Relationship between the concentrations of nitrogen compounds and the water discharge in the Chirchiq River, Uzbekistan

B K Karimov1, S S Shoergashova1, V N Talskikh2, and A T Salokhiddinov1

1Department of Ecology and Water Resources Management, Tashkent Institute of Irrigation and Agricultural Mechanization Engineers, Kori-Niyazov street 39, 100000 Tashkent, Uzbekistan
2Center of Hydrometeorological Service of the Republic of Uzbekistan (Uzhydromet). 72, 1st Bodomzor Yuli street, 100052 Tashkent, Uzbekistan

Email: bkarimov1960@gmail.com

Abstract. The Chirchiq River is one of the most human affected important drinking and municipal water source in the Republic of Uzbekistan. This work aimed to study the level of water pollution in the Chirchiq River by nitrogen compounds (ammonium, nitrite, and nitrate) over the last decade (2008-2018) with the identification of possible correlations between the level of water pollution and discharge. Most common pollutants: ammonium, nitrite, and nitrate concentrations in water were determined using generally accepted photometric methods. Correlation analysis of relationships between the river discharge and the concentrations of these compounds was carried out for each of 9 hydropost for each year and multiyear average values of the ten years (2008-2017). The water quality in the upstream part of the river is evaluated as a very good, however, in mid- and down streams due to diversion of nitrogen-containing organic and inorganic wastewater into the river worsened the water quality abruptly and concentrations exceeding MPC for fishery water bodies up to 5-8 times. Fortunately, according to the \([\text{NO}_3^-]:[\text{NO}_2^-]:[\text{NH}_4^+]\) ratio, the river has still enough assimilation capacity to transform hazardous ammonium and nitrite forms into nitrate nitrogen. Obtained results did not confirm the existence of significant interdependencies between the nitrogen compounds and water discharge. The results of the study will provide a theoretical and practical basis in terms of elucidating the mechanism of hydrochemical transformation of nitrogenous compounds along with the river ecosystem and predicting the dynamics of their concentrations in river water.

1. Introduction

Water resources play a vital role in arid Central Asia. The current practices of irrational and ineffective use of water resources causes a number of problems: an acute shortage of river water, widespread pollution, leading to increased morbidity of the population, salinization and degradation of irrigated lands, a decrease in biodiversity and disruption of ecosystem functioning [1; 2, 3, 4]. The ecological state of the Chirchiq river basin remains unsatisfactory, despite the measures taken to improve the ecological situation in its basin. Of particular concern is the pollution of clean river waters mainly by industrial and...
household wastewater in the upper and agricultural in the mid- and down streams, containing nitrogen compounds [5; 6].

Being a right-bank and high-water tributary of the Syr Darya River, the Chirchiq River has great importance for industry, agriculture, and household water supply. Its water resources are intensively used for hydropower production and irrigated agriculture, especially after reaching the piedmont area, in connection with which the river flow decreases rapidly. Upstream of the Gazalkent dam, the Bozsu canal diverts the water to the right from the Chirchiq, the Karasu canal diverts the water to the left above the Troitskaya dam, and below the Chirchiq it feeds the number of other canals. The cities of Gazalkent, Chirchiq, Tashkent are located in the river valley; as well as the villages of Charvaq, Iskandar, Bектemir, and Almazar. It is known that the water of open natural reservoirs always contains a certain percentage of nitrogen-containing compounds, which are either dissolved in it or present in the form of a suspension or a colloidal form. Under the influence of biochemical processes occurring in streams, as well as under the influence of physicochemical factors, they transsubstantiated, passing from one state to another. The main forms of mineral nitrogen in natural waters are ammonium, nitrite, and nitrate. All organic and inorganic sources of nitrogen after entering aquatic medium tending to be converted to nitrates – least harmful and stable form. The total nitrogen indicator determines the total saturation of the water with both mineral and organic nitrogen compounds [7; 8].

In usual, the concentration of nitrogen-containing compounds in water fluctuates. The limits of change are significant and depend on the specific characteristics of a particular aquatic ecosystem (in mg/l): 0.3–0.7 – for oligotrophic; 0.7-1.3 – for mesotrophic and 0.8-2.0 – for eutrophic water bodies. The total indicator of water saturation with mineral nitrogen reflects the total concentration of its nitrate, nitrite forms, and ammonium [8, 9]. Thus, the ratio [NO$_3^-$]:[NO$_2^-$]:[NH$_4^+$] plays an important diagnostic value. Increased content of nitrite and ammonium nitrogen is a very reliable indicator of recent pollution, and a large amount of nitrate may indicate that the water has been contaminated a long time ago [8]. Under conditions of irrigated agriculture where large quantities of nitrogen fertilizer application are practiced which can lead to direct pollution of water bodies, this rule can be disturbed (5).

