Longitudinal patterns of different pollutant concentrations in the Setun River

M Tereshina, O Erina, D Sokolov, G Shinkareva and J Vasilchuk
Lomonosov Moscow State University, Moscow, Russia

martereshina@yandex.ru*

Abstract. As one of the most well-studied rivers of the Moscow megalopolis with diverse landscape and anthropogenic impact conditions on its watershed, the Setun River is a unique system suitable for complex urban geochemical research. Data of our ecological monitoring of 2019-2020 show elevated content of multiple elements, including nutrients and heavy metals, in its water throughout the year with several distinctive types of concentration distribution along the course of the river. These patterns correspond to various major impacts in the watershed: concentrations of P, N, Mn and sometimes As are the highest in the upper reaches due to proximity of a landfill and decrease downstream; Cu has a drastic concentration increase below an industrial park, and concentrations of various metals consistently increase downstream from highways and railroads despite the fact that the lower reaches are protected as a part of a wildlife sanctuary. Our findings may serve as a basis for optimizing the water quality monitoring within the framework of comprehensive research of pollution transport in water, soil and air of an urban watershed.

1. Introduction

Small rivers, especially those draining urban and other transformed areas, are usually more heavily affected by anthropogenic pollution, exhibiting generally higher pollution levels and more drastic short-term fluctuations of pollutant concentrations [3, 8]. This effect is caused not only by the sheer number of polluting agencies, but also by the limited self-purification potential of small streams, as well as the absence of strict control over direct pollution in small basins. At the same time, their chemical load can play a significant part in global hydrogeochemical cycles, affecting the water quality on larger regional scales [11, 13].

Correct assessments of any river’s water quality, as well as allocation of specific pollution sources and determination of their effect on water chemistry in different parts of the river, are all dependent on the presence of sufficiently detailed monitoring data [9, 12]. Such monitoring has to take into account the entire structure of water use in the watershed and be combined with modelling or other studies to understand the entirety of processes controlling the water quality dynamics to formulate an effective strategy of environmental protection and provide efficient water management.

The Setun River is one of the few rivers in the Moscow city with a non-canalized channel [4]. Despite the fact that its watershed area partially belongs to a nature reserve, the river experiences a wide variety of human impacts. About a half of the watershed area is covered by residential and industrial land. In the headwaters, the recultivated Salarievo landfill – formerly the largest landfill in Europe – is located. Finally, there are a number of direct waste inflows into the river from multiple
industrial facilities with minimal treatment. There are also excessive studies concerning the geochemistry of different areas of the Moscow City, and specifically the Setun basin, including several works on the river’s water chemistry, which makes it one of the most well researched watersheds in terms of pollution transport and a good model object for further expanding the understanding of the pollution generation and transformation in the rivers of the Moscow metropolitan area.

2. Materials and methods

To examine the patterns of spatial and temporal variation of the Setun River’s water chemistry, a network of 7 stations was established (Fig. 1). The stations were spread nearly evenly along the river, taking into consideration the previously allocated key sources of pollution within the watershed: stations S1-S2 cover the headwaters of the river with the lowest overall level of urbanization but are located down the hill from the former Salarievo landfill; stations S3-S4 are located upstream and downstream from the intersection with the Moscow Ring Road, S5 – below the Ochakovo industrial park and the confluence with the Nareshka River, S6 – below intersections with a railroad and several highways. The S7 station is the final gauge, located at 1 km distance from the river’s mouth. At each station, water samples were taken seasonally – in April, August and November of 2019, and in February, April, June and August of 2020.

Some of the water was filtered through 0.45 μm Millipore filters to separate the dissolved forms of elements. Concentrations of nutrient elements were determined photometrically in filtered and unfiltered samples: phosphates and total phosphorus – by the Murphy and Riley method, total nitrogen – by alkaline persulphate digestion. Chemical oxygen demand (by dichromate method) was also measured in filtered and unfiltered samples. Concentrations of major ions were measured with ion chromatography. Concentrations of heavy metals and other trace elements in filtered water were determined through mass spectrometry and atomic emission spectrometry in an external lab.

For further analysis, only those trace metals were selected whose concentrations exceeded detection limits in the majority of samples: Al, As, B, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, Rb, Sr, V, Zn.

