The Monitoring for Pollution of the Sediments in the Volga River Basin (Russia)

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Abstract

Topical issues of modern geoecology related to the study of pollution of sediments of water bodies with heavy metals are considered. The Volga River basin, within which the research was carried out, is a rather heterogeneous picture, both in geological, geomorphological and hydrological terms, and in technogenic development and use. A four-level taxonomy is presented in the selection of sites for monitoring, based on a combination of natural-landscape-climatic and technogenic factors. The highest taxon (areas of category I) includes the basins of reservoirs with the adjacent slopes and the residential and industrial-agricultural structures located within them. Within these areas, smaller taxa are distinguished - areas of category II - industrial and urban areas. Areas of category III are the small rivers without significant pollution and areas of category IV are for special observations. The principles of sampling sediments, the placement of observation points and the frequency of these events in time are considered. Examples of special observations when studying the intra-annual migration of heavy metals in the system "sediments - water column" at the Ivankovo reservoir of the Upper Volga are highlighted. The studies were carried out under conditions of a standard flow rate for a given reservoir and under conditions of slow water exchange.

Introduction

Since 1992, within the framework of the Russian-German projects "Oka - Elba" and "Volga - Rhine", monitoring of pollution of sediments with heavy metals has been started. At different times, our partners were the University of Heidelberg, the Karlsruhe Research Center, the UFZ Leipzig-Halle, the Nizhny Novgorod State University of Architecture and Civil Engineering, and the Tver State Technical University. Sediments studies were carried out on the Ivankovo, Uglichs Saratov and Volgograd reservoirs, Lake Seliger, a natural flow regulator of the Upper Volga, on the Upper and the unsupported parts of the Lower Volga from Volgograd to Astrakhan, in the Oka river basin with the Moscow and Klyazma tributaries. Last years, much attention has been paid in the world to assessing the ecological state of water supply sources, as well as to comprehensive studies of ecosystems of various water bodies (Chen et al. 1996; Dekov et al. 1997; Domy 2001; Lemly 2002; Gleick et al. 2008; Kolomiytsev et al. 2017; Tolkachev et al. 2020).

The monitoring by various specialists means: a) observation of the processes; b) observation of the processes and forecast of their development; c) observation, forecast and process control; d) routine monitoring of processes. In the work under consideration, monitoring is understood as the observation of the state and pollution of sediments by heavy metals of water bodies of the Volga basin. The monitoring of the sediment's quality is the most important aspect of studying the ecological situation of water bodies. The sediments of water bodies play the role of a battery, a transformer of technogenic impact and are an indicator of its level. The main methodological problems are: 1) taking into account the differences in samples in terms of the mechanical composition and 2) taking into account the qualitative composition of the clay fraction minerals. Taking into account the differences in the sediment samples in terms of their texture is a fundamental methodological principle that makes it possible to optimize the

number of samples in accordance with the hydrology of a water body. In studies, when only the gross content of elements in samples is analyzed, as a rule, an irregular picture of pollution is obtained, since in adjacent points of sampling in local areas, the content of heavy metals can differ several times.

For the correlation of samples of different texture, it is recommended to use the determination of the contamination of the fraction less than 0.020 mm (Mueller 1979; Ackermann 1980; Mueller and Furrer 1998; Mueller et al. 2001). Fractions smaller than this value exhibit the properties of clay and are called "physical clay" (Voronin 1986). Currently, laboratory nylon sieves with a mesh size of 0.020 mm are commercially available. The use of these sieves to isolate the required fraction simplifies the procedure for preparing sediment samples for analysis. The samples taken from different parts of the river are brought to a "common denominator" (Mueller et al. 2001). For the initial selection of observation sites, available maps and aerial photographs of the investigated territory were used.

Justification Of The Choice Of The Observation Network

For the most complete study of the features of sediment pollution of water bodies in the process of research, areas of four categories were identified according to natural and man-made signs. The areas of category IV were allocated for special observations.

