

Review Article

Study of Pharmaceutical Pollution of Water Entering the Alazani River from the Treatment Facility of the Village Kondoli (Georgia) and Possible Consequences for the Ecology of the Kakheti Region

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Abstract - Over the past decade, the number of articles on the detection and analysis of pharmaceuticals in water has increased significantly due to improved methods and new, more accurate measurement tools. Antibiotics, painkillers, heart drugs, oral contraceptives and antidepressants are just some of the pharmaceuticals which concentrations is slowly increasing to disturbing level in river systems and underground water. Ecotoxicity data, as well as information on current pollutant dispersion levels, remain scarce and focus on prescription and widely used over-the-counter medicines. Even these chemical pollutants negatively affect living organisms, ecosystems and public health. The purpose of this article is to identify pharmaceutical contamination at the treatment facilities of the city of Telavi (Georgia). At the outlet of this facility, wastewater samples were taken for the presence of 13 pharmaceuticals and the sampling taken was analyzed on a UV-8200 spectrophotometer in the Water Resource Laboratory at the Georgian Technical University. There were found Antibiotics: Terbinafine, Clarithromycin, Enalapril detected less than 4.00 ng/L, Ciprofloxacin 12757.1193 ng/L, Cetirizine 1913.5679ng/L, Citalopram 391.8258 ng/L, Enrofloxacin 191.3568 ng/L, Ofloxacin - 50.1173 ng/L, Trimethoprim – 4.0094 ng/L, Metoprolol – 3.6449 ng/L, water-soluble alkaloid Caffeine at 54.4407 ng/L, Nicotine – 12.5046 ng/L, painkillers and antipyretic medicine Paracetamol is present at low concentrations – 2.5964 ng/L. Since the standard design of the Telavi city treatment facilities does not provide special equipment for the treatment of wastewater from active pharmaceutical elements, it'll be recommended to Telavi Municipality add one of the treatment equipment to the development project of this treatment facility.

Keywords - Pharmaceuticals contaminants, Treatment facilities, Wastewater treatment, Spectrophotometric method, Pharmaceutical market of Georgia.

1. Introduction

In the modern era, where the problem of maintaining the ecological balance is so acute, the cause of which is the local conflict existing in the "human-nature-society" system, particular importance is acquired modeling the physical, chemical and biological processes occurring in the biosphere, more precisely, modeling such systems that accurately describe the range of distribution of the number of pollutants in the environment, as well as the speed of distribution and their impact on biosystems and humans [35].

The methodological basis for such models will be a systemic analysis of qualitatively different processes: use and protection of natural resources, the impact of urbanization, anthropogenic loads and limit permissible concentrations of loads. Pharmaceutical contamination of surface and underground water that has not properly studied remains a

worldwide problem. To solve the large-scale problem of pharmaceutical pollution, it is important to simulate the interaction of a person with the environment, as a model of a complex "system," which, based on system analysis, will assist in identifying foci of pharmaceutical pollution, determining its spread and identifying the concentration of chemically active substances.

Qualitative and quantitative evaluation of pharmaceutical contaminants remains a subject of scientific research rather than part of a permanent monitoring program. This can be judged by the numerous articles that appeared in scientific journals. In the study of pharmaceutical pollution of water resources on the example of the Kura River (Tbilisi, Georgia), were identified and laboratory confirmed pollution with an increased content of psychostimulants, analeptics, antibiotics of the macrolide group and analgesics in the riverbed, within



city. The location of the sampling sites was chosen by the location of the accumulation of pharmaceutical, tourist and food facilities:

ZAHES-Tbilisi, Didube-Tbilisi, between Tbilisi and the Ponichala reserve and in front of the Algeti tributary. The results of the study were follows:

Table 1. Pharmaceutical pollutants in Kura River [6]

