MAPPING OF HEAVY METAL POLLUTION OF THE ZERAVSHAN RIVER ALONG THE LENGTH OF THE RIVER

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Abstract: The research paper examines the long-term (1990-2019) changes in the amount of heavy metals in the water of the Zeravshan River as a result of anthropogenic impact on the river flow at all observation points. In addition, the pollution of the river with heavy metals was mapped using a geographic information system.

Pollution of the Zeravshan River with heavy metals is caused by industrial, agricultural and municipal wastewater, which is negatively affected by large volumes of wastewater from the cities of Samarkand and Navoi.

According to research, the amount of chromium (VI, III) along the Zeravshan River along the length of the river increased from 1990 to 2019, while the amount of copper, zinc, manganese, nickel, lead, cadmium and mercury decreased along the river. It is obvious that the effluents discharged by mining and processing enterprises located on the territory of Tajikistan also have an impact on the territory of Uzbekistan. Therefore, it is necessary to monitor the chemical composition of wastewater.

Key words: Zeravshan river, observation points, heavy metals, copper, zinc, manganese, nickel, chromium (VI, III), lead, cadmium, mercury**.**

КАРТИРОВАНИЕ ЗАГРЯЗНЕНИЯ РЕКИ ЗЕРАВШАН ТЯЖЕЛЫМИ МЕТАЛЛАМИ НА ВСЕХ ТЕЧЕНИЯХ РЕКИ

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Аннотация: В научной работе рассмотрены многолетние (1990-2019 годы) изменения количества тяжелых металлов в воде реки Зеравшан в результате антропогенного воздействия на сток реки во всех пунктах наблюдения. Кроме того, с помощью геоинформационной системы было картировано загрязнение реки тяжелыми металлами.

Загрязнение реки Зеравшан тяжелыми металлами вызвано промышленными, сельскохозяйственными и коммунальными сточными водами, на что негативно влияют большие объемы сточных вод городов Самарканд и Навои.

По данным исследований, количество хрома (VI, III) по реке Зеравшан по длине реки увеличилось с 1990 по 2019 год, а по реке уменьшилось количество меди, цинка, марганца, никеля, свинца, кадмия и ртути. . Очевидно, что сбросы горнодобывающих и перерабатывающих предприятий, расположенных на территории Таджикистана, оказывают воздействие и на территорию Узбекистана. Поэтому необходимо следить за химическим составом сточных вод.

Ключевые слова: река Зеравшан, пункты наблюдения, тяжелые металлы, медь, цинк, марганец, никель, хром (VI, III), свинец, кадмий, ртуть.

1. Introduction. The Zeravshan River is formed at the confluence of the Mastchokhdarya and Fandarya rivers in the territory of the Republic of Tajikistan, enters the territory of Uzbekistan near the Ravotkhoja dam and flows through

Samarkand, Navoi and Bukhara regions [1].

Currently, the Zeravshan River is one of the water resources in Uzbekistan 85% in irrigated agriculture, 11% in hydropower and thermal power plants, 3% is used in industry, 1% in utilities [2].

Heavy metals are defined as metal elements that have a higher density than water [3]. Heavy metals fall into surface waters through atmospheric precipitation and wastewater discharges [4].

The toxicity and carcinogenicity of heavy metals are also important to study, as each metal has its own mechanism of toxicological action, physicochemical properties. This is because heavy metals in water bodies can accumulate in plants and animals and pass from one organism to another through “food chains” and pose a serious threat to living organisms due to their biological activity and toxicity.

When metals dissolve in water, their mobility increases in the order Pb <Cd <As <Hg. Metals are well absorbed into sedimentary rocks. In rivers, 90% of lead, 30-50% of cadmium and 20% of mercury are deposited in turbid [4]. When it falls into the sediment layer, heavy metals accumulate in the lower sediments and are a source of dangerous secondary contamination.

The Zeravshan River is heavily contaminated with heavy metals, with transboundary impacts and the formation of toxic metals (antimony, zinc) in the catchment area due to the effluents of the Tajik Mining Combine. The amount of landslides in the groundwater is 0.001-0.11 mkg/dm^3 in the First May Dam (Ravotkhodja observation point) and 0.001-0.008 mkg/dm^3 in the Choponota water intake post [5].

According to the Committee for Nature Protection, there are 93 industrial enterprises, 52 wastewater treatment plants, 46 water intake points and 46 recycling facilities, which have a negative impact on the ecosystem of the Zeravshan river basin.

According to Uzhydromet, the Zeravshan River is a highly anthropogenically influenced river in Uzbekistan, which is affected by water intake for various purposes, the development of collector-drainage systems and discharges into the river and other water management measures.

The aim of the study was to study the contamination of the Zeravshan River with heavy metals and to assess changes in river flow (length) and time.

