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Results of Chemical and Ecological Research of Surface and Waste Waters in Adjara and their Impact on Ensuring Environmental Security

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The monograph presents the findings from extensive chemical and ecological experiments conducted over several years on surface waters in the Autonomous Republic of Adjara. It discusses the current state of the chemical-ecological condition of the Black Sea coast and includes the results of microbiological research on certain fish species (such as Trachurus mediterraneus and Clupea harengus) that inhabitants the Ajara coastal waters of the Black Sea basin. Additionally, the monograph reveals the primary quality parameters and current issues related to the seasonal dynamics of the ecological condition of two lagoon type lakes, Nuri-Geli and Ardagani. It also covers the methods used for wastewater treatment in the Black Sea resort zone of Adjara.

The study was conducted in the Adjara Black Sea water area, both within the coastline and up to 400-500 meters from the shore. The experiments revealed significant findings about the current ecological state of the Black Sea coastline, as well as the waters of Ardagani and Nuri-Geli lakes, and certain hydrobionts inhabiting these areas. In most cases, the observed levels did not meet the established standards, which was attributed to the negative impact of anthropogenic factors. Analyzing the water characteristics, including, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Total Suspended Particles (TSP) in the wastewater treatment plant (sewage system) of Batumi, a correlation was discovered between TSP of inflow waters and a decrease of COD and BOD_5 indicators. The higher the concentration os suspended particles in the water, the greater the reduction of COD and BOD_5 are. In case of low concentration, the quality of treatment process decreases.

Considering the strategic significance of research objects and findings, the study provides recommendations for periodic implementation of sanitary-bacteriological and hydrochemical monitoring of surface water in the Adjara Black Sea coastline and its water area.

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PREFACE

A chemical examination was conducted in the south-eastern region waters of the Black Sea coastline, spanning from Kvariati to Pichvnari with a determination of the basic seasonal quality parameters at various observation points. This topic is of relevance importance because certain parameters related to seawater purity are being adversely affected by negative anthropogenic events (such as manure, household waste, industrial wastewater and oil spills, various waste disposal and other human-related factors). As a result, they are not meeting the maximum permissible concentration (MPC) limits.

According to the research, the quality of seawater along the Batumi port and marine station's coastline does not meet the required standards. This is evident from the deterioration in the smell and transparency of the water, as well as negative changes in various indicators such as pH, Dissolved Oxygen, BOD_5, nitrogenous compounds, certain toxic elements, dissolved oil products, coliform bacteria content. The utilization of electro-dialysis equipment with a minimum time regime (5 minutes) can effectively treat seawater, resulting in saving costs and improved water quality.

To remove oil products from seawater, it is suggested to employ a combined technique involving filtering through sawdust and Parallon. Sawdust can serve as a burning material, while Parallon can be regenerated for future sorption procedures. The final step in eliminating oil products should involve microfiltration. To reduce costs, it is recommended to use sorption and membrane technologies for cleaning up sources of seawater pollution, and then discharge the treated water back into the sea.

Given the strategic significance of the Black Sea, it is crucial to conduct a systematic chemical analysis of its waters to assess water quality and implement timely preventive measures. This becomes even more imperative since the Black Sea coastline is a popular destination for recreational activities such as fishing, water sports, swimming, and tourism.

INTRODUCTION

In nature, every living organism exists in a state of constant interaction with the ecosystem it inhabits, as none can survive independently. Therefore, any alteration in the ecosystem can immediately impact the physical-chemical characteristics of living organisms or other objects present. The world's ocean, which encompasses 98% of the hydrosphere and covers ¾ of the Earth's surface, is no exception to this natural law. It is in a constant interaction with the atmosphere and lithosphere, and it is where the first forms of life originated.

Although seawater composition remains relatively stable, human capacity and modern technology have dramatically increased to the point where irreparable harm can be inflicted upon the natural resources of the world's oceans. A prime example of this negative impact is the annual increase in pollution of seawater due to oil spills, industrial and household wastewater, fecal matter, and toxic substances from the atmosphere.

The Black Sea is a typical enclosed basin, also known as an internal sea, that connects to the Atlantic Ocean via narrow straits: to the southwest, it connects to the Sea of Marmara through the Bosphorus Strait, while to the northeast, it connects to the Sea of Azov through the Kerch Strait (picture 1). The Black Sea is situated in a deep basin between the Asia Minor and Crimea Peninsula and spans latitudinally from the coast of Georgia to the Balkan Peninsula. Its eastern border is formed by the Caucasus coast and the Colchis Lowland. The Black Sea covers an area of 420325 km^2 and its easternmost point lies between Batumi and Poti. Its longest length is 1150 km, and its widest point is 611 km. The volume of the Black Sea is 547015 km^3, with a maximum depth of 2212 m and an average depth of 1300 m.

The chemical content of the Black Sea water sets it apart from other seawaters due to its hydrological and morphological characteristics, as well as water structure, and dynamics. In the 1980s, pollution of the Black Sea waters became a major issue because of irregular fishing, ground dumping, reduced freshwater inflow, and poaching, threatening the normal functioning of the ecosystem along the coastline. Although the suspension of a range of factories in the 1990s significantly reduced pollution levels, the problem remains. The Black Sea coastline is of vital importance to those living in the area, as it affects several areas, such as:

1) conventional fishing and processing of sea products;

2) intensive exploitation of natural resources and economic development;

3) development of large resort and tourism infrastructure, as well as recreational resources.

Therefore, the Black Sea and particularly its coastline are high-risk areas that demand daily attention from humans, given that any actions taken by those residing in the region are closely linked to the uppermost living layer of the sea. Therefore, it is crucial to give special consideration to the Black Sea coastline and significant ports in Georgia (such as Batumi, Poti, and Sokhumi) during monitoring and research activities.

Our research aims to evaluate the chemical-ecological condition of seawaters in the southeaster region of the Black Sea, ranging from Kvariati to Pichvnari coastline, given their severity and urgency. To achieve this objective, we have identified specific observation points where we assess the main organoleptic, physical-chemical, and sanitary-hygiene parameters of water seasonally. This approach enables us to determine the chemical content and level of cleanliness of the mentioned water area.

Picture 1. Geographical Location of the Black Sea

The actuality of conducting systematic monitoring and comprehensive studies on the chemical composition and cleanliness level of the Black Sea basin waters is justified by the need to establish a database that can evaluate the present condition of this crucial ecosystem and enable the implementation of timely preventive measures.

The aims of the study are as follows:

- Illustrating significance of the sea coastline for human life and household needs, description of the components in the Black Sea water based on the literature review;

- Conducting chemical-examination study of seawater, based on the assessment of dynamics of its organoleptic, physical-chemical and sanitary-bacteriological parameters;

- Conducting multielement analysis of seawater with the Plasma Atomic Emission Spectroscopy;

- Assessment of sanitary-bacteriological state of seawater through filtration in membrane device;

- Determine a concentration of soluble oil products in seawater through filtration in different sorbents;

- Determine the most efficient and cost-effective method for treatment seawater from soluble oil products and microorganisms, through its filtering in membrane devices and different sorbents.

For the purposes of the mentioned above, we selected 8 locations in the Kvariati-Kobuleti coastline (Pictures 2-9):

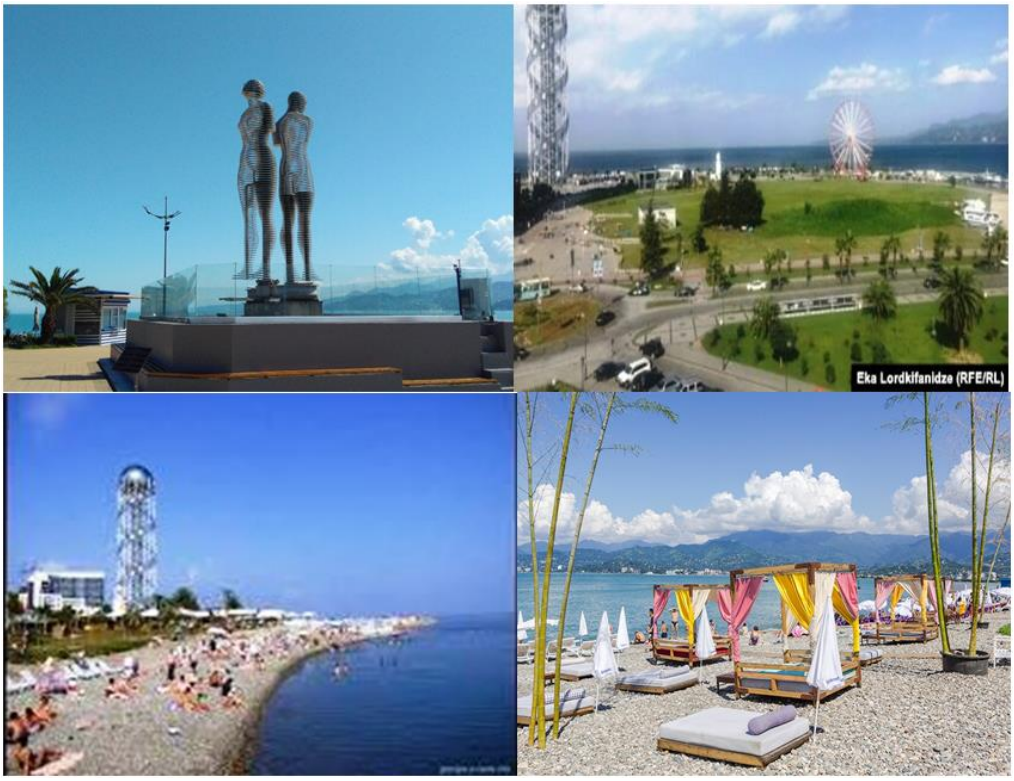
1. Kobuleti coast - Pitchvnari;
2. Kobuleti coast – Kintrishi estuary to the sea;
3. Chakvi coast – coastline near the railway station;
4. Settlement of Batumi oil refinery in Batumi –Korolistavie river estuary;
5. Coastline near the Batumi port;
6. Beach (active recreational and swimming zone) near the Batumi Marine Station;
7. Gonio - coastline in 50 m from the central route;
8. Kvariati – coastline near the central route.

Picture 2. Kobuleti coast - Pitchvnari

Picture 3. Kobuleti coast – Kintrishi river estuary

Picture 4. Chakvi coast – coastline near the railway station

Picture 5. Korolistavie river estuary



Picture 6. Beach near the Batumi Marine Station

Picture 7. Coastline near the Batumi port

Picture 8. Gonio coastline **Picture 9. Kvariati coastline**

The experimental research were carried out at the Institute of Agrarian and Membrane Technologies of Batumi Shota Rustaveli State University, on the material and technical base of the laboratories: of analytic chemistry, of electrodialysis processes and apparatuses, of baro-membranes synthesis and technologies, of sorption processes, of microbiology laboratories, as well as in the chemistry department of the Batumi Shota Rustaveli State University (pic.10-11).

Picture 10. The Institute of Agrarian and Membrane Technology

Picture 11. The Batumi Shota Rustaveli State University

The literature utilized in this paper is based on the normative acts under the Georgian legislation, in particular: the Georgian Law on water; a technical regalement on preventing pollution of surface waters in Geogia; sanitary rules and norms for preventing pollution of surface waters; the Convention on the Protection of the Black Sea against Pollution on the Black Sea Biodiversity and Landscape Conservation and other.

I.1. Importance of Sea Coastline in Human Life

The world's ocean encompasses 98% of the hydrosphere, covering ¾ of the Earth's surface. It is where the first forms of life originated. It is in a constant interaction with the atmosphere and lithosphere; thus it has huge impact over climate, flora and fauna of our planet. The coastline of the sea is particularly crucial for the development of maritime states. Georgia is not an exception, which has a south-eastern coastal area. The recreational value of the sea coastline is well recognized, and among our chosen observation points, Gonio beach stands out as a unique location. It is situated to the south of the confluence of the Chorokhi river, which shields the beach from excessive river runoff, making it the cleanest coastline in the area.

