Egyptian Journal of Aquatic Biology & Fisheries
Zoology Department, Faculty of Science,
Ain Shams University, Cairo, Egypt.
ISSN 1110 – 6131
Vol. 23(4): 659 – 666 (2019)
www.ejabf.journals.ekb.eg

Chemical composition and water quality of some rivers of the sverdlovsk oblast (Ural, Russia)

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ARTICLE INFO

Article History:
Received: Aug. 25, 2019
Accepted: Oct. 27, 2019
Online: Nov. 2019

Keywords:
Sverdlovsk oblast
Ural
Rissia
Chemical composition
water quality
Heavy metals
Biogenic compounds

ABSTRACT

The water quality of a river is very important as it is using for drinking and domestic purposes, agriculture and aquatic life including fish and fish farming. The concentration of the major ions (Cl^-, SO_4^{2-}, K^+, Na^+, Mg^{2+}, Ca^{2+}), nitrogen and phosphorus compounds (NH_4^+, NO_2^-, NO_3^-, HPO_4^{2-}), ions Ba^{2+}, Sr^{2+} , Heavy metals and trace elements (Ba^{2+}, Fe, Cd, Co, Si, Mn, Cu, Ni, Pb, Sr^{2+}, F^-, Zn), concentration was determined. The results showed that general indicators**,** according to the chromaticity value, samples of different rivers differed very strongly. According to the value of mineralization, the water of all samples was fresh. According to the cationic composition, 7 samples had calcium type and one (Pozarishka) had a mixed type. Also, the content of organic matter in the samples was generally significant. The lowest oxidation values were recorded in the samples of the Ufa river network (Nos. 6 and 7), The highest in the water of Iset river. The concentration of most elements in the water exceeded the standard values.

INTRODUCTION

The goal of water conservation in every country is to be achieved by strengthening watercare, which often means monitoring water quality. Chemical analysis and determination of tracing of heavy metals such as lead, cadmium, iron, copper, etc. are of great importance. Heavy metals include a number of physiologically important elements in their low levels, such as Cu, Fe, Zn; highly toxic like Pb, Mn, Cd, Hg, As, Sb and less toxic like Au, Ag, and Cr, etc (Odobasic 2012).

In water, heavy metals quickly decompose and settle in the form of soluble solid carbon, sulphates, and sulfides at the bottom. At that time, when the absorption capacity of the precipitate is exhausted, the concentration of metal ions in water increases (Biki 2016).

Water has become an important goods for the evolvement of industrial and agriculture. Water is completely not only important for the survival of human beings but also animals, plants and all other living things. (Palevitz 1999). Also, water is extremely important for the quality of life. Oceans, rivers, lakes, and streams together with the earth form the strengths on which life grows and react.. balance of environmental kept by the amount and water quality control the way of life of a people.. On the other hand, contaminated water is a huge source of disease, and, in addition to spoiling the earth, it also becomes unsuitable for life. (Siebe 1994).

Quality of water is a growing global challenge. Polluted water and poor sanitation are killing many children around the world every day. Quality of water is the physic-chemical and biological properties of water in relation to many of standards. The main uses considered for this feature are parameters that relate to drinking water, human contact safety, and ecosystem health. Interest in water analysis is associated with the tremendous importance of water for all categories of living things. It is necessary for the healthy development of humans, animals, and plants.

Water quality depends on the ion that dissolves in water. The main ions that are responsible for maintaining water quality are carbonate, bicarbonate, chloride, sulfate, nitrate, and fluorine. These ions are present in anionic form. Cation and anions must be equal in order to maintain water quality. Cations are also present in water in the form of hardness and salinity. Natural qualities of water are subject to destruction as a result of human activity. Municipal and industrial waters entering the water are the main source of organic and inorganic contaminants. (Kafia *et al.*, 2011). The chemical subject of water quality has become a cause of growing concern, as chemicals contaminated the environment in industrial effluents pose a great risk to humans, animals, and plants (Lou *et al.*, 2007).

The water quality may to give a detailed about of the concentration and state the organic and inorganic matter present in the water, together with certain physical characteristics of the water. the surface water composition is influenced by natural factors in the drainage basin and varies with seasonal differences in runoff volumes, weather conditions, and water levels (Mapfumo *et al.*, 2002). The purpose of the study is to assess water quality, the chemical composition, and determination of some heavy metals in some rivers of the Urals.

