Urban impact on water quality in the rivers of Central Russia

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Abstract. Comparative analysis of the urban impact on water quality in the main rivers of Central Russia has been performed based on hydrochemical observations dataset for the period 2005-2019. It was obtained from monitoring results at the gauging stations located upstream and downstream of 11 cities in the studied region. The pollution level was estimated by comparison of the annually-averaged concentration values for 43 water quality indicators with their defined maximum permissible concentrations. The most substantial growth in concentrations downstream of the cities compared to their upstream values was revealed for heavy metals, nitrogen compounds, phosphates and oil products. A much less significant negative impact was imposed by cities on transparency, oxygen and major ions content. The cities were ranked by the total number of hydrochemical indicators which concentrations 1) increase downstream of cities, 2) exceed the maximum permissible concentrations before and after entering cities, 3) exceed the maximum permissible concentration before and after entering cities while sufficiently increasing (>10%) at the downstream station. Additionally, the indicators were identified that experienced the most considerable impact from the urban areas. Among the studied cities, three groups were identified differing from each other in the degree of impact on the river water quality.

1. Introduction

The scientific literature published in the last two decades contains the results of the studies of individual cities [1-4] or several cities [5-15] influence on the water quality in several river basins of Central Russia. Within the Volga basin, the influence of the Rzhev, Tver’ and Staritsa towns on the quality of the Volga River was studied. Similar estimates were obtained for Kaluga and Murom cities in the Oka basin, for Donskoy town in the basin of the Don River, for the city of Smolensk in the Dnieper basin, etc. The problem of the influence of cities on the quality of river waters is given quite a lot of attention in various regions of the world [16-17].

The main purpose of this study was to perform the comparative evaluation of impact imposed by Central Russian cities on the water quality and level of water pollution in the Volga, Oka (and its tributaries, the Moscow and Upa rivers) and Don basins.

2. Materials

The study of the ecological condition of Central Russia rivers was carried out at 20 gauging stations of the State Observational Network (SON) located upstream and downstream of the cities [18]. The research included the cities of Rzhev and Tver’ (Volga River); Smolensk (Dnieper River); Zvenigorod
and Voskresensk (Moscow River); Vladimir (Klyazma River); Kaluga and Murom (Oka River); Donskoy (Don River) and Tula (Upa River). The influence of the city of Moscow on the water quality of the Moscow River was estimated based on comparison of measurement values in sections downstream of Zvenigorod and upstream of Voskresensk. In this case, not only the influence of the city of Moscow itself (considering city borders before their last change in 2012) was assessed, but also of the area between the indicated sections, which include other towns, agricultural lands, etc. Two groups of the river basins were considered regarding their area. The first group contains rivers with size from several (Upa River, Moscow River near Zvenigorod) to dozens (Volga River near Rzhev, Moscow River near Voskresensk, Klyazma River near Vladimir, Don near Donskoy) thousand square kilometres. Another group considers larger river basins with a catchment area from 40-50 (Oka River near Kaluga, Volga River near Tver’) to almost 200 (Oka River near Murom) thousand square kilometres.

The watershed of the Don River is located in the forest-steppe zone while the rest of the considered river basins belong to the forest zone. The climate of the area under consideration is moderate continental. Snow feeding predominates in the studied rivers. River basins in the region are characterized by significant anthropogenic pressure. Urban influence is considered as one of the most important factors that impose a negative impact on the water quality of rivers and reservoirs. The population of cities considered in this research according to data for 2020 varies from 20 (Zvenigorod) - 50 (Rzhev and Donskoy) and 100 (Murom and Voskresensk) to 300 (Vladimir, Kaluga and Smolensk) and 400 (Tula and Tver’) thousand people. Various enterprises of mechanical engineering, metal-working, chemical, food-processing and light industries are developed in them. A special place among the considered cities of Central Russia, also with regard to the negative impact on the environment, is occupied by the city of Moscow with its 13 million population and various industries, including mechanical engineering and oil refining and developed public utilities.

