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ECO-CHEMICAL MONITORING OF BASITCHAY

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Abstract
During environmental monitoring, the aquatic environment is considered a primary focus because pollutants can migrate long distances within a short time. Despite the self-cleaning capacity of rivers, the proximity of residential areas often requires regular monitoring. In aquatic environments, the presence of heavy metals and pH levels, which can affect biocenoses, must be taken into account. The impact of heavy metals on living organisms varies significantly. Our research examines cations and anions that influence ecosystem integrity, considering whether their concentrations exceed permissible limits. The study focused on elements such as manganese, copper, molybdenum, nickel, lead, cobalt, iron, and zinc, along with anions like chloride, sulfate, ammonium, nitrate, and nitrite. Additionally, their physicochemical parameters were analyzed. Seasonal changes and water flow were also considered.

Keywords: Basitchay, ecological monitoring, metal, drinking water, electrical conductivity, anion, cation, ecotoxicants.

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Introduction

Zangilan District is located in the southwestern part of the Republic of Azerbaijan. The district's landscape is characterized by a complex and fascinating terrain of alternating plains, elevations, and valleys carved by river flows. Four rivers flow through the district: Araz, Okhchuchay, Hakari, and Basitchay. Basitchay, a left tributary of the Araz River, originates in the Republic of Armenia. The river stretches 44 km in length (17 km of which lies within Azerbaijan's territory) and has a catchment area of 354 km² (156 km² within Azerbaijan's territory).

The river's flow varies: 0.65 m³/s during dry years, 2.10 m³/s during average years, and 4.05 m³/s during wet years. However, it is polluted by waste from pig farms in Armenia's mountainous villages. Within Zangilan District, Basitchay is a tributary of the Araz River and is locally referred to as

Balachay. The section flowing through Baharli village is called Baharli, while the section near Razdara village is known as Razdara [4].

The valley through which Basitchay flows, sometimes referred to as the Basutchay Valley in certain sources, is a state reserve that protects rare oriental plane trees. Basitchay merges with tributaries such as Sukhavuz, Khachinchay, Sobuchay, and Chopadara before flowing into the renowned Chinar Reserve (Kinav Valley)—the largest of its kind in Europe. The river primarily winds through dense forests (mainly plane and walnut trees).

The lower reaches of the river have been developed for horticulture and agriculture, particularly sericulture, viticulture, and grain farming [6]. A visual depiction of the river is presented in Figure 1.

Continuous monitoring of this river is of great importance. Regular monitoring efforts are crucial for maintaining the environmental balance. Following the liberation of the Karabakh region, conducting analyses of the section of Basitchay within Azerbaijan's territory has become a vital and necessary task [1,7]. Therefore, we have selected Basitchay as the focus of this study.