The sea coastline is significant for the economic development. As a rule, it is a key location for ports and other technical facilities (such as, terminal). Seawater is rich with biological resources. As it is widely known, the Black Sea phytoplankton biomass in 50 m deep amounts to 3,6 tonnes, while a total resource of seaweeds in the Black Sea is estimated to 9 tonnes. There are more than 2000 species of sea animals inhabiting the Black Sea, while fish and invertebrates are actively produced in the coastline. Studying chemical consistence of the Black Sea is a subject of high interest from chemical industry, as chemical substances produced from the Sea, such as magnesium, potassium, bromine, iodine, Glauber's salts are used in glass, pharmaceutical, textile, cellulose-paper and fertilizers production. The intermediary coastline of the sea and its bottom is particularly rich in mineral resources with a strategic significance. Seawater covers almost all of the elements known in nature.

It is estimated that $56 \cdot 10^{16}$ tonnes of substances have been dissolved in the world's ocean. There are billion tonnes of magnesium, potassium, calcium, million tonnes of gold, silver, uranium. As of today, up to 60 precious elements has been dissolved in water, however, four elements and their compounds are taken for industrial purposes, these are sodium, chloride, magnesium, bromine. Related technical complexities prevent obtaining of other elements. There are fields of iron, magnesium, rare metals like, phosphorite, red clay concretions, also oil and natural gas.

Recent studies carried in the Black Sea coastline prove that there are fields rich with oil and natural gas supplies, total area of which amounts to 20 km^2. Important natural gas fields were discovered in northern part of the Black Sea and currently exploration works are ongoing, also additional works are being carried in this regard in Batumo-Poti coastline. Precipitated manganese-ore has been found on 10 km^2 area at the Rioni river estuary, where total concentration of manganese amounts to 2-14%. Important coal mine has been discovered at the border of Turkey, which amounts to 30% of the Turkey's coal supply.

The Black Sea coast in Georgia is distinguished by a well-developed resort infrastructure. There are various types of resorts with specific purposes, representing imminent place for recovering health for millions of people. Thus, the Black Sea coastline is very important as it's the richest source for recreational resources, including, national parks, managed reserves and buffer zones of reserves. Therefore, carrying of multidirectional and well-thought works for solving socio-economic and ecological issues of the Black Sea, to ensure rational resource use of the Black Sea is of superior significance.

The word "ecology" has a Greek origin translating to "home". The ecology studies interaction between various organisms and their relation with environment. It's important to note that humans are a part of nature, and ecology considers human activities. Any modifications to the ecosystem can be attributed to both natural and human-induced changes in the environment, either ongoing or long-term. The world's oceans are a crucial component of the ecosystem, encompassing the majority of the Earth's hydrosphere, as well as certain lakes, rivers, swamps, and underground waters. The combined area of the oceans and seas on the planet's surface is approximately $1370 \cdot 10^6$.

A definition “water pollution” has a broad meaning considering high polluting levels in water threatening human health. There are two aspects distinguished in the water pollution:

I. Natural pollution, which considers intensive piling of organic compounds in the water due to inflow spills from river to the sea; also pollution of the sea from atmosphere and volcanic eruption;

II. II. Anthropogenic pollution refers to a damage caused to the natural resources of the world ocean as a result of human activities. The main anthropogenic factors of pollutions in seawater are as follows:

1) Industrial and household waste inflow, which introduces disease carrying bacteria into the seawater;

2) Toxic substances from atmosphere. The car emissions that use ethylated petrol, release about 50000 tonnes of leads to the atmosphere and then in the ocean annually, concentration of which in the seawater most frequently exceeds permissible limits;

3) The seawater contamination by heavy metals as a consequence of radioactive and nuclear explosions;

4) Disposing of fertilizers and harmful chemicals into the sea. These harmful substances are absorbed by fish-eating birds and transferred to human afterwards. The sea animals and seaweeds have a selective absorption of heavy metals: shellfish absorbs copper, radiolarians and phytoplankton – strontium, jellyfish absorbs zinc, tin, lead, lobsters and crawfish – cobalt. Heavy metals are present in seawater as a precipitation.

5) Oil and its byproducts are currently the primary pollutants of the ocean, and their contamination will continue to pose a major threat to the global ecosystem in a long-term perspective. Oil pollution originates from sources such as river runoffs, port areas, oil refineries and terminals, and even the atmosphere. The southeastern coastline of the Black Sea shelf, specifically the Batumi, Supsa, Tuapse, and Novorossiysk water areas, is particularly sensitive to oil pollution.

The world ocean is unable to combat a stress caused at the turn of XIX-XX centuries. A human equipped with the modern technology caused irreparable damage to the natural resources in the world ocean, which catastrophically reduced its self-cleaning ability and currently, to minimize pollution scale, it is imperative for humans to take targeted political, legal, chemical, biological and technological actions in a timely manner. Sanitary rules and norms of the sea coastline protection has been developed to safeguard human health and promote rational use of natural resources in seawater. The sanitary rules and norms are supposed to prevent seawater pollution, as polluted water is unsuitable for recreational, health and drinking-household purposes. Those rules apply from the maximum level of water along 2 km on the land, on the coast of territorial waters in Georgia, also, the city coastline and the river estuaries, which are also used for recreational, health and drinking-household purposes.

I.2. The Main Physical-Chemical Characteristics of the Black Sea Waters

The chemical composition of the Black Sea is similar to the world ocean structure. Multiple indicators of water dynamics structure (density, volume, resistance of water layer and vertical division) depends on the thermodynamic mode of the seawater and its salinity. The composition of the Black Sea is as follows:

1. Basic ions (Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-, Br^-, F^-, Na^+, K^+, Mg^{2+}, Ca^{2+});
2. Soluble gasses (N_2, O_2, CO_2, CH_4, H_2S);
3. Biogenic substances (nitrogen and phosphorus compounds);
4. Microelements (Cu, V, Nb, Sr, Zn, Sn, Pb, Co, Au, I, Al,);
5. Organic substances (carbohydrates, amino acids, fatty acids, vitamins), which are created from accumulation, transformation and decomposition of carbon containing organic compounds.

An average annual temperature of the Black Sea in the most of its coastline ranges from +17 to +20°C. The warmest regions of the Black Sea is its south-eastern region, as the Caucasus mountains prevent north winds in this region. Also, this region is affected by coastal flows coming from the south, thus, it is less affected by cooling impact of the inflow water from rivers. The Black Sea coastline of Georgia is located in this region.

A maximum average monthly temperature of surface waters in the Black Sea is detected in August, while minimal – in February. A change of temperature along increasing depth is not detected, thus the seasonal temperature fluctuations are observed up to 70 m deep. Constant temperature level +8,9°C is established at 500 m deep. pH of seawater depends on carbonic acid and concentration of its ions, as its defines balance between H_2CO_3 (acid reaction), carbonates (CO_3^{2-}) and hydro carbonates (HCO_3^-) (alkaline reaction). Seawater has a weak alkaline reaction.

pH depends on depth and pressure, as with their increase pH decreases. pH reaches its maximum (8-8,4) on surface level of the sea (0-50 m), as a result of intensive absorption of carbon dioxide during photosynthesis. pH decreases in the deep, because carbon dioxide concentration increases. Seasonal and day-night change of pH happens only at surface level of the sea and depends on the carbon dioxide concentration. pH reaches its maximum in spring and summer. pH in the Black Sea ranges between 8,1-8,5 interval, and in the surface waters - 8,31-8,33. A level of pH also depends on hydrogen sulphide, thus pH decreases in the depth of the seawater and reaches its minimum – 7,6.

Basic salt-forming ions in the Black Sea are: 1) chlorides - NaCl, KCl, $MgCl_2$; 2) sulphates - K_2SO_4, $MgSO_4$, $CaSO_4$; 3) carbonates - $CaCO_3$. The salinity in the surface waters of the Black Sea amounts to 18-18,5$‰_0$, while minimum salinity is 17,5$‰_0$. In the places of river inflows, as a rule, salinity decreases, thus a minimal level of salinity of the Black Sea is detected in its north-western part (13-15$‰_0$), where the main river inflows are. Salinity increases with an increase of depth. An average salinity of the Black Sea coastline waters amounts to 16-17$‰_0$ and its levels increases with increasing depth and with greater distance from the coastline towards the center.

Seawater contains variety of gasses, including atmospheric (N_2,O_2) and other origin gasses (CH_4, H_2S). The concentration of these gases varies depending on location and time. For instance, high concentration of O_2 deep in the ocean indicates positive vertical circulation, whereasthe presence of H_2S indicates absence of such circulation. The process of dissolving gasses in water is reversible. A maximum concentration of oxygen in seawater is in winter – 12 mg/l, related to the temperature drop, while in summer it is minimal amounted to 7-8 mg/l. A seasonal fluctuation of oxygen in seawater influenced by a temperature level, salinity and content of phytoplankton. Along with temperature increase, solubility of oxygen decreases and increases with an increase of pressure. Therefore, the oxygen solubility decreases in summer with a temperature increase. An average concentration of soluble oxygen in seawater amounts to 10 mg/l (7 ml/l); in winter its increases to 12 mg/l (8,5 ml/l), and drops in summer to 8 mg/l (5,5 ml/l).

Carbon dioxide in the seawater is both in free (CO_2) and compound form (H_2CO_3, HCO_3^-, CO_3^{2-}). CO_2 serves as a primary source of carbon in seawater: carbonate and bicarbonate ions define alkalinity and hydrogen ions created by H_2CO_3 dissociation define pH in the seawater. A seasonal fluctuation of CO_2 concentration is detected in the surface of the Black Sea. In particular,CO_2 increases in winter and autumn, as it is intensively absorbed from the atmosphere during cooling of water, while in spring and summer seawater becomes warmer and photosynthesis is particularly active, thus the CO_2 concentration decreases. In winter, the concentration of free CO_2 in surface water of the Black Sea amounts to 1 mg/l (0,5 ml/l), while in summer it is 0,4 mg/l (0,2 ml/l). It is notable that spilling of oil and soluble oil by-products in the seawater cause significant increase of CO_2 (6-14 mg/l) and intensive decreaseof pH to 0,3-0,5.

Hydrogen sulphide is a typical and constant characteristic of seawateraccumulated in deep and sometimes in surface layers within certain conditions. Hydrogen sulphide is present in seawater in both free and produced forms: hydrosulphide ions (HS^-) and sulphide ions (S^{2-}), which are products of H_2Sdissociation:

$$\mathbf{H_2S \leftrightarrow H^+ + HS^-} \qquad \mathbf{H_2S \leftrightarrow H^+ + S^{2-}}$$

O_2 is a primary precondition for formation of H_2S is in water. However, bio chemical renewal of sulphates (desulfurization) remains as one of the main sources, which is carried through anaerobic bacteria microspores. Another significant contributor to creation of hydrogen sulphide is a release of sulphur from decomposition of organisms, which is in the organic compound of those organisms. Creation of H_2S in the Black Sea is detected from 150-200 m deep, where its concentration amounts to 0,04-0,16 ml/l; at 300 m deep – 1 ml/l; at 500 m deep – 3 ml/l, and at 1000 m and more – 6 ml/l.

Nitrogen containing nonorganic compounds are represented by: nitrates, nitrites and ammonium salts. A fluctuation of nitrogen concentration in seawater is based on two contradictory processes: photosynthesis and decomposition of organic matters. There is about 8 μg/l NO_3^- in the Black Sea waters, at 150 m deep its concentration increases, and decreases in the zone of H_2S frees space for NH_4^+ ion. Concentration of nitrate ions in winter reaches 17 μg/l, as photosynthesis is weak, and minimal concentration is detected in summer 1 μg/l. NO_3^- increases to the coastline and reaches its maximum in the most polluted regions. Concentration of nitrate ions is much lower than nitrite ions in the Black Sea, as it is an intermediary product of nitrification process: $NH_4^+ + 2O_2 \rightarrow NO_2^- + 2H_2O$. Nitrite ionsare present in upper layers of the Black Sea (0,5-1 μg/l). The maximum volume is detected by the end of summer, while in autumn it decreases and is completely vanished in winter and transformed into nitrates (together with O_2): $2NO_2^- + O_2 \rightarrow 2NO_3^-$.