During the last decades, the strategic importance of the river as a source of drinking and industrial water supply for largest in Central Asia city and main industrial centre of the Republic of Uzbekistan - Tashkent city, as well as for other industrialized cities of Tashkent region has increased many times, especially after the construction of the Charvaq reservoir in the 1970s. However, profitability and industrial development must not be the sole objectives and aspirations. While nitrate is relatively nontoxic to adults, because of nitrate excretion from the kidneys, concentrations above 10 mg/L N-NO$_3^-$ are fatal for children under 6 months (10). That is why there is an urgent need to follow SDG-6 Clean water and sanitation goals. Clean water and the access to the local population to clean water is the basis for sustainable developments in the frame of the WFEC (Water-Food-Energy-Climate) Nexus, and are therefore crucial issues in sustainable development the use of water resources.

This work aimed to study the level of water pollution in the Chirchiq River by nitrogen compounds (ammonium, nitrite, and nitrate) over the last decade (2008-2018) with the identification of possible correlations between the level of water pollution and discharge. The level of water pollution with nitrogenous compounds depends mainly from the types and scales of pollution sources within the river drainage. It is expected, that changes in water discharge will also play considerable role in this process; however, this issue was still not investigated in the region. Therefore, obtained results of the detailed evaluation of mineral nitrogen compounds concentrations in the river water and their relationships with water discharge will provide a theoretical and practical basis in terms of elucidating the mechanism of hydrochemical transformation of nitrogenous compounds along with the river ecosystem and predicting the dynamics of their concentrations in river water.
2. Methods

Chirchiq river basin (40°90′ – 41°62′N, 68°71′ – 69°97′E), is located on the territory of three states: Kazakhstan, Kyrgyzstan, and Uzbekistan. The length of the river is 155 km, and the basin area is 14.9 thousand km².

The river is considerably supplied from glaciers, however, mainly snowmelt. Average water discharge in the source - 221 m³/s. Ice phenomena can be observed from November to March. The Chirchiq River has several tributaries; all of them fall on the upper part of its valley, bordered by mountains. Ugam, Kok-Su, Chatkal, and Pskem are the main rivers flowing into the Chirchiq River. Before the construction of the Charvaq reservoir, Chirchiq was formed from the confluence of two main rivers: Chatkal on the left side and Pskem on the right side. The Pskem River originates in the glaciers of the Talas Alatau, especially developed and numerous in the left top of the river, called Maidantal. In the low-lying part of the valley, tributaries are completely absent. [11].

These studies were carried out within the framework of the research program of the Department of Ecology and Water Resources Management, TIIAME. The study used a database on the water discharge and quality conducted by Uzbekistan Hydrometeorological Service (UZHYDROMET) and Chirchiq river branch of the State Specialized Inspection for Analytical Control (SSIAC) under the State committee of the Republic of Uzbekistan on ecology and environmental protection.

To study the current level of water pollution by various forms of nitrogen, during 2018, the authors carried out additional hydrochemical studies jointly with the staff of the SSIAC Chirchiq laboratory. The Uzhydromet conducts a monitoring program on 9 hydroposts (gauging stations) along the Chirchiq
river and collects water samples ones every month (12 times per year). We were kindly allowed by the Administration of Uzhydromet to use the results of these analyses for the multiyear assessment of water quality (Figure 1). Also, several samples were taken from the lower reach of Charvaq Dam (140 km to the mouth) as background for comparison (marked as hydropost No 0).

0 – The lower reach of Charvaq Dam
1 – Chirchiq river 0.3 km above Gazalkent city;
2 – Chirchiq river 0.35 km below Gazalkent city;
3 – 2.5 km above wastewater discharge of Transformer plant, 0.5 km before entering Chirchiq city;
4 – 3 km below the wastewater discharge of “Chirchiq-Makhsam” PO (production association), 0.5 km below Chirchiq city;
5 – 3 km below wastewater discharge of UzKTJM (Uzbek plant of refractory and heat-resistant metals);
6 – 7 km above the wastewater discharge of KSM - (Sergeli plant of building materials and structures), Tashkent city;
7 – 3 km below the wastewater discharge of KSM (Tashkent city);
8 – 11 km below the wastewater discharge of bast factory (village Novomykhaylovka)
9 – Chirchiq river 3.2 km above river mouth (Chinaz city).

For assessing water quality, we used the values of maximum permissible concentrations (MPC) of pollutants for various types of water use generally accepted in the Republic of Uzbekistan (Table 1). Established by US Environmental Protection Agency (12) drinking water standard for N-NO₂ is 1 mg/l, 10 mg/l for N-NO₃ which also corresponds to MPS stated in this table.

| Compound, mg/l | Types of water use and limiting hazard indicator: toxicological (toxic.), sanitary-toxicological (san-toxic.) |
|----------------|-------------------------------------------------------------------------------------------------------------|
|                | household, drinking and cultural (MPC)                                                                  | fishery (MPC) |
| N-NH₂/ NH₄⁺    | 2/2.6 (san-toxic.)                                                                                      | 0.39/0.5 (toxic.) |
| N-NO₂/ NO₂⁻    | 1/3.3 (san-toxic.)                                                                                      | 0.02/0.08 (toxic.) |
| N-NO₃/ NO₃⁻    | 10/45 (san-toxic.)                                                                                      | 8.89/40 (toxic.) |

determining ammonium nitrogen in the water, a photometric method was used according to the qualitative reaction with Nessler’s reagent [13]. Nitrate nitrogen was determined by the Griess’s reagent method with the formation of a diazo compound with 1-naphthylamine, and nitrate nitrogen by the colorimetric method using sodium salicylate [14].