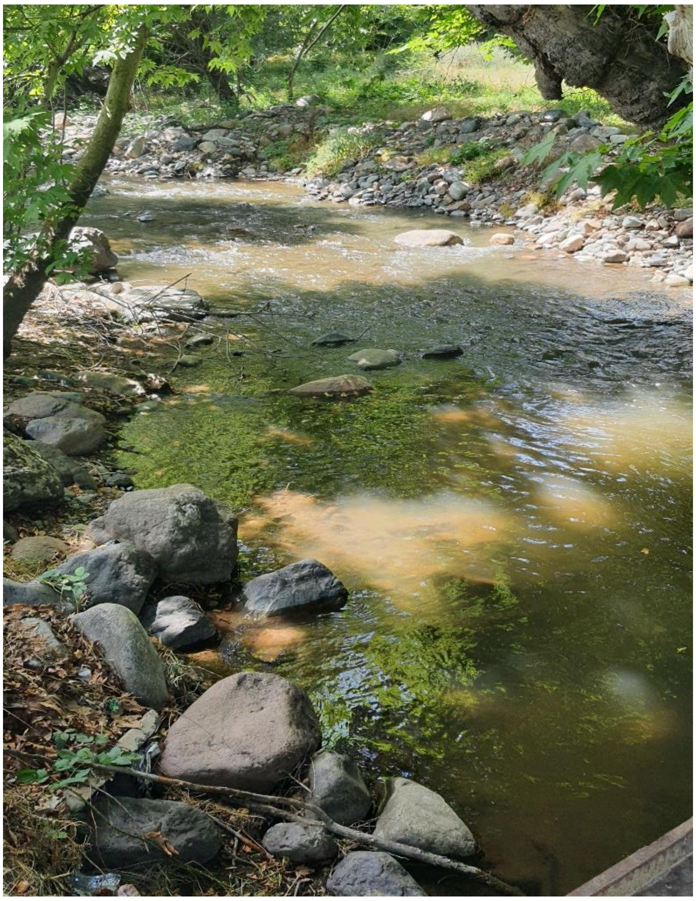

Figure 1. Basitchay

Materials and methods

To determine the GPS coordinates of the samples, a GARMIN Etrex 10 device was used. Sampling is a critical part of the analysis, as the reliability of the data depends on it. The location, frequency, and technique of sample collection must ensure representativeness to a certain extent, as conclusions about the state of the water body are drawn based on their analysis. Physical and chemical parameters were studied using atomic absorption and atomic emission methods, while anions and cations were analyzed spectrometrically [9, 12, 14, 18].

The obtained results were compared with the permissible concentration limits (PCL) for surface waters, as specified in the regulation "Rules for Protecting Surface Waters from Pollution by Wastewater," approved by the State Committee for Ecology and Natural Resource Use of the Republic of Azerbaijan on January 4, 1994 (Order No. 01) [17].

Results and discussion

Initially, monitoring was conducted for the upper, middle, and lower courses of Basitchay. Water samples were collected from sections of the river passing through the Razdara, Ordekli, and Baharli villages [5]. The GPS coordinates of the sampling locations are presented in Table 1.

Table 1. GPS Coordinates of Basitchay Sampling Locations

№	Territory	Coordinates	
1	Rəzdərə kəndi	39⁰04'08.0"	46⁰33'48.5"
2	Ördəkli kəndi	39⁰02'27.5"	46⁰38'42.7"
3	Baharlı kəndi	39⁰00'41.1"	46⁰41'03.4"

Water samples were analyzed on the following dates: December 19, 2022; January 16-18, 2023; January 25-26, 2023; February 2-3, 2023; February 9-10, 2023; and February 21, 2023. The research covers the winter months, and the effect of water flow rates on the concentration of substances was also studied. The results are presented in Tables 2, 3, 4, 5, 6, and 7.

Table 2. Results of Water Sample Analysis from Basitchay (December 19, 2022)

№	Component Name	Unit of Measurement	Component Quantities			PLC
			Razdara village	Ordekli village	Baharli village	
1	**Hydrogen indicator, pH**	–	7.9	8.0	8.1	6.5-8.5
2	**Dissolved oxygen**	mgO_2/L	8.2	8.2	8.2	≥4.0
		%	82.0	83.0	82.0	
3	**Electrical conductivity**	S/m	0.387	0.391	0.390	–
			0.406	0.403	0.402	
4	**Hardness**	meq/L	3.6	3.62	3.61	7.0
5	**Chloride ion, Cl^-**	mg/L	8.9	8.3	9.0	350
6	**Sulfate ion, SO_4^{2-}**	mg/L	40.5	42.3	42.0	500
7	**Ammonium ion, NH_4^+**	mg/L	0	0	0	0.5
8	**Nitrite ion, NO_2^-**	mg/L	0	0	0	3.3
9	**Nitrate ion, NO_3^-**	mg/L	0.31	0.42	0.29	45.0
10	**Zinc, Zn**	μg/L	1.58	2.47	5.07	1000
11	**Iron, Fe**	μg/L	5.03	3.34	<LOD	300

