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DETERMINATION OF IRON IONS IN RIVER WATERS AND THEIR IMPACT ON THE ECOSYSTEM

Iron is an important micronutrient in biocenoses. Its balanced presence ensures the normal functioning of ecosystems. However, anthropogenic pollution with iron or artificial addition of iron can disrupt the balance in ecosystems.

In this manuscript, we studied the influence of the iron ion in the Oxchu River passing through the Burunlu and Sayifli villages located in Azerbaijan on various ecosystems. The dynamics of iron ion concentration affecting biocenosis were investigated from January to August. The GPS coordinates of the sampling locations in the river were determined using an Etrex-10 device. Water samples were analyzed in the laboratory using the SM 3030 (A-K) and ISO 11885 methods. The main analyses were performed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The maximum concentration of iron ions in the Burunlu village section was observed in the first decade of May, reaching 2330 $\mu\text{g/L}$. In the Oxchu River flowing through Sayifli village, the highest concentration was also observed in the first decade of May. The migration of pollutants in the aquatic environment occurs rapidly; therefore, studying it is extremely important from both ecological and economic perspectives.

Keywords: clean water, river ecosystem, iron ion, ecology, Inductively Coupled Plasma Optical Emission Spectrometry.

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Өзен суларындағы темір иондарын және олардың экожүйеге әсерін анықтау

Темір биоценоздарда микроэлемент ретінде шешуші рөл атқарады. Оның оңтайлы деңгейлері экожүйелердің дұрыс жұмыс істеуіне ықпал етеді. Дегенмен адам әрекетінен немесе осы элементті жасанды енгізуден туындаған темірдің ластануы экожүйедегі теңгерімсіздікке әкелуі мүмкін.

Бұл мақалада біз Әзірбайжанда орналасқан Бурунлу және Сайфли ауылдары арқылы ағып жатқан Охчу өзеніндегі темір ионын зерттедік. Биоценозға әсер ететін темір ионының концентрациясының динамикасы қаңтар-тамыз аралығында зерттелді. Өзендегі сынама алу орындарының GPS координаттары Etrex-10 құрылғысының көмегімен анықталды. Су үлгілері зертханалық жағдайларда SM 3030 (A-K) және ISO 11885 әдістерін қолдана отырып талданды. Негізгі талдаулар индуктивті байланысқан плазмалық оптикалық эмиссиялық спектрометрияны (ICP-OES) қолдану арқылы орындалды. Бурунлу ауылы учаскесінде темір иондарының ең жоғары концентрациясы мамыр айының бірінші онкүндігінде байқалып, 2330 $\mu\text{g/L}$ -ге жетті. Сайфли ауылы арқылы өтетін Охчу өзенінде де ең жоғары концентрация мамыр айының бірінші онкүндігінде байқалды. Су ортасындағы ластаушы заттардың миграциясы тез жүреді, сондықтан оны зерттеу экологиялық жағынан да, экономикалық тұрғыдан да өте маңызды.

Түйін сөздер: таза су, өзен экожүйесі, темір иондары, экология, индуктивті байланысқан плазмалық оптикалық эмиссия спектрометриясы.

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Определение ионов железа в речных водах и их влияние на экосистему

Железо играет ключевую роль как микроэлемент в биоценозах. Его оптимальное количество способствует правильной работе экосистем. В то же время загрязнение железом, вызванное деятельностью человека, или искусственное внесение этого элемента могут привести к дисбалансу в экосистемах.

В данной статье был изучено влияние иона железа в реке Охчу, протекающей через села Бурунлу и Сайфли, расположенные в Азербайджане. Динамика концентрации ионов железа, влияющая на биоценоз, была исследована с января по август. GPS-координаты мест отбора проб в реке были определены с помощью прибора Etrex-10. Образцы воды были проанализированы в лабораторных условиях с использованием методов SM 3030 (A-K) и ISO 11885. Основные анализы были выполнены с помощью оптической эмиссионной спектрометрии с индуктивно связанной плазмой (ICP-OES). Максимальная концентрация ионов железа в створе села Бурунлу наблюдалась в первой декаде мая и достигала 2330 мкг/л. В реке Охчу, протекающей через село Сайфли, самая высокая концентрация также наблюдалась в первой декаде мая. Миграция загрязняющих веществ в водной среде происходит быстро, поэтому ее изучение крайне важно как с экологической, так и с экономической точки зрения.