Correlation analysis between the indicators of the river discharge and the concentrations of ammonium, nitrite, and nitrate nitrogen was carried out for each hydropost each year of the ten years (2008-2017). To find more reliable indicators of the correlation, the mean annual indicators for each hydropost were also calculated using the MS Excel program. We also used a method of quantitative analysis, which consists in determining the ratio of ions [NO₃⁻]: [NO₂⁻]: [NH₄⁺].

3. Results

The lowest average annual concentrations of ammonium, nitrite, and nitrate nitrogen have been observed in hydroposts located above Chirchiq city (from lower reach of Charvaq Dam to hydropost 2 - below Gazalkent city) amounting 0.02, 0.004 and 0.58 mg/l respectively (Table 2). The water quality of the Chirchiq River by the level of pollution by ammonium and nitrite nitrogen in the middle and lower reaches does not meet the established MPC standards in most cases. In particular, in the midstream of the river below the hydropost of Chirchiq-Maxam (hydropost No. 4), according to the average annual data for the study period increased concentrations of ammonium nitrogen with the average multiyear value of 0.52 mg/l has been observed. The range of average annual concentrations in this river section
for the period 2008-2017 changed from 0.04 to 0.86 mg/l. The highest average concentrations of ammonium nitrogen were observed in 2012 (0.86 mg/l) and 2014 (0.81 mg/l) (Figure 2). The increased concentration of ammonium nitrogen can be associated with wastewater discharge of “Chirchiq-Makhsam” enterprise, which is the largest producer of nitrogen fertilizers for agriculture in Central Asia.

Table 2. Average annual and multiyear concentrations of ammonium, nitrite, and nitrate nitrogen in the water of Chirchiq River

