Water Quality Monitoring of the Chirchik River Basin, Uzbekistan Murodjon NASEDJANOV*¹⁾, Hirozumi WATANABE²⁾, Izumi WATANABE²⁾, Yoshiko KAWABATA³⁾ and Dang Quoc THUYET⁴⁾

Abstract: The study investigates occurrence of ionic contaminants and pollutants in the tributaries of the Chirchik River in the northeast part of Uzbekistan. Water samples collected in the Chirchik River Basin were analyzed by ion liquid chromatography to determine ions such as Ca^{2+} , Mg^{2+} , K^+ , NH_4^+ , Na^+ , Li^+ , SO_4^{-2-} , NO_2^- , $C\Gamma$, F, PO_4^{-3-} . Plant available forms of heavy metals in soils were extracted according to the methods established by Japanese Ministry of Environment. Elements such as Cr, Ni, Cu, Zn, V, Mn, Fe, Ga, Ba, As, Mo, Rb, Sr, Sb, Se, Cd, In, Cs, Co, Ag, Hg, Tl, Pb were detected with the help of ICP-MS. Toxic heavy metals such as Hg, Cd and Pb were not detected in all water samples, while Fe and Ba exceeded the Maximum Admissible Concentrations (MAC) in several sites in the watershed. Contaminants such as NO_3^- , NO_2^{-2} , SO_4^{-2-} , NH_4^+ and PO_4^{-3-} exceeded the MAC values for some water samples probably due to discharges from agriculture and other industries. It was noticed that the level of most ions increased near to stationary sources, automobile road and residential area while the concentrations of As and Sb were initially high in the Charvak water reservoir.

Key Words: Chirchik River, Heavy metals, Ionic contaminants, Monitoring, Water quality

1. Introduction

Presently, water quality associated with agriculture and industrial activities in Uzbekistan is a great concern particularly in economic region of Tashkent province. Previous monitoring results carried out in 2001-02 in the northeast part of Tashkent province revealed heavy metals pollution in the Chirchik Watershed. The level of chromium (III) and nickel (II) were high in irrigation water and plough soils. The total concentration of chromium in irrigation water fluctuated from 0.5 to 20 mg/L, and nickel ranged from 0.35 to 2.29 mg/L, whereas allowable concentration of chromium and nickel was 0.5 mg/L and 0.1 mg/L, respectively. The concentration of chromium and nickel in plough soil layer ranged from 20 to 83.1 mg/kg and from 17 to 30.3 mg/kg, whereas admissible concentrations for serozem belt soils are 30 and 35 mg/kg for chromium and nickel, respectively (Riskieva et al., 2002). However, the source of pollutants was not discovered yet, and monitoring has not been carried out in the Chirchik Watershed since 2002. More data are required for investigating possible sources and effects on water quality and contamination level of plough soils.

The objective of this study was to monitor the concentrations of ionic contaminants and heavy metals in the tributaries of the Chirchik River.

2. Materials and Methods

2.1. Sampling and chemical analysis

Water samples were collected from the Charvak water reservoir along the Chirchik River to downward. Arable soils were sampled at low relief hills and near to urban areas (**Fig. 1**).

Sampling sites were appointed with the help of GPS device (Garmin). Sampling was conducted in the 14th, 17th, 21st of August and the 4th of September, 2008.

Water samples were filtered through 0.45 μ m Millipore filter (Millipore Co., USA) and introduced to ion liquid chromatography (Shimadzu, Japan) to analyze ions such as Ca²⁺, Mg²⁺, K⁺, NH₄⁺, Na⁺, Li⁺, SO₄²⁻, NO₃⁻, Br⁻, NO₂⁻, Cl⁻, F⁻, PO₄³⁻.

Plant available forms of heavy metals in soils were extracted according to the methods established by Japanese Ministry of Environment (Yamanaka, 2007).

Elements such as Cr, Ni, Cu, Zn, V, Mn, Fe, Ga, Ba, As, Mo, Rb, Sr, Sb, Se, Cd, In, Cs, Co, Ag, Hg, Tl, Pb were determined with the help of ICP-MS (Agilent, USA).

Soil pH and soil humus were measured with Horiba pH meter and Tyurin titration method, respectively. Bulk density was determined by gravimetrical method.