2. Materials and Methods. In the study of pollution of the Zeravshan river with heavy metals, monitoring was carried out at 11 checkpoints of the river:

1. Ravotkhodja (0.4 km below Ravotkhodja dam, around Ravotkhodja village).
2. Samarkand (3 km above the Ak-Karadarya watershed, from the city of Samarkand 6 km northeast).
3. Siab (21 km north-west of Samarkand, 0.5 km below the Siab collector discharge point).
4. Siab (additional) (22 km below the city of Samarkand).
5. Taligulyan (26 km north-west of Samarkand, 3.7 km below the discharge of Taligulyan collector).
6. Kattakurgan (7.2 km northwest of Kattakurgan, 0.8 km below the Chiganak reservoir).
7. Khatirchi (2 km south of Khatirchi village, 0.5 km below Karadarya foothills).
8. Navoi (upper) (3.5 km north-west of Navoi, 1 km above the Navoiazot water supply point).
9. Navoi (lower) (5 km north-west of Navoi, 0.8 km below the Navoiazot discharge point).
10. Bukhara (upper) (1 km above the city of Bukhara).
11. Bukhara (lower) (1 km below the city of Bukhara) [6] is controlled (Fig. 1).

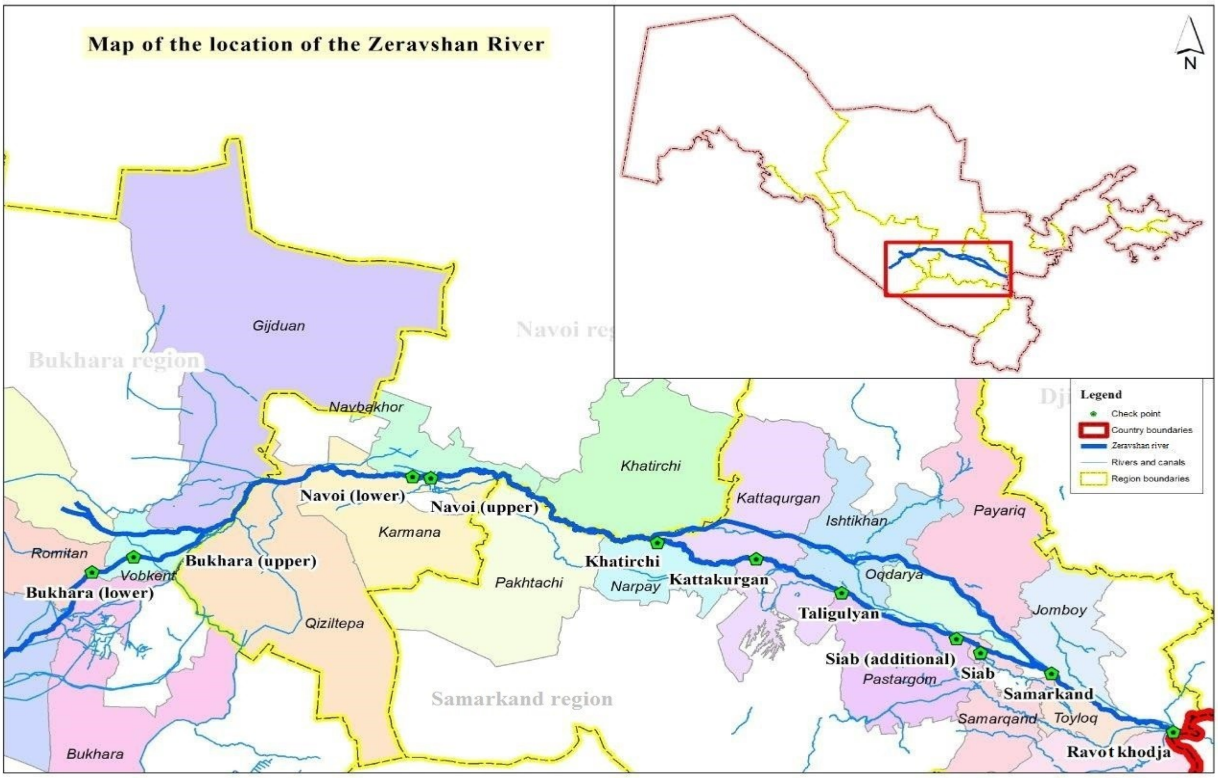

Figure 1. Map of Zeravshan river observation points

In order to assess the pollution of the Zeravshan River with heavy metals, data of the Uzhydromet monitoring network for 1990-2019 were collected, summarized and analyzed, taking into account that the monitoring points above and below Bukhara have been operating since 2011.

Water Analysis. Atomic absorption spectroscopy of heavy metals in the waters of the Zeravshan River was carried out using the method of analysis.

For analysis, 250 ml of the test water sample is placed in a measuring tube and evaporated. Evaporation is carried out until a dry salt residue is formed on the bottom of the pot. After evaporation, 1M HNO_3 acid solution is poured into it and measured by atomic absorption spectroscopy.

3. Results and discussion. The average perennial of the Zeravshan river water (1990-2019) The concentrations of heavy metals are given in Table 1.