| Compound (mg/l) | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 | 2008-2017 |
|----------------|------|------|------|------|------|------|------|------|------|------|----------|
| N-NH₃          | 0.03 | 0.01 | 0.02 | 0.04 | 0.07 | 0.01 | 0.04 | 0.01 | 0.02 | 0.01 | 0.03     |
| N-NO₂          | 0.005| 0.008| 0.006| 0.003| 0.003| 0.003| 0.002| 0.005| 0.001| 0.001| 0.004    |
| N-NO₃          | 0.95 | 0.76 | 0.68 | 0.67 | 0.61 | 0.51 | 0.47 | 0.46 | 0.84 | 0.75 | 0.67     |
| 1 - Chirchiq river 0.3 km above Gazalkent city |
| N-NH₃          | 0.02 | 0.01 | 0.02 | 0.03 | 0.03 | 0.02 | 0.03 | 0.02 | 0.01 | 0.02 | 0.02     |
| N-NO₂          | 0.004| 0.005| 0.009| 0.007| 0.004| 0.005| 0.001| 0.002| 0.003| 0.004| 0.004    |
| N-NO₃          | 0.66 | 0.65 | 0.48 | 0.65 | 0.55 | 0.47 | 0.46 | 0.42 | 0.74 | 0.73 | 0.58     |
| 2 - Chirchiq river 0.35 km below Gazalkent city |
| N-NH₃          | 0.04 | 0.02 | 0.04 | 0.04 | 0.04 | 0.03 | 0.03 | 0.05 | 0.04 | 0.01 | 0.03     |
| N-NO₂          | 0.005| 0.010| 0.009| 0.009| 0.014| 0.004| 0.003| 0.001| 0.003| 0.005| 0.006    |
| N-NO₃          | 1.08 | 0.88 | 1.31 | 1.59 | 1.15 | 1.30 | 1.01 | 0.98 | 1.52 | 1.21 | 1.2      |
| 3 - 2.5 km above wastewater discharge of Transformer plant, 0.5 km before entering Chirchiq city |
| N-NH₃          | 0.04 | 0.03 | 0.42 | 0.62 | 0.86 | 0.53 | 0.81 | 0.68 | 0.67 | 0.54 | 0.52     |
| N-NO₂          | 0.005| 0.025| 0.078| 0.099| 0.086| 0.132| 0.086| 0.098| 0.160| 0.054| 0.082    |
| N-NO₃          | 0.73 | 0.6  | 1.64 | 2.3  | 1.89 | 2.25 | 1.5  | 1.67 | 2.99 | 1.42 | 1.7      |
| 4 – 3 km below the wastewater discharge of “Chirchiq-Maxam” PO (production association), 0.5 km below Chirchiq city; |
| N-NH₃          | 0.29 | 0.72 | 0.08 | 0.18 | 0.26 | 0.33 | 0.49 | 0.3  | 0.34 | 0.17 | 0.32     |
| N-NO₂          | 0.074| 0.118| 0.062| 0.068| 0.032| 0.091| 0.050| 0.037| 0.046| 0.028| 0.061    |
| N-NO₃          | 1.23 | 0.95 | 1.2  | 2.14 | 1.17 | 1.89 | 1.12 | 1.12 | 1.48 | 1.31 | 1.36     |
| 5 – 3 km below wastewater discharge of UzKTJM (Hydropost Troitsky); |
| N-NH₃          | 0.04 | 0.39 | 0.11 | 0.1  | 0.19 | 0.22 | 0.29 | 0.21 | 0.2  | 0.2   | 0.2      |
| N-NO₂          | 0.071| 0.109| 0.049| 0.054| 0.040| 0.122| 0.098| 0.061| 0.080| 0.068| 0.075    |
| N-NO₃          | 1.23 | 1.36 | 1.82 | 2.79 | 1.64 | 2.99 | 1.7  | 1.64 | 2.75 | 1.94 | 1.99     |
| 6 – 7 km above the wastewater discharge of KSM (Tashkent city); |
| N-NH₃          | 0.08 | 0.29 | 0.13 | 0.13 | 0.14 | 0.08 | 0.16 | 0.1  | 0.09 | 0.25 | 0.14     |
| N-NO₂          | 0.021| 0.074| 0.058| 0.028| 0.024| 0.029| 0.018| 0.015| 0.024| 0.038| 0.033    |
| N-NO₃          | 2.78 | 1.27 | 1.09 | 1.3  | 1.61 | 1.42 | 1.34 | 0.66 | 2.22 | 1.84 | 1.55     |
| 7 – 3 km below the wastewater discharge of KSM (Tashkent city); |
| N-NH₃          | 0.19 | 0.21 | 0.1  | 0.1  | 0.12 | 0.08 | 0.15 | 0.08 | 0.08 | 0.09 | 0.12     |
| N-NO₂          | 0.029| 0.051| 0.032| 0.023| 0.023| 0.027| 0.019| 0.015| 0.015| 0.024| 0.026    |
| N-NO₃          | 2.05 | 1.48 | 1.01 | 0.82 | 1.4  | 1.43 | 1.17 | 0.72 | 1.77 | 1.35 | 1.32     |
| 8 – 11 km below the wastewater discharge of bast factory (village Novomykhaylova) |
| N-NH₃          | 0.08 | 0.07 | 0.01 | 0.01 | 0.28 | 0.06 | 0.05 | 0.09 | 0.03 | 0.06 | 0.07     |
| N-NO₂          | 0.023| 0.046| 0.013| 0.004| 0.043| 0.046| 0.026| 0.048| 0.060| 0.041| 0.035    |
| N-NO₃          | 1.07 | 1.08 | 0.81 | 1.19 | 1.75 | 1.91 | 1.22 | 1.14 | 1.92 | 1.68 | 1.38     |
| 9 – Chirchiq river 3.2 km above river mouth. |
Based on the results of changes in the average annual concentrations of nitrite nitrogen, it was revealed that the highest average multiyear value of nitrite nitrogen concentration - 0.082 mg/l observed after the Chirchiq-Maxam discharges (hydropost No. 4). The highest average annual concentrations of nitrite nitrogen on this river hydropost are observed in 2011 (0.099 mg/l), 2013 (0.132 mg/l) and in 2016 (0.16 mg/l), these values exceed MPC for fishery water bodies by 5, 6, 6 and 8 times respectively. Further, a significant increase in the content of nitrites was observed in the hydroposts above Tashkent city - 0.075 mg/l and Chinaz - 0.035 mg/l (hydroposts №6 and 9), however, remains below the level after the Chirchiq-Maxam discharges.

**Figure 2.** Dynamics of the ammonium nitrogen concentrations in the Chirchiq river water in 2008-2017 at hydroposts No. 4, 5 and 6

**Figure 3.** Changes in the mean multiyear values of nitrate-nitrogen concentration along the Chirchiq River (2008-2017). See section 2 “Study area and methods” for hydroposts names
Along the length of the Chirchiq river, for the studied period, the average annual concentrations did not exceed the MPC for nitrate-nitrogen, the range of fluctuations varied within 0.58-1.98 mg/l (Table 2 and Figure 3). The concentrations of nitrogen compounds did not exceed water quality standards in terms of household, drinking, and cultural water use during our field studies in 2018. At the same time, in many water samples, the concentrations of ammonium and nitrite nitrogen have significantly exceeded permissible norms for fishery waterbodies (Table 3). Starting from the summer season, the increase of the concentration of ammonium nitrogen below hydropost Chirchiq-Maxam for fishery water bodies has been observed. The maximum ammonium concentration – 0.61 mg/l has been observed in October, in November it has declined to 0.5 mg/l, and in December it increased again to 0.58 mg/l. The average annual ammonium concentration was equal to the fishery MPC - 0.39 mg/l. In the rest of the hydroposts the excess of MPC was not observed.