Statistical analysis was performed by using SPSS -11 Version for MacOSX based on Pearson_Spearman's rank correlation. The values of p <0.05, <0.01, <0.001 were considered to indicate statistical significance; all tests were two-tailed.

^{*} Corresponding author: nmurodjon@gmail.com

Str. Kamarniso-3, Almazar district, P.O.Box 100179, Tashkent, Uzbekistan

³⁾ International Center, Tokyo University of Agriculture and Technology, Japan

Research Institute of Soil Science and Agrochemistry, Tashkent, Uzbekistan
Faculty of Agriculture, Tokyo University of Agriculture and Technology, Japan

⁴⁾ United Graduate School of Agricultural Science, Tokyo University of Agriculture and Technology, Japan

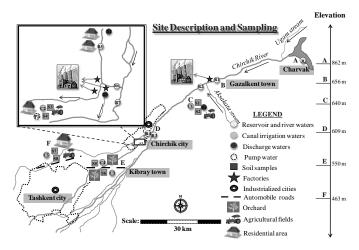


Fig. 1. Sampling Sites in the Chirchik Watershed. Legend: R is water sample in Charvak reservoir; R1, R2, R3, R4, R5, R6 and R7 are water samples in the Chirchik River and its tributaries; C1, C2, C3, C4, and C5 are water samples in irrigation canals; D1 and D2 are water samples in discharge water from agricultural fields; D3 is water sample in discharge outlet from "C" factory; P1 is pump water sample (3 m in depth); S1, S2, S3, S4, S5, S6, S7 and S8 are plough soil samples collected in agricultural fields.

3. Results and Discussion

3.1. Physical and chemical parameters of water body

Water pH was about 7.5 which is similar to the pH in the Chirchik River observed in August and September varying from 7 to 7.8 (Toderich, 2000). Only in D3 point the pH resulted in 6.6 possibly because of discharge of acidic chemical from factory (Kuiyi *et al.*, 2008). Hydrocarbonate (HCO₃) concentration in Gazalkent town was 119 mg/L, while it increased in Chirchik city resulting in 232 mg/L. Oxygen regime of the river was in normal condition fluctuating from 10.7 to 11.47 mg/L (Toderich, 2000). According to the sanitary norms, in summer and winter seasons dissolved oxygen must not reduce below 6 mg/L and 4 mg/L, respectively (Guseva *et al.*, 2000). COD (chemical oxygen demand) in canal waters fluctuated from 8 to 50 mg/L.

3.2. General characteristics of irrigated soil

Soil humus varied from 1.33 to 1.85%, nitrogen 0.064 - 0.210%, phosphorus 0.165 - 0.210%, potassium 2.0 - 2.43%, affirming average statistical database on humus and nutrient contents in serozem belt soils in Central Asia (SoyuzNIXI, 1963). In the serozem belt soils humus fluctuates from 1.06 to 1.96%, nitrogen from 0.04 to 0.15%, phosphorus 0.12 - 0.18%, and potassium 1.32 - 1.58% (Riskieva *et al.*, 2002). Soil pH varied from 8.1 to 8.4. Average soil moisture was 17.86%, with average bulk density of 1.49 g/cm³ in plough soil (15-20 cm). Similar result of bulk density was observed in clay loam soil (agricultural field in northern Jordan) varying from 1.4 to 1.5 g/cm³ in the 10-20 cm plough soil layer.

3.3. Average concentration of soluble ions and elements

The average concentrations of several ions and elements in water sample were presented (**Table 1**). Contaminants such as NH_4^+ , NO_3^- , NO_2^- , SO_4^{2-} and PO_4^{3-} exceeded the MAC values. However, the level of Cr, Ni, Cu, Zn, V, Mn, Ga, As, Mo, Rb, Sr, Sb, Se, Cd, In, Cs, Co, Ag, Hg, Tl, and Pb elements and Ca^{2+} , Mg^{2+} , Li^+ ions did not exceed corresponding the MAC values in both water and soil samples. Only, Fe and Ba exceeded the MAC values in R1, R2, R7, C5, D1, and P1 sites.