The study of the urban impact on the ecological condition in rivers is based on long-term datasets of observations at gauging stations of the State Observation Network (SON) covering the period from 2005 to 2019 [18]. The analysis used a set of annually averaged values of various hydrochemical indicators, including smell, transparency, colour, temperature, major ions content (Ca$^{2+}$, Na$^+$, K$^+$, Mg$^{2+}$, HCO$_3^-$, Cl$^-$, SO$_4^{2-}$), pH, chemical oxygen demand (COD) by dichromate method, nitrogen compounds (NH$_4^+$, NO$_2^-$, NO$_3^-$), biochemical oxygen demand over 5 days (BOD$_5$), phosphates, heavy metals (Fe, Cu, Ni, Zn, Cr, Pb, Mn, Cd), phenols, oil products, formaldehyde, etc. To identify water pollution imposed by each city, comparison of water quality indicators with the maximum permissible concentrations in natural waters values was made according to restrictions for fishery purposes [19].

3. Results and discussion

3.1. Generalised urban impact on river water quality in the region

It should be noted that the analysed period could be characterized by the absence of any significant persistent long-term temporal trends in differences of hydrochemical indicators values between river sections upstream and downstream of the cities. Therefore, long-term averaged characteristics give a fairly adequate representation of features inherent to urban impact on the river water quality in the current socio-economic and climatic conditions of the region. During the studied period, the annual river flow in the region refers to a long phase of its decreased values.

The most noticeable increase in the long-term averaged annual concentrations downstream of the cities compared to their upstream values, considering all of the studied cases, was revealed for heavy metals (HM), nitrogen compounds, phosphates and oil products (figure 1). Furthermore, cities tend to have a much less noticeable impact on indicators such as transparency and oxygen content in water (decrease downstream of the city reaches 5 and 2%, respectively).

Few separate groups of hydrochemical indicators were considered during the analysis. So, among the major ions, the highest relative difference between the river sections upstream and downstream of the cities is revealed for chlorides (Cl$^-$) and sulfates (SO$_4^{2-}$) - about 12-15%, while the salinity of water increases by an average of 10% (figure 1). Regarding organic matter transformation downstream of
the cities, the most significant increase was observed for ammonium (NH$_4$), nitrites (NO$_2$) and phosphates (up to 53, 37 and 36%, respectively). Heavy metals concentration also inclines to change significantly within the urban influence zone (figure 1). The relative difference between the concentrations of cadmium (Cd) and trivalent chromium (Cr$^{3+}$) could reach more than 70%. Significant transformation also occurs in concentrations of hexavalent chromium (Cr$^{6+}$), manganese (Mn), zinc (Zn), copper (Cu) and iron (Fe). Their relative changes are varying within 15-45%. Regarding other chemical indicators, urban impact significantly increases the concentration of oil products (by 40%), anionic synthetic surfactants (ASSAA) and phenols (up to 25%).

Two city groups could be identified regarding the set of hydrochemical indicators on which city has the most significant impact via an increase in their downstream concentrations. The first of them includes the cities of Rzhev and Tver’ located on the Volga River, Zvenigorod on the Moscow River, Donskoy (Don) and Kaluga (Oka). This type of urban impact is characterised by the greatest increase in the content of biogenic elements (ammonium, nitrites, phosphates) and COD (according to the dichromate method) in studied rivers. The cities of the second group were found to significantly increase the concentrations of heavy metals, phenols and oil products in the river water downstream of the urban area.

![Figure 1](image.png)

**Figure 1.** Long-term averaged relative difference between concentration values of various hydrochemical indicators upstream and downstream of the city; spatially averaged for all studied urban areas.

### 3.2. Features of urban impact on river water quality and the level of their pollution

The major ions content does not exceed the maximum permissible concentration values in all the sections under consideration (both upstream and downstream of the cities). Among the studied cities, few are identified (Kaluga and Murom on the Oka; Rzhev on the Volga; Vladimir on the Klyazma and
Zvenigorod on the Moscow River) where the concentrations of the major ions comply with the natural background value at both upstream and downstream sections. The river water there corresponds to bicarbonate-calcium type with significantly lower concentrations of other cations and anions (less than 20%). No particular difference in the content of ions between the sections upstream and downstream of the cities is observed (figure 2a). Thereby, these cities do not imply any noticeable changes in the major ions concentration. The same conclusion holds for the Upa River section near Tula. While the relative share of \( \text{SO}_4^{2-} \) is substantially higher there (35%), the difference in upper and lower sections could also be considered insignificant. In other words, in this case a high proportion of the sulphate ions is most likely caused by the natural features of the catchment area. The second group unites the cities of Donskoy on Don and Moscow on the Moscow River (considering section between Zvenigorod and Voskresensk) (figure 2b). In the downstream sections of these urban areas, a considerable growth in sulphate and chloride ions could be observed, evidently due to insufficiently treated municipal wastewater discharge.