The plots of category I include reservoirs with adjacent slopes, on which industrial and residential zones, farmland and other technogenic objects are located. The reservoir itself is characterized by a leaching regime below the culverts of the upstream hydroelectric complex, a regime of transit and local accumulation of heavy metals in the middle part, and a powerful sedimentation zone of heavy metals in the dam part. The cities, industrial zones and tributaries contribute to the pollution. These objects can contribute to the cleaning effect by diluting contaminated sediments with cleaner sediments. To assess the general tendency of sediment pollution, it is advisable to repeat the studies in the upstream of the dam zone of the reservoir once every 5-10 years. On the reservoirs designated as sites of category I, there is no single picture of pollution, which is explained by their different volumes, wave regimes, lithological composition of the slopes abraded during the processing. So, on the relatively small the Ivankovo and the Uglich reservoirs, pollution from residential areas to varying degrees covers most of them. On the Kuibyshev and the Volgograd reservoirs, which are an order of the magnitude larger in volume, the situation is significantly different. Quite a lot of clay material is involved in the processing of the shores of these reservoirs, actively absorbing heavy metals. At 20 km downstream from the city of Saratov, all sediments tests for the content of heavy metals showed values that did not exceed the background values, although within the city the background heavy metals values were exceeded several times. The Seliger lake, as a natural regulator of the Upper Volga runoff, is quite unambiguously assigned to sites of category I. The town of Ostashkov, which is the main contaminant of sediments in terms of Cr (Kolomiytsev et al. 2004), is identified as a category II site.

On the basis of monitoring at the sites of the 1st category, the sites of the 2nd category are distinguished - those in which the pollution of the sediments by heavy metals is a scientific and environmental interest,

i.e. areas where the background values for heavy metals are significantly exceeded (several times). These areas include both cities with industrial zones located on the banks of the Volga, for example, Tver, Yaroslavl, Kostroma, Nizhniy Novgorod, etc., and located on tributaries of various orders, for example, Shchelkovo and Noginsk on the Klyazma river, Podolsk on the Pakhra river, Penza on the Sura river and others. In the areas of category II, the contamination pattern of sediments is rather variegated. The settlements on the Ivankovo and the Uglich reservoirs such as Konakovo, Dubna, Kimry, Beliy Gorodok, Kalyazin and Uglich introduce pollutants into sediments, creating local contaminated sites.

The town of Shchelkovo on the Klyazma river, in conjunction with treatment facilities, creates a rather long plume of the contamination by heavy metals in sediments with several times the background excess (Wedepohl 1995; Matschullat et al. 2000). In the process of monitoring next years, a decrease of pollution in sediments was noted due to a decrease in economic activity and the introduction of new progressive technologies for the production and treatment of wastewater. For the town of Noginsk on the Klyazma, the picture is quite peculiar. Above the city, sediment pollution is greater than below, which is explained by the inflow of solid "relatively clean" runoff from the surface of town and nearby territories (Novoseltsev et al. 2002).

Out of competition is the Moskva river below the city of Moscow, where the background values for a number of metals in sediments are exceeded tenfold. In such areas, monitoring should be carried out once every 1-2 years. Such observations make it possible to evaluate the results of the application of environmental protection measures, both by individual enterprises and in general within the industrial and residential areas. For more accurate identification of sources of pollution or purification of a water body in such cases, it is advisable to place several sites of IV category. The category III sites includes conditionally clean small rivers, the role of which in pollution is usually insignificant. In some cases, when they bring in clean sediments, the polluted zones in the water body into which they flow are purified. Small rivers with significant industrial zones should be classified as category II or IV sites. In the areas of category III, in the absence of strong human expansion, the repetition of observations once every 5-10 years seems to be sufficient.

Methods Of The Sediment Investigation

At the sites of categories I-III, monitoring answers the general questions of sediment pollution by heavy metals. At the special observation sites – IV category – both specially set scientific tasks and more detailed aspects of water pollution can be studied. An example of ranking the territory of the Ivankovo reservoir by monitoring categories is shown in Figure 1. The content of Cr, Co, Ni, Cu, Zn, As, Cd, Pb, Fe, Mn in the bottom water horizons, pore solutions and solid phase was monitored on the reservoir in the intra-annual mode sediments. The research was carried out at the observation stations "Ploski" and "Shoshinskiy reach". Station "Ploski" is located in the channel part of the reservoir in the section near the village of Ploski – under the conditions of the standard flow velocity for this reservoir. The "Shoshinskiy reach" station is located in the channel part of the Shoshinskiy reach, 600 meters above the highway – in conditions of a slow water exchange. Integral sediment samples were separated into a solid phase and a

pore solution. The method of chemical phase analysis was used in the solid phase, which included its sequential treatment with three selective extracts (Tolkachev 2012). The 1st extract extracts exchangeable and readily soluble forms of heavy metals using an acetate-ammonium buffer solution with $\text{pH} = 4.8$ (108 ml 98% CH_3COOH + 78 ml 25% NH_4OH + 800 ml H_2O). The 2nd hood extracts of heavy metals associated with organic matter. A 30% H_2O_2 solution is used. The 3rd extract extracts only heavy metals associated with amorphous Fe and Mn hydroxides at $\text{pH} = 7.3$ (0.5 M citric acid Na + NaHCO_3 + $\text{Na}_2\text{S}_2\text{O}_4$). To determine the heavy metals content, we used a "Plasma Quad 3" inductively coupled plasma ionization mass spectrometer (Fisons Instruments Elemental Analysis, UK).

