Content of heavy metals in bed loads of gully systems within the limits of the Saratov city in summer season

A S Sheshnev and D S Majeed
Saratov State University, 83 Astrakhanskaya str., 410012, Saratov, Russia
sheshnev@inbox.ru

Abstract. The article presents the results of the analysis of the chemical composition of bed loads (layer of 0–1 cm) entering through streams in gullies from the limits of the Saratov city to the Volgograd Reservoir. The content of six heavy metals (Ni, Cu, Cd, Cr, Pb, Zn) having the property of accumulation and high toxicity were analysed. The most polluted sediments are found in gully systems, the drainage basins of which are located in industrial zones. The results demonstrate that in the absence of surface runoff treatment systems contaminated waters as well as soils enter water bodies from urbanized areas.

1. Introduction
Gullies in cities are often used by municipal services as a natural transportation route for surface runoff. Significant volumes of pollutants come with runoff from roads to storm drains [1], therefore, due to high contamination, it is recommended to collect and purify water from roads before it is discharged [2]. Hazardous substances such as heavy metals also enter the receiving basin from urban watersheds [3]. Various pollutants are deposited in gully areas of the city [4]. The study of the transportation process of pollutants through gullies and the identification of the chemical composition of bedload sediments is a relevant issue.

The Volgograd Reservoir closes the Volga-Kama water reservoir cascade. It is located in an industrially developed region and accumulates the entire spectrum of chemicals of both natural and anthropogenic origin [5]. As a result of the long-term intake of pollutants to the Volgograd Reservoir, the conditions for water use deteriorate and it gives a rise for issues of hygienic and environmental nature. A set of measures is required in order to restore the ecological potential of the reservoir.

Saratov is the largest city situated on the banks of the Volgograd Reservoir inhabited by around 840 thousand people. The city limits of Saratov are crossed by large gullies with a permanent watercourse flowing into the Volgograd Reservoir. There are residential areas, industrial facilities, and transport infrastructure located in the drainage basin of the gullies. The streams in the gullies receive contaminated groundwater, wastewater from industrial sites, and often household sewage water from low-rise residential buildings that are not connected to the central sewerage system. Unauthorized dumps of household and construction waste are often found in the gully areas. All surface runoff from the city of Saratov flows through the gullies into the Volgograd Reservoir without treatment.

In urban settings, even small streams can deteriorate the quality of water in rivers and reservoirs [6]. The volume of inflow and the chemical composition of runoff are influenced by the intensity of precipitation and the morphology of the drainage basin [7], the type of man-caused impact and the characteristics of urban development [8–10].
The chemical composition of water runoff is often subject to significant seasonal fluctuations [11]. Earlier studies of the water runoff of gullies in Saratov showed that a decrease in the concentration of pollutants is observed in 58.6% of cases, an increase in 30% of cases, and no changes in 11.4% of cases during the summer-autumn runoff minimum compared with the spring runoff maximum [12].

Gully complexes are an important channel for sedimentary material to enter the receiving water body by means of water flows. The formed channel sediments enriched with technogenic materials can be designated as modern technogenic gully alluvium.

Contribution of different sources to the supply of sedimentary material to urban gully complexes during the year is different. By analogy with other water bodies, we should expect the manifestation of seasonal cycles of sediment deposition, differences in physical and mechanical properties and the content of a number of substances. Pollutants enter the soil surface mainly in aerogenic way, then they are carried away to gully complexes, transported in the form of sediments and partially deposited in bed loads. The erosional pattern performs a drainage function, receiving water and solid runoff from the urban storm drains. In conditions of industrial cities, the study of a composition of bed load sediments samples from outflow areas provides fairly reliable information on the technogenic contamination of watercourses [13].

From a geoecological point of view, bottom sediments are of particular interest, reflecting the complex characteristics of the catchment area, the water body, and technogenic sources of discharge. The contamination data of the surface layer (0–1 cm) of bed loads pose as a composite index for a particular time, for example, hydrological seasons. The choice of heavy metals as indicators to be specified is associated with their accumulative ability and high toxicity.

2. Materials and methods

The right bank of the Volgograd Reservoir is an area of high erosional dissection of the slopes of the Volga Upland. The studies on the geochemical features of sediments passing through gullies into the reservoir were carried out on 11 gully systems in the city of Saratov (figure 1). The right bank of the Volgograd Reservoir is an area of high erosional dissection of the slopes of the Volga Upland. The studies on the geochemical features of sediments passing through gullies into the reservoir were carried out on 11 gully systems in the city of Saratov (figure 1).