Ключевые слова: чистая вода, речная экосистема, ионы железа, экология, оптическая эмиссионная спектрометрия с индуктивно связанной плазмой.

Introduction

Constant monitoring of environmental pollution is of great importance in terms of its impact on the biosphere. Pollutants can enter the food chain in the environment and cause serious consequences. Therefore, it is necessary to regularly monitor pollutants in the environment. Chemical components have the ability to migrate within the environment [4]. This migration occurs particularly rapidly in aquatic environments. In this regard, continuous monitoring of freshwater sources such as rivers, lakes, and reservoirs is essential. Pollution by metals can spread over long distances [2,8,13,19]. Therefore, rivers are of particular importance in this context. Migrating metals can enter various biocenoses and affect their integrity. For this reason, we have chosen iron as our target element. Iron mainly limits the growth of phytoplankton in aquatic ecosystems. This affects the carbon cycle and climate change. Overall, both phytoplankton and zooplankton are sensitive to high concentrations of iron. The decline of these organisms impacts the entire trophic chain, including fish, amphibians, and birds. Excessive amounts of iron, especially in water, can be toxic to certain organisms [17,18]. It can lead to oxidative stress and cellular damage, resulting in reduced species diversity. High levels of iron salts (Fe^{2+} and Fe^{3+}) can alter the pH level of water and affect the bioavailability of other elements. This poses a risk of stress or poisoning for fish and other aquatic organisms. Iron reacts with oxygen to form iron hydroxide ($\text{Fe}(\text{OH})_3$) precipitates. This process reduces the amount of available oxygen in the water, leading to oxygen deficiency for fish and other aerobic organisms [1,3,9,11]. Iron precipitates (rust-colored layers) accumulate at the bottom of rivers, polluting the habitats of benthic organisms and hindering their development. These sediments also pose serious problems for spawning fish, as the eggs sink and cannot develop in an ox-

xygen-deficient environment. Additionally, iron can react with sulfides and other compounds to produce toxic substances. These substances are directly poisonous to aquatic life and can cause fatalities. As a result, fish farm productivity decreases [12,15].

Materials and methods

Water samples were taken from the sections of the river passing through the villages of Burunlu and Sayifli, located in the territory of Azerbaijan. The GPS coordinates of these locations were determined using an Etrex-10 device. The coordinates are presented in Table 1.

Table 1 – Sampling coordinates

| Areas | Coordinates | |
|----------|-------------|-------------|
| Burunlu | 39°02'43.1" | 46°44'09.0" |
| Shayifli | 39°07'19.1" | 46°34'19.7" |

For the determination of iron, the SM 3030 (A-K) and ISO 11885 methods were used. SM 3030 (A-K) and ISO 11885 are standard laboratory methods for the determination of metals and some non-metal elements in water, wastewater, soil extracts, and other sample types. Both standards utilize ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) technology. In the case of Inductively Coupled Plasma (ICP), plasma is a high-temperature (approximately 6000–10000 K) ionized gas state. Argon gas (Ar) is ionized in a plasma generator under the influence of a high-frequency electromagnetic field. The high temperature causes the atoms and ions in the sample to ionize and transition to a high-energy state. With Optical Emission Spectrometry (OES), when atoms and

ions of each element return from a high-energy to a lower-energy state, they emit light (emission) at characteristic wavelengths. The spectrometer captures this light and conducts spectral analysis. The intensity of the emitted light is proportional to the concentration of the element. Using these methods, elements such as Aluminum (Al), Arsenic (As), Antimony (Sb), Bismuth (Bi), Barium (Ba), Beryllium (Be), Calcium (Ca), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Iron (Fe), Copper (Cu), Molybdenum (Mo), Manganese (Mn), Nickel (Ni), Phosphorus (P), Tin (Sn), Lead (Pb), Strontium (Sr), Zinc (Zn), Vanadium (V), Selenium (Se), Lithium (Li), Sodium (Na), Potassium (K), Silicon (Si), Boron (B), Titanium (Ti), Tungsten (W), and other elements and rare metals can be determined. ISO 11885 covers 33 elements including: Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ti, Tl, V, W, Zn, etc. The standard defines procedures for sample preparation, calibration, quality control, and reporting.