Table 1

The average perennial of the Zeravshan river water contamination with heavy metals (1990-2019)

Observation point	Heavy metals, mkg / dm 3								
	Cu	Zn	Mn	Ni	Cr (VI)	Cr (III)	Pb	Cd	Hg
Ravotkhodja	0,13-4,55	1,25-12,3	0,83-3,93	0,83-3,93	0,01-2,0	0,03-3,5	0,05-2,12	0,0008-0,82	0,0008-0,12
Samarkand	0,16-4,13	1,36-14,2	0,27-3,6	0,27-3,6	0,05-2,23	0,02-4,02	0,02-2,12	0,0008-0,85	0,0008-0,07
Siab	0,43-4,47	1,94-16	1,05-7,77	1,05-7,77	0,13-4,06	0,21-3,9	0,06-2,79	0,01-1,17	0,0008-0,13
Siab (additional)	0,37-5,49	1,94-15,1	1,9-6,19	1,9-6,19	0,07-4,22	0,07-3,93	0,05-1,75	0,008-0,92	0,0005-0,15
Taligulyan	0,67-3,55	1,47-15,7	1,47-9,9	1,47-9,9	0,1-2,53	0,11-3,52	0,06-1,21	0,001-0,82	0,0008-0,64
Kattakurgan	0,4-3,85	1,6-34,6	0,78-3,69	0,78-3,69	0,1-2,81	0,22-3,87	0,02-1,72	0,006-0,98	0,0008-1,26
Khatirchi	0,26-4,23	0,46-16,4	0,04-3,69	0,04-3,69	0,22-2,5	0,06-3,15	0,008-1,83	0,005-1,06	0,0008-0,03
Navoi (upper)	0,33-3,84	0,15-10,8	-	-	0,14-5,59	0,84-10,8	0,01-2,77	0,001-0,81	0,0008-0,02
Navoi (lower)	0,45-4,15	0,27-9,29	-	-	0,3-11	1,15-9,8	0,01-1,22	0,004-0,81	0,0008-0,01
Bukhara (upper)	0,6-2,36	1,45-12,2	-	-	0,03-1,01	1,42-3,1	0,05-1,02	0,002-0,51	0,0008-0,001
Bukhara (lower)	0,65-2,57	1,84-13,3	-	-	0,08-0,94	1,2 -2,61	0,1-0,8	0,03-0,52	0,001-0,003

*- not observed in river water.

Copper is widespread in nature and its man-made origin is associated with its use in electrical, construction, automotive and mining industries. In water, copper is suspended, colloidal, and in molten form, often migrating in molten form.

Copper forms relatively stable complexes (carbonates, nitrates, sulfides, chlorides, ammonia, and hydroxyls) with solid bases.

The average perennial (1990-2019) amount of copper in the Zeravshan River water varies in the range of 1.18-2.03 mkg dm^3 along the river length (Table 1). The maximum allowable concentration (MAC) is 1 mkg/dm^3. Contamination of Zeravshan river water with copper concentration exceeds MAC at all observation points, especially when the highest concentration is twice as high as AN at Navoi (lower) observation point (Figure 2).

The main sources of contaminants for copper salts in the Zeravshan region are industrial wastewater from enterprises in the Republic of Tadjikistan and the Navoiazot Production Association [2].

Copper salts belong to class II, its toxic properties are poorly studied. Ingestion of large amounts of copper in humans leads to pilson's disease, in which the bulk of copper accumulates in brain tissue, skin, liver, pancreas.

Zinc is a relatively rare element in nature in the form of sulfide and carbonate ores. It falls into the river waters from the soil and plants.

Zinc iron plating is used in the automotive industry, copper production, textile industry and so on. Zinc dissolves in river water and is well absorbed into sedimentary rocks.

The average perennial (1990-2019) amount of zinc in the Zeravshan River water varies along the river length in the range of 3.2-6.1 mkg/dm^3 (Table 1). This is much lower than MAC for drinking water, but in some cases higher than MAC used for fishing purposes. The allowable norm is 10 mkg/dm^3.

Although the contamination of the Zeravshan river water with zinc concentrations did not exceed MAC at all observation points, the highest concentration was observed at the Kattakurgan observation point of the river (Figure 2).

The oxidizing ability of **Manganese** and the widespread adsorption (superficial absorption, absorption) processes contribute to its accumulation in the lower sediments.

When heavy metals were studied in the river between 1990 and 2019, manganese and nickel concentrations in the Zeravshan River were not observed at the observation posts in Navoi and Bukhara regions, and since 2002 at all monitoring points [7].

The average perennial (1990-2019) amount of manganese in the water of the Zeravshan River varies in the range of 2.04-4.17 mkg/dm^3 along the length of the river.

(Table 1).

The highest manganese content (4.17 mkg/dm^3) was observed at the Taligulyan observation point of the river (Figure 2).