Name of Pharmaceuticals	ZAHES-Tbilisi, most upstream point	Didube	Between Tbilisi and Ponichala Reserve	Before Algeti Tributary
	Concentrations (ng/l)			
Caffeine (psychostimulant and analeptic)	4284	6500	786	2982
Clarithromycin (macrolide antibiotic)	120	179	–	–
Cotinine (nicotine)	120	231	152	74
Nicotine (nicotine)	864	1283	1493	480
Paracetamol (analgesic–antipyretic)	230	138	310	129
The total amount of pharmaceuticals by site	5618	8331	2741	3665

According to the research results, the highest concentrations of pharmaceutical pollutants were observed at the places of discharge into the river of insufficiently treated sewage and wastewater (Didube and between Tbilisi and Ponichala). The lowest concentrations indicate the places with the least anthropogenic impact (before the Algeti tributary and ZAGESI - Tbilisi). Pharmaceutical pollution of the Kura River can have a negative impact on the environment (especially the river ecosystem) and human health, especially if they use the water of the Kura River for drinking or agriculture. After analyzing the pharmaceutical markets, in particular, the increase in sales of medicines in the USA, Europe, Japan, as well as in Georgia, the authors draw a parallel between the increase in the quantitative indicator of water pollution with an increase in this economic component [6].

Noteworthy is the analytical work of Chinese scientists, which describes the distribution of identified antibiotics in global rivers. The work is based on the analysis of more than 600 scientific articles from 1999 to 2021; a database has been created containing 90,000 records of 169 antibiotics and their metabolites in the surface waters of 76 countries. During the study of materials, high levels of pollution were found in rivers in Africa and South America (for example, concentrations of Sulfamethoxazole (SMX) and Trimethoprim (TMP) significantly exceeded the predicted value). The paper presents the results of a study to identify areas of high concentration of antibiotic contamination and maps of high-risk areas at regional and global levels. According to the authors, it is necessary to create a specific plan for combating surface water pollution with antibiotics for each region and to implement the coordination of the measures described in this plan at the level of sectoral, regional and international cooperation [15].

Recently, the number of studies to establish the impact of pharmaceuticals on the underwater world has increased. The interest deserves a study by the Toxicology Research Center of the University of Guelph (Guelph, Canada), where a group of scientists created an experience in an irrigation pond (in an underwater microcosm in which there were fish, plankton,

bacteria and algae), where several fences were arranged. A cocktail from the medicines of ibuprofen (a nonsteroidal anti-inflammatory drug), fluoxetine (an antidepressant, a selective serotonin reuptake inhibitor), and ciprofloxacin (an anti-infective anti-inflammatory drug) drugs were administered at predetermined intervals at concentrations of 6, 10, and 10 μ g/L, respectively (low contamination). 60, 100, 100 μ g/l (average contamination level), 600, 1000, 1000 μ g/l (high contamination level).

The duration of this exposure in water was 35 days. The results of the studies were as follows: with a low level of pollution, no changes were found in the aquatic microcosm, however, with medium and high pollution, the death of fish and macrophytes, a decrease in their diversity and an effect on the level of biocenosis in plankton populations were noted.

In conclusion, the authors point to the need to expand research, determine the homology of sensitivity, form a list of the combination of ecotoxic pollutants and assess the risks of their impact on the underwater world. This information can be used to determine the state of the ecosystem the selection of cleaning methods to reduce toxic effects on the environment [28]. To achieve high environmental safety, it is necessary to implement the correct environmental policy, which implies monitoring the environment at any time, as well as in any part of the investigated facility, which will guarantee timely and necessary measures to maintain an environmental balance.

2. Main Part

The article discusses the detection of antibiotics and other pharmaceuticals in city Telavi wastewater at the outlet of the treatment facility.

Treatment facility is located on the right bank of the Alazni River (the length of the river is 390 km, the basin area is 11 800 km², the average water discharge is 98 m³/sec.), at an altitude of 356 meters above sea level, on the territory of the old treatment facility, northwest of the villae Kondoli, Telavi municipality and occupies about 86,500 m² [8].