During the laboratory work, the following equipment and reagents are required:

1. ICP-OES device (Plasma generator (RF generator, typically 27–40 MHz), argon gas supply (99.999% purity), autosampler for sample injection, optical spectrometer and detectors (CCD, PMT, etc.), computer and software (for calibration and data processing)).
2. Other equipment (pipettes, markers, filtration filters (0.45 μm), glass containers and materials for chemical reactions, chemical fume hood (for protection against toxic vapors), safety equipment: gloves, goggles, lab coats).
3. Argon gas (Ar) – high-purity for plasma.
4. Acids (ultra-pure nitric acid – HNO_3 , ultra-pure hydrochloric acid – HCl).
5. Standard element solutions (commercially produced or high-purity solutions prepared in the laboratory).
6. Distilled or deionized water.

According to sampling procedures, clean plastic or glass containers should be used for water analysis. Samples should be analyzed as soon as possible; otherwise, they must be stored at 2–4°C. For certain elements (such as Fe and Mn), samples are preserved by acidification (e.g., with HNO_3 to maintain $\text{pH} < 2$).

During the preparation procedure, if necessary, water samples are filtered using a 0.45 μm filter. Acid is added (typically 2 mL of HNO_3 per 100 mL of sample) to stabilize metal ions, which is essential

for preserving the sample until it is transported to the laboratory from a distant location [7].

During ICP-OES analysis, argon gas is connected to the plasma, the device is turned on, and the plasma is stabilized (~10–15 minutes). For calibration, at least a 5-point standard series is prepared (e.g., 0, 0.1, 0.5, 1, 5 mg/L). Characteristic wavelengths are selected for each element (according to ISO 11885 and the device manual). A calibration curve is created (intensity vs. concentration). The sample is introduced into the plasma using an autosampler. The emission spectrum is measured at the appropriate wavelength for each element (for Fe, it is 238.204 nm). Duplicate analyses (repeat measurements) are performed to ensure accuracy of the results. The concentrations are calculated using the software. Concentration units are typically in mg/L (for water samples).

This method can be used for monitoring the quality of drinking water, determining the pollution level of wastewater, environmental control of industrial processes, analysis of soil and environmental samples, and metal analysis in food products (with appropriate sample preparation).

This method offers several advantages, including simultaneous determination of multiple elements, high sensitivity, a wide dynamic range, automation capability, simple sample preparation (for water samples), and a short analysis time (a few minutes).

Thus, samples are collected in clean glass or plastic containers, and if there is a delay, acid is added for preservation. Then filtration, acid digestion, and dilution are performed. Various concentration standard solutions are prepared next. Calibration with standards and selection of the wavelength follow. The sample analysis involves injection into the plasma and measurement of the emission. Afterwards, data processing takes place, meaning the results are calculated using the calibration curve. Measurements and evaluation of blanks, replicates, and internal standards are also carried out.