12	**Cobalt, Co**	µg/L	1.86	1.83	3.0	100
13	**Lead, Pb**	µg/L	<LOD	<LOD	<LOD	30
14	**Nickel, Ni**	µg/L	0.159	<LOD	<LOD	100
15	**Molybdenum, Mo**	µg/L	20.3	8.02	6.22	250
16	**Manganese, Mn**	µg/L	7.62	1.49	<LOD	100
17	**Copper, Cu**	µg/L	4.47	5.16	5.42	1000

Table 3. Analysis Results of Samples Taken from Basitchay on January 16-18, 2023

№	**Component Name**	**Unit of Measurement**	**Component Quantities**			**PLC**
			Razdara village	**Ordekli village**	**Baharli villa**	
1	**Hydrogen indicator, pH**	–	7.8	8.0	8.1	6.5-8.5
2	**Dissolved oxygen**	mgO_2/L	8.6	8.5	8.6	≥4.0
		%	91.0	90.0	90.0	
3	**Electrical conductivity**	$x10^{-3}$ S/m	0.397	0.399	0.393	–
4	**Hardness**	meq/L	3.51	3.51	3.5	7.0
5	**Chloride ion, Cl^-**	mg/L	8.3	8.3	8.3	350
6	**Sulfate ion, SO_4^{2-}**	mg/L	39.6	42.0	41.6	500
7	**Ammonium ion, NH_4^+**	mg/L	0	0	0	0.5
8	**Nitrite ion, NO_2^-**	mg/L	0	0	0	3.3
9	**Nitrate ion, NO_3^-**	µg/L	0.3	0.35	0.27	45.0
10	**Zinc, Zn**	µg/L	<LOD	<LOD	109	1000
11	**Iron, Fe**	µg/L	5.87	6.45	10.8	300
12	**Cobalt, Co**	µg/L	3.57	4.4	4.72	100
13	**Lead, Pb**	µg/L	<LOD	<LOD	1.92	30
14	**Nickel, Ni**	µg/L	0.099	0.223	<LOD	100
15	**Molybdenum, Mo**	µg/L	3.91	24.9	32.3	250
16	**Manganese, Mn**	µg/L	20.2	19.4	39.8	100
17	**Copper, Cu**	µg/L	6.35	5.16	11.3	1000

Table 4. Analysis Results of Samples Taken from Basitchay on January 25-26, 2023

№	**Component Name**	**Unit of Measurement**	**Component Quantities**			**PLC**
			Razdara village	**Ordekli village**	**Baharli villa**	
1	**Hydrogen indicator, pH**	–	8.2	8.3	8.4	6.5-8.5
2	**Dissolved oxygen**	mgO_2/L	9.0	9.4	9.3	≥4.0
		%	94.0	98.0	97.0	
3	**Electrical conductivity**	µS/m	0.3880	0.390	0.391	–
4	**Hardness**	meq/L	3.4	3.5	3.5	7.0
5	**Chloride ion, Cl^-**	mg/L	8.1	8.0	8.2	350
6	**Sulfate ion, SO_4^{2-}**	mg/L	41.2	34.9	32.5	500
7	**Ammonium ion, NH_4^+**	mg/L	0.4	0.1	0.1	0.5

8	**Nitrite ion, NO_2^-**	mg/L	0	0.01	0	3.3
9	**Nitrate ion, NO_3^-**	µg/L	0.02	0.01	0	45.0
10	**Zinc, Zn**	µg/L	<LOD	<LOD	<LOD	1000
11	**Iron, Fe**	µg/L	<LOD	<LOD	0.026	300
12	**Cobalt, Co**	µg/L	2.44	3.64	2.88	100
13	**Lead, Pb**	µg/L	<LOD	<LOD	<LOD	30
14	**Nickel, Ni**	µg/L	<LOD	<LOD	<LOD	100
15	**Molybdenum, Mo**	µg/L	5.18	4.38	4.88	250
16	**Manganese, Mn**	µg/L	<LOD	3.25	<LOD	100
17	**Copper, Cu**	µg/L	7.1	7.33	3.32	1000