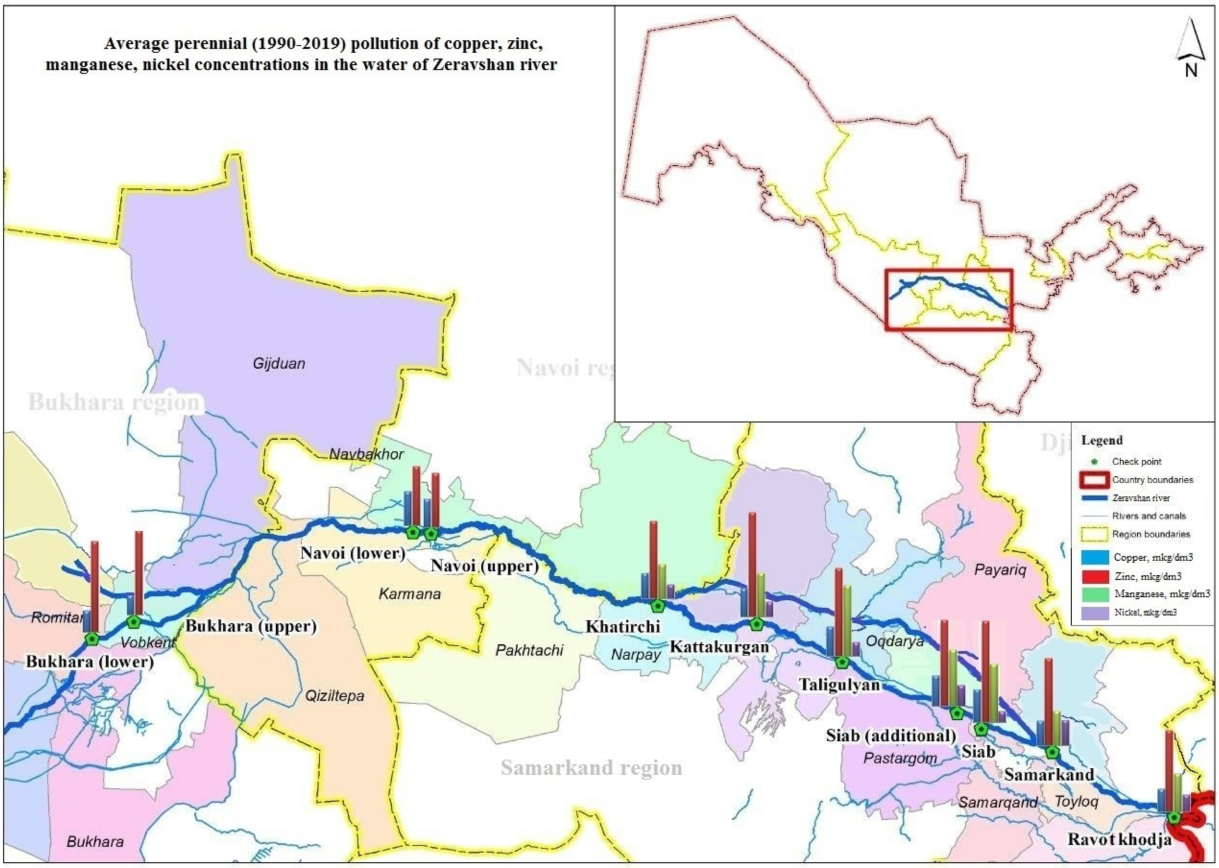

Figure 2. Average perennial (1990-2019) pollution of copper, zinc, manganese, nickel concentrations in the water of Zeravshan river

Nickel is widely used in industry. Its natural origin is associated with soil and volcanic particles, anthropogenic - fuel (57%) and industrial wastewater (25%). Nickel is dissolved and migrates to sedimentary rocks when it is bound to organic matter [8]. Nickel can accumulate in bottom sediments due to adsorption processes [9].

The average perennial (1990-2019) amount of **nickel** in the Zeravshan river water varies along the river length in the range of 0.72-1.51 mkg/dm^3 (Table 1).

The highest level of nickel content (1.51 mkg/dm^3) is observed at the Samarkand checkpoint on the river (Figure 2).

Chromium occurs in nature in the form of the mineral chromite, which contains up to 68% chromium oxide [4]. Chromium is widely used in many industrial processes and as a result pollutes many environmental systems [8]. Chromium is used in metallurgy, chemical industry, agriculture and others. In the high boiling point type, chromium vapors quickly condense in aerosols. Chromium enters surface waters with industrial and agricultural effluents. Chromium mainly migrates along with suspended solids and bottom sediments.

The average perennial (1990-2019) amount of **chromium (VI**) in the Zeravshan River varies in the range of 0.40-2.21 mkg/dm^3 along the river length (Table 1).

Along the length of the river, the concentration of chromium (VI) increases at the Siab (additional), Navoi (upper) and Navoi (lower) observation posts, the highest concentration (2.21 mkg/dm^3) is observed at the Navoi (lower) observation post (Figure 3).