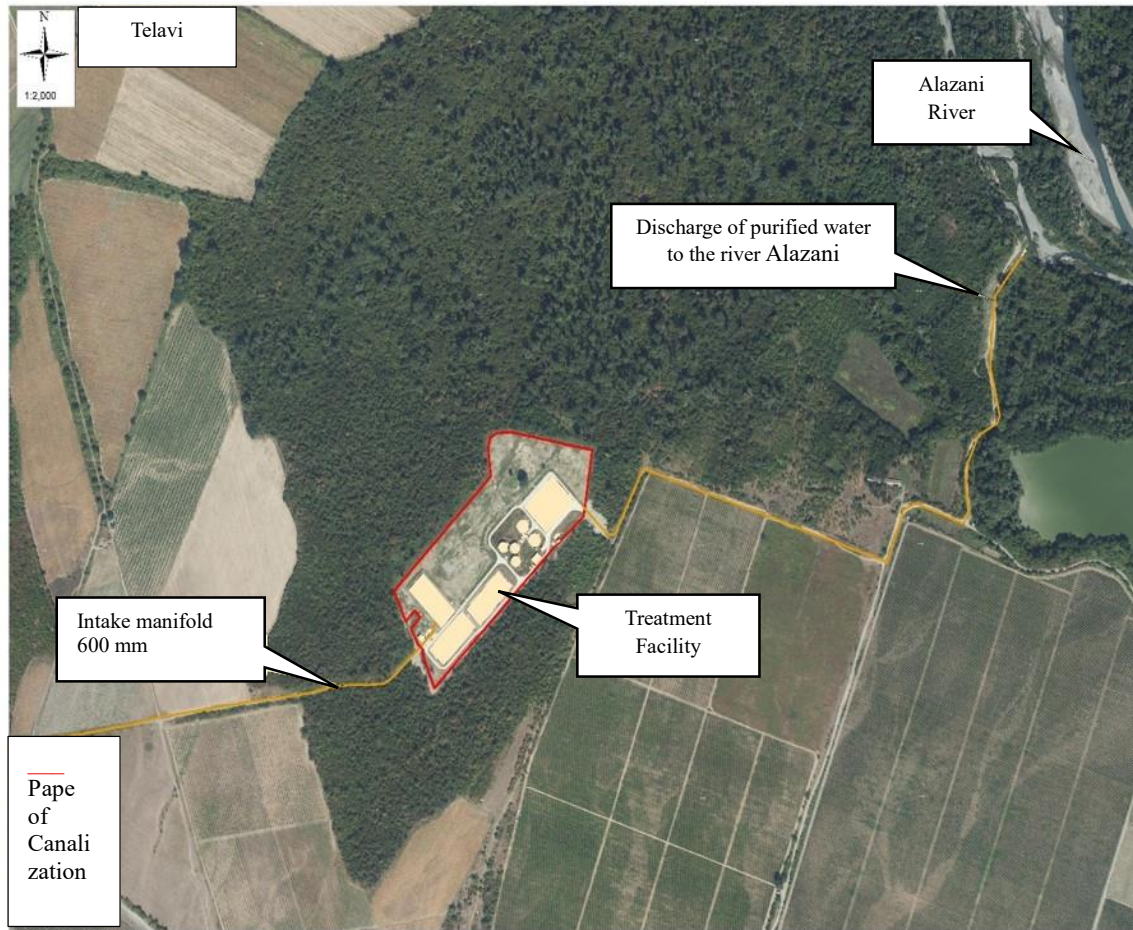


Fig. 1 Telavi treatment facility

The treatment plant project was funded by the Swedish government through the Swedish International Development Agency (SIDA) and was implemented by the Municipal Development Fund of Georgia (GMDF). The construction of treatment facilities will be carried out in two stages: Stage I, until 2030, when the population will be 52,000, and Stage II, until 2040, when the population will reach 91,000. Currently, in 2026, it is 31,027 people, and the annual flow is 1,531,130 m³/year. Large industrial facilities are connected to the system, in particular: Kartuli Marani LLC, Rtvelisi LLC, Telavis Gvynis Marani LLC, Vaziani Company LLC, Alcoholic Beverages Company LLC, 16 medical institutions in the municipality Telavi (including hospitals, clinics and ambulance stations with a total number of 260 units), about 30 hotels, 70 catering facilities, and travel companies. In the vicinity of the treatment facilities, agriculture is quite well developed [19].