3.3.1 Reservoir Water

The level of NO₂⁻ (nitrite) was two folds of the MAC values and three folds of previous result (Glavgidromet, 1998). According to Marcel (2006) nitrite is originated due to increase of "nitrosomonas" bacteria which oxidizes ammonium transforming to nitrite form. It is usually found on surface water under pH condition 6.0 - 9.0, and 20 - 30°C water temperature.

3.3.2 River Waters

The concentration of soluble ions and elements sharply increased in water samples collected in R1 and R2 sites after Gazalkent town (Table 1). The concentration of nitrate (NO_3^-) in the river water was high than the MAC values in 1.7 times and nitrite (NO_2^-) exceeded 2 times in R1 and 3 times in R2, where the MAC values for nitrite and nitrate were 0.02 and 9.1 mg/L, respectively for surface waters in Uzbekistan republic (Razakov *et al.*, 2003).

For phosphate ion (PO_4^{3-}) 0.3 and 3.5 mg/L were adopted as the MAC values for fishery pond and drinking waters, respectively (Razakov *et al.*, 2003). However, the phosphate ion concentration in R1 and R2 sites showed 9.18 and 6.27 mg/L, respectively. Some forms of phosphorus are applied to control corrosion in water supply or in cooling water system in industrial sector, including a production of synthetic detergents (Tchobanoglous and Schroeder, 1985) and its usage in households in Gazalkent town which probably increased the level of phosphate ion in the river waters.

In R2 point, the concentration of most ions decreased, it is very likely due to tributary stream the Aksakata which inflows between R1 and R2. The concentration of ions in R3 and R4 sites collected before entering Chirchik city was lower than the samples collected in residential area in R5, R6, R7 sites, however the concentration of all ions did not exceed the MAC values except Fe and SO_4^{2-} in R7 site which is the down part of Chirchik city.

3.3.3. Canal and Pump Irrigation Waters

It must be pointed out that there is no MAC values for irrigation waters in Uzbekistan however, based on the standards offered by the EU directives, and in consideration of present sanitary norms used in Uzbekistan, France, the USA,

Table 1. Average concentrations of ions and elements in the Chirchik Watershed. Note: nd for not detected, -- for not available.

| Sampling | Water samples, mg/L | | | | | | Water samples, µg/L | | | |
|-------------|---------------------|----------|----------|-------------|-------------------------------|------------------|---------------------|--------|------|------|
| sites | NH_4^+ | NO_3^- | NO_2^- | SO_4^{2-} | PO ₄ ³⁻ | Ca ²⁺ | Fe | Ba | Cr | Ni |
| R | 0.02 | 0.63 | 0.04 | 11.29 | 3.61 | 27.75 | 143.40 | 60.60 | nd | 0.01 |
| R1 | 0.01 | 16.24 | 0.04 | 17.55 | 9.18 | 66.98 | 321.60 | 145.80 | 3.28 | 0.17 |
| R2 | nd | 9.87 | 0.06 | 22.07 | 6.27 | 45.06 | 289.80 | 124.8 | 1.29 | 0.12 |
| R3 | 0.01 | 1.85 | nd | 16.97 | 3.43 | 19.43 | 180.60 | 60.57 | nd | nd |
| R7 | nd | 8.36 | nd | 124.4 | 5.40 | 55.07 | 312.20 | 89.57 | 1.60 | 0.19 |
| C1 | 0.05 | 0.56 | nd | 10.26 | 3.00 | 25.16 | 138.90 | 46.95 | nd | 0.01 |
| C2 | 1.18 | 8.46 | 0.50 | 39.51 | 3.00 | 34.45 | 189.90 | 54.15 | 0.87 | 0.12 |
| C3 | 0.02 | 0.79 | nd | 10.59 | 3.16 | 18.93 | 139.90 | 50.00 | nd | nd |
| C4 | 0.53 | 0.60 | nd | 11.95 | 3.56 | 26.83 | 143.00 | 48.74 | nd | 0.15 |
| C5 | 0.03 | 26.3 | nd | 246.30 | 8.56 | 74.34 | 559.30 | 38.17 | 1.00 | 0.83 |
| P1 | 3.71 | 96.14 | nd | 58.19 | 7.89 | 62.15 | 463.70 | 69.93 | nd | 0.52 |
| D1 | nd | 18.32 | nd | 56.50 | 9.33 | 75.92 | 392.30 | 140.1 | 1.90 | 0.34 |
| D2 | 0.04 | 0.56 | nd | 26.69 | 3.06 | 24.09 | 149.60 | 49.69 | nd | 0.06 |
| D3 | nd | 28.43 | nd | 84.99 | 2.88 | 45.78 | 219.40 | 49.45 | nd | 0.40 |
| MAC (river) | 0.50 | 9.10 | 0.02 | 100 | 0.3 | 180 | 300 | 100 | 500 | 100 |
| MAC (canal) | 1.50 | 25.00 | 0.50 | | 1.00 | | | | | |