MATERIALS AND METHODS

Study area and sampling

Water sampling was carried out in the winter of 2017 from the surface of Sverdlovsk oblast's 8 rivers (Russian Federation). The sampling locations are presented in Table 1 and Fig. 1.

Table 1: Sampling sites on the rivers of the Sverdlovsk oblast in 2017

№	River	Location
1	Pozarishka	Kamensky district, Pozarishka village
2	Brusyanka	Beloyarsky district, Studencheskij village
3	Iset	Yekaterinburg city
4	Baltym	Verkhnyaya Pyshma city, Sadovij village
5	Pychma	Sukholozhsky district, Kuryi village
6	Manchazh	Artinsky district, Manchazh village
7	Ufa	Krasnoufimsky district, Kljuchiki village
8	Tura	Nizhneturinsky district, Nizhnyaya Tura

Sample preparation and analysis

In winter, eight surface water samples were taken, as well as from areas adjacent to the agricultural sector located near settlements, using 1000 ml polyethylene terephthalate (PET) bottles. All PET bottles were rinsed with the surface water of each area before sampling, and samples were taken 100 mm below the level of surface water, away from the edge of each surface river. Samples were appropriately labeled for on-site identification and immediately delivered to the laboratory immediately after sampling for storage and analysis.

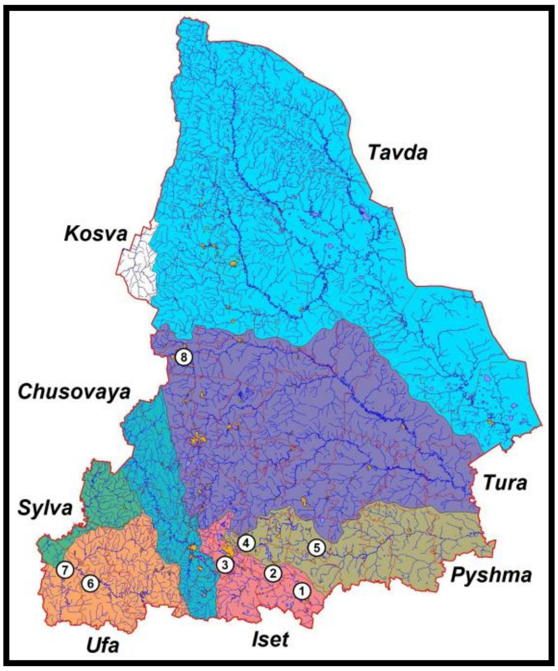

Fig. 1: Sampling locations on the map of the river basins of the Sverdlovsk oblast.

The storage time for the water samples was seven days at 4°C (in the refrigerator) by adding HNO_3 to maintain a pH of <2 in accordance with the guidelines for industrial waste resources (EPA and Victoria 2009).

The concentration of the major ions (Cl^-, SO_4^{2-}, K^+, Na^+, Mg^{2+}, Ca^{2+}), nitrogen and phosphorus compounds (NH_4^+, NO_2^-, NO_3^-, HPO_4^{2-}), and ions Ba^{2+}, Sr^{2+} was determined by capillary electrophoresis (“Capel-103R", Lumex®, St. Petersburg, Russia).

The data collection was obtained using electropherograms’ analysis and calculations with calibration curves were performed in the package “Multichrom for Windows” (version 1.52u, Ampersand Ltd, Moscow, Russia). The total alkalinity, the content of bicarbonate and carbonate ions were calculated by the inflection point of the titration curve for 30 mL of the sample with a 0.02 mL HCl. The calculations were performed in the Alkalinity calculator software (version 2.22) (Rounds 2013).

Photometric measurements were taken using a CFC-2 concentration photoelectric colorimeter (OJSC "Zagorsk Optical-Mechanical Plant", Sergiev Posad, Russia), potentiometric measurements were performed on I-160 MI ion meter (LLC “Measuring technique”, Moscow, Russia), and conductometric on conductometer EZ-1 (Meterics®, China).

Heavy metals

The analysis of the metal content in water was carried out after preliminary filtration on the atomic absorption spectrometer MGA-915MD (Lumex®, St. Petersburg, Russia). As calibration solutions the mixtures of state standard reference samples of individual ions were used.