* For the Moscow River near the city of Moscow: upstream section – station downstream of Zvenigorod, downstream section – station upstream of Voskresensk

**Figure 2.** Major ions concentration (mg/l) in Volga River near the city of Rzheiv (a) and Moscow River near the city of Moscow (b).

* For the Moscow River near the city of Moscow: upstream section – station downstream of Zvenigorod, downstream section – station upstream of Voskresensk.

**Figure 3.** Hydrochemical indicators content in Oka River near the city of Murom (a) and Moscow River near the city of Moscow (b) as maximum permissible concentration value multiplier \((n \times \text{MPC})\).
Regarding other hydrochemical indicators, the city of Murom represents the least polluted situation of all studied cases (figure 3a). The rise of concentration with a transition to the downstream section occurs for only 4 indicators, while the resulting difference could be considered as somewhat significant (more than 10%) for only one of them. For the rest of the considered urban areas, specific sets of hydrochemical indicators could be identified: the concentrations of which increase significantly downstream of the city (figure 3b); and those whose concentrations do not increase sufficiently, or even decrease.

It was found that 13 out of 14 considered indicators experience a certain growth in their concentrations between upstream and downstream sections of the Moscow River near the city of Moscow (table 1). 12 such indicators are revealed near the city of Tula. This number reaches 11 downstream of the city of Rzhev, while 10 of them are observed further down the river in Tver’, Smolensk and Zvenigorod. Finally, 8 indicators with values increasing from upper to lower section of the river were found near Kaluga, Vladimir and Donskoy. However, even a sufficient increase in concentrations downstream of the city in many cases does not lead to the exceedance of maximum permissible concentration values.

**Table 1.** Long-term averaged river water quality indicators values in the rivers of Central Russia upstream and downstream of the studied urban areas.

