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Phosphorus accumulation in a lowland reservoir during the spring flood

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Abstract. On the basis of detailed observations of 1984, 2012 and 2016 we estimated the accumulation of reactive phosphorus in the Mozhaysk reservoir during the spring flood. The results of this assessment depend on the completeness and origin of the used data: the absence of discharge gauging stations on the tributaries of the reservoir introduces an error of 30-40%, a decrease in the frequency of water quality monitoring from daily to 2 times a month or the use of empirical dependences in the absence of monitoring – up to 50-60% or more. During the flood, an overwhelming amount of reactive phosphorus accumulates in the reservoir due to a significant inflow (50-60% of the annual) and low outflow (from 1 to 13% of the annual). Over the past 30 years, there has been a significant reduction in the external phosphorus load on the reservoir.

1. Introduction

Anthropogenic eutrophication of lakes, i.e. increase of their primary productivity as a result of the inflow of nutrients with wastewater and non-point sources from fertilized agricultural fields, is recognized as one of the most dangerous human impacts on the environment [1-5]. In many cases, phosphorus serves as an element which (co)limits this process.

According to various estimates, between 20 and 80% of the phosphorus delivered from the catchment is captured in bottom sediments of reservoirs. This negatively affects the quality of water in them, due to more active algal bloom compared to rivers that don't have dams, even in the absence of anthropogenic impact. However, the phosphorus content downstream from the dams decreases [6], and thus the general effect of dams on the amount of nutrients which find their way into the seas with the river runoff is estimated as positive. But for reservoirs which serve as water supply sources, the negative effects associated with cyanotoxins release into the water outweigh the advantages. Also, sedimentation of phosphorus in lakes, especially shallow ones, increases the internal nutrient loading on the water body, due to which the blooming intensity does not decrease even when the input of anthropogenic phosphorus from the catchment stops.

The main source of phosphorus inflow into reservoirs is river runoff [7], and intra-annual variability of the phosphorus content in rivers is very high. In temperate zones, the major part of phosphorus finds its way into reservoirs during the flood period, when increased flow is combined with an increased concentration of phosphorus due to intensive washout from the catchment.

Accumulation of phosphorus during the flood period largely determines the functioning of the reservoir ecosystem throughout the year [8]; on the one hand, it depends on the hydrometeorological

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conditions for water and chemical runoff formation during the flood period, and on the other, on the operational mode of the dam. However, the accuracy of estimates of such accumulation largely depends on the available initial data [9]. Given the steady decrease in the number of hydrological observation stations in Russia, and insufficient frequency of water quality observations (down to their complete absence), the conclusions on the long-term dynamics of phosphorus accumulation in reservoirs can be misleading, even leading to incorrect inferences regarding current trends.

2. Materials and methods

The object of this study was the Mozhaysk reservoir, which is located in the west of the Moscow region (N 55°35', E 35°50'). This is the largest reservoir in the Moskva river water system, which supplies drinking water to the Moscow metropolitan area. It is about 235 million m³ in volume, and covers an area of about 30.7 km² at normal retaining level, with a catchment area of 1,360 km². Three main tributaries: the Moskva river (catchment area 755 km²), the Lusyanka (170 km²), and the Koloch (279 km²) provide 83% of the water inflow into the reservoir from 91% of the catchment area. Russian federal monitoring gauging stations operate on the Moskva and Lusyanka rivers, essentially at the point of their inflow into the reservoir (the upper boundary of the backwater area). The river Koloch runoff is regulated by the dam, which pumps water from the Koloch to the Mozhaysk reservoir.

The data included in this study was taken from three years with different annual flow: 1984 (average, with the annual inflow $\Sigma IN = 263$ million m³), 2012 (high, $\Sigma IN = 360$ million m³) and 2016 (average, $\Sigma IN = 287$ million m³). During these years detailed observations of water quality were carried out at the reservoir and its catchment area, including more frequent sampling during floods on the tributaries (in 1984 and 2016 almost daily, in 2012 on average twice a week), and downstream from the dam (2-3 times a week) [10, 11]. The inorganic phosphorus content in the samples was measured using Murphy-Riley method [12].