Statistical Analysis

To build the Piper chart, we used the package GW_Chart (version 1.29), a new version of the MODFLOW Graphical User Interface for Argus ONE (MODFLOW

GUI) that adds support for the U.S. Geological Survey's MODFLOW-2000 and the Reservoir, Transient Leakage, Interbed Storage, Lake, and Gage packages. MODFLOW is a groundwater modeling program. It can be compiled and remedied according to the practical applications. Because of its structure and fixed data format, MODFLOW can be integrated with Geographic Information Systems (GIS) technology for water resource management. The new version can also import existing MODFLOW-88 and MODFLOW-96 models. A utility program, GW_Chart, was developed in conjunction with the MODFLOW GUI and is used for post-processing of the output of MODFLOW (Winston 2000). For the exploratory data analysis, the Principal Coordinates Analysis (PCoA) technique was used in the package PAST (version 3.24) (Hammer *et al.*, 1999).

RESULTS AND DISCUSSION

The results of the analysis are presented in Table 2.

Table 2: Chemical composition of water in some Sverdlovsk oblast rivers (excess standards for fisheries in bold)

№	Indicators	1	2	3	4	5	6	7	8
General indicators									
1	Alkalinity, mg/L	5.22	3.30	1.52	2.37	2.00	5.15	2.95	1.32
2	Chromaticity, ºchrome-cobalt scale	57.5	31.4	25.4	17.9	25.1	4.5	7.8	33.1
3	Conductivity, μS/cm	928	393	385	332	396	544	312	250
4	Mineralization, mg/L								
	- Residue at 180 ºC	509	227	138	148	272	335	192	115
	- Total dissolved solids	839	357	279	284	337	535	292	191
5	pH, scale	7.13	7.28	6.80	7.09	7.66	7.18	8.00	7.99
6	Total hardness, mg/L	8.99	3.86	3.24	3.27	3.87	6.03	3.53	2.41
Major ions and carbonate system, mg/L									
7	Bicarbonate (HCO_3^-)	318.4	201.3	92.7	144.6	122.0	314.2	180.0	80.5
8	Potassium (K^+)	11.9	2.3	2.0	5.2	4.8	1.6	1.6	.9
9	Calcium (Ca^{2+})	103.2	57.5	44.1	47.4	50.3	99.6	56.4	35.5
10	Carbonate (CO_3^{2-})	.27	.21	.03	.09	.31	.27	.96	.41
11	Magnesium (Mg^{2+})	46.7	12.0	12.6	11.0	16.5	12.9	8.7	7.8
12	Sodium (Na^+)	65.3	13.7	13.2	9.8	18.2	8.9	6.9	5.7
13	Sulphate (SO_4^{2-})	218.4	32.8	75.2	33.0	87.7	49.1	25.5	46.1
14	Chloride (Cl^-)	63.4	20.7	29.1	26.1	31.9	11.8	8.4	8.3
Biogenic compounds, mg/L and organic matter									
15	Ammonium (NH_4^+)	.41	.18	.46	.28	.10	.14	.03	.15
16	Nitrate (NO_3^-)	2.23	11.3	4.44	1.84	2.86	24.1	1.49	.58
17	Nitrite (NO_2^-)	**2.04**	**.16**	**1.10**	**.15**	**1.06**	**.38**	**.16**	**2.24**
18	Phosphate (HPO_4^{2-})	**.43**	**.20**	.14	.02	**.27**	**.53**	**.23**	**.25**
19	Permanganate oxidability, mgO/L	5.09	5.52	7.49	5.62	5.17	1.47	2.06	7.44
Heavy metals and trace elements, mg/L									
20	Barium (Ba^{2+})	**1.84**	.44	.13	.21	.09	**2.11**	.34	.15
21	Iron (Fe)	.029	.045	.097	.064	.029	.045	.037	**1.91**
22	Cadmium (Cd)	**.0063**	.0047	.0031	.0047	.0015	.0015	.0047	.0015
23	Cobalt (Co)	**.317**	**.121**	**.138**	**.105**	**.061**	**.043**	**.036**	**.024**
24	Silicon (Si)	3.64	4.25	2.71	4.07	.66	5.44	.46	1.41
25	Manganese (Mn)	**.019**	**.016**	**.013**	**.013**	**.013**	**.013**	**.019**	**.019**
26	Copper (Cu)	**.012**	**.010**	**.006**	**.008**	**.003**	**.003**	**.002**	**.003**
27	Nickel (Ni)	**.103**	**.086**	**.035**	**.086**	**.052**	**.069**	**.035**	**.035**
28	Lead (Pb)	**.106**	**.083**	**.062**	**.083**	**.083**	**.106**	**.133**	**.083**
29	Strontium (Sr^{2+})	**.67**	.25	.28	.20	.08	**4.60**	**.58**	.16
30	Fluorine (F^-)	.15	.14	.45	.10	.16	.14	.10	.08
31	Zinc (Zn)	**.057**	**.187**	**.063**	**.084**	**.084**	**.107**	**.106**	**.084**