| River-City          | Smell | Colour | Hardness | COD | BOD_{5} | NH_{4} | NO_{3} | Phosphates | Fe | Ca | Zn | Mn | Phenols |
|---------------------|-------|--------|----------|-----|---------|--------|--------|------------|----|----|----|----|---------|
| Volga-Rzhev         | MCPUP | 0.93   | 5.22     | 0.28| 1.00    | 0.62   | 0.17   | 0.07       | 0.29| 0.78| 4.35| 1.20| 0.59    | 1.33|
|                     | MPCDN | 1.02   | 5.08     | 0.30| 1.02    | 0.69   | 0.21   | 0.08       | 0.42| 0.78| 5.16| 1.35| 0.65    | 1.40|
| Volga-Tver’         | MCPUP | 0.94   | 4.37     | 0.39| 0.88    | 1.55   | 0.09   | 0.16       | 1.24| 1.13| 5.31| 1.41| 0.58    | 1.33|
|                     | MPCDN | 0.84   | 4.48     | 0.21| 0.98    | 1.69   | 0.11   | 0.23       | 1.70| 1.11| 6.17| 1.94| 0.64    | 1.47|
| Oka-Kaluga          | MCPUP | 0.5    | 1.12     | 0.61| 0.54    | 0.92   | 0.2    | 0.29       | 1.71| 0.62| 2.02| 0.28 | -       | 1.50|
|                     | MPCDN | 0.5    | 1.16     | 0.67| 0.69    | 0.87   | 0.27   | 0.40       | 2.44| 0.55| 2.92| 0.40 | -       | 1.30|
| Oka-Murom           | MCPUP | -      | 4.36     | 0.62| 0.88    | 1.57   | 0.24   | 0.44       | 2.72| 0.79| 2.97| 0.8  | 0.44    | 2.58|
|                     | MPCDN | -      | 3.89     | 0.61| 0.86    | 1.52   | 0.22   | 0.47       | 2.60| 0.56| 3.10| 0.87 | 0.5     | 3    |
| Moscow-Zvenigorod   | MCPUP | 1.05   | 1.14     | 0.55| 0.65    | 1.02   | 0.21   | 0.31       | 1.47| 0.49| 2.75| 1.19 | 0.92    | 2.33|
|                     | MPCDN | 1.08   | 1.10     | 0.55| 0.79    | 1.31   | 0.24   | 0.35       | 1.65| 0.49| 3.23| 1.30 | 0.98    | 2.93|
| Moscow-Voskresensk  | MCPUP | -      | 1.43     | 0.61| 2.55    | 2.41   | 1.68   | 3.65       | 7.79| 0.53| 4.23| 1.58 | 0.93    | 3.42|
|                     | MPCDN | -      | 1.30     | 0.65| 2.97    | 3.38   | 2.06   | 4.27       | 10.3| 0.65| 5.28| 1.87 | 1.06    | 5.17|
| Moscow-Moscow       | MCPUP | 1.08   | 1.10     | 0.55| 0.79    | 1.31   | 0.24   | 0.35       | 1.65| 0.49| 3.23| 1.30 | 0.98    | 2.93|
|                     | MPCDN | -      | 1.43     | 0.61| 2.55    | 2.41   | 1.68   | 3.65       | 7.79| 0.53| 4.23| 1.58 | 0.93    | 3.42|
| Klyazma-Vladimir    | MCPUP | 1.28   | 6.21     | 0.51| 1.10    | 2.2    | 0.47   | 1.29       | 2.33| 3.02| 5.21| 1.05 | 0.88    | 2.75|
|                     | MPCDN | 1.28   | 6.13     | 0.5 | 1.10    | 2.06   | 0.46   | 1.37       | 2.21| 3.16| 5.42| 1.08 | 1.01    | 3.17|
| Upa-Tula            | MCPUP | 1.07   | 2.66     | 1.66| 0.63    | 1.46   | 0.10   | 0.64       | 1.77 | -   | 2.33 | 0.6  | 0.71    | 2.23|
|                     | MPCDN | 1.09   | 2.57     | 1.66| 0.81    | 1.79   | 0.25   | 1.02       | 2.20 | -   | 3.26 | 1.02 | 2.97    | 2.77|
| Dnieper-Smolensk    | MCPUP | 0.42   | 4.65     | 0.50| 0.8    | 1.01   | 0.20   | 0.14       | 8.33| 7.99| 1.66 | 0.38 | 1.25    | 1.38|
|                     | MPCDN | 0.42   | 4.61     | 0.52| 0.86    | 1.45   | 0.43   | 0.22       | 11.8| 8.26| 1.93 | 1.46 | 1.14    | 1.31|
| Don-Donskoy         | MCPUP | 1.10   | 2.60     | 1.23| 0.97    | 2.09   | 1.04   | 1.17       | 6.35| 0.71| 2.26 | 0.64 | 1.39    | 2.07|
|                     | MPCDN | 1.11   | 3.01     | 2.16| 0.88    | 1.82   | 1.22   | 0.90       | 2.99| 3.43| 2.48 | 0.49 | 1.93    | 2.21|

* MPCUP – MCP multiplier upstream of the city.
* MPCDN – MCP multiplier downstream of the city.
* For the Moscow River near the city of Moscow: upstream section – station downstream of Zvenigorod, downstream section – station upstream of Voskresensk.
Often, the content of certain elements was found to exceed their maximum permissible concentrations (MPC) value upstream and downstream of the urban areas. The studied cities could be arranged according to the total number of hydrochemical indicators exceeding their MPC values in relevant sections of the river: Vladimir 10-11 (10 indicators above MPC upstream against 11 elements downstream of the city); Donskoy 10-10; Voskresensk 9-10; Moscow 8-10; Smolensk 7-8; Zvenigorod 7-7; Rzhev 4-6; Murom 5-5 and Kaluga 4-4 (table 1).

The largest number of indicators with values increasing downstream of the city was observed in Moscow (10, of which for 8 the concentration change is higher than 10%). Further, water of the Moscow River near Voskresensk is represented by 9 such indicators with significantly large downstream differences for each of them. Then cities of Tula, Donskoy and Vladimir follow with 8 increasing indicators. However, only 6 of them meet the “10% or more” threshold near the city of Tula, while for the city of Donskoy its number reached 5, and for the city of Vladimir only 2. These are followed by Tver’ and Zvenigorod with five indicators with increasing concentrations. Nevertheless, only 4 of them change sufficiently downstream of both cities. Likewise, 5 indicators with growing concentration were identified for the Dnieper River sections near Smolensk (with 3 of them being significantly large) and Rzhev (downstream of which only 1 indicator changes significantly).