Content of microelements in the seawater is less than 1mg/l. It shall be mentioned that seawater contains almost all known microelements, additionally, sea animals and seaweeds have a selective absorption regards to microelements: shellfish absorb copper; ascidians and gloturias - vanadium and niobium; radiolarians - strontium; jellyfish - zinc, tin, lead; Phytoplankton-gold; seaweeds - iodine and aluminium. The majority of microelement compounds is unstable and quickly precipitates.

Organic substances in seawater are in a colloidal state and are classified in two groups: 1) substances in composition of seaweeds and sea animals; 2) dissolved organic substances, that are products of vital activity or incomplete decomposition. The sources of organic substances are: 1) Products from Biochemical decomposition of organisms; 2)Products of vital activity; 3) River runoffs; 4) Atmospheric precipitation.

The Black Sea waters contain on average 3-4 mg dry organic substance per litre. The change of concentration in organic substances depend on the water temperature and intensity of photosynthesis. Along the increasing depth in the seawater, a concentration of dissolved organic compounds decreases.

Biochemical Oxygen Demand (BOD) - is one of the primaryindicators of chemical-ecological state of seawater, which is a sensitive and reliable indicator of seawater pollution. Biochemical Oxygen Demand – this is a volume of oxygen spent by microorganisms for oxidation of organic substances in seawater within certain time and temperature conditions. The average BOD shall not exceed 1,8 mg per O_2/l in surface waters, and 1,1 per O_2/l in 10 meters deep to maintain purity in seawater.

I.3. The Present Chemical-Ecological State of the Black Sea Coastline

According to the definition provided by the United Nations 1982, sea pollution refers to direct or indirect introduction of substances or energy sources, that harm living organisms, are dangerous for human health, prevent fishing and general marine activities, have negative influenceon water quality and recreational conditions. Protection of the Black Sea requires common effort by not only the Black Sea coast countries, but the whole world. This is particularly crucial in south-eastern region of the Black Sea – from the Chorokhi river to Rioni river estruary, in 30 km length coastline, where two important ports – Batumi and Poti are located and currently there are powerful oil terminals.

The main polluters of the Black Sea are its feeding rivers: Danube, Dnieper, Dniester, Don, Rion, Enguri, Chorokhi and other. Any runoffs (including, sewage), which are spill in the sea without any processing, cause chemical and microbiological pollution of water. Currently, the main polluters of the Black Sea are following: 1) Household and sewage waters; 2) industrial waste (paints, plastic and polyethylene produce); 3) oil and soluble oil products; 4) various types of fertilizers; 5) heavy metals and radioactive pollution.

Pollution of the Black Sea is explained by the accumulation of large volume of organic substances by river runoffs (organic pollution), which causes increased limits of H_2S and deficit of oxygen in water. H_2S concentration is directly and proportionally related to the water salinity. It is commonly known that salinity increases along with depth and at 300 m deep reaches 21,7$\%_0$. The volume of salinity H_2S depends on interactions of various polluting substances and microflora in the sea. H_2S is created as a result of decomposition of organic substances by microorganisms and restoration of sulphates to sulphides. Radioactive pollution of water it the most severe in terms of sea pollution.

After the Chernobyl nuclear power plant accident, the study has been commenced to evaluate contamination by radioactive substances. This study revealed maximum level of radioactive Cesium. Before the accident its distribution amounted to 0,5 Bq, while after the accident this was increased by almost 30 and amounted to 45 Bq/per litre. The same data was revealed in the case of ^{90}Sr. Currently, the Black Sea is also polluted by heavy metals, distribution of which according to increase are arranged in the following order: Hg < Cd < Cr < Pb < Zn.

The risk of water pollution by oil is increasing due to significant importance of its extraction and transportation for the global economy development. Oil is a complex mixture of various types of hydrocarbons, which contains sulphurous, nitrogen and oxygen compounds. Seawater is vulnerable to both raw oil and oil produce. The largest spill of oil on the sea surface typically occurs as a result of tanker accident during oil transportation. In this case, the crew members may intentionally release oil in the sea to prevent tanker from sinking, which may cause serious ecological disaster

Oil is usually burnt or frozen during such accidents, however, it results in atmosphere pollution, as the wind might catch some portion of unburnt oil, which than comes down as “black rain” in the polluted area. A threat of oil pollution is in the sea port locations, where oil is being loaded on the tankers and might be spilled in the sea. One of the sources of oil pollution in the sea is the oil refineries operating near to the coastline, which frequently release waste in the sea.

In modern days, construction of oil pipelines on the large distances is becoming global, which in the case of accident creates serious pollution threat. For instance, the largest oil pipelines are: Trans-Arabian, Trans-Alpine (carrying 70-100 million tonnes of oil daily), recently added by Trans-Caucasia pipeline, which transits oil from Baku, Georgia and middle Asia to west Europe and American countries. Another source of oil pollution of the sea is oil storages, in other words, terminals, which frequently leak oil to the ground and then to seawater.

Oil is present in the seawater in soluble and dispersed forms, thus up to 5 tonnes of oil could penetrate 5 m seawater just in 1 day. After appearing in the seawater, hydrocarbons in oil are transformed as follows: 1) evaporated from the surface to the atmosphere; 2) dissolved and distributed in water; c) precipitated in the bottom; d) absorbed by sea flora and fauna; e) destructed.

A diameter of oil emulsion drops is 0,5 μm, volume – $6\ 10^{-14}$ ml, while surface area amounts to $8 \cdot 10^{-9}$ cm^2. 1 ml oil may produce $15 \cdot 10^{-12}$ drops, a total area of which amounts to 12 m^2. Oil spilled in the sea produces 10^{-4} cm slick for 40-100 hours, which disappears from the sea surface within 24 hours.

The Black Sea is considered as one of the most polluted seas in the world. The current condition of its ecosystem has been drastically declined in the recent decades. Therefore, protection of the Black Sea is a main concern for many countries and it requires international cooperation. The main international political instrument provided for the protection of the Black Sea ecosystem is the Convention for the Protection of the Black Sea against Pollution (Bucharest Convention, valid since 1994) and the Strategic Action Plan for the Environmental Protection and Rehabilitation of the Black Sea (1996, updated in 2009). Georgia has signed both of the documents.

1.4. The Research Methodology

Action plans for water protection, also, the construction projects influencing chemical content of the surface waters shall be submitted to the government-ecological expertise, the rule of which is defined by the Ministry of Environment and Natural Resources Protection. The monitoring programme of the surface waters applies to whole Georgia implemented by the Ministry of Environment and Natural Resources Protection, also based on the government regulation on approving technical regalement on surface waters. The sea pollution refers to direct or indirect introduction of such substances or energy sources, that harm living organisms, are dangerous for human health, prevent fishing and general marine activities, worsen water quality and recreational conditions.

Like the majority of the inland seas, the Black Sea pollution level is high as a result of anthropogenic influence. About $4 \cdot 10^5$ tonnes of organic substances flow into the sea. The Black Sea has a significant economic purpose, particularly, for its surrounding countries. Oil and gas are extracted in the north-western region of the sea. There are magnetite and titano-magnetite sands in Taman, Ureki and other places. The Black Sea holds significant importance in terms of transportation. Odessa, Novorossyisk, Tuapse, Batumi, Poti, Nikolaev, Kherson, Feodosia, Sevastopol, Burgas, Varna, Constanta, Trabzon, Samsun and Zonguldak are its distinguished ports. Almost all kinds of materials and products, passengers, are being transported to and out of those ports. The Black Sea is an important fishing destination. The sea and its surrounding climate lays an important foundation for the development of resorts and tourism. Currently, there are several popular resorts operating on its coastline: Yalta, Sochi, Bichvinta, Gagra, Sokhumi, Batumi, Anapa, Gelendzhik, Varna and many others.

Georgia is a maritime country, as it is bordered by the Black Sea on its west. The Black Sea coastline in Georgia runs for 315 km. It commences at the Psou river estruary and ends in village Sarpi. Importance of the Black Sea for Georgia is invaluable. It represents the most significant resource potential, recreational zone and the main channel for external interrelations. Within Georgia, small and narrow capes are located in the sea like, Bichvinta, Gudauta, Sokhumi, Kodori, Anaklia, Poti, Tsikhisdziri and Green Cape. The bays along these capes are more or less favourable for construction of ports. Those bays are the location for the most important ports in Georgia: Poti, Batumi, Sokhumi, Ochamchire and Gagra. Warm climate,beaches, long period of swimming season, high seawater temperature, unique landscape and diversity of the coastline, mineral springs with healing properties in some places create the most favourable conditions for recreation and certain disease treatment. All of these provoked creation of well-known resorts at the Black Sea coastline, there is a high potential for the development of international cruise tourism in the coastline.

Batumi serves as the final stop for cruises operating in the Black Sea. Unfortunately, for a variety of objective and subjective reasons, seaside resort infrastructure has been partly damaged, many of the facilities are out of order. Currently, rehabilitation works for many of them is underway. An increasing role of the Black Sea in the development of strategic power of Geogia is related to the reconstruction and expansion of existing ports.

As mentioned earlier, regular monitoring of organoleptic, physical-chemical, sanitary-hygiene and toxicology indicators of the Black Sea is crucial. This enables the determination of water quality and opportunity for regular checks, for ensuring household and sanitary safety. Determination of chemical consistence, including, concentration of pollutant substances in seawater regarding to its Maximum Permissible Concentration (MPC) is necessary for conducting expertise. Maximum Permissible Concentration is defined considering background concentration of each parameter. Background concentration reflectes condition of water before influence of water user.

Considering direct and indirect effect of the Black Sea water on the development of various economic fields and human cultural-household life, the aim of our dissertation is to carry out chemical-expertise study on the Black Sea water, to assess its current quality, while taking into account the seasonal dynamics of the key physical-chemical and sanitary-hygiene parameters. At the same time, we aim to define the chemical and bacteriological purification methods through revealing optimal version.

Analysis for any origin water requires sampling, to assess its quality and reveal certain changes. The sample is taken according to the norms defined by the state standard (GOST 24481-80). The sample is taken in the chemically clean container with a screw cap. The container is exposed to sample water two times, then filled with water and tightly closed by the cork.

The types for water sampling are: point, periodic, continuous, serial, compound and large volume. Point water sampling is reasonable for:

a) research of potential water pollution, pollution level and existence of pollutants;

b) definition of variable parameter, such as: dissolved gas concentration, residual chlorine, soluble sulphide and other.

Analysis on physical-chemical water indicators required filling up of container, to ensure there is no oxygen under the cork which decreases shaking during container transportation. In the case of analysis, the sanitary-hygiene indicators, the container shall in sterilized in autoclave in advance and shall not be fully filled, to avoid accidental contamination of the sample. For partial analysis (to define certain parameter), 1-2 litres of water are enough, analysis for sanitary-hygiene indicators require 0,5 liter of water sample.

The organoleptic indicators are inspected right upon taking the sample, as after certain time its concentration in the water changes. During transportation container shall be placed in a package to avoid contamination, damage or excessive shaking. The samples shall be transported quickly with a special care. Cooling to 2-5°C and storage in dark is the method applied to determine organoleptic parameters, for storage and conservation of the water samples. The maximum recommended storage period for particular actions: to determine smell – 6 h; colour- 24 h; turbidity – 24 h; temperature shall be determined on-site. It is necessary to have dark container, to avoid negative exposure of light on the water compounds.

After pouring water into the sample container, it shall be labelled with an indication of: sample number, sample description, taking time and place, environmental climate conditions, name of the person taking the sample, the research purpose. It is recommended to take samples on a regular basis, seasonally, which allows for drafting comprehensive image on the water quality. If the sample is stored for two-three days, conservation is necessary via adding 0,5 ml of chloroform on per 300 ml of sample. We took water samples from 0-50 cm deep in the sea in certain points and got average sample by mixing them. We did three parallel trials during each type of analysis. Then we did arithmetic average of the results, if the permissible variation between the parallel trials did not exceed 0,02%.