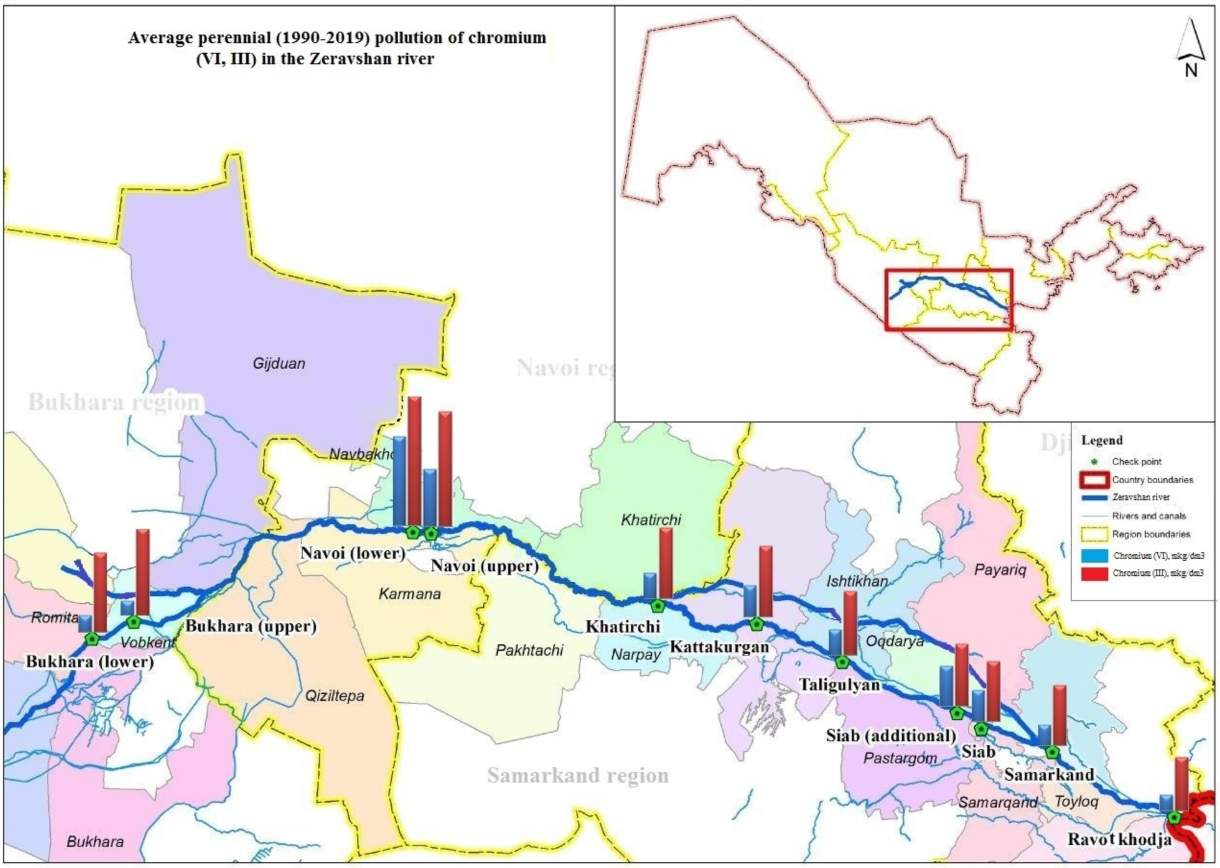

Figure 3. Average perennial (1990-2019) pollution of chromium (VI, III) in the Zeravshan river

The average perennial (1990-2019) amount of **chromium (III)** in the Zeravshan River varies in the range of 1.35-3.21 mkg/dm^3 along the river (Table 1).

The concentration of chromium (III) increases along the length of the river, with the highest concentration (3.21 mkg/dm^3) observed at the Navoi (lower) observation point (Figure 3).

According to the research of Rubinova F.E and Ivanov Yu.N. [10], among the rivers in the Aral Sea basin, near the city of Navoi on the Zeravshan River, the highest level of chromium pollution is observed.

Lead enters river water from the atmosphere and various industrial effluents. While more than 50 percent of lead is produced by humans by burning gasoline and oil, the second most powerful source is metallurgy.

Lead affects the kidneys, liver, heart, brain and other soft tissues of the human body.

The average perennial (1990-2019) amount of lead in the Zeravshan River varies in the range of 0.3-0.88 mkg/dm^3 along the river length (Table 1).

The lead concentration decreases from top to bottom along the length of the river, with the highest concentration being observed at the Siab observation point (Figure 4).