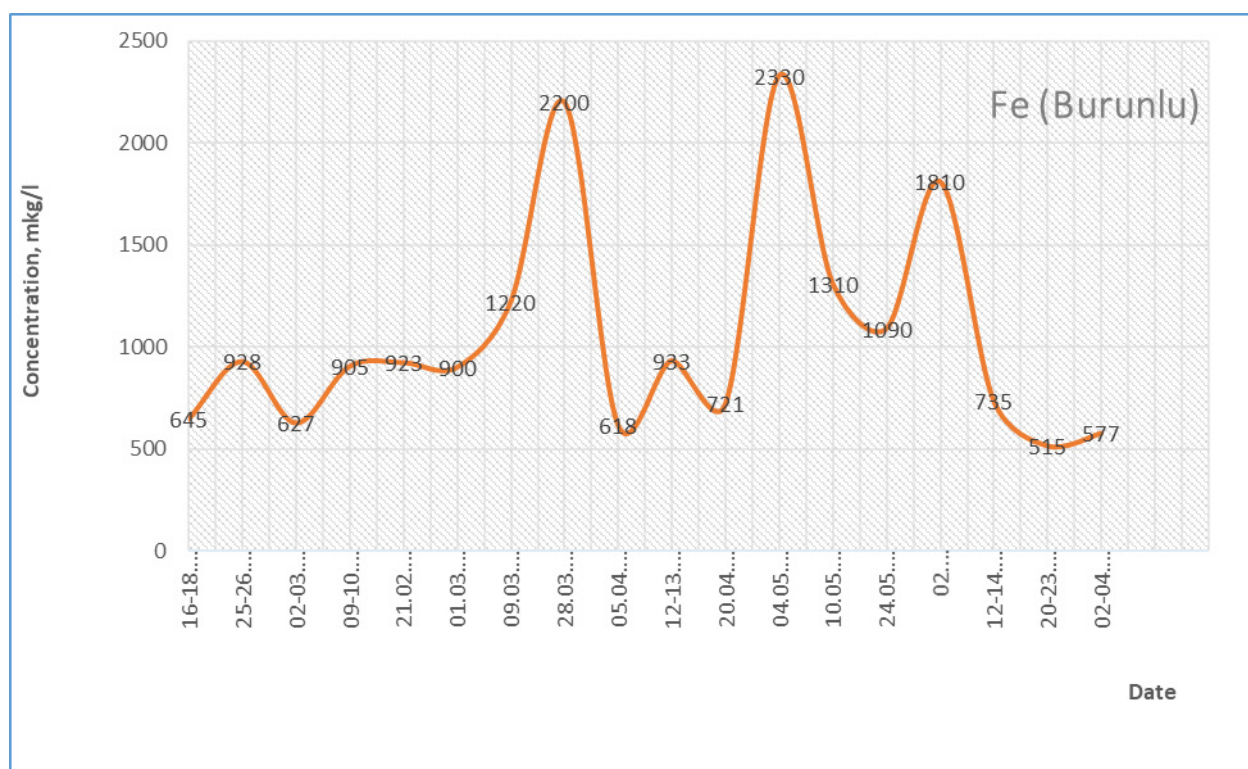
Results and discussion

During the study, it was found that the iron concentration was high between January and August 2023. The dynamics of iron concentration changes during this period are shown in Table 2.

The concentration dynamics of iron in samples taken from the sections passing through Burunlu and Sayifli villages were determined, and their graphical representations are shown in Figures 1 and 2.

Table 2 – Dynamics of Chenges in Iron Concentration Within 2023 (January-August) in mkg/l

| № | Fe- Date | Measurements | Burunlu village | Shayiffi village |
|----|---------------|--------------|-----------------|------------------|
| 1 | 16-18.01.2023 | mkg/l | 645 | 392 |
| 2 | 25-26.01.2023 | mkg/l | 928 | 908 |
| 3 | 02-03.02.2023 | mkg/l | 627 | 638 |
| 4 | 09-10.02.2023 | mkg/l | 905 | 808 |
| 5 | 21.02.2023 | mkg/l | 923 | 811 |
| 6 | 01.03.2023 | mkg/l | 900 | 875 |
| 7 | 09.03.2023 | mkg/l | 1220 | 1040 |
| 8 | 28.03.2023 | mkg/l | 2200 | 1830 |
| 9 | 05.04.2023 | mkg/l | 618 | 223 |
| 10 | 12-13.04.2023 | mkg/l | 933 | 886. |
| 11 | 20.04.2023 | mkg/l | 721 | 664 |
| 12 | 04.05.2023 | mkg/l | 2330 | 2330 |
| 13 | 10.05.2023 | mkg/l | 1310 | 1110 |
| 14 | 24.05.2023 | mkg/l | 1090 | 946.0 |
| 15 | 02.06.2023 | mkg/l | 1810 | 1540 |
| 16 | 12-14.06.2023 | mkg/l | 735.0 | 705.0 |
| 17 | 20-23.06.2023 | mkg/l | 515.0 | 444.0 |
| 18 | 02-04.08.2023 | mkg/l | 577.0 | 564.0 |