The water samples were analysed on organoleptic parameters – colour, smell, transparency, floating particles according to the GOST 3351-74. At first, we were defining the smell by sniffing it from 0 to 5 degree (Table 1). To define colouring we were pouring it in the transparent cylinder and were observing on a daylight. We were describing the water colouring by the terminology defined by the state standard: colourless, weak yellowish, yellowish, green, greenish, green-yellowish.

Table 1

The water smell intensity and demonstration nature

Smell intensity	***Smell demonstration nature***	***Smell intensity, degree***
No	There is no smell	0
Very weak	A user experiences very weak smell	1
Weak	A user experiences weak smell	2
Noticeable	smell is highly noticeable and promotes negative feedback regarding water	3
Sharp	Sharp smell attracts attention	4
Strong	The smell is so strong the water is unusable	5

The water transparency was assessed using smooth metal disc by measuring the average water depth at which the disc disappeared and reappeared at the boundary. This value, expressed in centimetres (Table 2), represents a conditional measure of water transparency. The water temperature is crucial factorinfluencing its physical-chemical and biological processes. An oxygen saturation level of water and self-cleaning intensity depends on temperature. Usually, the water is warmed up in the basins from top to bottom. The basins where water is contaminated from the runoffs, increase of temperature by more than +5°C from its natural temperature level is not permitted.

The average annual temperature of water in the surface of the Black Sea depends on a geographical location of the observation object and the sea streams, distance from the shore has a minimal influence on the temperature fluctuations in water. A maximum temperature of the Black Sea coastline is detected in August, while minimal in January-February. The seasonal temperature fluctuation usually happens in 70 m deep. We were defining the temperature of the water samples right upon taking.

Table 2

Classification of surface waters according to degree of transparency

№	*Water transparency in cm*	*Degree of transparency*
1	> 30	transparent
2	25-30	slightly turbid
3	20-25	medium turbid
4	10-20	turbid
5	< 10	Strongly turbid

pH in the seawater depends on correlation of carbonic acid molecules and its ions:

$$\mathbf{CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}}$$

The seawater has weak alkaline reaction (8,31-8,33), pH decreaseswith depth to 7,6. The water pH has been defined as pH-Meter pH meter from Mettler Toledo (AG Analytical CH-8603), which was calibrated in advance towards 3 buffer solutions: pH 4 ,01; pH 7,0; pH 9,21. Division of natural waters by *pH* is presented in the Table 3.

Table 3

The classification of natural waters by pH

Strong acidic waters	<3	Result of hydrolysis the heavy metals salts (waters of shafts and ores)
Acidic waters	3-5	Organic compounds decompose and release carbonic acid, fulvic acids, and other organic acids into water.
Weak acidic waters	5-6,5	Humic acids get into the waters from ground and swamps (mainly forest zone waters)
Neutral waters	6,5-7,5	There are $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$
Weak alkaline waters	7,5-8,5	„ ———— "
Alkaline waters	8,5-9,5	There are Na_2CO_3 and $NaHCO_3$
Strong alkaline waters	>9,5	There are high volumes of Na_2CO_3 and $NaHCO_3$

Chlorides are most frequently found in water in the form $NaCl$. Chlorides are introduced into water from the soil, and their concentration can be elevated due to the presence of human and animal excrement (including, feces and urine). Increase of chloride distribution in the water indicated on pollution. Permitted limit of chloride per 1 liter of water is 350 mg. If chlorides exceed 500 mg per liter, this water has bitter taste. To determine concentration of chlorides in seawater samples, argentometric titration method developed by Mor and Knudsen has been applied, the principle of which is as follows: applying $AgNO_3$ on Cl^- ion composed solution created $AgCl$ white precipitation:

$$NaCl + AgNO_3 \rightarrow AgCl \downarrow + NaNO_3$$

Cl^- ions are titrated by $AgNO_3$ solution with participation of indicator-reagent K_2CrO_4. A completion of titration is checked as follows: when all Cl^- ion is bound in $AgCl$, new portion of $AgNO_3$ in the solution enters into reaction with K_2CrO_4 and produces reddish brown precipitation of $AgCrO_4$: $2Ag^+ + CrO_4^{2-} \rightarrow AgCrO_4 \downarrow$. To calculate the salinity of seawater, we multiplied the concentration of chloride ions by a defined coefficient for seawater - 1,65, which converts the amount of chloride ions to salinity.

The higher the concentration of free oxygen in water, the more clear and high quality it has. Decrease of temperature, increased pressure or reduction of mineralization quality increased absorption speed of oxygen from the atmosphere. The concentration of dissolved oxygen in the surface waters ranges within wide limits from 0 to 14 mg/l and undergoes seasonal changes. In particular, its maximum concentration is detected in winter, when the water temperature is minimal. The concentration of dissolved oxygen in the surface waters shall be at least 4-6 mg/l. The classification of pollution level in surface waters by the degree of dissolved oxygen concentration and oxygen saturation is represented in Table 4.

Dissolved oxygen in water has been determined by applying classical iodometric titration method (reverse titation) by Winkler. To determine BOD_5 we were keeping one portion of water brought in laboratory in incubator at 20°C for 5 days. Biochemical oxidation of organic compounds occurred in the water during this process. We were determining free oxygen volume in the samples by iodometric titration afterwards. This oxygen remains unused during aerobic microorganisms vital activity and represents amount of oxygen required for oxidation of organic compounds in water by microorganisms before nitrification process. By determining difference between initial concentration of free oxygen and oxygen left in water after incubation, we defined Biochemical Oxygen Demand within 5 days. This provided us with an indication of the level of water purity.

Table 4

Pollution level and quality class of surface water

№	Pollution level and quality class of water	*Dissolved oxygen, mg/l*		
		Summer	*Winter*	*Oxygen saturation level,%*
1	Very clean I class	9	14-13	95
2	Clean II class	8	12-11	80
3	Moderately polluted III class	7-6	10-9	70
4	Polluted IV class	5-4	8-5	60
5	Dirty V class	3-2	5-1	30
6	Very dirty VI class	0	0	0

The oxidation indicator is related to the water pollution level – this is the concentration of oxygen in water which is equivalent to the amount of oxidizers spent for oxidation of organic compounds. We determined the seawater oxidation by applying the Schulze method according to the GOST 23268.12-78. This method is based on oxidation of organic compounds found in the water sample by 0,01N $KMnO_4$ solution. Potassium permanganate releases free oxygen in an acidic environment, which is spent on oxidation of organic compounds in water:

$$2KMnO_4 + 3H_2O_4 \rightarrow K_2SO_4 + 3H_2O + 50.$$

We were determining sulphate concentration in the seawater samples by the turbidimetric method. The method is based on the principle of SO_4^{2-} ion precipitation in the form of $BaSO_4$ in the area of hydrochloric acid by applying glycol reagent (Table 5, Figure 1). Glycol which enters into reaction area causes stabilisation of $BaSO_4$ - suspension after precipitation of barium sulphate and allows for turbidimetric determination of sulphate micro amounts. The sensitivity of the method amounts to 2 mg/l SO_4^{2-}. To conduct the analysis, we prepared calibration curve for standard solutions in advance. We defined optical density of solutions on the ultraviolet spectrometer UV-1800 (cuvette 20 mm, wavelength λ - 364 nm).

Table 5

Concentration of standard solutions and their respective optical density

№	*Concentration of the solution C, mg/l*	*optical density of the solution D*
1	1,0	0,038
2	2,0	0,029
3	4,0	0,057
4	6,0	0,081
5	8,0	0,089
6	10,0	0,111
7	12,0	0,149
8	14,0	0,156
9	16,0	0,172
10	18,0	0,191
11	20,0	0,198

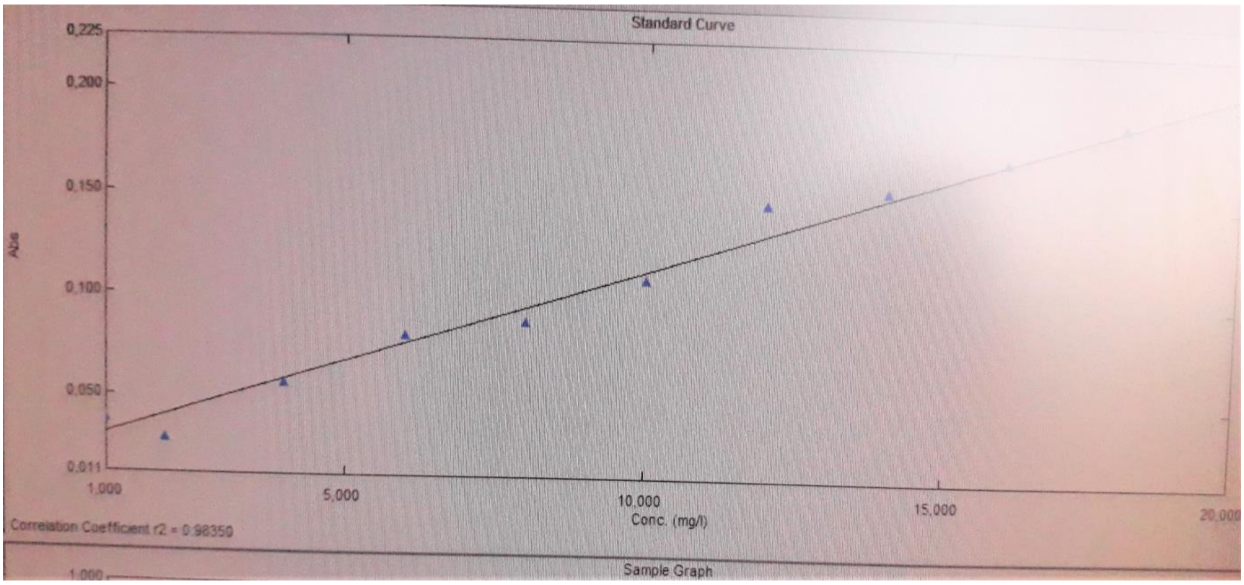


Figure 1. SO_4^{2-} **standard solutions' calibrated curve**

The photometric method for determination of NO_2^- is based on the principle of interaction of nitrites with sulfanilic acid $C_6H_7NO_3S$ with a participation of α-naphthylamine. Optical density of solutions was defined photometrically on spectrometer UV1800. The method detection limit is 0,003 mg/l NO_2^-. A relative error of analysis is ±5%. We were building calibrated curve for standard solutions before the analysis. Optical density of solutions was determined on the wavelength – λ=520 nm, cuvette volume is – 10 mm (Table 6, Figure 2).