We analyzed the pollutants identified as priority ones during lithgeochemical studies in the limits of cities in the north of the Lower Volga region. Samples were collected using a plastic scoop and stored in sealed plastic bags taking into account the nature of water bodies (watercourses in gully complexes) and their hydrodynamic regime. The surface layer of sediments was sampled from a depth of 0–1 cm. Sediments in this layer are formed in the form of a saturated suspension, and reliably reflect seasonal changes in their chemical composition. Samples in the outflow areas of watercourses were taken in August 2020 away from the Volgograd Reservoir outside the flood zone during a flood season. All samples were taken from the permanent watercourses (table 1).

The combined sample consisted of 3–5 individual samples taken along the watercourse cross section. The samples of sediments were dried, brought to an air-dry state at room temperature under laboratory conditions, and grounded. The average sample was taken by the quartering method. As an extracting medium we used extracts of 1 mol/dm³ by hydrogen nitrate solution, which describe the content of acid-soluble forms of metals. The content of heavy metals (Ni, Cu, Zn, Cd, Pb, Cr) in the resulting solution was defined by atomic absorption spectrometry in a flame atomization mode on a Kvant-2A spectrophotometer in the laboratory of geocology of Saratov State University.

3. Results and discussion

In order to assess the results of the study, we applied a simplified technique [14]. In the original technique developed for lake water systems, a “standard pre-industrial level” is taken as a background value, which is determined from deep bed loads that were formed before the technogenic impact. In this study, the content of heavy metals in the bed loads of the stream outside the zone of technogenic impact at a distance of more than 20 km from the city of Saratov is taken as the local background value.
Figure 1. Location of sampling sites, outflows of watercourses:
1 – Nazarovka, 2 – Tokmakovskiy, 3 – Zaletaevskiy, 4 – Mutnyj Klyuch, 5 – Krutenkiy,
6 – Mahannyj, 7 – Secha, 8 – Bezymyannyj, 9 – Visyachiy, 10 – Alekseevskiy, 11 – Dudakovskiy.

Table 1. Results of quantitative chemical analysis of bed load samples, mg/kg.

| Sampling sites     | Ni   | Cu  | Cd   | Cr   | Pb   | Zn   |
|-------------------|------|-----|------|------|------|------|
| Nazarovka         | 13.43| 42.99| 0.68 | 1.33 | 13.76| 69.98|
| Tokmakovskiy      | 12.37| 29.03| 3.09 | 4.64 | 9.26 | 97.34|
| Zaletaevskiy      | 10.09| 7.6  | 0.51 | 0.41 | 6.97 | 28.46|
| Mutnyj Klyuch     | 17.3 | 13.02| 10.23| 0.32 | 10.33| 34.81|
| Krutenkiy         | 6.92 | 8.32 | 1.05 | 0.53 | 12.26| 43.12|
| Mahannyj          | 9.41 | 15.62| 0.18 | 0.52 | 19.11| 41.9 |
| Secha             | 3.78 | 4.2  | 0.06 | 0.44 | 4.94 | 12.06|
| Bezymyannyj       | 4.94 | 4.93 | –    | 0.13 | 2.77 | 16.79|
| Visyachiy         | 8.02 | 4.07 | 0.14 | 0.21 | 5.1  | 28.53|
| Alekseevskiy      | 2.91 | 3.06 | 0.1  | 1.17 | 3.02 | 13.27|
| Dudakovskiy       | 2.79 | 2.48 | 0.02 | 0.14 | 2.48 | 9.14 |
| background content| 7.84 | 3.4  | 0.09 | 0.1  | 2.87 | 10.97|

A degree of technogenic contamination of bed loads was estimated by the contamination coefficient 
\( C_f \):
\[
C_f = \frac{C_i}{C_n}
\]
where \( C_i \) – actual element concentration, \( C_n \) – background concentration.
A degree of contamination for each element was defined according to the scheme: $C_f < 1$ – no contamination; $1 \leq C_f < 3$ – moderate degree of contamination; $3 \leq C_f < 6$ – considerable degree of contamination; $C_f \geq 6$ – high degree of contamination (table 2).