For all studied elements, except for Pb and Cd, their concentration in the pore solution in all seasons is higher than in the bottom water, which indicates the existence of a constant flow of matter from BS into the water mass. At the same time, no obvious regularities in the change in the concentration difference between water and pore solution were noted for the most heavy metals. The lack of correlation between the concentrations of heavy metals in the water and pore solution may indicate that their chemical composition is formed independently of each other under the influence of various processes.

A high percentage of the sum of mobile compounds in the solid phase of sediments was noted for the almost all studied elements (Table 1). A particularly high percentage is "flat" for Cu, Zn, Cd, Cr, and for station "Shoshinskiy Reach" - for Zn, Cd. At the station "Ploski" elements such as Co, Cd, Mn are mostly found in ion-exchange forms, and for Cr, Ni, Pb, Fe this form is of decisive importance. Almost all mobile Cu is in the forms associated with the organic matter of BS. For Cr, Co, Ni, Cd, it plays a significant role. For Pb, As, Fe, the most typical form is associated with Fe and Mn hydroxides; for Co, Ni, Cu, Cd, Mn, it is practically atypical. For Zn, all three forms of existence have the same distribution.

Table 1. Percentage of mobile forms of heavy metals from their gross concentration in the solid phase of sediments of the Ivankovo (numerator) and Shoshinskiy Reach (denominator) (%) after (Tolkachev 2012)

	June	August	October	January	May
Cr	58.1/10.88	51.35/13.02	50.7/15.31	50.78/11.16	54.08/15.6
Co	17.3/19.12	20.64/21.5	19.11/24.23	20.01/6.42	24.27/17.48
Ni	23.14/23.0	24.36/27.08	22.46/22.19	23.24/4.93	21.49/17.78
Cu	75.56/18.11	75.27/21.58	78.03/22.35	87.74/13.59	70.08/17.09
Zn	52.9/59.1	58.55/64.47	37.46/70.25	43.13/41.02	41.12/58.59
As	14.4/11.68	10.42/13.27	9.2/15.21	12.14/5.96	13.04/15.7
Cd	60.16/58.16	68.69/66.91	61.1/61.09	59.74/26.95	60.44/49.86
Pb	11.05/8.48	12.49/11.75	15.16/16.43	15.13/4.17	15.1/11.0
Mn	19.1/23.3	31.4/59.6	19.1/25.5	20.9/15.7	20.7/17.6
Fe	39.2/30.1	56.8/42.1	56.7/56.8	54.4/22.1	67.8/38.7

Note that, according to the monitoring results, Co, Cd, Mn, Cr, Ni, Pb are in the most mobile forms in sediments at station "Ploski". At station "Shoshinskiy Reach", the patterns of distribution of moving forms of elements are generally preserved. Most of Co, Zn, Cd are in ion-exchange forms, for Cr, Ni, Pb, As this form plays an essential role, especially in winter conditions. Most of the mobile Cu is in the form associated with the organic matter of sediments, and for Cr, Co, Ni, Zn, Cd it is essential. For Pb, As, the form associated with Fe and Mn hydroxides dominates only in summer, while in winter and spring the value of ion-exchange forms sharply increases. It can be stated that Co, Cd, Zn, and in winter, Pb, As are in the most mobile forms in sediments of station "Shoshinskiy Reach".

The mobile forms of the studied microelements are characterized by the maximum variability. For them, the values of the coefficient of variation (Cv) vary in the interval 0.18-1.04 for "Ploski" station and in the interval 0.42-1.06 for "Shoshinskiy Reach". Very low Cv values are noted for inactive (crystalline) forms. The Cv values vary in the range 0.001-0.055 for the "Ploski" station and in the range 0.002-0.040 for "Shoshinskiy Reach" (Tolkachev 2012). It can be concluded that it is the change in the content of heavy metals in mobile forms that contributes to the change in their total content in sediments. The oxidation-reduction potential of the near-bottom water horizons at the stations varied from +340 mV in winter to +410 mV in spring. Measurement over the depth of sediments showed that within 3 cm there is an oxidized layer with a value of Eh = 70-80 mV, and deeper, a reducing environment is observed. At a depth of 10-12 cm, Eh = -170-180 mV. The reaction of the bottom layer of water and pore solution throughout the year remains at the level of neutral and slightly alkaline with an insignificant amplitude of fluctuations. Thus, it can be stated that at the permanent observation stations in the bottom water and sediment pore solution, there were no sharp seasonal changes in such environmental parameters as the redox-potential and pH.