Table 3. Concentrations of ammonium, nitrite, and nitrate nitrogen in the Chirchiq River water during the field studies in 2018

| Hydropost | 0. Lower reach of Charvaq Dam | 4. Below the Chirchiq-Maxam | 7. Below the KSM (Tashkent city) | 9. Above river mouth |
|-----------|-------------------------------|-----------------------------|----------------------------------|---------------------|
| Compound (mg/l) | min – max average | | | |
| N- NH₄⁺ | n.d. | 0.25 – 0.61 | 0.12 – 0.4 | 0.1 – 0.26 |
| N- NO₂⁻ | n.d. | 0.013 – 0.02 | 0.042 – 0.177 | 0.028 – 0.121 |
| N- NO₃⁻ | 0.29 – 0.9 | 0.88 – 1.53 | 1.5 – 2.3 | 1.58 – 2.9 |

[NO₃⁻]:[NO₂⁻]:[NH₄⁺] – 1:0.02:0.32 1:0.05:0.03 1:0.03:0.03

Note n.d. – not detected.

Figure 4. Average long-term fluctuations in the dynamics of water discharge in the Chirchiq River (2008-2017). See section 2 “Study area and methods” for hydroposts names.
Regarding the nitrite nitrogen, an increase in concentration was observed up to MPC for fishery water bodies - 0.02 mg/l in summer in the Chirchiq-Maxam hydropost. In the hydropost below the Sergeli KMS, cases of excess concentrations of nitrite nitrogen were observed throughout 2018, ranging from 0.042 to 0.177 mg/l. A similar situation was observed in the Chinaz hydropost, where concentrations ranged from 0.028 to 0.121 (on average 0.064) mg/l. A similar situation was observed in the Chinaz hydropost, where concentrations ranged from 0.028 to 0.121 (on average 0.064) mg/l.

At the same time, concentrations of nitrate-nitrogen did not exceed of MPC either for household drinking and cultural water use or for fishery water bodies (Table 3).

Analysis of the dynamics of water discharge in the Chirchiq River over a 10 years showed that the highest discharge was observed in the hydropost below UzKTJM – 232.91 m³/s (Figure 4). An increase in water discharge in the UzKTJM hidropost also occurs as a result of the waste water discharge from the plant engaged in hydrometallurgical production, powder metallurgy, and the production of cermet hard alloy.

The results of the correlation analysis between the values of water discharge and the concentrations of ammonium nitrogen in different sections of the Chirchiq River showed that in the period from January to September 2008 in section No. 5 (below wastewater discharge of UzKTJM) there was a significant, although moderate ($R^2=0.75$) direct correlation between these indicators established (Table 4 and Figure 5).

![Figure 5. Relationship between river discharge and ammonium nitrogen concentrations in hydropost No.5 - below wastewater discharge of UzKTJM, 2008](image)

For 2008, the correlation analysis was carried out only for the period of from January to September, since there was no data for river discharge for the period October - December. There was a moderate correlation between river discharge and ammonium nitrogen. At the same time, in 2009 no reliable relationships were found between these indicators.

In the period from January to November 2010, in hydroposts No. 2 and 3, a moderate direct correlation between the river discharge and the content of ammonium nitrogen was found ($R^2=0.78$ and 0.68 respectively). However, in hydropost No. 5 in the same year, an inverse correlation was observed ($R^2=-0.55$, Figure 6).

The correlation analysis showed that in 2011, 2013, 2014, and 2016, no significant interrelationships between the river discharge and ammonium nitrogen were found at all 9 hydroposts. In 2012, it was found that in hydroposts No. 6, 7, 8 and 9 there was moderate direct correlation between these indicators ($R^2=0.74$; 0.68; 0.68; 0.67 respectively). In 2015 and 2017, there was a weak direct correlation between the river discharge and ammonia nitrogen at hydroposts No. 8 and 7 ($R^2=0.55$ and 0.64 respectively). In 2017 at hydroposts No. 8 and 9 very weak inverse correlation ($R^2=-0.49$ and -0.51 respectively) was established (Table 4).
Figure 6. Relationship between river discharge and ammonium nitrogen concentration in hydropost No.5 - below wastewater discharge of UzKTJM, 2010

Table 4. Significant correlation coefficients between the water discharge and the concentration of ammonium nitrogen at different hydroposts of the Chirchiq River

| Year/ Hydropost | 2008 | 2010 | 2012 | 2015 | 2017 |
|-----------------|------|------|------|------|------|
| 2               | c.i. | 0.78 | c.i. | c.i. | c.i. |
| 3               | c.i. | 0.68 | c.i. | c.i. | c.i. |
| 5               | 0.75 | -0.55| -    | -    | -    |
| 6               | c.i. | c.i. | 0.74 | c.i. | c.i. |
| 7               | -    | c.i. | 0.68 | c.i. | 0.64 |
| 8               | c.i. | c.i. | 0.68 | 0.55 | -0.49|
| 9               | c.i. | c.i. | 0.67 | c.i. | -0.51|

Notes: c.i. – correlation insignificant; - no data on river discharge

Figure 7. Relationships between river discharge and nitrites concentration in hydropost No.4 - below the wastewater discharge of “Chirchiq-Makhsam” in 2011

For nitrites it was found that in 2008 in hydropost No. 5 there was a direct correlation ($R^2=0.62$), in hydropost No. 6 – inverse correlation ($R^2= -0.45$) between river discharge and concentration. Thus below UzKTJM with an increase in water discharge, the concentration of nitrites also increases. Correlation analysis for 2009 showed the presence in 3 hydroposts (No. 2, 6, 7) of inverse relationships
between the river discharge and nitrites, $R^2$ were -0.51; -0.47; -0.50 respectively. In 2011, the correlation analysis showed in 4 hydroposts a direct relationship between the river discharge and nitrites; in hydroposts No. 3, 4, 5, 8, the $R^2$ indicators were equal to 0.45; 0.81; 0.76; 0.72 respectively. In hydropost No. 4, the highest direct correlation was observed. Thus based on this, it can be assumed that excessively concentrated discharges from the Chirchiq-Maxam enterprise diverted to the river (Figure 7).