The accumulation of inorganic phosphorus in the Mozhaysk reservoir during the flood period was calculated as the difference between the input from the catchment (external phosphorus load) and the discharge in the lower reach of the Mozhaysk dam. The external load was calculated as the sum of phosphorus inflow with the runoff from the Moskva, Lusyanka, and Koloch rivers and the lateral inflow.

The mass of inorganic phosphorus M_P (tons/day) brought in with a certain volume of water per day was calculated as the product of the average daily discharge Q (m³/s) and the corresponding phosphorus content P (mg/l) with 0.0864 coefficient to take into account the dimensions and the number of seconds in a 24-hour period. Then the daily values were calculated for the main flood period, which was identified as the period of sustainably high water with discharge less than 33.3% exceedance, including the flood peak, starting and ending with the days with discharge exceedance of more than 33.3% (3.82 and 0.83 m³/s for the Moskva and Lusyanka rivers, respectively).

One of the objectives of the present study was to assess the sensitivity of the calculation methods to particular features of the initial data. Obviously, estimates of phosphorus accumulation would be more reliable if there was daily data on both discharge and phosphorus content. However, in practice, researchers rarely have such detailed field data.

Data on discharges from the Mozhaysk and Koloch dams is present in the operational schedules produced by the Mozhaysk dam facility's hydrological section, which are available in the database of the Krasnovidovo station for all the years since its construction.

Official data on daily discharges at the federal monitoring hydrological stations on the Moskva and Lusyanka rivers is available only for 1984. Since the 1990s only water levels have been measured at these stations, and for 2012 and 2016 we only have data on daily water levels. The curve Q = f(H) is often used to recalculate water level H into discharge Q. However, this curve should be regularly updated, which did not happen for the Moskva and Lusyanka rivers for more than 20 years (the most "up-to-date" curve coordinates we have in the Krasnovidovo station database are from 1996).

In addition to the curve itself, sets of reduction coefficients k_Q are also needed, which take into account the influence of ice and vegetation. These coefficients vary widely at different phases of the

hydrological regime and also must be regularly updated, and their correct application requires knowledge of the ice conditions in the winter and aquatic vegetation growth in the summer. There's no data on these coefficients in the Krasnovidovo station database. We used two techniques to estimate them for the floods of 2012 and 2016 broadly. The first method was to calculate the daily k_Q coefficients in the spring of 1984 as the ratio of discharges published in annual printed archives of runoff data and derived using the Q = f(H) curve. The obtained coefficients predictably increase from 0.2 in the period of continuous ice cover to 1.0 at the flood peak and then decrease again as the channel overgrows. Such coefficients were applied for 2012 and 2016 taking into account the dynamics of ice cover and vegetation (according to our field observations). The second method involved calculating k_Q for each calendar date according to yearbooks for a long-term period and applying these coefficients without taking into account the 2012 and 2016 specifics.

As an alternative to Q = f(H) curve, we used the daily data on the total surface inflow into the Mozhaysk reservoir quoted in the operational schedules to estimate discharges from the Moskva and Lusyanka rivers. The shares of runoff from the catchments of the Moskva and Lusyanka were calculated in proportion to their shares in the total catchment of the reservoir.

As to inorganic phosphorus content in the river water, in 1984 and 2016 they were measured during daily observations, and the few existing gaps could be reliably filled by linear interpolation of the measured values. However, in 2012 some gaps were up to 4 days long; was linear interpolation acceptable in this case? To answer this question, we have consistently "thinned out" the series of measured phosphorous content to imitate sampling once a week, once every ten days, and once a fortnight, using the data for 1984 – the year for which the fullest observational data was available. The deleted data was substituted by linear interpolation of the remaining values. The estimates of external phosphorus load and phosphorus accumulation in the reservoir, based on the "thinned out" data, were compared with the most reliable estimates based on the daily discharges and phosphorus content data.