### Table 2. Contamination coefficient ($C_f$) and degree of contamination ($C_d$) of bed loads.

| Sampling sites     | Ni   | Cu   | Cd   | Cr   | Pb   | Zn   | $C_d$ |
|-------------------|------|------|------|------|------|------|-------|
| Nazarovka         | 1.71 | 12.64| 7.56 | 13.3 | 4.79 | 6.38 | 46.38 |
| Tokmakovskiy      | 1.58 | 8.54 | 34.33| 46.4 | 3.23 | 8.87 | 102.95|
| Zaletaevskiy      | 1.29 | 2.24 | 5.67 | 4.1  | 2.43 | 2.59 | 18.32 |
| Mutnyj Klyuch     | 2.2  | 3.83 | 113.67| 3.2  | 3.6  | 3.17 | 129.67|
| Krutenkiy         | 0.88 | 2.45 | 11.67| 5.3  | 4.27 | 3.93 | 28.5  |
| Mahannnyj         | 1.2  | 4.59 | 2    | 5.2  | 6.66 | 3.82 | 23.47 |
| Secha             | 0.48 | 1.24 | 0.67 | 4.4  | 1.72 | 1.09 | 9.6   |
| Bezmyannyj        | 0.63 | 1.45 | –    | 1.3  | 0.97 | 1.53 | 5.88  |
| Visyachiy         | 1.02 | 1.2  | 1.56 | 2.1  | 1.78 | 2.6  | 10.26 |
| Alekseevskiy      | 0.37 | 0.9  | 1.1  | 11.7 | 1.05 | 1.2  | 16.32 |
| Dudakovskiy       | 0.36 | 0.73 | 0.22 | 1.4  | 0.86 | 0.83 | 4.4   |

The cumulative impact of several pollutants in the sample was estimated by an integral indicator – the degree of contamination ($C_d$):

$$C_d = \sum C_f = \sum C_i / C_n$$

Assessment of the degree of contamination was performed according to a classification, taking into account the number of analysis elements (N): $C_d < 2N$ – moderate degree of contamination, $2N \leq C_d < 4N$ – considerable degree of contamination, $C_d \geq 4N$ – high degree of contamination [15].

Six elements were defined in the study, so the gradation of $C_d$ levels has the following form: $C_d < 6$ – no contamination; $6 \leq C_d < 12$ – moderate degree of contamination; $12 \leq C_d < 24$ – considerable degree of contamination; $C_d \geq 24$ – high degree of contamination (table 2).

According to the degree of contamination of bed loads, the gully systems are classified as follows: no contamination – 2 (Bezmyannyj, Dudakovskiy), moderate degree of contamination – 2 (Secha, Visyachiy), considerable degree of contamination – 3 (Alekseevskiy, Zaletaevskiy, Mahannnyj), high degree of contamination – 4 (Krutenkiy, Nazarovka, Tokmakovskiy, Mutnyj Klyuch).

In a general picture, the attention is drawn to the high degree of contamination of bed loads in streams, the catchment areas of which are located in industrial zones. There are chemical, petrochemical and machine-building enterprises located in the basins of Nazarovka and Tokmakovskiy streams. These streams as well as Krutenkiy and Mutnyj Klyuch streams receive sewage of unknown origin from the residential area and industrial zones.

There are unauthorized dumps of household and construction waste in all gullies in the southern part of Saratov and in Mahannnyj gully in the north of the city. Pollutants from these dumps enter the stream courses, accumulate in bed loads and flow with runoff to the Volgograd Reservoir.

The minimum degree of contamination of bed loads is recorded in areas where drainage basins are occupied by summer cottages, gardens and woodlands (Secha, Dudakovskiy, Visyachiy, Bezmyannyj gullies). These areas have a sparse road network and there are no permanent sources of polluted wastewater discharge.
4. Conclusion

1. Heavy metals accumulate most intensively in the bed loads of gully systems in industrial areas of cities. In cities situated on the banks of the Volgograd Reservoir, including Saratov, contrary to environmental legislation and urban planning standards, there is no system for treating surface runoff. Watercourses in gullies should be considered as sources of long-term negative impact on the Volgograd Reservoir.