Table 5. Analysis Results of Samples Taken from Basitchay on February 2-3, 2023

№	**Component Name**	**Unit of Mea urement**	**Component Quantities**			**PLC**
			Razdara v lage	**Ordekli villa**	**Baharli village**	
1	**Hydrogen indicator, pH**	–	7.9	7.7	8.0	6.5-8.5
2	**Dissolved oxygen**	mgO_2/L	8.5	8.1	7.8	≥4.0
		%	91.0	87.0	83.0	
3	**Electrical conductivity**	µS/m	0.389	0.389	0.390	–
4	**Hardness**	meq/L	3.3	3.32	3.41	7.0
5	**Chloride ion, Cl^-**	mg/L	8.6	7.9	7.9	350
6	**Sulfate ion, SO_4^{2-}**	mg/L	30.4	31.4	27.3	500
7	**Ammonium ion, NH_4^+**	mg/L	0.03	0.05	0.04	0.5
8	**Nitrite ion, NO_2^-**	mg/L	0	0.02	0	3.3
9	**Nitrate ion, NO_3^-**	mg/L	0.44	0.46	0.45	45.0
10	**Zinc, Zn**	µg/L	<LOD	<LOD	<LOD	1000
11	**Iron, Fe**	µg/L	10.5	4.36	5.2	300
12	**Cobalt, Co**	µg/L	3.06	3.46	2.98	100
13	**Lead, Pb**	µg/L	<LOD	<LOD	<LOD	30
14	**Nickel, Ni**	µg/L	2.38	1.03	1.49	100
15	**Molybdenum, Mo**	µg/L	4.17	19.2	11.3	250
16	**Manganese, Mn**	µg/L	18.3	21.7	22.1	100
17	**Copper, Cu**	µg/L	14.8	10.1	8.82	1000

Table 6. Analysis Results of Samples Taken from Basitchay on February 9-10, 2023

№	**Component Name**	**Unit of Meas urement**	**Component Quantities**			**PLC**
			Razdara vill	**Ordekli vill**	**Baharli village**	
1	**Hydrogen indicator, pH**	–	7.8	7.7	7.7	6.5-8.5
2	**Dissolved oxygen**	mgO_2/L	7.7	8.4	8.3	≥4.0
		%	80.0	87.0	86.0	
3	**Electrical conductivity**	µS/m	0.387	0.386	0.385	–

4	**Transparency**	cm	29	29	29	>30
5	**Hardness**	meq/L	3.9	3.9	3.87	7.0
6	**Calcium ion, Ca^{2+}**	mg/L	56.1	54.7	54.3	–
7	**Magnesium ion, Mg^{2+}**	mg/L	14.6	14.2	14.7	–
8	**Chloride ion, Cl^{-}**	mg/L	7.91	8.57	8.6	350
9	**Bicarbonate ions**	mg/L	192.0	185.1	193.0	–
10	**Carbonate ions, CO_3^{2-}**	mg/L	27.4	27.6	30.0	–
11	**Sulfate ion, SO_4^{2-}**	mg/L	30.1	30.8	25.2	500
12	**Ammonium ion, NH_4^{+}**	mg/L	0.04	0.03	0.04	0.5
13	**Nitrite ion, NO_2^{-}**	mg/L	0	0	0	3.3
14	**Nitrate ion, NO_3^{-}**	mg/L	0.51	0.47	0.55	45.0
15	**Na^{+} + K^{+} ions**	mg/L	2.0	0.3	1.2	–
16	**Zinc, Zn**	µg/L	0.165	0.0539	3.99	1000
17	**Iron, Fe**	µg/L	8.1	7.11	8.93	300
18	**Cobalt, Co**	µg/L	4.06	4.0	1.34	100
19	**Lead, Pb**	µg/L	<LOD	<LOD	<LOD	30
20	**Nickel, Ni**	µg/L	1.75	<LOD	0.913	100
21	**Molybdenum, Mo**	µg/L	4.17	21.9	8.63	250
22	**Manganese, Mn**	µg/L	3.18	25.8	24.7	100
23	**Copper, Cu**	µg/L	7.19	4.37	4.44	1000