The design of treatment facility project is implemented by LLC "United Water Supply Company of Georgia". The data on the project have been kindly provided by the above-mentioned organization after the appeal of the Faculty of Civil Engineering of the Georgian Technical University [19].

According to the standard project (first phase up to 2030), the treatment facilities ensure the removal of biochemical oxygen consumption and chemical consumption of oxygen, suspended particles from wastewater, and at second phase (up to 2040), the removal of nitrogen and phosphorus will be added to this list. At the first stage of treatment, wastewater entering the treatment facilities is subjected to mechanical treatment on large-sized grates, two automatic fine-grained grates and a sand trap. Being based of the corresponding project contract, household waste that got on the grates is transported to the household waste landfill, and settled sand is pumped into the sand storage using a sand pump.

After the mechanical purification stage, the purified water undergoes a biological purification process in anaerobic tanks (3 units), where organic substances decompose, and silt stabilization is carried out, and suspended particles (crude silt) settle in anaerobic tanks. Settling is carried out up to a certain limit (600 mm) and is pumped to silt fields for drying silt using a floating boat (amphibian), pipelines and pumps. After anaerobic tanks, water is purified using biofilters. Purified water continuously sprays onto biofilters by means of rotary sprinklers, organic particles dissolved in water are purified by

aerobic process and microorganisms. Purified water enters the perforated bottom of the biofilter and overflows into the drainage channel, from where water is supplied to the secondary settling tank.

After passing through biofilters, the removed particles of microorganisms settle in the secondary settling tank and are periodically pumped by pumps to the silt drying field [19].