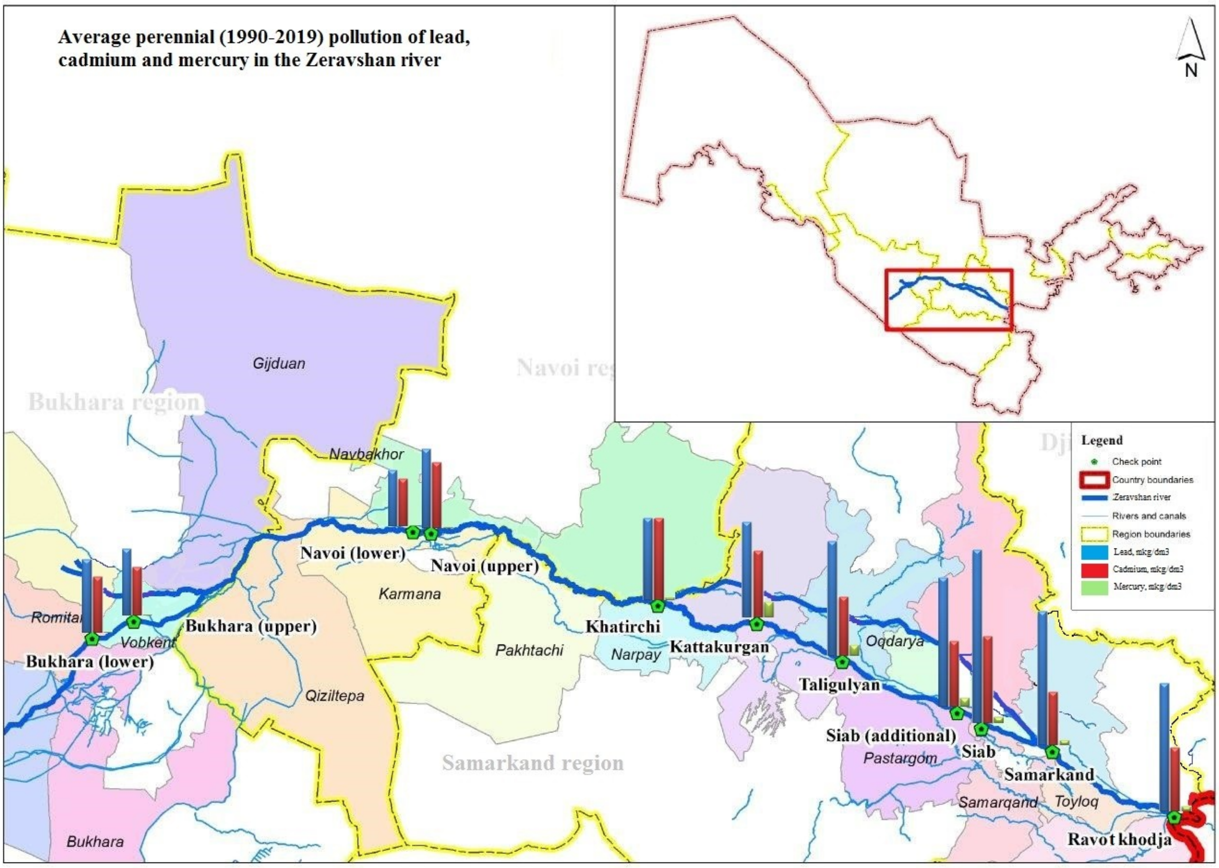

Figure 4. Average perennial (1990-2019) pollution of lead, cadmium and mercury in the Zeravshan river

Cadmium is present in zinc in carbonate and sulfide ores, and its toxicity is similar to that of mercury and arsenic. Anthropogenic pollution occurs due to wastewater from metallurgy, mining, chemical industries and others [4]. The highest levels of cadmium compounds in the environment accumulate in sedimentary rocks [8]. Cadmium is well absorbed into underwater sediments, but as mineralization increases and pH decreases, it enters solutions and causes secondary contamination.

The average perennial (1990-2019) amount of cadmium in the Zeravshan river water varies in the range of 0.23-0.44 mkg/dm^3 along the river length (Table 1).

Cadmium concentration decreases from top to bottom along the length of the river, the highest concentration is observed at Siab and Khatirchi checkpoints (Figure 4).

Mercury is a common toxic and polluting substance in the environment, causing serious changes in body tissues and causing various adverse effects on health [8]. However, about 50 percent of its presence in river waters is related to economic activity. Mercury is widely used in electrical appliances, chemical industry, pharmacology and others. In natural waters, mercury and its compounds are well absorbed into sediments, especially where sulfur is present, it is intensively absorbed. The formation of organic mercury compounds can lead to mercury mobility and secondary pollution of water bodies.

The average perennial (1990-2019) mercury content in the Zeravshan River water varies in the range of 0.001–0.07 mkg/dm^3 along the river length (Table 1).

The mercury concentration along the river length does not exceed the MAC, however, the highest concentration (0.07 mkg/dm^3) is observed at the Kattakurgan observation point (Figure 4).

When analyzing the changes in the average perennial heavy metal content of **Zeravshan rive**r water every 5 years between 1990-2019, the concentration of copper, zinc, chromium (VI) in 1990-1994 was higher than in other years and decreased every 5 years compared to 2015-2019. the amount of lead and cadmium increased inversely (Table 2).