Table 6

Concentration of standard solutions and their respective optical density

№	***Concentration of the solution C, mg/l***	***optical density of the solution*** *D*
1	0,002	0,001
2	0,004	0,003
3	0,01	0,005
4	0,02	0,008
5	0,04	0,018
6	0,10	0,059
7	0,20	0,129
8	0,30	0,200

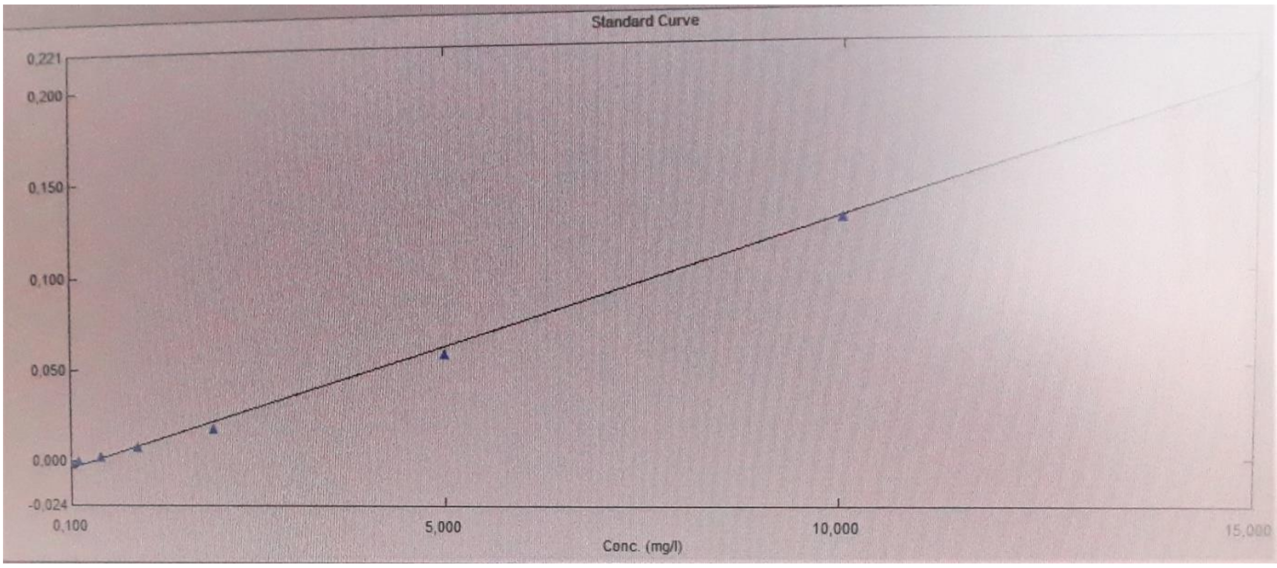


Figure 2. NO_2^- **- standard solutions' calibrated curve**

The method for determining the total amount of mineral nitrogen-containing compounds in water is based on the ability of ammonia and ammonium ions to react with Nessler's reagent via creating yellow-brownish compound. It colour intensity is determined photometrically. The method determination limit is 0,05mg/l NH_4^+. We were building calibrated curve for standard solutions before analysis. The optical density of solutions was determined on ultraviolet spectrometer UV-1800, the wave length – λ=520 nm, cuvette volume = 50 mm (Table 7, Figure 3).

Table 7

Concentration of standard solutions and their respective optical density

№	*Concentration of the solution C, mg/l*	*optical density of the solution D*
1	0,100	0,017
2	0,200	0,105
3	0,500	0,436
4	1,000	0,743
5	1,500	1,122
6	2,000	1,355
7	3,000	1,801

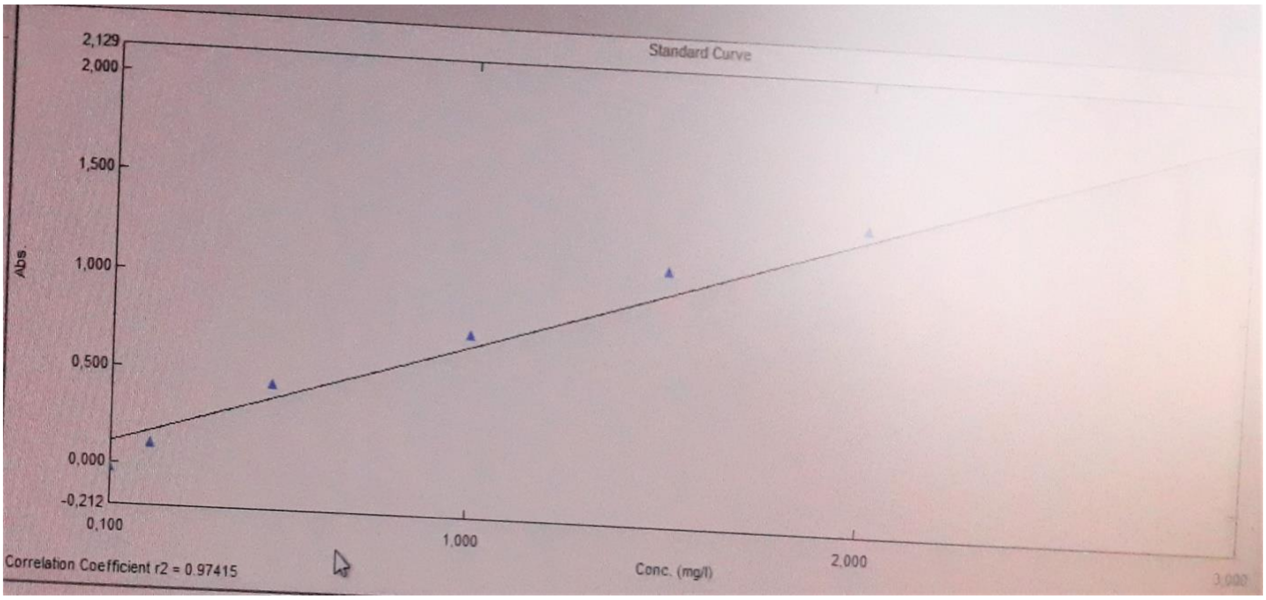


Figure 3. NH_4^+ **- standard solutions' calibrated curve**

Total harness of water has been determined according to the GOST 4151-72. The method is based on ability of creation stable complex by trillon Б with $Ca^{2+}$and Mg^{2+}ions. The indicator was defined by titration of the sample with trillon Б solution in pH 10 area, with a participation of indicator - chromogen black $C_{20}H_{12}N_3O_7SNa$. Ca^{2+}andMg^{2+} ions were determined by the complexometric method the principle of which is based on the ability of complex III (Trilon Б) to create stable complexes with interacting Ca^{2+} and Mg^{2+} ions in the alkaline area (pH12). The method allows for determination of ions more than 1 mg, the relative erroramounts to$\pm$0,02 mg.

It is of vital importance to study purification of water resources polluted by natural and anthropogenic influence (oil polluted especially) by sorption methods through combination of various sorbents and filtering material. To study the topic, we filtered the seawater and used glass made special columns, which had a locker in the bottom for capacity (the amount of water flowed during certain time) regulation (capacity amounted to 1 l/h). We used 200 g sawdust as a filter in the first column, 100 g of finely chopped sponge made of polyurethane material in the second. Using the gravimetric method, we analysed the soluble oil products present in both the unfiltered and filtered samples.

To determine the concentration of oil products in seawater, we applied the gravimetric method, which involves extracting the oil products from water using chloroform. The polar and non-polar hydrocarbons obtained from the extraction were then treated with n-hexane (in a non-polar solvent) for further processing. After passing the extract through a column containing a sorbent Al_2O_3 that adsorbs all polar compounds, the remaining extract is evaporated on a water bath. The residue is then dried (during which time the solvent completely evaporates). The residue is weighed (non-polar and least polar compounds).

To conduct analysis, we added 10% HCl solution to the sample to reach $pH5$. The entire volume (1 litre) of acidified water, was transferred into a separating funnel. We then periodically added 15 ml of chloroform, shook the mixture for a few minutes, and allowed it to settle for 15 minutes until the layers separated. The lower chloroform layer was carefully removed from the separatory funnel by dropping it several times, and the separated extract was collected in a flask. We repeated this process 3-4 times and evaporated the collected extract on a water bath until only 15 ml of solution remained in the flask. Afterward, we transferred this remaining solution to a beaker, which was then reduced to a constant weight, and we washed the flask with a small amount of chloroform. The extract in the beaker was evaporated with a ventilator until only about 0,5 ml remained. We then continued to evaporate the solution until it was dry and weighed the residue every 2 minutes until two consecutive weighing showed the same weight (reaching a constant weight). Following the evaporation process, we added waterless Na_2SO_4 to the dried residue treated, treated with 1-2 ml of n-hexane and poured it carefully into a column filled with aluminium oxide. We made sure to maintain the hexane level above the lower limit of the aluminium oxide while pouring each subsequent portion into the column. Below the column was embedded a weighing bottle, which was reduced to a constant weight. The contents of the weighing bottle were evaporated using the same method as with the chloroform. Finally, we weighed the weighing bottle together with the dried residue to a constant weight.

In order to prepare the sorbent column, we used a glass tube with 1 cm in diameter and 10 cm in length. A glass plate was inserted into it and one end of the tube was narrowed down to 1 mm. We placed 1 cm of glass wool on the lower side of the tube, followed by 2-3 cm of sorbent - aluminium oxide, and then another thin layer of glass wool. Prior to use, the column was washed with pure hexane (3-5 ml), and a new column was prepared for each analysis.

To investigate the most effective method of cleaning seawater, we carried the water purification through electrodialysis method using a model electrodialysis unit that operated in circulation mode, the hydraulic scheme of which is illustrated in Figure 4. the material and technical base was represented by the laboratory of the electrodialysis process and equipment at the Agrarian and Membrane Technology Institute.

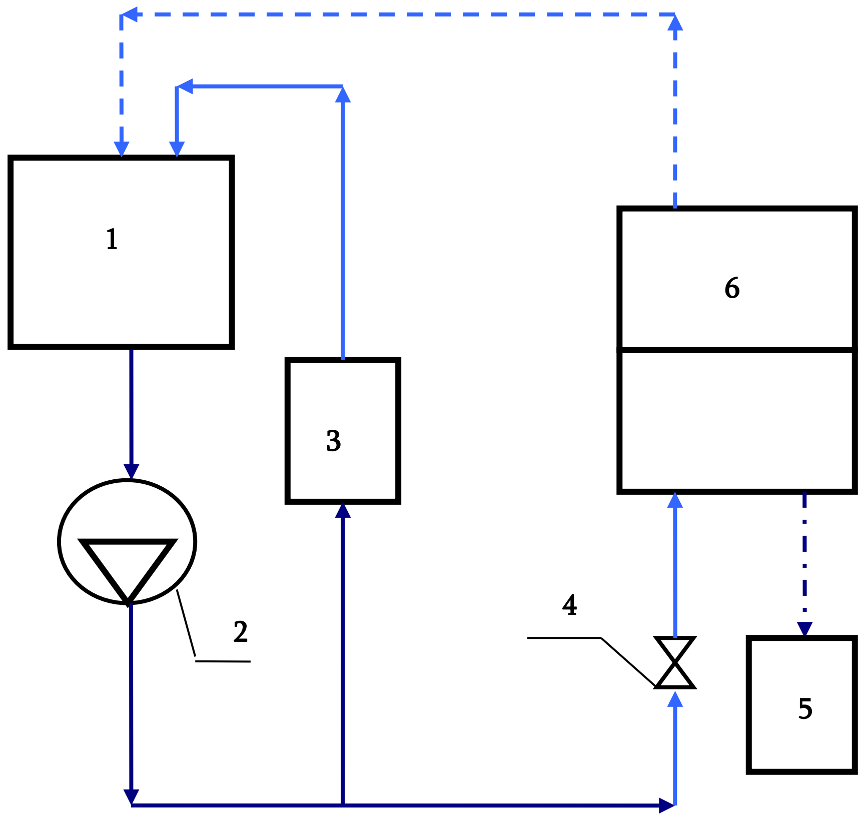


Figure 4. The hydraulic scheme of a model electrodialysis device
1 - tank; 2 - pump; 3 - filter; 4 - tap; 5- concentration receiving tank; 6 – electrodialysis device

10 liter of seawater (this is the minimum initial water volume required for the model device) is supplied to the filter (3) from the tank (1) by a pump (2). During this process, tap (4) remained closed. Once the admixtures were removed, the solution was directed to the dialysate sections of the electrodialysis unit, and tap (4) was opened at this stage. After passing through the dialysate chambers, the water was returned to the tank (1). The concentrate that formed in the chambers flowed out on its own through the outlet collector and into the concentrate collection tank. As the electrodialysis unit was a model and the water path length was short

(as the machine was assembled in a parallel scheme), we applied the circulation mode to determine the amount of time required to clean the water of microbes.

Electrodialysis is a process that involves the movement of ions through membranes in an electric field. The electrodialysis method is a membrane-based process for separating substances, which is based on the transfer of electrolyte ions through ion-selective, ion-exchange membranes under the influence of an electric field. The main advantages of electrodialysis method includes: low operating costs, no need for reagents, absence of solution phase transition, and relatively low specific electricity costs.