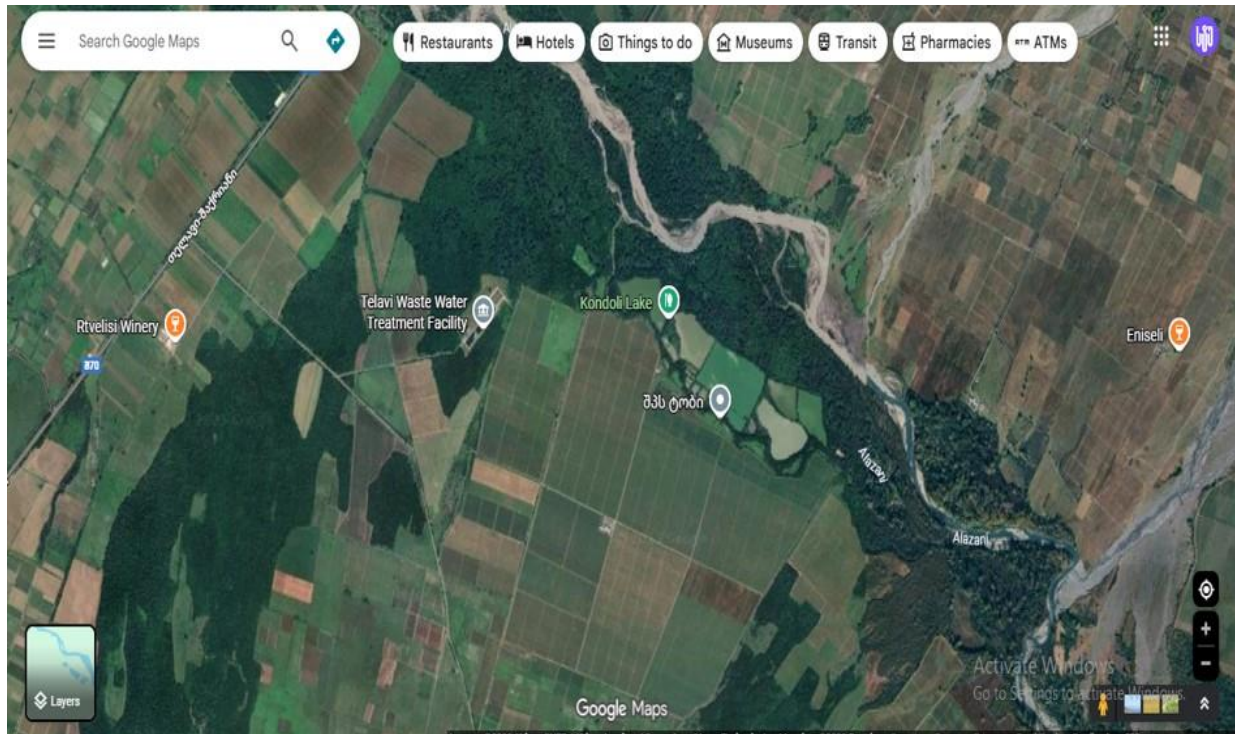


Fig. 2 Fish farm LLC "Tobi"

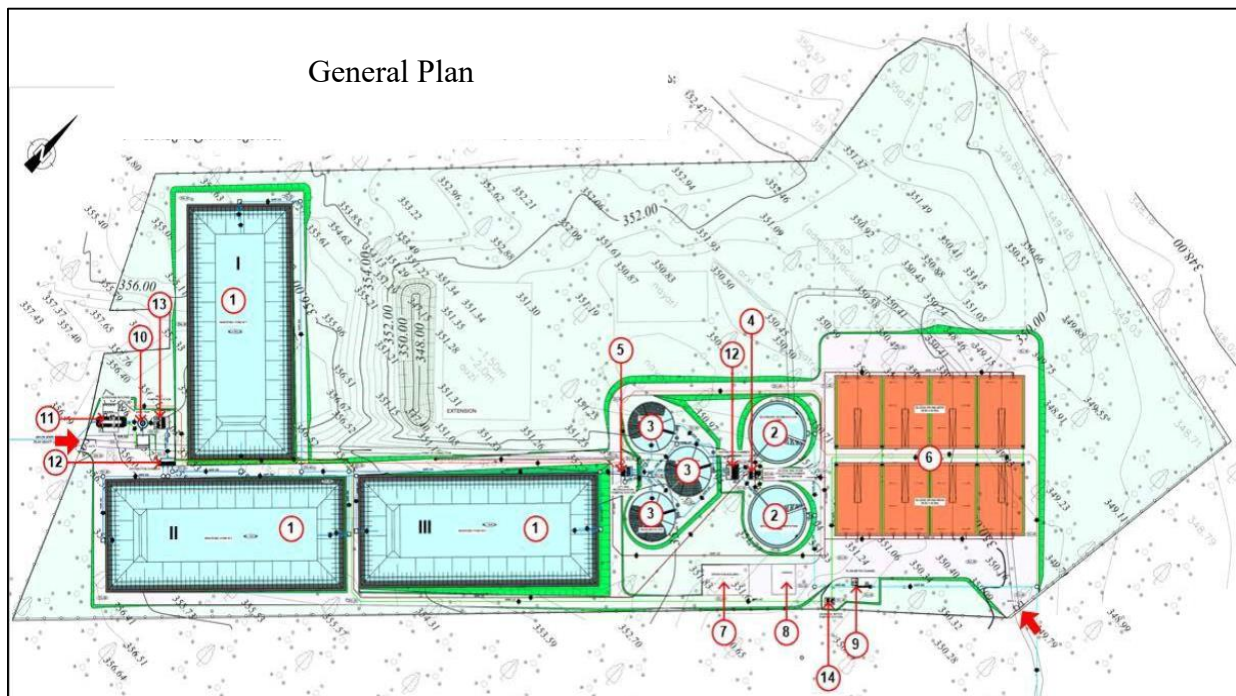


Fig. 3 Treatment plant plot plan, 1:500. Anaerobic tank (1), Secondary sedimentation reservoir (2), Biological filter (3), Silt collection well and pumping station (4), Biological filter pump (5), Silt field (6), Operating building (7), Garage (8), Hydrometer (9), Sand trap (10), mechanical cleaning building (11), Distribution chamber (12), Pumping station (13), and Drainage water pumping station (14). [19]

Treated water is discharged into the river in Alazni at one point. According to the project quality of wastewater meets the requirements of the technical regulation of the Government of Georgia dated December 31, 2013, No. 425, " Regulation of activities having impact on surface waters and discharging pollutant substances in waters" [19, 21].