Table 7. Analysis Results of Samples Taken from Basitchay on February 21, 2023

№	**Component Name**	**Unit of Me urement**	**Component Quantities**			**PLC**
			Razdara v lage	**Ordekli vi lage**	**Baharli village**	
1	**Hydrogen indicator, pH**	–	8.1	8.0	8.1	6.5-8.5
2	**Dissolved oxygen**	mgO_2/L	7.8	7.8	8.0	≥4.0
		%	82.0	82.0	85.0	
3	**Electrical conductivity**	µS/m	0.390	0.389	0.388	–
4	**Transparency**	cm	29	29	29	>30
5	**Hardness**	meq/L	4.12	3.89	3.99	7.0
6	**Calcium ion, Ca^{2+}**	mg/L	57.7	54.6	56.0	–
7	**Magnesium ion, Mg^{2+}**	mg/L	15.0	14.2	14.6	–
8	**Chloride ion, Cl^{-}**	mg/L	8.5	8.47	8.48	350
9	**Bicarbonate ions, HCO_3^{-}**	mg/L	207.5	197.0	195.1	–
10	**Carbonate ions, CO_3^{2-}**	mg/L	6.0	8.3	9.7	–
11	**Sulfate ion, SO_4^{2-}**	mg/L	30.17	31.5	30.73	500
12	**Ammonium ion, NH_4^{+}**	mg/L	0	0	0	0.5
13	**Nitrite ion, NO_2^{-}**	mg/L	0	0	0	3.3
14	**Nitrate ion, NO_3^{-}**	mg/L	0.62	0.51	0.54	45.0
15	**Na^{+} + K^{+} ions**	mg/L	8.0	8.5	5.65	–
16	**Zinc, Zn**	µg/L	0.159	0.0402	4.02	1000
17	**Iron, Fe**	µg/L	8.4	7.3	8.95	300
18	**Cobalt, Co**	µg/L	3.99	3.95	1.26	100

19	**Lead, Pb**	µg/L	2.1	1.1	3.45	30
20	**Nickel, Ni**	µg/L	1.63	<LOD	0.875	100
21	**Molybdenum, Mo**	µg/L	4.02	19.4	8.02	250
22	**Manganese, Mn**	µg/L	3.05	20.3	23.4	100
23	**Copper, Cu**	µg/L	7.23	5.11	3.96	1000

The hydrogen indicator holds great significance. The increase or decrease in its amount in water can lead to serious ecological consequences. A low pH value indicates an acidic environment. This implies that, in an acidic environment, metals become active and more dangerous for the surrounding environment. In other words, conditions arise for metals to easily react with any compound or substance [2, 3, 8, 10, 11, 13]. For this reason, this parameter should be analyzed first. Dissolved oxygen affects the integrity of the ecosystem.

The salinity of water is associated with dissolved salts (chlorides, sulfates, bicarbonates of metals) in the water. Salinity is measured in g/L. In freshwaters, 80% of the dissolved salts consist of calcium and magnesium bicarbonates. The hardness of water can be carbonate or temporary. Temporary hardness can be removed by boiling. Sulfates and chlorides, however, cause permanent hardness, which cannot be eliminated through boiling.

The parameter of electrical conductivity quantifies the ability of aqueous solutions to conduct electric current. The electrical conductivity of natural waters depends on the concentration of mineral salts and temperature. Natural waters are mixtures of strong electrolytes. Other ions, such as Fe^{3+}, Fe^{2+}, Mn^{2+}, Al^{3+}, NO_3^-, and HPO_4^{2-}, do not significantly affect electrical conductivity unless present in high concentrations.