The ion-exchange membranes are the crucial component of the electrodialysis device, produced through the process of hot casting a blend of ionite and polyethylene, and then reinforced with Capron fabric (or without reinforcement). The transfer of electricity in the machine is achieved by the ion-counter diffusion of the solution to and from the membrane under the influence of an electric field. The working module of the electrodialysis device is constructed by arranging anionic and cationic membranes.

The electrodialysis device comprises of platinized titanium electrodes and a package of membranes placed between them, with alternating MK-40 and MA-40 type membranes forming 20 pairs of working chambers in the device. Net-turbulizers and fluid distribution frames are positioned between the membranes. To ensure the initial liquid flows turbulently within the frame made of propylene material (to ensure the strength and tightness of the structure), a polymer mesh is positioned between the membranes. The body frames form a collector system, which enables electrolyte solutions to be supplied to the electrodialysis machine and separated solutions (dialysate and concentrate) to be extracted from it. The membrane package is enclosed between the two electrodes and is hermetically sealed.

We selected a single-stream configuration of the electrodialysis device, whereby the initial solution would flow through only one channel - the desalination (dialysate) chamber - and the hydrated salt ions from the concentration chamber would exit the device together with water. In order to equally distribute the initial solution flow, we assembled a parallel configuration of the working package, where the initial solution was simultaneously fed into all dialysate chambers of the electrodialysis device from one end and exited from the other end. It took a minimum of 5 minutes for the parameters to stabilize on the aforementioned model device, thus we collected the dialysate after 5 minutes. Subsequently, we replaced the water and took the dialysate again after 10 minutes. For the third time we took the dialysate after 15 minutes (Table 8).

Table 8

Experiment parameters for the electrodialysis machine operation

Time, min	*Electric power, amper*	*Water cost, ml/min (l/h)*	*Membrane area, m²*	*Height of net-turbulizers, mm*	*Thickness of fluid distribution frame, cm*	*Height of one chamber cm*	*Volume of water sample, L*
15	1,5						
10	1,0	500					
5	0,5	(30)	0,0525	0,7	0,09	15	10

Membrane filtration processes (microfiltration and ultrafiltration) involve the separation of substances using porous polymeric or non-organic materials. Unlike conventional filtration, in membrane filtration the mixture is divided into concentrate and filtrate (permeate) on opposite sides of a semi-conductor membrane. Based on the size of the membrane pores and the amount of operating pressure, the type of baro-membrane filtration used are: micro-, ultra-, nano-, or reverse-. Microfiltration is applied to separate colloidal and insoluble microparticles (size range 0.1-10µm, pressure range 0.03-0.1MPa). While ultrafiltration is used to separate low-molecular-weight compounds from high-molecular-weight particles (size range 0.001-0.02 µm, pressure range 0.1-0.5 MPa).

We used microfiltration and ultrafiltration methods to study the seawater filtration process. In particular, we applied a fluoroplastic microfiltration membrane (with a working area of 0.01 m^2, an average pore size of 0.2µm, and a working pressure of 0.1MPa=1atm) and a polyoxadiazole ultrafiltration membrane (area of 0.01m^2, an average pore size - 0.02µm, working pressure 0.3-0.5 MPa=3-5 atm). The experiments were conducted using laboratory equipment comprising of: a membrane cell (3), manometer (4), compressor (2), connecting pipes, tanks (1, 5), and tap (6) (Figure 5).

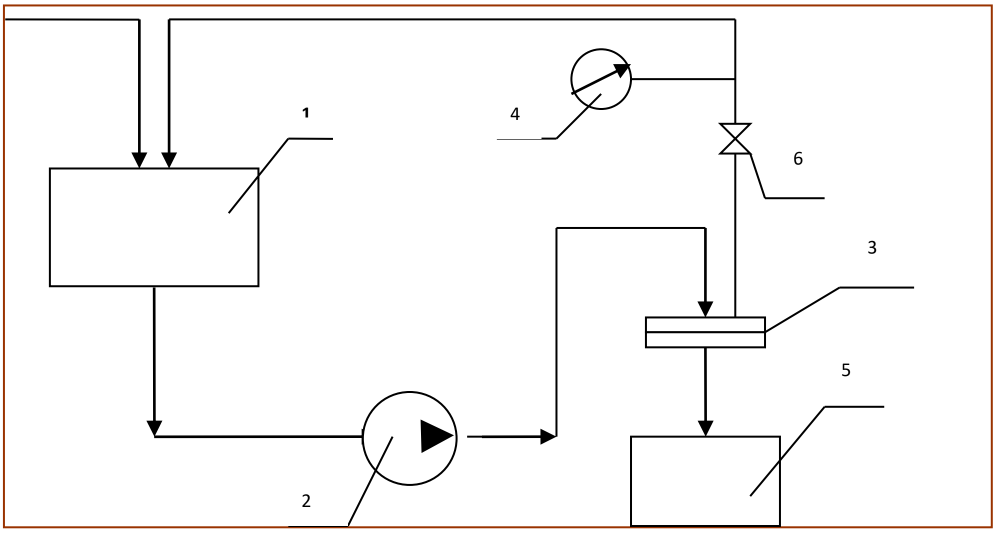


Figure 5.

1, 5 –Tanks 2 – Compressor 3 – Membrane cell 4 - Manometer 6 - Tap

A schematic diagram of a membrane cell is shown in Figure 6.

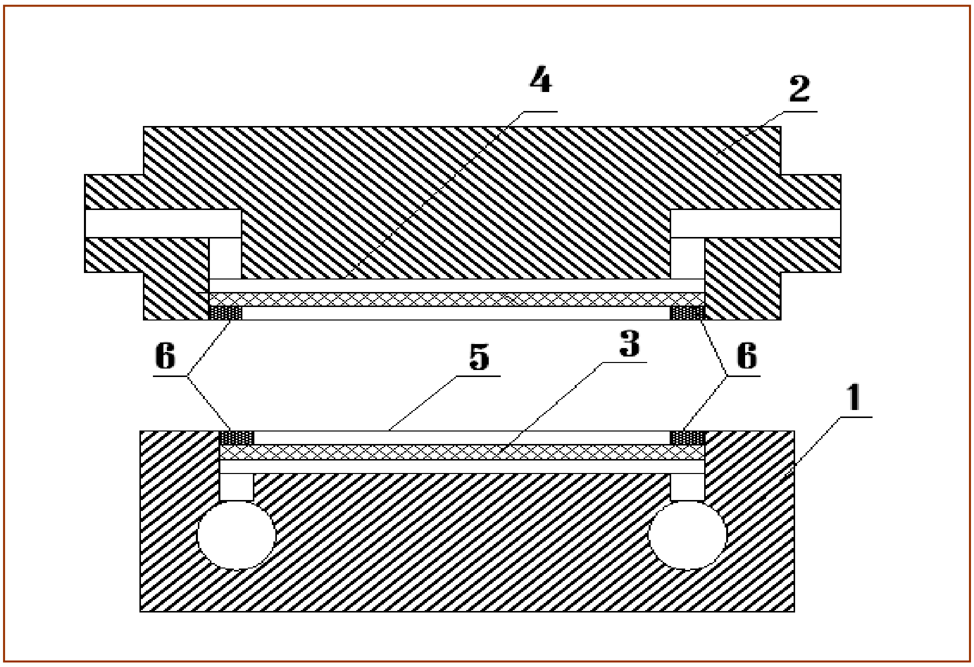


Figure 6.Laboratory Filtration Cell

1. Foundation. 2. Cap. 3. Pore layer.
4. Net (polyvinyl chloride). 5. Membrane. 6. Hermetic layers

Initial solution was placed in the tank (1) and pressured using a compressor (2), P=0,05-0,1MPa (0,5-1 atm) and provided to filtration cell containing a microfiltration membrane composed of fluoroplastic (with a pore average size of 0.2 μm). About 95-97% of the solution was filtered and collected in tank (5), we were pouring out the remaining 3-5% of concentration. After that, the filtrate (permeate) was subjected to chemical and sanitary-hygienic (total number of coliform bacteria) analyses. The same rule was applied to further filter the filtrate obtained through laboratory equipment with an ultrafiltration membrane made of polyoxadiazole (with a pore size of 0.02 μm).

To conduct a multi-elemental analysis of waters, we used the plasma atomic emission spectrometry, a device ICPE-9820 (SHIMADZU product) (Figure 7). The plasma atomic emission spectrometry method determines the intensity of light emitted by element atoms that are excited by inductively coupled argon plasma at different wavelengths. Prior to analysis on the plasma atomic emission spectrometer, we prepared standard solutions, with one solution serving as an internal standard. We made standard solution by applying multi-element standards. We used Yttrium (*Y)* as an internal standard with a concentration of 0,1ppm. Standard solution №2 contained concentrations of 5ppb and 25ppb, standard solution №3 - 2ppm and 5ppm, and standard solution №4 had a concentration of 0,5ppm.

Inductively coupled spectrometry is a form of atomic emission spectrometry that employs inductively coupled argon plasma to excite atoms. This method relies on the fact that each element in Mendeleev's periodic table emits a light quantum with a specific wavelength during excitation and ionization. The qualitative analysis is determined by the wavelength, while quantitative – by the intensity of the wave radiation. Thus, the main value of this method lies in its capacity to conduct both types of analysis simultaneously, enabling the determination of over 20 elements with high accuracy in less than two minutes per sample.

Picture 12. Plasma Atomic Emission SpectrometryICPE-9820

The multielement standard solutions contain:

$Al, Sb, Ba, Pb, B, Ca, Cd, Cr, Co, Fe, K, Cu, Mg, Li, Mn, Mo, Na, Ni, P, Si, Ti, V, Zn, As, Be, Se, Tl$.

Inductively coupled plasma is a type of discharge of highly ionized argon gas generated by an induction coil through an alternating magnetic field. As the plasma reaches high temperatures, the atoms of the sample undergo desolation, vaporization, excitation, and ionization. The device can detect elements ranging from 1 μg/l (10^{-6} g/l) to 1 nanogram/l (10^{-9} g/l) and less. The metal coil acts as the inductor, wrapped around the top end of the lamp and connected to the generator. The sample solution in the form of an aerosol enters the central channel of the lamp, where it undergoes drying, dissociation, ionization, and thermal excitation within the plasma. When the carrier gas flows through the lamp, a spark ignites, removing some electrons out of the gas. Those electrons are then kept by the magnetic field and their moving speed rapidly increases. The process of providing high energy to electrons using the device coil is referred to as inductive coupling, which enables the plasma to remain stable through a continuous energy supply from the inductive coupling between the lamp and coil. A correlation coefficient amounts to at least 0,99.

Sea water samples were analysed to determine the total number of coliform bacteria (intestinal lactose-positive rods) in accordance with methodological instructions 4.2.2959-11. This type of bacteria consist of around 100 types of microbes, which are commonly represented in the intestinal microflora of humans, animals, and birds. They are also referred to as pathogenic microbes. The titrimetric method was used to estimate the total number of coliform bacteria in the seawater samples: 1 ml of the sample was inoculated onto liquid lactose-peptone “ground” to facilitate bacterial growth. To prepare the “ground”, a 1 ml aliquot of lactose-peptone solution was dissolved in 10 ml of distilled water and sterilized in an autoclave for 12 minutes at 0.5 atm and 112°C.

After cooling down, the resulting medium was transferred into 9 test tubes, following a 3-parallel row scheme. After inoculation, the solutions were incubated at 37°C for 24 hours. If no colour change (from green to yellow) or gas formation was observed, the result was negative, indicating the absence of microbes in the water. However, if there was a colour change and gas formation, one drop of the test solution was streaked onto a new “ground” - endo fuchsin-sulphite agar - using a microbiological loop, and further incubated. If this led to a colour change and the formation of colonies with a dark red or metallic shining colonies on the surface, the third stage of inoculation was carried out. In this stage, a mass peeled from the discoloured solid nutrient “ground” with a sterilized microbiological needle was inoculated onto semi-liquid nutrient “ground” broth, and sterilized at 120°C for 15 minutes. This was then incubated at 37°C for 24 hours. If a colour change (red to yellow) and gas formation was observed, it confirmed the presence to lactose fermentation or in other words coliform bacteria. These nutrient areas mentioned above are recommended by ISO as indicators for detecting coliform bacteria. Using a three stage inoculation scheme (Table 9), we estimated the approximate number of bacteria in 100 ml of seawater at the end of the analysis.