Moderate inverse correlation ($R^2=-0.61$) in hydropost No3 and a strong direct correlation ($R^2=0.81$) in hydropost No9 was found between river discharge and nitrites in 2012. Similarly, an inverse correlation in hydroposts No6 and 9 ($R^2=-0.78; -0.62$ respectively) and a weak direct correlation ($R^2=0.56$) in hydropost No9 has been established in 2014 was found between these indicators. In all other cases: ($R^2$ from -0.47 to -0.68) in hydropost No9 in 2015, hydroposts No 2 and 6 in 2016 and hydroposts No6 and 8 in 2017 a very weak or slightly moderate inverse correlation was found between river discharge and nitrites (Table 5).

Thus, according to the analyzes, a significant increase ($R^2=0.7-0.8$) in the concentration of nitrites with an increase in water discharge was observed only in 2011-2012. After 2012, a significant direct correlation between these indicators was either not observed or it was slightly inverse proportional ($R^2=0.55$ to -0.68).

**Table 5.** Significant coefficients of correlations between the value of water discharge and the concentration of nitrites at different hydroposts of the Chirchiq River

| Year/ Hydropost | 2011  | 2012  | 2014  | 2016  | 2017  |
|----------------|-------|-------|-------|-------|-------|
| 2              | c.i.  | c.i.  | c.i.  | -0.57 | c.i.  |
| 3              | c.i.  | -0.61 | c.i.  | c.i.  | c.i.  |
| 4              | 0.81  |      |      |      |      |
| 5              | 0.76  |      |      |      |      |
| 6              | c.i.  | c.i.  | -0.78 | -0.58 | -0.68 |
| 8              | 0.72  | c.i.  | 0.56  | c.i.  | -0.52 |
| 9              | c.i.  | 0.81  | -0.62 | c.i.  | c.i.  |

Notes: c.i. – correlation insignificant; - no data on river discharge

The relationships between river discharge and nitrates concentrations were mostly inversely proportional and ($R^2$) changed between from -0.48 to 0.68. Only in hydropost No9 in 2008 and in hydroposts No4 and 5 in 2011 0.61-0.82 moderate direct correlation has been found (Table 6).

For nitrates in 2008, it was found that in hydroposts No. 2, No. 3, No. 6 there was a weak inverse correlation ($R^2=-0.48; -0.50; -0.68$), and in hydropost No. 9 - moderate direct correlation ($R^2=0.79$), between river discharge and nitrate concentration (Table 6). In 2009 it was found that in hydroposts No. 6 and No. 7 there is a weak inverse correlation ($R^2=-0.55; -0.52$), between river discharge and nitrates. In 2010 it was found that in hydropost No. 2 there is a very weak direct correlation ($R^2=0.48$), and in hydroposts No. 6, No. 7 and No. 8 - weak inverse correlation ($R^2= -0.50; -0.55; -0.53$ respectively), between these indicators.

In 2011, the correlation analysis showed the presence in 4 hydroposts of a direct interdependence between the river discharge and nitrates. In hydroposts No. 2, No. 3, No. 4, No. 5, the $R^2$ were equal 0.45; 0.49; 0.82; 0.61 respectively. As can be seen, the highest direct correlation was observed in hydropost No. 4. In this hydropost, a similar situation was observed for nitrates in the same year. For all other years of observations, the correlations between the river discharge and the concentration of nitrates were either very weak straight ($R^2$ from 0.49 to 0.58) or weak inverse ($R^2$ from -0.46 to -0.53).

After performing calculations for each year from the period 2008-2017, a correlation analysis was carried out using average long-term multiyear data for 9 hydroposts. The results of this analysis have shown no significant relationships between river discharge and ammonium and nitrate nitrogen ($R^2= -
0.28). Only a weak direct correlation was found in hydropost No. 7 between the river discharge and nitrites ($R^2=0.54$).