Finally, let's assume that there is no observational data on phosphorus content for the study period. In this case empirical relationships between the content and discharge are often used to estimate the inflow of various substances. Generally, inorganic phosphorus content tends to be directly dependent on the river discharge, since the washout of phosphorus from the soil, agricultural lands, etc. is the highest when the runoff is increased. However, this relationship may significantly vary in different seasons and years [13, 14]. In this study we have tested the equations describing the relationship between inorganic phosphorus content and runoff of the Moskva and Lusyanka rivers obtained separately for the ascending and descending flood limbs, using the data of long-term water quality studies in the Mozhaysk reservoir's catchment basin (table 1).

Table 1. Empirical dependence of inorganic phosphorus content P in the water of the Mozhaysk reservoir tributaries on the water discharge Q.

River	Flood stage	Dependence equation	R^2	n
Moskva	Ascending	$P = 0.660 e^{-0.019 Q}$	0.819	15
	Descending	$P = 0.058 e^{0.002 Q}$	0,022	38
Lusyanka	Ascending	$P = 0.766 e^{-0.042 Q}$	0.285	9
	Descending	$P = 0.057 Q^{0.166}$	0.321	20

Daily inorganic phosphorus content values in the water discharged by the Mozhaysk dam and pumped over from the Koloch reservoir were in all cases obtained by linear interpolation of the measured values. This seems to be quite acceptable since the variability of the phosphorus content in water of the Mozhaysk and Koloch reservoirs is much lower than in the rivers.

A summary of all applied techniques to calculate the external phosphorus load and accumulation of inorganic phosphorus in the Mozhaysk reservoir is presented in table 2.

3. Results

The years significantly differed regarding both the origin of river floods, and the dam operational schedule (figure 1). The year 2012 had the latest, the highest, and the most rapid flood, while in 2016

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it was the earliest, lowest, and prolonged, with two peaks. Discharges from the Mozhaysk dam during the floods of 1984 and 2016 mostly did not exceed the minimum flow $(1.5 \text{ m}^3/\text{s})$, while during the ascending and descending limbs of the 2012 flood they were at least 9-12 m³/s, reaching 124 m³/s at the peak.

Table 2. Methodologies for assessing the accumulation of inorganic phosphorus in the Mozhaysk reservoir during the flood period.

Calculation	Data sources and specific features of calculation method				
method	Discharge Q	Inorganic phosphorus content P			
Q_1	1984 – printed archives of runoff data; 2012 and 2016 – Q(H) + k_Q estimates based on 1984 data	All observational data +			
Q_2	Q(H) without k _Q	linear interpolation (LI)			
Q_3	$Q(H)$ + mean average k_Q				
Q_4	Dam operational schedules + catchment areas				
T_1		Observations every 7 days + LI			
T_2	Similar to Q ₁	Observations every 10 days + LI			
T_3		Observations every 14 days + LI			
\mathbf{P}_1	Similar to Q ₁	Empirical dependencies D(O)			
P_2	Similar to Q ₂	Empirical dependencies P(Q) for ascending and descending flood limbs			
P_3	Similar to Q ₃				
P_4	Similar to Q ₄				

The highest inorganic phosphorus content in the rivers was recorded in the spring of 1984, reaching 0.55 mg/l in the Moskva river (figure 1) and 0.83 mg/l in the Lusyanka. In 2012 and 2016 the phosphorus content was much lower and did not exceed 0.15 and 0.21 mg/l in the Moskva river, and 0.20 and 0.43 mg/l in the Lusyanka, respectively. This change was probably due to reduced anthropogenic load on the catchment area (size of agricultural area, use of inorganic fertilizers).