Table 9

Estimation of an approximate number of bacteria in 100 ml of seawater by applying three stage inoculation scheme

Number of positive results			Approximate number of bacteria in 100 ml	Number of positive results			Approximate number of bacteria in 100 ml
From 1 liter volume	*From 0.1 liter volume*	*From 0.01 liter volume*		*From 1 liter volume*	*From 0.1 liter volume*	*From 0.01 liter volume*	
0	0	0	< 30	2	0	0	91

0	0	1	30	2	0	1	140
0	0	2	60	2	0	2	200
0	0	3	90	2	0	3	260
0	1	0	30	2	1	0	150
0	1	1	61	2	1	1	200
0	1	2	92	2	1	2	270
0	1	3	120	2	1	3	340
0	2	0	62	2	2	0	210
0	2	1	93	2	2	1	280
0	2	2	120	2	2	2	350
0	2	3	160	2	2	3	420
0	3	0	94	2	3	0	290
0	3	1	130	2	3	1	360
0	3	2	160	2	3	2	440
0	3	3	190	2	3	3	530
1	0	0	36	3	0	0	230
1	0	1	72	3	0	1	390
1	0	2	110	3	0	2	640
1	0	3	150	3	0	3	950
1	1	0	73	3	1	0	430
1	1	1	110	3	1	1	750
1	1	2	150	3	1	2	1200
1	1	3	190	3	1	3	1600
1	2	0	110	3	2	0	930
1	2	1	150	3	2	1	1600
1	2	2	200	3	2	2	2100
1	2	3	240	3	2	3	2900
1	3	0	160	3	3	0	2400
1	3	1	200	3	3	1	4600
1	3	2	240	3	3	2	11000
1	3	3	290	3	3	3	>11000

I.5. The Organoleptic Characteristics of Seawater

We conducted seasonal assessments of organoleptic indicators in seawater samples according to GOST 3351-74 (Tables 10, 11, 12). The port beach had the most noticeable smell, which ranged between 4-5 points seasonally, exceeding the permissible norm by 2-3 points. The water at this location was highly turbid with an uncharacteristic greenish-yellow colour. Floating particles were observed at 0-50 cm deep from the water surface throughout all seasons. At the confluence of Kintrishi and Korolistskali to the sea, the smell was noticeable a 3-point in autumn, the water was slightly turbid and turbid (seasonally), while floating particles were observed in spring and winter at 40-50 cm deep from the surface and in autumn at 30-40 cm deep from the surface.

In comparison to other seasons, the smell of the water samples taken at Korolistskali and Kintrishi estuaries was higher in the autumn period, which could be related to the rise of temperature and lack of atmosphere precipitation. the water at Pichvnari, Gonio and Kvariati locations had no smell with 0 point, it was transparent with no visible floating particles on the surface throughout all three seasons. At Chakvi beach, the water had a slight smell of 2 points in autumn and 1 point in spring and winter, and was slightly turbid in autumn, which led to the presence of floating particles up to a depth of 0-10 cm from the surface. The colour and turbidity of natural waters are key factors affecting their transparency or light transmission, and the presence of large dispersed particles in the water can cause pollution and a decrease in transparency.

Table 10

Organoleptic parameters of seawater in autumn season

№	*Location*	**sample volume ml**	**Smell, points**	**transparency**	**chromaticity**	**floating particles**
1	***Pichvnari coast***	**2000**	0	Transparent	_	_
2	***Kitrishi estuary to the sea***		3	turbid	_	Observed up to a depth of 0-40 cm
3	***Chakvi beach***		2	slightly turbid	_	Observed up to a depth of 0-10 cm
4	***Korolistskali river estuary to the sea***		3	slightly turbid	_	Observed up to a depth of 0-30 cm
5	***Coastline near port***		5	Strongly turbid	Green-yellowish	Observed up to a depth of 0-50 cm
6	***Gonio beach***		0	Transparent	_	_
7	***Kvariati beach***		0	Transparent	_	_
	Norm		***2 points***	***It should be transparent from 0-30 cm***	***It is not allowed at 0-10 cm***	***Floating particles uncharacteristic to the seawater shall not be observed on the water surface or upper layer***

Table 11

Organoleptic parameters of seawater in winter season

№	Location	sample volume ml	Smell, points	transparency	chromaticity	floating particles
1	*Pichvnari coast*	**2000**	0	Transparent	_	_
2	*Kitrishi estuary to the sea*		2	slightly turbid	_	Observed up to a depth of 0-50 cm
3	*Chakvi beach*		1	Transparent	_	_
4	*Korolistskali river estuary to the sea*		2	slightly turbid	_	Observed up to a depth of 0-40 cm
5	*Coastline near port*		4	strongly turbid	Green-yellowish	Observed up to a depth of 0-50 cm
6	*Gonio beach*		0	Transparent	_	_
7	*Kvariati beach*		0	Transparent	_	_
	Norm		***2 points***	***It should be transparent from 0-30 cm***	***It is not allowed at 0-10 cm***	***Floating particles uncharacteristic to the seawater shall not be observed on the water surface or upper layer***

Table 12

Organoleptic parameters of seawater in spring season

№	Location	sample volume, ml	Smell, points	transparency	chromaticity	floating particles
1	*Pichvnari coast*	**2000**	0	Transparent	_	_
2	*Kitrishi estuary to the sea*		2	slightly turbid	_	Observed up to a depth of 0-50 cm
3	*Chakvi beach*		1	Transparent	_	_
4	*Korolistskali river estuary to the sea*		2	slightly turbid	_	Observed up to a depth of 0-50 cm
5	*Coastline near port*		5	strongly turbid	Green-yellowish	Observed up to a depth of 0-50 cm
6	*Gonio beach*		0	Transparent	_	_
7	*Kvariati beach*		0	Transparent	_	_

	Norm		***2 points***	***It should be transparent from 0-30 cm***	***It is not allowed at 0-10 cm***	***Floating particles uncharacteristic to the seawater shall not be observed on the water surface or upper layer***

I.6. The Physical-Chemical Characteristics of Seawater

Right upon taking water samples, we measured the temperature on-site as it is a variable parameter. Seasonal temperature data for the water samples are presented in Table 13. Throughout our seasonal observations, the highest temperature in different locations along the Adjara coastline was recorded in spring, ranging from 16-21°C, whereas the lowest was recorded in winter – within 10-16°C. In comparison to other areas, coastal waters near the port had an increase in temperature of 1-6°C in all seasons.

The pH of seawater is influenced by the concentration and nature of dissolved gases and organic compounds. The accumulation of high levels of soluble molecular CO_2, oil, and organic compounds result in an increase of acidity, while an inflow of freshwater leads to its decrease. The pH of seawater in the Black Sea is regulated by the carbonic acid-carbonate system, which functions as a buffer system. The pH of seawater in the surface water is within 8,1-8,5. But in depth, it decreases to 7,48-7,6. Our observation revealed that the pH of seawater was the highest in winter and lowest in autumn and spring, with a range of 7,20-8,20. An exception is the coast near the Batumi port, where the lowest pH was recorded in autumn amounted to 6,35, which exceeds the limits of the MPC (Table 13, Diagram 1).

Table 13

Temperature and pH of seawater

\№	Location	Autumn		Winter		Spring	
		T, °C	pH	T, °C	pH	T, °C	pH
1	***Pichvnari coast***	15	7,90	13	8,13	19	8,0
2	***Kitrishi estuary to the sea***	17	7,20	15	8,03	20	7,50
3	***Chakvi beach***	16	7,28	15	7,84	18	7,4
4	***Korolistskali river estuary to the sea***	16	7,60	14	8,00	19	7,93
5	***Coastline near port***	18	6,35	16	7,90	21	7,53
6	***Gonio beach***	13	8,00	11	8,20	17	8,07
7	***Kvariati beach***	12	8,03	10	8,10	16	8,0
MPC			**6,5-8,5**		**6,5-8,5**		**6,5-8,5**

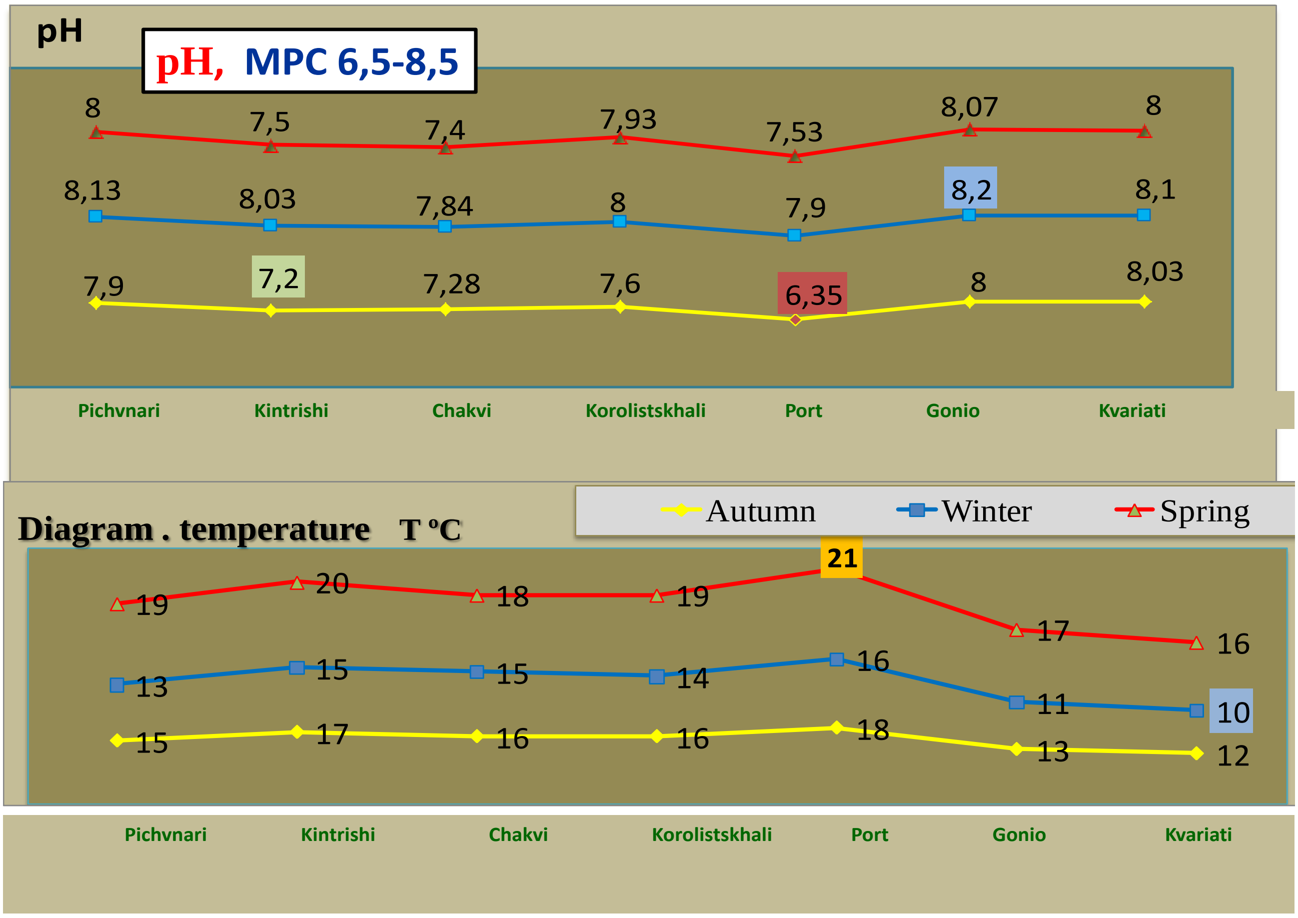


Diagram 1. Temperature and pH in seawater samples in various locations

The salinity of seawater can be determined by measuring the concentration of chloride ions. The seawater samples taken near river estuaries had low chloride levels: 10509-10918 mg/l - in autumn, 9900-10000 mg/l - in winter, and 4000-5000 mg/l - in spring. The highest concentration of chlorides were found near the port throughout the year - 7500-12600 mg/l. The concentration of NaCl showed a consistent correlation with the concentration of chloride ions. Salinity was the lowest in spring, which could be related to high levels of precipitation, and highest in autumn (Table 14). Concentration Ca^{2+} and Mg^{2+} decreases starting from autumn to spring, in parallel to seasonal increase of precipitation volume and water desalination (this is particularly found in the river estuaries). Concentration of those ions are in consistent correlation with water hardness (Table 15).