General indicators

According to the chromaticity value, samples of different rivers differed very strongly: from 1.52 in the Iset River to 57.5 in the Pozarishka River. The water of 5 rivers had a neutral reaction, 3-slightly alkaline. According to the value of mineralization, the water of all samples was fresh (<1000 mg/L). The water of most (6) samples was soft (<4 mg/L), in Manchazh river had medium hardness (4–8 mg/L) and in Pozarishka river had high hardness.

Major ions

The ratios of principal ions equivalent concentrations are presented in Fig. 2. According to the cationic composition, 7 samples had calcium type and one (Pozarishka) had a mixed type due to a slightly higher proportion of sodium and magnesium. On the cation's ternary plot all the samples formed a line, which indicates cation's similarity of the sources in the waters of the studied rivers. According to the anionic composition, 5 samples had a bicarbonate type and 3 samples had mixed sulphate-bicarbonate. On the anion field of the graph, the samples formed two clusters differing in the relative proportion of sulfate ions. In general, the presence of one cationic and two anionic trends should be interpreted as the source of the main ions' origin in the studied rivers is the leaching of calcium and magnesium carbonates from carbonate sediments: limestone, dolomite and anhydrite (Olkowska *et al.,* 2017). It can be assumed that the role of anhydrites in the formation of the anionic composition of the Pozarishka, Iset, Pyshma and Tura rivers is higher.

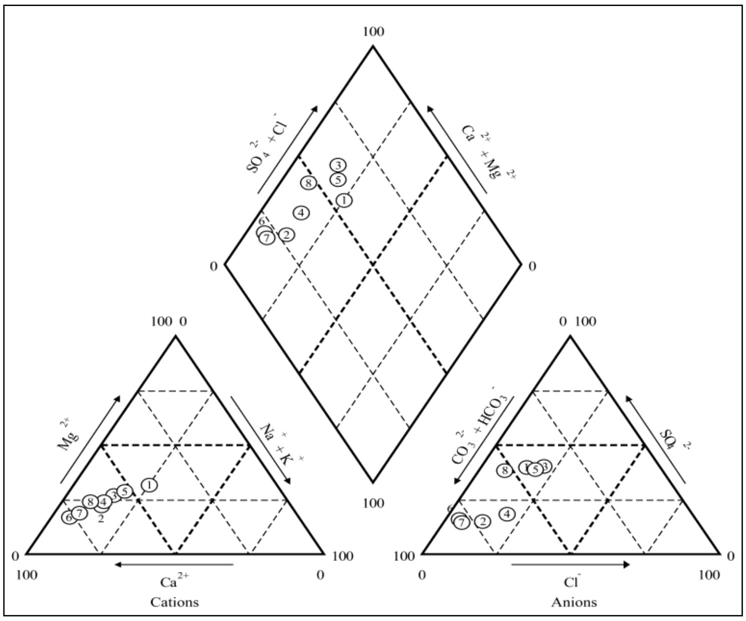

Fig. 2: Piper diagram of water samples in the study area

Biogenic compounds and organic matter

The content of organic matter in the samples was generally significant. The lowest oxidation values were recorded in the samples of the Ufa river network (Nos. 6 and 7), The highest in the water of Iset River. Total ammonia (TAN), in particular, the union compound, is one of the main environmental pollutants in freshwater systems that are physiologically harmful to aquatic organisms and affect the functionality of ecosystems (Leoni *et al.,* 2018). Ammonium concentrations were low, indicating a lack of fresh organic water pollution. However, in all the samples the concentration of nitrate was increased. Nitrites are the last part of the oxidation of organic nitrogen in the chain: ammonium - nitrite - nitrate. Therefore, the presence of nitrite should be interpreted as the incompleteness of the nitrogen oxidation processes as a result of oxygen deficiency (Olkowska *et al.*, 2017; Leoni *et al.*, 2018). Since the sampling was carried out in winter, when the rivers are covered with ice, the lack of oxygen is natural. Thus, elevated nitrate concentrations should be considered as a seasonal phenomenon, not associated with anthropogenic impact. The concentration of phosphates in most samples exceeded the standards for eutrophic water bodies (0.2 mg/L), but not too high.