Thus, the largest number of indicators increasing significantly within a studied section and, at the same time, exceeding their maximum permissible concentration could be found near the city of Voskresensk and is equal to 9. Then the city of Moscow (8) and Tula (6) follow. Further, the towns of Donskoy, Smolensk, Tver’ and Zvenigorod have 5 such indicators. Finally, the cities of Vladimir and Kaluga come with 2 indicators, while Murom and Rzhev only have 1. Moreover, each city is characterized by a specific impact on the water quality via different sets of pollutants prevailing in river waters (table 1).

Significant changes in concentration (more than 10%) downstream of the cities was found to be typical for Cu (observed downstream of all the cities considered), phosphates (occurred downstream of 7 cities), phenols (downstream of 6 cities), Zn and BOD$_5$ (downstream of 5 cities). It is also observed for NH$_4$ and Mn (downstream of 3 cities), COD using dichromate method, NO$_2$ and Cr (downstream of 2 cities), as well as for hardness (downstream of 1 city).

Among 154 pairs of “hydrochemical indicator – city” combination considered (14 indicators upstream and downstream of 11 cities), 106 cases concluded in an increase in concentrations downstream of the city. Yet, in 70 of them, an increase in concentrations downstream of the city is revealed when MPC is exceeded in both upper and lower sections of the river. The substantial growth in concentrations which concluded in MPC exceedance only downstream of the city, in its turn, was observed in 41 cases.

Thus, among the cities considered, three groups are identified, differing from each other in terms of the impact they impose on the water quality of the studied rivers. The first of them includes cities (Murom and Kaluga on the Oka River, Rzhev on the Volga River) which insignificantly increase the concentrations of analysed hydrochemical indicators and thereby cause relatively small harm to aquatic ecosystems. The intermediate group includes the towns of Rzhev on the Volga River, Zvenigorod on the Moscow River and Smolensk on the Dnieper River, whilst the cities of the last group, namely Moscow, Tula, Voskresensk and Donskoy, imply the most significant negative impact on the rivers Moscow, Don and Upa, respectively.

4. Conclusions

Several conclusions could be drawn based on long-term monitoring datasets of water quality condition at the gauging stations of the State Observation Network located upstream and downstream of 11 cities of Central Russia covering the period 2005-2019. Observational data included a wide range of annually-averaged values of hydrochemical indicators such as the major ion content and their sum (TDS), heavy metals, biogenic elements, indicators of the organic matter content (BOD$5$, COD) and others (O$_2$, pH, oil products, phenols, suspended matter). The estimation of pollution level was
conducted by comparison of annually-averaged concentrations of about 20 water quality indicators with the defined maximum permissible concentrations for fishery purposes.

1. The most significant increase in the long-term averaged annual concentrations among all analysed hydrochemical indicators downstream of the city, averaged over all the considered sites, was revealed for heavy metals, nitrogen compounds, phosphates and oil products. Cities tend to have a much smaller negative impact on transparency and oxygen content in water, as well as major ions content.

2. Studied cities could be arranged according to the number of indicators, which rise sufficiently (more than 10%) with transition downstream of the city. The following order occurs: Voskresensk, Moscow, Tula, Donskoy, Smolensk, Tver’, Zvenigorod, Vladimir, Kaluga, Rzhev, Murom.

3. 154 pairs of “hydrochemical indicator – city” combinations were considered (all indicators except major ions content). 106 cases concluded in the growth of concentrations downstream of the city, whilst 70 of them have shown this increase only when MPC is exceeded in both upper and lower sections of the river. The major increase in concentrations which concluded in MPC exceedance only downstream of the city, in its turn, was observed in 41 cases.

4. Three city groups were identified among the studied sites. Each of them differs from another depending on the degree of urban impact on the water quality in the analysed rivers of Central Russia. The first of the groups includes cities (Murom and Kaluga on the Oka River, Rzhev on the Volga River) which cause only a limited increase in the concentration of water quality indicators and, thereby, lead to relatively small harm to aquatic ecosystems. The intermediate group includes the cities of Zvenigorod on the Moscow River, Tver’ on the Volga River, and Smolensk on the Dnieper River. The last group consisting of Moscow, Tula, Voskresensk and Donskoy cities have the largest negative impact on the rivers Moscow, Upa and Don, relatively.

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