In general, the highest inorganic phosphorus content was noted in the rivers at the beginning of the flood; during rising discharges and in the descending flood limb these values decreased. Downstream of the Mozhaysk dam the phosphorus content changed smoothly, not exceeding 0.11 mg/l in 1984, and 0.05 mg/l in 2012 and 2016.

In line with the fluctuations of discharge and phosphorus content, the highest external phosphorus load on the reservoir was noted during the ascending flood stage. The highest inflow of inorganic phosphorus into the reservoir with surface runoff in 1984 reached 4 tons/day, in 2012 more than 3 tons/day, and in 2016 less than 1.5 tons/day (according to the results of the most reliable calculation method Q_1).

The maximum phosphorus washout from the catchment in each of the three years was observed 2 days before the flood peak (in 2016 it was 9 days before the second peak in which, however, the phosphorus content in the rivers was already lower). Phosphorus outflow from the reservoir was negligible: even in 2012 when the discharges from the reservoir were the biggest it didn't exceed 0.4 tons/day (figure 1).

The total inorganic phosphorus inflow during the flood in 1984 amounted to 23.3 tons (59% of the total annual inflow), in 2012 to 18.6 tons (56% of the annual inflow), and in 2016 to 14.8 tons (51%). The total phosphorus outflow in 1984 was 0.2 tons (2% of the annual value), in 2012 - 2.7 tons (13%), and in 2016 - 0.1 tons (1%).

Thus, almost all inorganic phosphorus brought into the Mozhaysk reservoir during the flood (from 85% of the external load in 2012 to 99% in 1984 and 2016) was accumulated in the reservoir, subsequently providing nutrition for algae during the growing season.

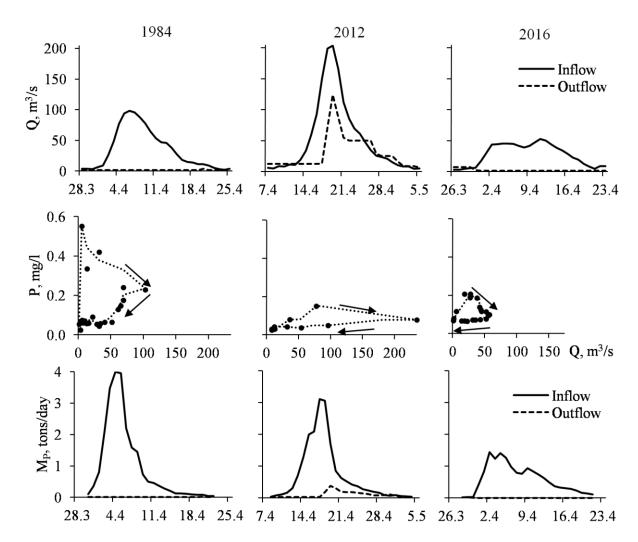


Figure 1. Total surface inflow and outflow discharge hydrographs of the Mozhaysk reservoir Q (top row); graphs of correlation between inorganic phosphorus content and discharges of the Moskva river (middle row); mass of inorganic phosphorus inflow M_P into the reservoir with river runoff, and discharged into the dam's downstream section (bottom row) during flood peaks in 1984, 2012 and 2016.

4. Discussion

Table 3 presents the results of estimating inorganic phosphorus accumulation in the Mozhaysk reservoir during the flood period obtained using all of the tested techniques. Since the Q_1 method (see Table 2) is based on the most complete and reliable data and seems to be the most accurate, we compared the results of the other assessments with this "reference" one. The deviation δ (%) describes the relative error which is due to specific features of the initial data and the calculation method.

In the absence of data on the river discharge and relevant values of k_Q coefficients, the most effective way to quantify river runoff is to use Q(H) curve and mean average k_Q values (method Q_3). When this technique is applied, the estimation error does not exceed 6% (compared to Q_1), while daily δ values remain relatively small during the entire flood (from 19 to 78%).