3. Results

Based on collected data, we were able to identify several groups of elements with distinctive types of longitudinal variation in the Setun River.
Total water salinity and concentrations of major ions remained relatively constant between stations. During our monitoring, differences between water salinity at the first and the last stations rarely exceeded 25-30% with a slight decreasing trend towards the mouth. Its maximum was observed during the winter low-flow period and in the spring flood (500-1000 mg/L), and in summer and fall typical water salinity was 450 mg/L. Most of the major ions also had limited variation along the length of the river: for example, hydrocarbonate concentrations were within the range of 250-350 mg/L in all collected samples and varied slightly between the stations.

A steady decrease towards the river mouth was also observed for nutrient concentrations: the highest concentrations of total nitrogen and phosphorus (6.4-12.7 mgN/L and 0.56-1.06 mgP/L, respectively), as well as phosphate (0.11-0.67 mgP/L) were consistently observed at the S1 station. The headwaters were also richer in organic matter, with COD values of 48-88 mgO/L, as opposed to the range of 27-65 mgO/L observed at the rest of the river.

Figure 2. Concentrations of phosphate, copper, manganese and strontium in the Setun River in different seasons.

Trace elements had more heterogeneous patterns of distribution along the length of the river. For Cu, a sharp increase was observed at the S5 station at almost all dates, with concentrations below this point being 1.5-3.6 times higher than at previous stations. For Li and B, similar steep increases were observed at stations S6-S7 (up to 1.3-2.1 times higher than at upstream stations). Sr concentrations
also increased at these points, but had another section with rapidly increasing values between the stations S2 and S3.

For other trace elements, trends with different direction and smaller magnitudes of variation were observed. For example, the highest concentrations of Mn (up to 300-720 μg/L) were observed at headwaters, and then its concentration gradually decreased (similarly to nutrient concentrations) and reached 50-100 μg/L at the river mouth. Likewise, As, Cr, Ni and Rb concentrations also decreased smoothly along the river’s length. By contrast, other trace metals, such as Zn and Mo, exhibited a steady increase of concentrations from the headwaters to the mouth.

For several parameters, such as salinity and turbidity, COD, concentrations of Al, Cd, Rb, V and Li, short-term spikes can also be observed outside of typical spatio-temporal patterns. In these events, the concentrations at one or two stations may increase 2-3 times compared to the remaining part of the river. Most frequently, such short-term increases are observed below the mouths of tributaries that drain industrial areas (rivers Navershka, Ramenka) and are concurrent with dramatic changes in water temperature, specific conductance etc. In winter, sharp increases in water turbidity and concentrations of some elements (Co, sulphates) occur at the S2 station, which is located downstream from a snow-melting facility.

4. Discussion

The features determined in this study indicate a high level of anthropogenic transformation of the Setun River’s water chemistry, expressed by unusual seasonal patterns of nutrient content and salinity and elevated concentrations of elements not typical for the region. Among the considered elements, exceedances of national environmental guidelines [10] were found for phosphate (up to 3.3-fold exceedance) and nitrite (8-fold and more), Mn (up to 14.4-fold), Sr, V, B, Zn, Mo and Cu. This correlates well with the data of municipal water quality monitoring [7].

Both gradual and sharp longitudinal changes of pollutant concentrations are observed in the river, which indicates the presence of both point and diffuse sources of pollution, although some particular sources might not have been uncovered by the extent of this study.

Elevated content of phosphate, total phosphorus and total nitrogen are strictly limited to the headwaters of the river, and their concentrations almost always monotonously decrease downstream, even as the river flows through heavily urbanized and industrialized areas. Furthermore, their highest annual concentrations are observed during the warm period, especially during the summer low flow, while in winter and during floods the maximum concentrations are less extreme. Combined with relatively low concentrations of heavy metals and only slightly elevated COD values, this suggests that a massive inflow of nutrients comes from the Salarievo landfill via leaching and seepage into groundwater [5-6]. Intensity of nutrient loading from this source is therefore dependent on soil temperature and permeability, and on the balance between different genetic types of water inflow, with greatest levels of pollution potentially occurring during dry summer periods when the aquatic ecosystem is already most vulnerable. It is also noteworthy that concentrations of the nitrite form of nitrogen are fairly consistent throughout the river’s length because of constant nitrogen transformations in the river, showing that even a localized nutrient input affects the entire river.

Similar patterns of spatial and temporal dynamics were observed for As, which is also likely to be contained in high quantities in the landfill leachate [1]. Some metals (Mn, Ni, sometimes Cr and Fe), that also had the highest concentrations at the upper stations, had an opposite seasonal regime to that nutrient elements, with maximum concentrations in spring or winter, which may be explained by its inflow with surface runoff during snowmelt and rain events [2]. It is unclear whether excessive amounts of these elements originate in the landfill or have a more natural genesis and come from the least anthropogenically affected parts of the watershed.