### Table 6. Values of the correlation coefficient between the water discharge and the concentration of nitrates at different hydroposts of the Chirchiq River

| Year/Year/ | Hydropost/2 | 2008/2008 | 2009/2009 | 2010/2010 | 2011/2011 | 2012/2012 | 2014/2014 |
|-----------|-------------|-----------|-----------|-----------|-----------|-----------|-----------|
| 2         | -0.48       | c.i.      | 0.48      | c.i.      | -0.49     | c.i.      |
| 3         | -0.50       | c.i.      | c.i.      | 0.49      | c.i.      | c.i.      |
| 4         | c.i.        | c.i.      | c.i.      | 0.82      | -         | -         |
| 5         | c.i.        | c.i.      | c.i.      | 0.61      | -         | -         |
| 6         | -0.68       | -0.55     | -0.50     | c.i.      | c.i.      | -0.56     |
| 7         | -          | c.i.      | -0.55     | c.i.      | c.i.      | c.i.      |
| 9         | 0.79        | c.i.      | c.i.      | c.i.      | 0.58      | c.i.      |

Notes: c.i. – correlation insignificant; - no data on river discharge

4. Discussion

Analysis of the available literature data suggests that the spatial and temporal characteristics of concentrations of nitrogen mineral compounds: ammonium, nitrites, and nitrates in river water depend, along with natural fluctuations in hydrological and hydrochemical characteristics, also to a decisive extent on the level of anthropogenic pollution [5, 15]. On the example of Azerbaijan's rivers shown that non-point sources of anthropogenic impacts (runoff of fertilizers from agricultural land) are strongly increased in the river water concentration of all nutrients, and particular ion NO$_3^-$ (from 220-480 to 1200-1450%) [16]. The content of dissolved biogenic elements (nitrogen compounds, phosphates) is dependent on the flow rate, but in the distribution of these characteristics, the key role is played by biogeochemical processes (respiration of hydrobionts, destruction of organic matter) and anthropogenic influence (flushing from agricultural land, etc.) [17]. An exponential relationship with a relatively high correlation coefficient ($R^2=0.9093$) between nitrate and nitrite nitrogen concentrations in the waters of Tundzha River and its four feeders in Bulgaria was drawn (18). However, no one of the previous investigations did not analyze in detail interdependences between water discharge and nitrogen compounds in river waters applying correlation analyses.

In water bodies with high aquatic plant development theoretically expected that the minimum concentrations of nitrogen, especially nitrates be expected in summer during the vegetation period and maximum concentrations during the late autumn-winter. Indeed, high concentrations of nitrogen compounds (eutrophication) can lead to oxygen deficit by nitrification, extreme aquatic alga, and high plant growth, exhibit toxicity toward aquatic life (19). However, in the case of the Chirchiq River, it has a very poorly developed plant cover due to rather high current velocity low water temperature. Therefore, there is little vegetation impact on nitrogen compounds dynamics during vegetation season. At the same time, a high load of domestic and industrial sewage waters (9), as well as drainage waters diversion from agricultural fields in mid- and downstream (3) can lead to high nutrient concentrations during the whole year. In natural conditions, the optimum water temperature for denitrification was 35°C and for nitrification 25°C, respectively (20), however, in Chirchiq river such water temperatures are possible only on the downstream part. The results of the forecast showed that by 2020, the sanitary standards of water quality in Chirchiq river may be exceeded for ammonium, nitrites, and nitrates 2.9; 9.3 and 3.2 times respectively (6).

Our results on the study of long-term dynamics of concentrations of mineral forms of nitrogen in the water of the Chirchik river, as well as the first correlation analyses of the relationship between different forms of nitrogen and water discharge, have given interesting results. Thus, it was found that water quality in the river before entering Chirchiq city (hydropost 3) during the whole study period was within all MPS criteria. However, starting from the “Chirchiq-Maxam” hydropost, the average annual value of ammonium and nitrite nitrogen (2008-2017) exceeds MPC by 1.33 and 4.1 times for fisheries purposes,
while the water quality according to these indicators is suitable for household and drinking water supply. The average annual values of nitrate-nitrogen were also low (within the range of 0.58-1.98 mg/l), which did not exceed MPC for both drinking, cultural and household (10 mg/l) and fishing (8.89 mg/l) purposes along the entire length of the Chirchik River. Thus, comparing to ammonium and nitrite nitrogen nitrate-nitrogen cannot be classified as a contaminant requiring permanent monitoring, which was also the case in freshwaters in Stara Zagora Region, Bulgaria (18).

If we judge by the highest average annual concentrations of ammonium and nitrite nitrogen, they also do not exceed the MPC of household, drinking and cultural purposes throughout the Chirchik river for the entire period of research. However, judging by fisheries regulations, the greatest concern is the water quality after the “Chirchik-Maxam” PO. From this hydropost water quality begins to deteriorate sharply with highly toxic nitrite nitrogen concentrations exceeding MPS for fishery up to 5-8 times and ammonium nitrogen concentrations exceeding MPS up to 2 times almost during the whole study period except 2008-2009. Starting from hydropost 5 (below wastewater discharge of UzKTJM) ammonium nitrogen concentrations are declining again below MPS values. However, nitrite nitrogen concentrations are staying above allowable concentration up to the river mouth. Thus, nitrite nitrogen can be classified as the most dangerous aquatic pollutant. Perhaps N-NO$_2^-$ belongs also in other countries to most hazardous, e.g. in Bulgaria, it was classified as a potential pollutant that requires effective removal by appropriate methods from the natural surface water bodies (18).