2. When organizing a network for monitoring quality of water in the Volgograd Reservoir, special attention should be paid to waters and bed loads in outflow sites of urban gullies, through which water and solid runoff enters both in an open stream and in storm drains.

3. In some cases, sediments carried by watercourses form debris cones and shallows in the reservoir. Long-term accumulation of pollutants in the bed loads of urban watercourses makes it possible to classify such soils as contaminated and provide that they to be referred as a waste of the corresponding hazard class.

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References

[1] Wang Q, Zhang Q, Dzakpasu M, Chang N and Wang X 2019 Transferral of HMs pollution from road-deposited sediments to stormwater runoff during transport processes Frontiers of Environmental Science & Engineering 13 pp 1–11

[2] Zhang M, Chen H, Wang J and Pan G 2010 Rainwater utilization and storm pollution control based on urban runoff characterization Journal of Environmental Sciences 22 pp 40–46

[3] Sakson G, Brzezinska A and Zawilski M 2018 Emission of heavy metals from an urban catchment into receiving water and possibility of its limitation on the example of Lodz city Environmental Monitoring and Assessment 190 pp 1–15

[4] Potapov A D and Senyushchenkova I M 2010 Geohimicheskie issledovaniya gorodskikh ovrazhno-balochnyh territorial (na primere g. Bryansk) [Geochemical studies of urban territories in rugged relief (by the example of Bryansk)] Geocology. Engineering geology. Hydrogeology. Geocryology 3 pp 213–222

[5] Shashulovskaya E A, Mosiyash S A, Filimonova I G, Grishina L V and Cousina E G 2016 Hydrochemical basis of biological productivity in the closing reservoirs of the Volga cascade Proceedings of the Zoological Institute RAS 320 pp 367–376

[6] Aleksander-Kwaterczak U and Plenzler D 2019 Contamination of small urban watercourses on the example of a stream in Krakow (Poland) Environmental Earth Sciences 78 pp 1–13

[7] Hall K J and Anderson B C 1988 The toxicity and chemical composition of urban stormwater runoff Canadian Journal of Civil Engineering 15 pp 98–106

[8] Jamwal P, Mittal A K and Mouchel J-M 2008 Effects of urbanisation on the quality of the urban runoff for Delhi watershed Urban Water Journal 5 pp 247–257

[9] Voronov A A, Malyskhina E S, Vyalikova E I and Maksimova S V 2018 Sovershlenstvolvane racionalnyh gorodskih inzhenernyh sistem ochistki poverhnostnnyh stochnych vod [Development of the Rational Urban Engineering Systems for the Surface Wastewater Treatment] Urban Construction and Architecture 8 pp 43–50

[10] Zelenáková M, Vranayová Z, Repel A and Kaposztasová D 2019 Surface runoff in urban area – case study New Trends in Urban Drainage Modelling Champ, Springer pp. 152–156.

[11] Ignatavičius G, Valskys V, Bulskaya I, Palulis D, Zigmontienė A and Satkūnas J 2017 Heavy metal contamination in surface runoff sediments of the urban area of Vilnius, Lithuania Estonian Journal of Earth Sciences 66 pp 13–20

[12] Sheshnev A S 2020 Sezonnaya dinamika himicheskogo sostava vod ovrazhno-balochnyh sistem gorodskih territorij (na primere Saratova) [Seasonal dynamics of the chemical composition of
waters from gully systems in urban areas (by the example of Saratov)\] *Bulletin of the Tomsk Polytechnic University. Geo Assets Engineering* 331 pp 7–14

[13] Yanin E P 2002 Tekhnogennye geohimicheskie asociacii v donnyh otlozheniyah malykh rek (sostav, osobennosti, metody ocenki) [Technogenic geochemical associations in sediments of small rivers (the composition, characteristics, assessment methods)] Moscow: IMGRE p 52

[14] Håkanson L 1980 An ecological risk index for aquatic pollution control – a sedimentological approach *Water Researches* 14 pp 975–1001

[15] Fonovoe soderzhanie tyazhelyh metallov v donnyh otlozheniyah poverhnostnyh vodnyh ob"ektov Respubliki Tatarstan. Regional'nye normativy [Background content of heavy metals in bottom sediments of surface water bodies of the Republic of Tatarstan. Regional standards] 2019 URL: http://pravo.tatarstan.ru/rus/oiv/min/eco/?npa_id=352971 (Accessed 20.01.2021)