**Figure 1** – The concentration dynamics of iron ions in water samples taken from the section of the Oxchu River passing through Burunlu village during the year 2023

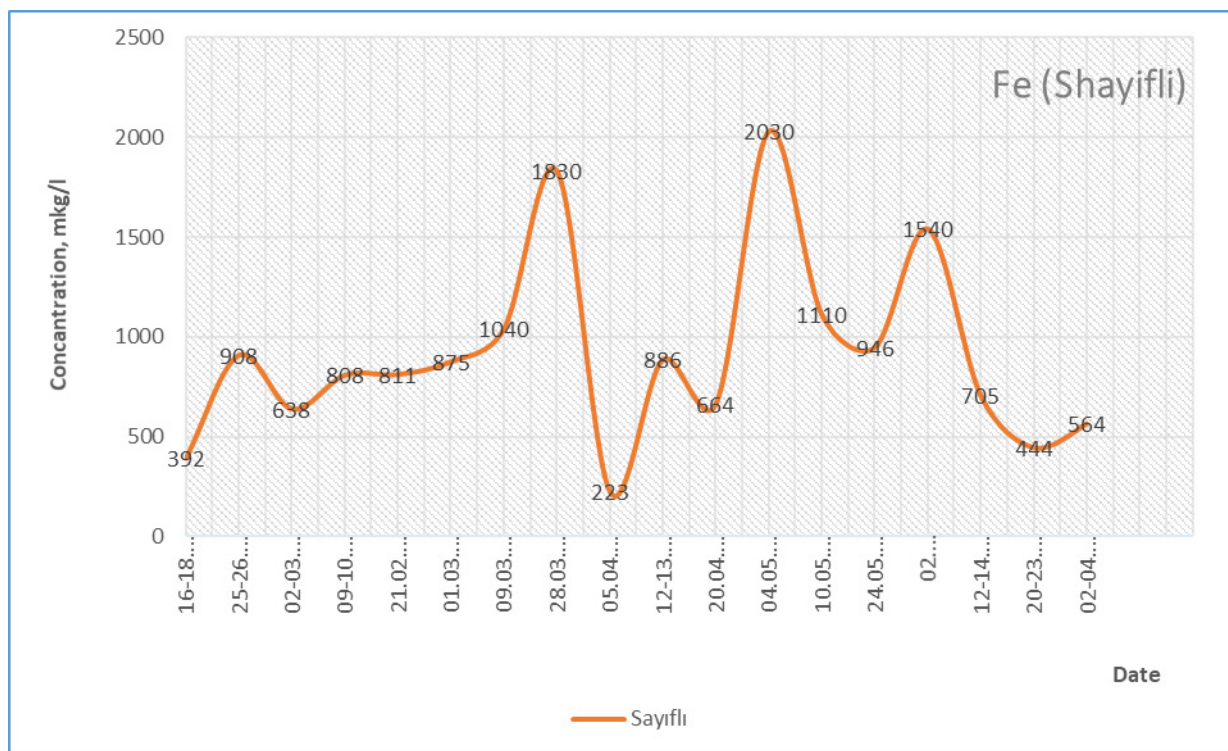


Figure 2 – The concentration dynamics of iron ions in water samples taken from the section of the Oxchu River passing through Sayifli village during the year 2023

Conclusion

Iron is an essential microelement in biospheres. Its balanced presence ensures the normal functioning of ecosystems. However, anthropogenic iron pollution or artificial iron additions can disrupt the balance in ecosystems. During the

studied months, the iron concentration in the river was found to be very high. The increase of iron levels in the river ecosystem can disturb the ecological balance, make living conditions difficult for organisms, and damage trophic relationships. This can lead to serious ecological and economic consequences.

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