Table 2

Changes in the average perennial heavy metal content of Zeravshan river water in different periods (1990-2019)

Observation point	Time interval	Heavy metals, mkg / dm 3								
		Cu	Zn	Mn	Ni	Cr (VI)	Cr (III)	Pb	Cd	Hg
Ravotkhodja	1990-1994	2,31	9,45	-	0,73	1,16	0,48	-	-	0,07
	1995-1999	0,41	7,05	2,65	1,41	0,18	0,61	1,2	0,02	0,015
	2000-2004	0,97	4,43	1,27	0,25	0,34	0,9	0,51	0,06	0,01
	2005-2009	1,83	2,82	-	-	0,32	2,46	0,93	0,17	0,006
	2010-2014	1,47	2,11	-	-	0,36	1,89	0,27	0,55	0,012
	2015-2019	1,38	2,63	-	-	0,14	1,74	0,53	0,62	0,001
Samarkand	1990-1994	2,35	8,98	0,27	-	1,14	0,33	0,001	-	0,05
	1995-1999	0,69	6,77	1,98	1,1	0,21	0,76	0,77	0,01	0,01
	2000-2004	0,64	7,01	2,15	2,12	0,7	1,01	1,24	0,04	0,02
	2005-2009	1,98	2,83	-	-	0,29	3,03	0,67	0,1	0,005
	2010-2014	1,47	2,18	-	-	0,55	1,93	0,22	0,47	0,008
	2015-2019	1,8	2,84	-	-	0,26	1,93	0,82	0,69	0,001
Siab	1990-1994	1,99	11	-	0,23	2,5	0,39	-	-	0,1
	1995-1999	1,75	7,67	4,38	0,68	0,61	1,47	1,14	0,08	0,02
	2000-2004	1,35	4,46	1,81	0,84	0,79	0,67	0,9	0,22	0,01
	2005-2009	2,49	3,22	-	-	0,35	2,31	0,89	0,32	0,01
	2010-2014	1,83	3,54	-	-	0,51	1,86	0,35	0,55	0,017
	2015-2019	2,37	5,62	-	-	0,31	2,06	0,87	0,89	0,001
Siab (add.)	1990-1994	2,81	7,11	-	0,65	3,31	0,57	0,002	-	0,107
	1995-1999	1,47	7,09	3,57	1,31	0,92	1,67	0,52	0,03	0,048
	2000-2004	1,04	5,35	1,9	1,09	0,47	1,21	0,86	0,12	0,008
	2005-2009	2,27	2,9	-	-	0,38	1,88	0,76	0,25	0,007
	2010-2014	1,79	2,98	-	-	0,51	2,12	0,31	0,53	0,006

	2015-2019	1,87	5,13	-	-	0,52	1,85	0,85	0,72	0,001
Taligulyan	1990-1994	2,18	11,2	-	0,3	1,94	0,45	0,001	-	0,201
	1995-1999	1,13	6,59	4,83	0,97	0,41	0,99	0,59	0,02	0,019
	2000-2004	1,9	4,23	2,54	0,3	0,5	1,83	0,72	0,24	0,002
	2005-2009	1,99	2,65	-	-	0,36	2,54	0,86	0,17	0,008
	2010-2014	1,52	2,21	-	-	0,49	1,85	0,24	0,45	0,01
	2015-2019	1,9	4,12	-	-	0,27	1,89	0,67	0,64	0,0011
Kattakurgan	1990-1994	2,14	20	0,78	6,56	1,95	0,45	-	0,01	0,344
	1995-1999	1,56	7,07	2,43	0,93	0,96	1,98	0,61	0,04	0,02
	2000-2004	1,1	5,23	2,82	1,02	0,71	1,49	0,25	0,05	0,011
	2005-2009	2,09	2,67	-	-	0,42	2,53	0,51	0,22	0,004
	2010-2014	1,5	3,45	-	-	0,55	2,19	0,22	0,52	0,008
	2015-2019	1,94	3,67	-	-	0,24	1,96	0,72	0,72	0,0008

Continuation of Table 2

Khatirchi	1990-1994	1,37	9,14	0,53	0,36	1,49	0,33	0,08	0,002	0,02
	1995-1999	0,79	6,23	2,3	0,87	0,89	1,43	0,47	0,05	0,021
	2000-2004	1,29	3,79	1,43	0,92	0,95	1,09	0,39	0,29	0,002
	2005-2009	2,28	2,73	-	-	0,34	2,46	0,24	0,31	0,007
	2010-2014	1,64	2,17	-	-	0,62	2,32	0,27	0,57	0,013
	2015-2019	1,7	3,96	-	-	0,34	2,12	0,69	0,68	0,001
Navoi	1990-1994	2,83	3,46	0,25	0,21	3,82	7,23	-	-	-
(upper)	1995-1999	1,69	2,68	-	-	1,99	2,11	1,44	-	-
	2000-2004	1,08	1,86	-	-	1,43	1,72	0,22	0,14	0,007
	2005-2009	2,01	2,91	-	-	0,63	2,43	0,07	0,22	0,001

	2010-2014	1,84	1,65	-	-	0,72	1,93	0,28	0,53	0,01
	2015-2019	1,13	6,7	-	-	0,44	2,52	0,51	0,35	0,0009
Navoi (lower)	1990-1994	3,23	3,89	-	0,74	7,08	7,44	0,25	-	-
	1995-1999	2,33	3,14	-	-	2,99	2,84	-	-	-
	2000-2004	1,37	2,17	-	-	1,92	2,32	0,18	0,036	0,004
	2005-2009	2,29	3,71	-	-	0,65	2,87	0,16	0,24	0,004
	2010-2014	1,84	2,05	-	-	1,14	2,15	0,31	0,26	0,005
	2015-2019	1,37	5,98	-	-	0,48	2,47	0,54	0,32	0,0008
Bukhara (upper)	2011-2014	1,21	1,91	-	-	0,57	1,74	0,11	0,21	-
	2015-2019	1,15	7,34	-	-	0,26	2,5	0,47	0,26	0,001
Bukhara (lower)	2011-2014	1,34	2,49	-	-	0,57	1,82	0,23	0,208	-
	2015-2019	1,27	7,57	-	-	0,32	2,1	0,45	0,32	0,002