As can be seen from the description of the technical capabilities of the Telavi treatment facility, neither in the first nor in the second phase of operation of this facility are wastewater pharmaceutical pollution treatment technology identified.

3. Materials and Methods

The purpose of this article is to show the results of a study that was carried out at the outlet of the sewer of the Telavi treatment facility. Water quality analysis is carried out by the Resolution No 425 of 2013 of Georgian Government on Protection of Surface Waters of Georgia from Pollution [22].

To solve the problem, the following steps were taken:

- A group of specialists for sampling was formulated (environmental specialists from the municipality of Telavi and employees of the Treatment Plant)
- Update sampling area. Since the section of the river where the treated water is discharged from the treatment facilities has a high and steep bank, it was not possible to take a sample directly from the river. Therefore, as an exception, sampling was carried out in the area between the treatment facilities and the river. In addition, it should be borne in mind that the concentration of pharmaceuticals in the water is very small, the probability of their detection in the river far from the place of water discharge (taking into account the flow rate, temperature, dilution coefficient, turbulence, turbidity, etc.) is extremely low.
- According to a special USGS protocol, to prevent contamination of water samples, when taking samples, dark glass bottles (5 mL), 13 disposable syringes, filters (0.40 - 0.45 μ m) for filtering water for each sample, and a treated bucket (500 mL) were used.
- All samples are placed in a collection chamber, preserved and inserted into a portable refrigerator (-10⁰) for transportation. [12, 13, 32].

The analysis was carried out by spectrophotometry on a UV 8200 apparatus (wavelength range 190-1100 nm, spectrum width 4 nm, wavelength accuracy $\pm$ 1 nm, photometric error $\pm$ 0.5%T, stability 0.002A/h @ 500 nm), in the laboratory "Water Resources of the Georgian Technical University."

Laboratory safety protocols were followed to ensure the reliability and veracity of the results. The sequence of actions was as follows:

- Solutions of standard samples concentration (2, 4, 6 mg/l) were prepared for all tested medicaments. Wavelength range 200-400 nm (For each medicament individually according to the existing protocol), for setting up the Behr-Lambert-Bouguer standard curve: (1) was measured the absorbance in a fixed wavelength point; (2) were measured standard samples; (3) test results were stored in the RAM;
- The new curve was used for measuring the unknown sample's concentration; the result was stored in the RAM [34].

Overall, the measurement results clearly indicate that treated wastewater is an important route for the penetration of various xenobiotic pharmaceuticals into surface water and groundwater as well. The study reports the presence of Ciprofloxacin (12757.1193 ng/l), Cetirizine (1913.5779 ng/l), Citalopram (391.8258 ng/l), and Enrofloxacin (191.3568 ng /l) in wastewater after leaving the treatment plant. The results of the full analysis of the sampling are shown in Table 2. For determination Risk Quotient (RQ) was defined PNEC (Predicted No-Effect Concentrations) from the NORMAN Ecotoxicology Database [17]. The results of screening by risk coefficient classifieds on three categories, $RQ \geq 1$ showed that the Measured Environmental Concentrations (MEC) of Ciprofloxacin and Ofloxacin are high risk to aquatic organisms; Medications such as Cetirizine, Citalopram and Enrofloxacin, fall into the moderate risk $0.1 < RQ < 1$ category; other drugs $RQ < 0.1$, do not cause concern during the sampling period. But these results cannot show the whole picture of the impact of drug pollution over a long period of time, taking into account the expanding range of drugs, the sanitary component of the region, climate change, etc.