An absence of any accurate data on the chemical composition of wastewater that is discharged from the Ochakovoo industrial park into the Setun River and its tributaries limits the detailed analysis of point-source pollution in its watershed, but the magnitude of changes occurring between stations S4 and S5 clearly implies its major effect on the Cu concentration. For other elements, though, the
industrial impact is not observed permanently and is limited to short-term increases of peak concentrations. Such extreme variability, introduced primarily by the inflow of the Navershka River that specifically drains some of the most industrialized areas, acts as an additional complication for water quality control in the watershed.

Interestingly, the highest concentrations of a vast array of elements, most notably B, Li, Mo and Sr, are observed in the lowest part of the river at a significant distance from the most industrialized areas. Their seasonal dynamics are also unstable, and no clear relation to higher or lower water flow is identified. We assume that road dust and runoff from the railroad must be the main source of these elements, as most of them also increase below the Moscow Ring Road, but further examination of available water quality and soil chemistry data is necessary to confirm this hypothesis.

5. Conclusion

Our analysis has allowed to allocate several distinctive subsections of the Setun River that are characterized by different combinations of key pollutants due to different impacts dominating in the genetic composition of water. A wide array of pollution sources causes a variety of patterns in both spatial and temporal dynamics of element concentrations, creating a system where different environmental risks may arise in different hydrological and meteorological conditions. Another major threat comes from the complete volatility of short-term wastewater surges from industrial areas, which can provide manifold increases of concentrations for some elements.

Wide ranges of element concentrations along the river’s length dictate the need to conduct monitoring studies on a dense network of stations, as opposed to gauging the river at its mouth. With further geochemical research on the watershed, it should be possible to assess the entirety of factors affecting the chemical flow of the Setun River and obtain a better understanding of such factors in the Moscow City.

Acknowledgements

Determination of pollutant concentrations and identification of pollution sources was conducted with financial support of the RSF, project number 19-77-30004. Assessment of seasonal differences in pollutant content was funded by RFBR and NSFC, project number 21-55-53039.

References

[1] Aucott M 2006 The fate of heavy metals in landfills: A Review New Jersey: New Jersey Department of Environmental Protection
[2] Cidu R, Biddau R 2007 Transport of trace elements under different seasonal conditions: effects on the quality of river water in a Mediterranean area Applied Geochemistry 22 12 pp 2777–2794
[3] Dassenakis M et al. 1998 Effects of multiple source pollution on a small Mediterranean river Applied Geochemistry 13 2 pp 197–211
[4] Goryunova S V 2010 Vliyanie antropogennogo vozdeystviya na ekologicheskoye sostoyanie maloy gorodskoy reki [Anthropogenic impact on the ecological state of a small urban river] Vestnik MGPU. Seriya Estestvennye nauki [MSPU Bulletin. Series Natural Science] 2 pp 57–64
[5] Kjeldsen P et al. 2002 Present and long-term composition of MSW landfill leachate: a review Critical reviews in environmental science and technology 32 4 pp 297–336
[6] Kulikowska D, Klmiuk E 2008 The effect of landfill age on municipal leachate composition Bioresource technology 99 13 pp 5981–5985
[7] Markin I M 2016 Ekologicheskoye sostoyanie kachestva vody reki Setun’ [Ecological state of water quality in the Setun River] Nauka I obrazovaniye segodnya [Science and education today] 6 7 pp 1–5
[8] Meybeck M, Helmer R 1989 The quality of rivers: from pristine stage to global pollution Global and Planetary Change 1 4 pp 283–309
[9] Meyer A M et al. 2019 Real-time monitoring of water quality to identify pollution pathways in small and middle scale rivers *Science of the Total Environment* **651** pp 2323–2333

[10] Order of the Ministry of Agriculture of the Russian Federation No. 552 of December 13, 2016 (as amended to March 10, 2020) “About approval of water quality standards for fishery waterbodies, including maximum concentration limits of pollutants in the water”

[11] Puczko K, Jekatieriynczuk-Rudczyk E 2020 Extreme hydro-meteorological events influence to water quality of small rivers in urban area: A case study in Northeast Poland *Scientific Reports* **10** 1 pp 1–14

[12] Zhang S, Xin X 2017 Pollutant source identification model for water pollution incidents in small straight rivers based on genetic algorithm *Applied Water Science* **7** pp 1955–1963

[13] Zhang X, Wu Y, Gu B 2015 Urban rivers as hotspots of regional nitrogen pollution *Environmental Pollution* **205** pp 139–144