Special surveillance in the areas of category IV - the Vorya, Severka, Pakhra, Desna and Mocha rivers - were carried out to study the effect of road traffic flows on the pollution of sediments in small rivers. In these cases, the placement of observation points was as follows: 2-3 points were tested upstream of the bridge and 5-6 below during the initial survey. When re-evaluating the results of primary observations, taking more than 2 samples above the bridge was deemed unnecessary. Downstream pollution of sediments by heavy metals decreased to the background value at a distance of 150-200 m from the mainline (Korzhenevskiy et al. 2018).

The entire area of the reservoir and adjacent slopes, which are the sources of solid material input into the reservoir and tributaries, is defined as the largest taxon - a category I site. Within its limits, two sections of the II category are identified - the cities of Konakovo and Dubna, which are the sources of individual pollution of the reservoir. The Soz river is allocated to a category III section, to which other small rivers can also be assigned. The above-described stations "Ploski" and "Shoshinskiy Reach" are classified as sites of category IV.

Justification For The Selection Of Sampling Points.

The sediment sampling is carried out depending on the research objectives. The water body is divided into a series of sections. If there is a floodplain, the section extends to its periodically flooded part. Sediment samples in each section must characterize the water body or its part for a certain period of time and meet the requirements that meet the assigned tasks. The volume of the sample taken must be sufficient to carry out the planned analytical laboratory tests.

In each section, 1-3 samples are taken, depending on the hydrological characteristics and their features in a given section of the water body. When using the technique (Novoseltsev et al. 2002; Kolomiytsev et al. 2017) it is enough to take samples weighing 300-500 grams. It is known that the top 3...5 cm of sediments characterize the pollution of the water body over the last 3...12 months. In the distribution of pollutants along the depth, as well as in the study of changes in the nature of pollution over the years, cores of undisturbed sediments are taken. For long-term storage, it is recommended to freeze samples to -20°C .

The rationale for sampling points is not uniform, since plots of different categories are somewhat unique and require an individual approach. In general, the following principles should be followed:

- in the areas of category I, during the initial surveys, it is necessary to test 2-4 points along the sections across the reservoir or the river in the areas below the industrial and residential agglomerations and on conditionally clean areas; during repeated sampling, the sampling points should be adjusted in accordance with the objectives of the study and the results of previous studies (one should not look for highly dispersed sediments in the sections of the reservoir with a leaching regime);
- on the sections of the II category, i.e. in areas of industrial and civil development of the territory, sampling sites should be placed above and below the survey object to the area with background heavy

metals values at the primary stage with the correction or preservation of previous sampling sites depending on the results obtained (in some cases, after the initial survey, observation points may not be located across, but downstream);

- in the areas of category III, it is recommended to take several samples at the confluence of small rivers (during the initial survey, you can sample several points upstream);

- plots of category IV are individual and here the specificity of sampling depends on the purpose of the study. Examples of such monitoring were given above for the stations "Ploski" and "Shoshinskiy reach" (Tolkachev 2012).

Conclusion

Proceeding from the fact that monitoring by the authors means observation of the state and pollution of sediments in water bodies of the Volga basin of heavy metals, according to the totality of natural and technogenic factors, several categories of objects with similar characteristics were identified, within which they were monitored. The hierarchical subordination of the sites makes it possible to rationally treat the points of sampling of sediments and their number and observation time.

As a result of monitoring, the following patterns were noted:

- in areas of category I, the pollution of the basin outside the zone of influence of technogenic objects is the less, the larger the water body; the factors characterizing the object may include water consumption, geological structure, which determines the amount of sorbent fractions in the sediments, the time and volume of their intake, etc.;

- in the areas of the II category, during the active economic development of the catchment area, sediment pollution occurs, which in some cases spreads to the areas of the I category; sources of pollution are mostly industrial waste, often with individual characteristics, for example, tanning industry - chrome, glass - lead, engines - iron and copper, etc.;

- plots of category III more often manifest themselves as a factor that improves the ecological state of a water body of a higher category, the exception is abnormally rainy years, when, due to the intensification of erosion processes, an increased amount of pollutants is washed off from the catchment area in comparison with ordinary conditions;

- plots of IV category allow solving some particular issues of studying the pollution of water bodies by heavy metals.

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Figures

Figure 1

Ranking of the Ivankovo reservoir by research category for monitoring the pollution of sediments (prepared using the online service "Yandex.Maps" maps.yandex.ru) Legend: Category I - the entire catchment area; II - the towns of Konakovo and Dubna with the adjacent water area; III - the river Soz; IV1 - station "Shoshinskiy Reach"; IV2 - station "Ploski"