It is known that the bioaccumulation of pharmaceuticals in the tissues of living organisms results in higher concentrations of compounds than in the environment (water or soil). Such characteristics of pharmaceuticals as bioactive components of drugs, lipophilicity and stability of most drugs in the aquatic environment pose a threat to living organisms in the described region (and not only) and the health of people consuming these products.

The Alazani River is one of the rivers of the basin (Kura, Iori, Araks, Ganjachay) of the South Caucasus, which is the main drainage resource and belongs to the Caspian water basin. The Alazani River directly flows into the Mingachevir reservoir (area 605 km²), created on the Kura River, and is used for electricity generation, agricultural irrigation and fishing. As described in the article, the discovery of antibiotics and other medicines in the water directly flowing into the Alazni River (taking into account the discovery of pharmaceutically active substances in the Kura River [6]), the water entering the territory of Azerbaijan is highly likely already polluted.

Table 2. The results of the full sampling analysis of contamination

Name of Pharmaceuticals	CAS	Type of Pharmaceuticals	Measured Environmental Concentration ng/l	Predicted No-Effect Concentrations (PNEC)	Risk Quotient (RQ) $RQ = \frac{MEC}{PNEC}$
Ciprofloxacin	85721-33-1	Antibiotic, fluoroquinolone	12757.1193	5200	2.453292
Cetirizine	83881-51-0	Antihistamine	1913.5679	4360	0.438892
Citalopram	59729-33-8	Selective serotonin reuptake inhibitor	391.8258	1600	0.244891
Enalapril	75847-73-3	Angiotensin-converting enzyme inhibitor	2.0047	7050	0.000284
Enrofloxacin	93106-60-6	Antibiotic, fluoroquinolone	191.3568	600	0.318928
Metoprolol	51384-51-1	Beta-adrenoreceptor antagonist	3.6449	8600	0.000424
Ofloxacin	82419-36-1	Antibiotic, fluoroquinolone	50.1173	26	1.927588
Terbinafine	78628-80-5	Antimycotic	0.1093	44	0.002484
Trimethoprim	738-70-5	Antibiotic, folic acid synthesis inhibitor	4.0094	100	0.040094
Caffeine	58-08-2	psychostimulant and analeptic	54.4407	62000	0.000878
Clarithromycin	81103-11-9	macrolide antibiotic	1.4992	130	0.011532
Nicotine	54-11-5	nicotine	12.5046	5450	0.002294
Paracetamol	16110-10-4	Analgesic-antipyretic	2.5964	14100	0.000184