Thus, a sharp increase in concentrations of ammonium and nitrite nitrogen is observed mainly in the Chirchik-Maxam, UzKTZhM, and Chinaz hydro stations. Indeed, the main polluter of Chirchik river in its midstream is “JV Chirchik-Maxam” producing ammonium, ammonium nitrate, carbamide, non-concentrated nitric acid, ammonium sulfate, and acidic melange. The generated wastewater is discharged into the Chirchik river after it is averaged into a buffer-ponds (6). Above hydropost Chinaz (downstream) in addition to industrial pollution sources large-scale agricultural sources of pollution such as fertilizer application in rural areas, surface water runoff from cotton fields, discharges of domestic, animal husbandry and poultry sewage waters into water bodies without proper treatment also largely contribute to water quality worsening.

The ratio of forms of mineral nitrogen: [NO$_3^-$]: [NO$_2^-$]: [NH$_4^+$] was in all cases about 1:0.05:0.31, which indicates that the assimilation capacity of the river ecosystem, despite permanent contamination with nitrogen-containing compounds, successfully copes with their transformation to a relatively harmless form of nitrogen – nitrates.

Our analysis based on of long-term data to identify the presence of possible interdependencies between the ammonium, nitrite, and nitrate forms of nitrogen and water discharge allowed us to establish the absence of any systematic clearly expressed and directed correlations between these parameters. In the vast majority of cases, these dependencies were extremely unreliable. The rare cases of very weak, weak, and average correlation reliability were found to be either directly or inversely proportional.

5. Conclusions

In detail water quality analyses based on the dynamics of multiyear concentrations of nitrogen compounds in the water of Chirchik river between 2008 and 2017 have revealed full correspondence of water quality in upstream of the river up to industrialized city Chirchik. However, downstream of Chirchik city starting from PO “Chirchik-Maxam” enterprise the situation is rapidly worsening according to average multiyear and multiannual concentrations of ammonium and nitrite nitrogen, exceeding allowable limits for fishery water bodies. The nitrate-nitrogen concentrations were within all MPS along the whole river channel with maximum levels on mid- and downstream with maximum values after Tashkent city caused by the diversion of domestic and agricultural drainage waters. However, [NO$_3^-$]: [NO$_2^-$]: [NH$_4^+$] ratio analyses have revealed that the river ecosystem has enough assimilation capacity to transform nitrogen-containing organics and sewage into less harmful nitrate nitrogen.

Obtained results of correlation analyses did not confirm expected interdependencies between the mineral nitrogen compounds and water discharge in Chirchik river. Thus, the changes in water
discharge alone cannot be used as an indicator for predicting biogenous compounds concentrations in water quality assessments.

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References
[1] Tornqvist R, Jarsjo J, Karimov B 2011 Environment International 37(2) 435-442.
[2] Karimov BK, Matthies M, Kamilov BG 2014 Unconventional water resources of agricultural origin and their re-utilization potential for development of desert land aquaculture in the Aral Sea basin. Bhaduri, Bogardi, Leentvaar, Marx (Eds.) The Global Water System in the Anthropocene: Challenges for Science and Governance, Springer International Publishing Switzerland 183-200.
[3] Karimov BK, Matthies M, Talskikh VN, Plotsen MA, Karimov EB 2019 Asian Journal of Water, Environment and Pollution 16(3) 109-114.
[4] Kulmatov R, Mirzaev J, Abduwuiali J, Karimov B 2020 Journal of Arid Land 12(1) 90–103.
[5] Bazarov DR, Akhmedova TA 2002 Journal Voprosy melioratsii 27 5-6.
[6] Usmanov IA 2017 Ecology and Construction 1 10–14.
[7] Pawelczyk A 2012 Water Science and Technology 66(3) 666-672.
[8] Guseva TV, Molchanova YaP, Zaika EA, Vinichenko VN, Averochkin EM 2000 Hydrochemical indicators of the state of the environment Moscov Ecoline 8-16.
[9] Akhmedova TA, Sharipov OO, Pulatov SM, Karimova DF, Azimov SS 2018 Web of Scholar 6 (24) 2.
[10] Niculescu V, Sandru C, Paun N, and Miricioiu, M 2017 Progress of Cryogenics and Isotopes Separation 20(2) 31-42.
[11] Usmanov S, Mitani Y, Kusuda T 2016 Computational Water, Energy, and Environmental Engineering 5(03) 87.
[12] EPA (Environmental Protection Agency) 1990 Drinking Water Criteria Document on Nitrate/Nitrite, Office of Drinking Water, Washington, DC.
[13] Demutskaya LN, Kalinichenko IE 2010 Journal of Water Chemistry and Technology 32(2) 90-94.
[14] Semenov AD 1977 A guidance on chemical analyses of surface land waters. Gidrometeoizdat, Leningrad.
[15] Drolc A, Koncan JZ 2008 Desalination 226(1-3) 256-261.
[16] Abduev MA 2011 Geographical Bulletin 3 9.
[17] Ovsyaniy EI, Orekhova NA 2018 Marine Hydrophysical Journal 34(1) 82-94.
[18] Georgieva N, Yaneva Z, Dospatliev L 2010 Desalination 264(1-2) 48-55.
[19] Huang W, Zhang Y, Li D 2017 A review. Journal of Environmental Management 193 470-482.
[20] Lu GH, Xu HP, Pan T 2019 In IOP Conference Series: Earth and Environmental Science 344(1) 012075.