Razakov *et al.* (2003) suggested standard values for 20 parameters for the irrigation waters in Uzbekistan. The parameters are indicated as follows: water pH 6.5-7, mineralization 1000 mg/L, PO_4^{3-} 1 mg/L, NH_4^+ 1.5 mg/L, NO_2^- 0.5 mg/L, NO_3^- 25 mg/L, F 1 mg/L, As 0.1 mg/L, Fe 5 mg/L, Cr^{6+} 0.1 mg/L, Cu 1 mg/L, Zn 5 mg/L, and Pb 0.2 mg/L. Considering these parameters for irrigation waters, PO_4^{3-} ion exceeded the MAC values in all cases. For example, in C1, C2, C3 sites it exceeded 3 times, in C4 - 3.5 times, while in C5 and P1 - 8.5 and 7.9 times, respectively. The mean concentration of PO_4^{3-} in canal waters resulted in 4.2 mg/L, NO_2^- in C2 and NO_3^- in C5 were above the MAC values (Table 1).

In the pump water (P1) NO_3^- exceeded the MAC values 3.8 times resulting in 96.14 mg/L, due to nitrification process in soil layers, probably derived initially from ammonium and converted to nitrate by "nitrobacter" in soil (Jalali *et al.*, 2005), as ammonium (NH_4^+) level was also higher than the MAC values.

Sulfate $(SO_4^{2^\circ})$ ion, collected near to "Tashkent Ring Automobile Road" where intensive transport activities have been observed, was high resulting in 246.3 mg/L in C5 point. According to Nurrohim *et al.* (2005) sulfur-dioxide (SO₂) is mainly derived from road vehicles and cause air pollution. Meanwhile, the concentrations of heavy metals did not exceed the MAC values in C5 point.

3.3.4. Discharge Waters

All discharge waters were free from NO₂⁻, NH₄⁺ and Br⁻, only at D2 point NH₄⁺ concentration was 0.04 mg/L. Concentration of NO₃⁻ at D1 and PO₄³⁻ at D1, D2, D3 are higher than the MAC values (Table 1). PO₄³⁻ is mainly derived from P-fertilizers, manures or sewage sludge applied to fields to support plants to uptake phosphorus, and soil is one of bulk sources for both organic and inorganic phosphorus (Guseva *et al.*, 2000; Marcel, 2006, Tchobanoglous and Schroeder, 1985). The level of Fe, Cu and Ni was high at D1 point probably due to their strong interaction with organic matter (Charlesworth *et al.*, 1999).

3.4. Average concentration of elements in soils and waters

Water extractable forms of heavy metals were lower than that of acid extractable (1M HCl) forms except for molybdenum (Mo), probably due to abundance of molybdate ion (MoO_4^{2-}) in soils which is soluble in water, whereas other compounds of Mo are less soluble (Fig. 2). Toxic heavy metals such as Cd, Pb, and Se had the highest concentrations in soil samples obtained at S1 and S2 agricultural plots, ranging 4.27 - 3.64 µg/kg, 336.3 - 278.6 µg/kg and 23.15 - 18.82 µg/kg, respectively. Moreover, the level of other metals such as Cs, Fe, Co, Ni, Zn, Ga, Ba, Rb and Cr was higher in S1 and S2 plots as compared to the other plots downward. Those elements may be derived from a stationary source located uppermost between R1 and R2, where the ions and elements trend showed sharp increase. Some elements such as Co, Se and Cs are known to be used in glass or mirror factories, where Co is mostly used to impart blue color to glass stuff, while cesium is used to etch the surface of glass, due to CsOH form is a very strong base and can etch the surface of glass. The concentration of Cr and Ni in all water samples did not exceed admissible norms and did not support previous results.