The main sources of pollution of the Zeravshan river. The main sources of water pollution in the Zeravshan River in Uzbekistan are Siab, Chiganak, Khauzaksay, Taligulyan collectors and Boynazar sewage treatment plants in Samarkand region [11], Navoi Upper, Central, Mirza-Mumin, Bishkent, Sanitary collectors in Navoi region [12].], In Bukhara region are Dengizkul, Central Bukhara, Ogitma, Parsankul, Main drainage tract, Main Karakul, Central Alat, Southern Alat, West Karakul, Bibishirin, West Romitan collectors [13]. However, the discharge volume is higher in Siab and Navoi (upper) collectors than in other collectors (Figure 5).

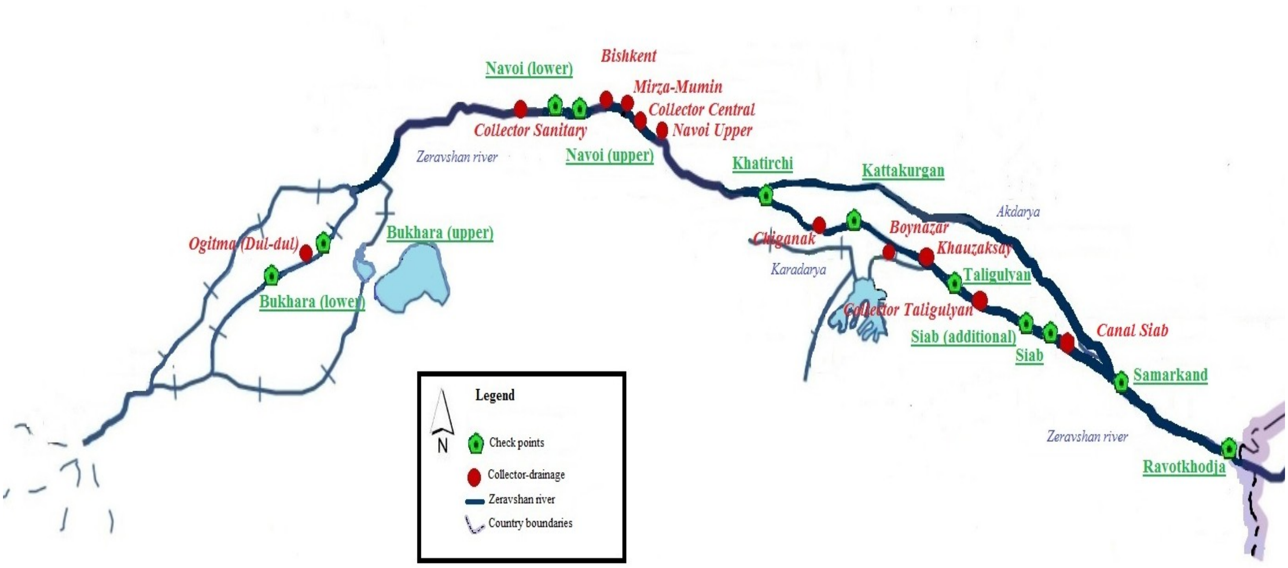

Figure 5. The main sources of pollution of the Zeravshan river

Heavy metals are among the major pollutants that need to be controlled in all areas. Due to the high levels of cadmium, chromium, lead and mercury poisoning among public health metals, these metal elements are considered systemic toxicants, the low concentration of which also leads to damage to human body organs. In determining the number of hazardous pollutants, their toxicity, stability, and level of accumulation in the external environment are important.

4. Conclusion. The high concentration of copper in the Zeravshan River water exceeds the MAC at all observation points along the river length. Also, the amount of chromium (VI, III) is highest at the Navoi (lower) checkpoint. Although the levels of zinc, manganese, nickel, lead, cadmium and mercury did not exceed MAC, they were higher in Siab, Kattakurgan, Navoi (upper) and Navoi (lower) observation posts than in other observation posts. Although river water is often used for irrigation purposes, it is toxic and migratory, and the use of water for recreation and fishing is dangerous to human health.

The Zeravshan River is heavily polluted by heavy metals, starting in Tadjikistan and migrating along the length of the river in Uzbekistan.

The analysis shows that in the period from the beginning of the river to the confluence of the river, there is an increase in the amount of heavy metals in the areas where large industrial enterprises are located and in the areas where wastewater is discharged.

According to research, the water of the Zeravshan River is polluted with heavy metals due to the discharge of wastewater.

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