The mineral composition of natural waters can be inferred from their electrical conductivity. Challenges in determining the total mineral content based on specific electrical conductivity arise due to varying conductivity values for different salts and the increase in conductivity with temperature. The normal mineralization level of 2 mS/cm (1,000 mg/dm^3) and 3 mS/cm (1,500 mg/dm^3) approximately corresponds to chloride and carbonate mineralization in terms of specific electrical conductivity.

The value of specific electrical conductivity primarily reflects the total concentration of inorganic electrolytes and is used in water quality monitoring programs. Specific electrical conductivity is a reliable indicator of anthropogenic impacts. Electrical conductivity, denoted as k (EC), quantifies the ability of aqueous solutions to conduct electric current. Conductivity depends on the presence of ions, their total concentration, mobility, valency, and the measurement temperature.

Solutions of certain inorganic compounds are relatively good conductors. Conversely, solutions of organic compounds whose molecules do not dissociate in solution either do not conduct electricity or conduct very poorly.

One of the most important indicators of water quality in natural water bodies is transparency. The approximate value of water transparency is measured using a Secchi disk, a 30 cm diameter white metal disk. The disk is lowered into the water until it is no longer visible. The depth at which it disappears characterizes the transparency of the water.

In natural waters, the amount of hydrogen ions is determined by the concentration of carbonic acid and the ratio of its ions. Surface waters with low carbon dioxide content are typically characterized by an alkaline reaction. Changes in pH are closely related to the process of photosynthesis. The source of hydrogen ions is the humic acids found in soil. The hydrolysis of heavy metals only plays a role when large amounts of sulfates from metals like Al, Fe, Cu, and others are present in the water.

The pH value in river waters typically ranges from 6.5 to 8.5; in atmospheric precipitation, it ranges from 4.6 to 6.1; in swamps, it is 5.5 to 6.0; and in seawater, it is 7.9 to 8.3. Seasonal changes also influence pH levels. In most cases, the pH of river water is 6.8-7.4 in winter and 7.4-8.2 in summer. According to the requirements for the properties and composition of freshwater, the pH value should not exceed 6.5-8.5. The pH value of water is an essential characteristic of its quality. It plays a significant role in the chemical and biological processes occurring in water. Additionally, the pH value influences the transformations of various forms of biogenic elements and alters the toxicity of pollutants [15, 16].

Dissolved oxygen exists in water in a molecular form. Two opposing processes affect its concentration in water: one increases the oxygen concentration, while the other decreases it. The absorption of atmospheric oxygen occurs at the surface of the water body. The rate of this process increases with rising pressure and decreasing mineralization. Aeration—the saturation of lower water layers with oxygen—occurs as a result of the mixing of water masses. The photosynthetic release of oxygen happens during the assimilation of carbon dioxide by aquatic plants. The process of photosynthesis intensifies with increases in water temperature, the intensity of sunlight, and the quantity of biogenic substances. Oxygen forms in the upper layers of the water.

Processes that reduce oxygen concentration include reactions where oxygen is consumed for the oxidation of organic substances. These reactions are biological (respiration of organisms), biochemical (respiration of bacteria and oxidation of organic matter), and chemical (oxidation of Fe^{2+}, Mn^{2+}, NO_2^-, NH_4^+, CH_4, and H_2S). The rate of oxygen consumption increases with the amount of bacteria and substances subjected to chemical and biochemical oxidation. Additionally, a reduction in dissolved oxygen levels occurs as oxygen escapes from the surface into the atmosphere.

Conclusion

The amount of dissolved oxygen in surface waters depends on seasonal and daily variations. Dissolved oxygen concentrations can reach values as low as 2.5 mg/dm^3. The distribution of oxygen during winter and summer has a seasonal character.

Thus, due to Basitchay's proximity to residential areas, it is crucial to conduct regular ecological monitoring. This is vital for ensuring the safety of living organisms in the environment.

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