Statistical analysis showed that in water samples (treated by concentrated HNO₃) Cr significantly correlated with Se (P<0.001), with Li, Ca, Fe (P<0.01) and with V (P<0.05), while Ni with Li (P<0.001), with Ca, V (P<0.01) and with Se, Rb (P<0.05).

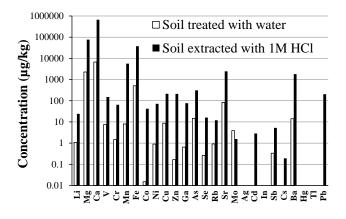


Fig. 2. Concentration of elements in soil samples (ICP-MS).

4. Conclusion

Toxic metals such as mercury, cadmium and lead were not detected in all water samples, while Fe and Ba exceeded the MAC values in several sites of the watershed. Contaminants such as nitrate, nitrite, sulfate, ammonium and phosphates exceeded the MAC values for some water samples probably due to discharges from agricultural sector and other industries. It was noticed that the level of most ions increased near to stationary sources, automobile road and residential area while the concentration of As and Sb was initially high in the reservoir water. Consequently, further investigation on the watershed is needed to reveal the exact sources of contaminants and pollutants under holistic way and systematical approach.

Acknowledgements

This work was supported in part by Japanese Grant-in-Aid for Human Resource Development Scholarship (JDS).

Special thanks for scientific advice to Dr. Riskieva Khurshida at the Research Institute of Soil Science and Agrochemistry.

References

- Charlesworth S.M., Lees J.A. (1999): Particulate-associated heavy metals in the urban environment: their transport from source to deposit, Coventry, UK. *Chemosphere*, **39**(5): 833-848.
- Guseva T.V., Molchanova Y.P., Zaika E.A., Vinichenko V.N.,

Averochkin E.M. (2000): *Gydrochemical indicators of the environment condition*. Ecoline, Russia, pp. 322.

- Kuiyi Y., Mao L., Yin D., Liu P., Luo H. (2008): Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam catalyzed by sulfonic acid resin in DMSO. *Catalysis Communications*, 9: 1521-1526.
- SoyuzNIXI (1963): *Methods on agrochemical, agrophysical and microbiological investigations in irrigated cotton regions*, Tashkent.
- Mohsen J. (2005): Nitrates leaching from agricultural land in Hamadan, western Iran. *Agriculture, Ecosystems and Environment*, **110**(3-4): 210-218.
- Nurrohim A., Sakugawa H. (2005): Fuel-based inventory of NO_x and SO_2 emissions from motor vehicles in the Hiroshima Prefecture, Japan. *Applied Energy*, **80**(3): 291-305.
- Razakov R.M., Toryanikova R.V., Talskikh V. N. (2003): Methods of surface waters quality evaluations: Standards and guidelines. *Materials of Central-Asian International Research Workshop*, Alma-Ata, 5-8th of May, Kazakhstan Republic.
- Riskieva Kh., Bairov A., Kuzieva A., Riskiev R., Nasedjanov M., Umarov M., Taipova Kh., Azimov R., Khodjaev A. (2002): Report: I-01-76 "Clean Soil – Healthy Population", *Research Institute of Soil Science and Agrochemistry of* Uzbekistan, Tashkent. pp.1-98.
- Tchobanoglous G, Schroeder D.E. (1985): "Phosphorus and phosphorus cycle"- Water Quality. University of California, Davis. Addison-Wesley Publishing Co., pp. 74-184.
- Toderich K., Tsukatani T., Mardonov B., Gintzburger G, Zemtsova O., Tsukervanik E., Shuyskaya E. (2002): Water quality, cropping and small ruminants: A challenge for the future agriculture in dry areas of Uzbekistan, *Research Project № 12372008*, Japan.
- Van der Perk M. (2006): Nutrients: Nitrogen cycle Part II. Soil and Water Contamination. Taylor & Francis Group, The Netherlands. pp. 113-124.
- Yamanaka M. (2007). "Application for soil samples". General Environmental Analysis for Field Survey. Elemental Analysis of Water and Soil. ISBN978-4-274-20464-7. Omsha, Tokyo, Japan. pp. 144-15.