If we calculate daily discharge using Q(H) curve without applying decreasing coefficients (method Q_2), the relative error increases significantly (up to 40% or more). The external phosphorus load is particularly overestimated during ascending flood stage (up to 300% on certain days), due to overestimation of discharges.

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Table 3. Estimates of inorganic phosphorus accumulation in the Mozhaysk reservoir during flood obtained using various techniques (M_P , tons), and their errors compared to the "reference" estimate made using method Q_1 (δ , %).

Calculation	1984		2012		2016	
method	M_P , tons	δ, %	M_P , tons	δ, %	M_P , tons	δ, %
Q_1	23.1	_	15.9	_	14.7	_
Q_2	32.8	+42	17.0	+6	18.4	+25
Q_3	22.0	-4	16.0	0	13.8	-6
Q_4	19.9	-14	10.9	-31	12.2	-17
T_1	24.625.1	+6+9	13.018.0	-18+13	12.815.4	-13+5
T_2	27.827.9	+21	13.114.5	−17…−9	13.014.4	-112
T_3	8.734.0	− 62…+48	7.322.2	-54+39	10.816.1	-26+10
\mathbf{P}_1	15.9	-31	20.8	+31	20.9	+42
P_2	16.2	-30	21.9	+38	21.7	+48
P_3	15.8	-32	21.4	+34	24.0	+63
P_4	17.1	-26	18.4	+16	23.8	+62

If we use an assessment of the river runoff based on the reservoir operational data in the absence of Q(H) curve, phosphorus accumulation in the reservoir (method Q_4) turns out to be underestimated (by 14-31%). In 1984 and 2012 the phosphorus inflow was particularly underestimated for the ascending flood stage (up to 60% on some days), and overestimated for the descending one (up to 30%); in 2016, on the contrary, the phosphorus inflow during the first days of the rapid rise in discharge was overestimated by 123%, while for the remaining period it was underestimated (up to 72%).

If the frequency of water quality monitoring is reduced from once a day to once a week (method T_1), the estimation error for phosphorus accumulation during the flood changes from 13 to 18% (table 3). Reducing the frequency of monitoring to once per ten days (method T_2) increases the error slightly (to 17-21%) and to once a fortnight (method T_3) – much more significantly (up to 50% or more).

Note that the error depends not only on the frequency but also on sampling dates, i.e., on how they relate to the dynamics of the water and nutrient flow. E.g., in 1984, depending on which days of the week were chosen to take samples every 14 days, phosphorus accumulation may be underestimated by more than 60% or overestimated by almost 50%. The distribution of errors within the calculation period is random.

Using empirical dependences of phosphorus content on discharge in the absence of observations of water quality in the reservoir tributaries (methods P_1 - P_4) results in significant errors. The external phosphorus load during the ascending flood stage was significantly overestimated for all three years.

In 1984, phosphorus accumulation, which was based on P(Q) dependencies, was underestimated by 26-32% compared with the "reference" (Q_1) value, with daily errors remaining within 70-363% range. In 2012 use of empirical equations resulted in overestimating the values by 16-38%, and in 2016 by 42-63%, while on certain days during the ascending flood stage the errors increased to 2,300%. The steady increase in errors over the years may indicate a change in the nature of the correlation between water and nutrient flow, and the need to regularly review it.

5. Conclusion

The majority of inorganic phosphorus is accumulated in the reservoir during flood periods due to its significant inflow (50-60% of the annual volume) and low outflow (between 1 and 13% of the annual volume).

Estimates of phosphorus inflow and accumulation in the reservoir during the flood period significantly depend on the completeness and origin of the data. The absence of monitoring stations on

the reservoir's tributaries leads to an error of up to 30-40%; reduced frequency of water quality monitoring from daily to twice a month, or use of empirical dependencies in the absence of monitoring result in an error of 50-60% or more.

A significant decrease of the inorganic phosphorus content in rivers and its inflow into the reservoir in 30 years indicates a change in the land use of the catchment.

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