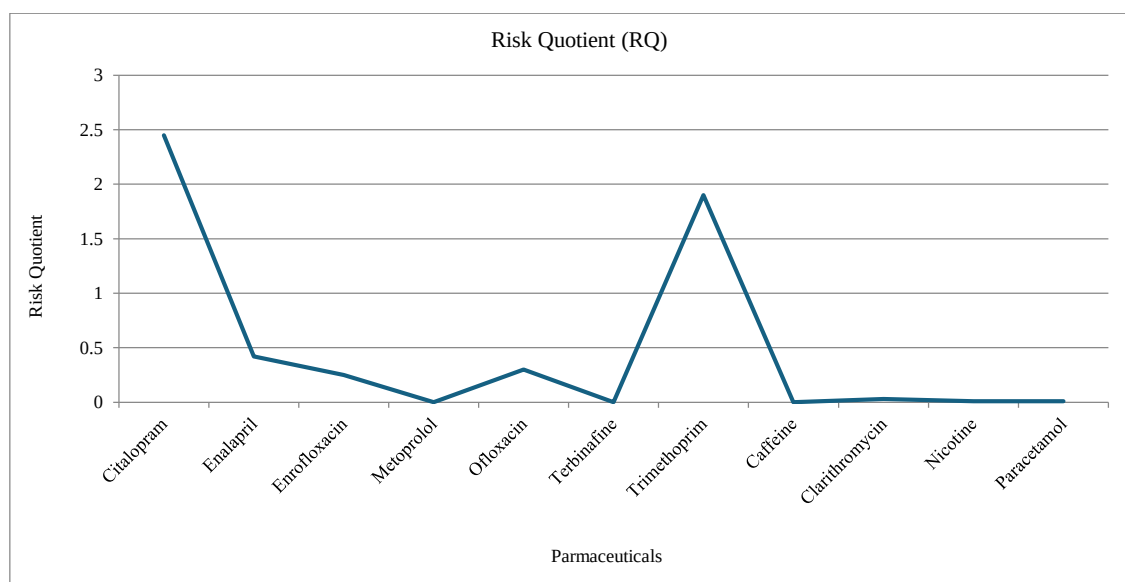


Fig. 4 Risk Quotient (RQ)

4. Results and Discussion

Being based on the fact that special cleaning methods and devices from pharmaceuticals are not considered at the standard treatment plant, it can be said that the amount of concentration of antibiotics and painkillers found will be completely discharged into the Alazani River. Presence pharmaceuticals in surface water can lead to unpredictable environmental consequences in region, impacts on aquatic

organisms, and to human health. Taking into account this impact, significantly exceeding environmentally significant levels, studies should be carried out according to a thorough prescribed monitoring schedule.

The next stage of research should be a reclamation canal and a fishery pond located downstream from the point of discharge of wastewater. Several studies show that some drugs

can bioaccumulated in aquatic organisms. The various impacts have been studied predominantly for fish and included changes in reproductive behavior, aggression, activity, etc. For example, nonsteroidal anti-inflammatory drugs, such as paracetamol, accumulate in the muscles of some fish species used for human consumption. It's known that antibiotics trigger the development of antibiotic resistance genes and contribute to the increase of antibiotic-resistant bacteria in surface and underground water [27]. One more source of the appearance of pharmaceuticals in the environment is the excretion of livestock treated with antibiotics, growth stimulants and other formulations. The drugs used in animal husbandry are less studied, but they cannot be neglected due to the extensive list of registered medicines.

The Alazani River basin is densely populated and characterized by developed agriculture. This is a fishing and recreation area. The local population is engaged in growing agricultural products, the leading industry of which is viticulture. Livestock farming is also developed in the region. The water of the Alazani River is used to irrigate agricultural land, as well as for the needs of livestock. Pollution of the river will lead to unfavorable results. If we take into account the popularity of grapes and especially the wine produced from them in Georgia and abroad, as well as the fact that they are the main source of income for the population, the negative economic effect is real.

Numerous experiments show that pharmaceutical compounds can be efficiently removed from the water by implementation of several processes in treatment plants, namely adsorption, ozonation, membrane technologies (nanofiltration and reverse osmosis) and etc. It will be important to use and include in the design of the treatment facility one of the modern treatment methods, such as the ozonating method, and reverse osmosis [36]. On the one hand, traditional wastewater treatment methods are not effective for removing pharmaceutical pollutants, on the other hand, deep treatment methods are associated with high economic and resource costs. But if wastewater is not treated, it can lead to serious consequences.

5. Conclusion

Using pharmaceuticals leads to pollution of the surface waters of the Alazani River, which can have unpredictable

environmental consequences. The article identifies the main source of infiltration of pharmaceuticals in the aqueous environment and provides evidence that conventional wastewater treatment technologies are not effective for the removal of pharmaceutical compounds, which can have environmental consequences.

It should also be noted that according to the United Nations COMTRADE database on international trade in Georgia, the import of drugs in 2024 amounted to 755.08 million US dollars, and a systemic trend of sales growth is observed in the country's pharmaceutical market [31].

Pharmaceutical pollution of water resources is a key issue in protecting the environment in the short term for human health, unwittingly exposed due to contaminated water and food. Pharmaceutical preparations appear not only in the form of active chemicals, but in the form of a combination of compounds exhibiting various bioactive properties. It is necessary to consider the effects of pharmaceuticals on the environment are long-term in nature, and the effect has not been sufficiently investigated.

Conflicts of Interest

“The author Mariam Kavrelishvili declares that there is no conflict of interest regarding the publication of this paper.”

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