Heavy metals and trace elements

The concentration of most elements in the water exceeded the standard values. It should be noted that in the Russian Federation the standards for the quality of natural waters for trace elements are quite strict because they imply the use of waters for the fishery. Elevated relative to the standards, the concentration of elements is usually for the Ural region and is associated with the peculiarities of the geochemical background. It is dominated by natural-man-made biogeochemical provinces in places of natural mineral deposits (brown coal, peat, metals, sand, clay, stones, and minerals) and industrial enterprises associated with them for their extraction and processing. Thus, the observed state is fairly common to the studied area's waters(Bobrova 2016).

In an attempt to identify possible patterns of microelements, we applied a multivariable PCoA technique. Its results are interpreted similarly to the analysis of PCA; however, not only the Pearson correlation, but also other similarity measures can be used, and we used the non-parametric Spearman correlation. The results of the analysis are presented in the ordination diagram (Fig. 3).

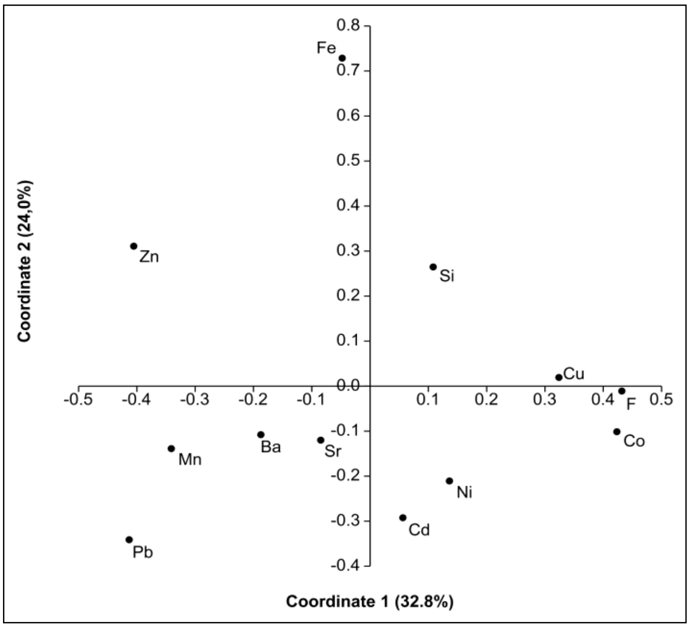

Fig. 3: Heavy metals and trace elements in the space of the first two principal coordinates of the metric scaling analysis (similarity – Spearman's Rho).

It can be seen that the first two axes explained more than 50% of the data's variability, with the first axis being about a third. With the greatest positive loadings, it included F, Co, Cu, and with the smallest – Pb, Zn, Mn. Despite the small sample, the pattern of elements on the right side of the diagram is well interpreted. Cobalt, nickel, chromium and copper in the Urals are often in association, as they have a common origin, namely, the ultrabasic hyperbasites (ultrabasites) of the Ural mountains. As a result of the weathering processes, rocks are destroyed and this group of elements is consistently present in soils, as well as in bottom sediments and water of water bodies. The presence of fluorine in this pattern is also explicable. It is known that, unlike most other ultrabasites, which usually contain 20 mg/kg of fluorine, the Urals ultrabasic contains an average of 590 mg/kg (up to 1300 mg/kg) of fluorine (Yanin 2007). As can be seen from table 2, the highest concentrations of Co, F and Cu were noted in samples 1, 2 and 3. Thus, the results of PCoA indicate that the formation of the trace element composition of the Iset river basin's waters is significantly influenced by the natural weathering processes of the Ural ultrabasites.

For coordinate 2, the largest multidirectional loadings gave Fe vs Pb, Cd. This pattern is interpreted worse. It can only be noted that Pb and Cd can have a technogenic origin, and the variability of iron is most likely due to natural causes.

CONCLUSION

The concentration of most elements in the water exceeded the standard values. It should be noted that in the Russian Federation the standards for the quality of natural waters for trace elements are quite strict since they imply the use of water for fishing. Elevated concentration of elements relative to standards is usually for the Ural region and is associated with the peculiarities of the geochemical background. Also, the content of organic matter in the samples was generally significant, ammonium concentrations were low, indicating a lack of fresh organic water pollution. Mining and minerals activities in the Urals region have a negative impact on water bodies in terms of increased pollution, which affects water quality, characteristics and components.

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