Table 14

Concentration of Cl-ion and NaCl in sea water

Location	Cl^-, mg/l			NaCl, mg/l		
	Autumn	Winter	Spring	Autumn	Winter	Spring
Pichvnari coast	11500	11122	5000	18975	18351	8250
Kitrishi estuary to the sea	10509	9900	4000	17340	16335	6600
Chakvi beach	11600	10200	6000	19140	16830	9900
Korolistskali river estuary to the sea	10918	10000	5000	18015	16500	8250
Coastline near port	12600	11200	7500	20790	18480	12375
Gonio beach	11632	10000	7000	19193	16500	11550
Kvariati beach	11700	11000	6700	19305	18150	11055

The concentration of dissolved oxygen in surface waters fluctuates seasonally and on a daily basis, and its deficit is mainly detected in water bodies with high levels of polluting organic compounds, biogenic compounds, and humus substances. A minimum of 5 mg/l of dissolved oxygen is necessary for normal aquatic organism activity, and levels dropping to 2 mg/l can lead to fatal results. The dissolved oxygen content in water samples taken before 12 pm should be at least 4-6 mg/l, regardless of the time of year. Table 16 presents the results of dissolved oxygen content analysis for the water samples, showing that the highest concentration level occurred in winter (5,46-10,08 mg/l) and the lowest in spring (3,95-9,70 mg/l). In all three seasons, the seawater in Kvariati and Gonio locations had the highest levels dissolved O_2 (9,10-10,08 mg/l), while the port location had the lowest (3,95-5,46 mg/l). Level of dissolved O_2 in the port waters was even lower than MPC - in the spring.

The level of water pollution in any water basin is measured by the amount of organic compounds present, which are oxidized by aerobic microorganisms, leading to a decrease in dissolved oxygen levels known as Biochemical Oxygen Demand (BOD_5). An indicator of water pollution by organic compounds is called the Biochemical Oxygen Demand over 5 days and nights, the level of which ranges from 0,5-4,0 O_2 mg/l - in surface waters and fluctuates seasonally and daily. We determined the BOD_5 in all water analysis samples on a seasonal basis. The determination of BOD_5 provided insight into the level of water pollution. The results of experiment analysis on BOD_5 are presented in Table 16.

Table 15

Ca^{2+}, Mg^{2+} - ions and water hardness

Location	Ca^{2+} mg/l			Mg^{2+} mg/l			* Hardness, mg/l / mg.equivalent/l		
	Autumn	Winter	Spring	Autumn	Winter	Spring	Autumn	Winter	Spring
Pichvnari coast	220,18	212,64	180,40	753,92	715,60	449,92	974,1 / 72,9	928,24 / 69,4	630,32 / 46,0
Kitrishi estuary to the sea	200,0	180,36	100,16	680,96	559,36	316,16	880,90 / 65,9	739,72 / 55,0	416,32 / 30,99
Chakvi beach	230,18	192,80	172,60	693,12	547,20	522,90	923,30 / 68,4	740,0 / 54,6	695,5 / 51,6
Korolistskali river estuary to the sea	200,40	190,40	100,20	690,30	522,90	425,60	890,7 / 66,7	713,3 / 52,5	525,8 / 40,0
Coastline near port	240,48	200,40	190,20	678,0	522,88	499,92	918,48 / 67,7	723,28 / 53,0	690,12 / 50,6
Gonio beach	180,0	170,30	165,20	510,72	425,60	404,0	690,72 / 50,9	595,9 / 43,4	569,2 / 41,4
Kvariati beach	185,4	170,50	150,40	670,0	540,20	401,28	855,4 / 64,3	710,7 / 52,9	551,68 / 40,5

* **Hardness:** in nominator - mg/l; in denominator – mg equivalent / l

Table 16

dissolved O_2 and BOD_5, mg/l

Location	dissolved O_2 , მგ/ლ						BOD_5, mg/l		
	Autumn		Winter		Spring		Autumn	Winter	Spring
	X_1	X_2	X_1	X_2	X_1	X_2			
Pichvnari coast	8,79	7,79	9,70	8,59	7,60	5,85	1,0	1,11	1,75
Kitrishi estuary to the sea	8,10	7,0	9,40	8,26	7,49	5,69	1,1	1,11	1,80
Chakvi beach	7,85	6,74	9,0	7,08	7,40	5,40	1,11	1,20	2,00
Korolistskali river estuary to the sea	8,10	6,60	8,44	7,23	7,15	5,31	1,50	1,21	1,84
Coastline near port	4,80	1,4	5,46	2,36	3,95	0,3	3,40	3,10	3,65
Gonio beach	9,40	8,50	10,06	9,20	9,10	8,0	0,9	0,86	1,10
Kvariati beach	9,76	8,98	10,08	9,710	9,70	8,66	0,78	0,38	1,04
MPC	not less than 4 mg/l						not more than 3 mg/l		

The BOD_5 was within limits in all locations, except of the coastal area near the port. The minimum levels of BOD_5 were found in Gonio-Kvariati coastline (0,3-1,10 mg/l), which correlated with the dissolved oxygen concentration in these locations. The BOD_5 exceeded the permissible limit in waters near the port in all three seasons (3,10-3,65 mg/l). Such oxygen deficit in water was confirmed by the experimental results of oxygen concentration determination after water retentions for 5 days and nights. Considering seasonal dynamics, this parameter was regularly decreasing during autumn-winter and increasing in spring, related to seasonal fluctuations in temperature and the reduced activity of microorganisms during colder periods.

The oxidability of water is an important indicator of pollution as it provides an estimation of the amount of organic substances present, which require significant volume of oxygen for oxidation. Based on this parameter, water samples collected from the Kvariati-Gonio coastline had the highest oxygen level and the lowest oxidation levels (0,98-1,8 mg/l). High oxidation levels were observed in coastal waters near the port throughout all seasons (4,0-6,05 mg/l), indicating a high degree of pollution potentially caused by the accumulation of organic substances and decreasing oxygen concentration. Based on seasonal dynamics, the level of oxidation in the water was minimal during winter and maximum in spring, which is related to an increase in organic substances during this season (Table 17, Diagram 2).

Table 17

Oxidizability, mg O_2/l

Location	Autumn	Winter	Spring
Pichvnari coast	1,52	1,04	2,4
Kitrishi estuary to the sea	1,36	1,12	3,0
Chakvi beach	1,36	1,04	2,6
Korolistskali river estuary to the sea	1,60	1,20	3,0
Coastline near port	5,68	4,0	6,05
Gonio beach	1,12	1,00	1,8
Kvariati beach	1,12	0,98	1,36
MPC, mg O_2/l	not more than 3		

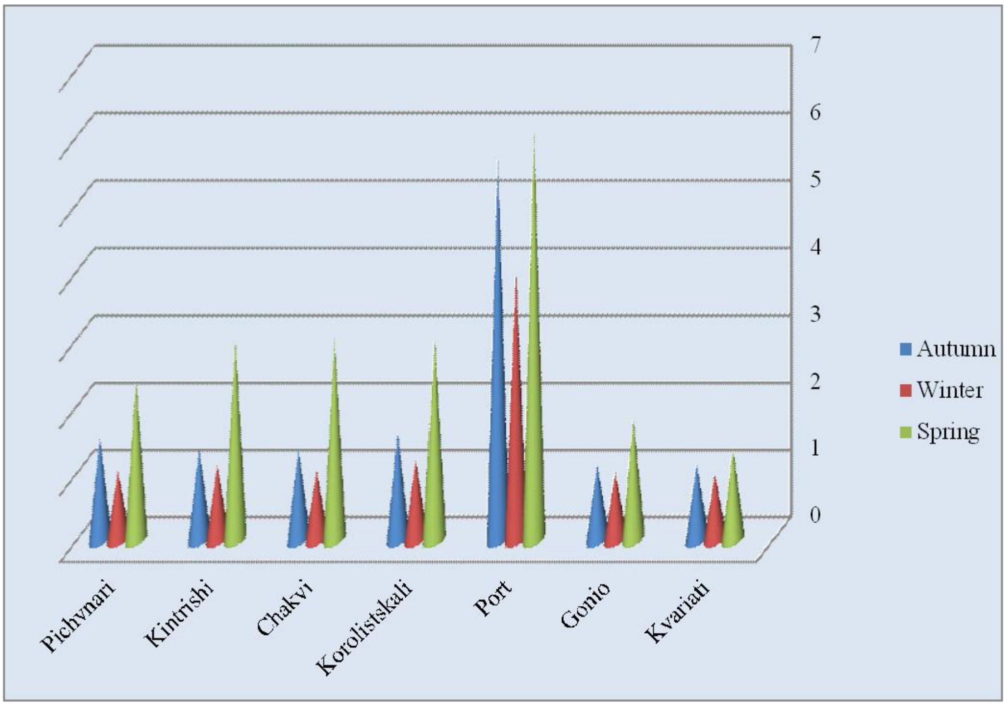


Diagram 2. Oxidation, mgO2/

Picture 13. Multi-element analysis of seawater samples on ICPE-9820

Picture 14. Toyota Centre near to Kintrishi bridge

Picture 15. Car washes near to Kintrishi bridge

Picture 16. Wastewater from restaurant Bella Costa at the estuary of Korolistskali river

Picture 17. Construction and household waste, sewage water, at the estuary of Korolistskali river

Table 18

Elemental analysis of seawater by plasma atomic emission spectrometry (ICPE 9820), mg/l

Location	Al	As	B	Ba	Ca	Co	K	Mg	Na	P	Pb	Si	Zn	Cu
Kitrishi estuary to the sea	0,473	0,0318	0,436	0,0165	160,0	0,009	5,40	418,0	892	0,192	0,0695	1,17	0,421	0,04
Kvariati beach	0,0012	0,0078	0,211	0,0012	174,39	0,0034	1,98	439,49	1104	0,008	0,0004	0,05	-0,06	- 0,0184
Gonio beach	0,0084	0,0171	0,259	0,0014	171,80	0,0033	1,20	448,8	1156	0,0126	0,0008	0,065	-0,277	-0,002
Chakvi beach	0,009	0,0245	0,461	0,0018	188,0	0,0035	3,30	550,0	1310	0,161	0,0029	0,173	0,0273	0,0026
Korolistskali river estuary to the sea	0,007	0,0226	0,408	0,0016	121,0	0,0042	1,43	471,0	882	0,142	0,0047	0,083	0,270	0,0012
Pichvnari coast	0,0058	0,0235	0,299	0,0022	193,6	0,0043	2,40	536,04	1134	0,0257	0,0014	0,0963	-0,269	-0,015
Coastline near port	0,0037	0,0368	0,489	0,0024	227,09	0,0044	2,61	587,0	1434	0,147	0,0085	0,206	0,680	0,45
MPC, mg/l	**1,0**	**0,05**	**5,0**	**0,1**	-	**0,005**	-	-	-	**0,028**	**0,01**	**10,0**	**0,05**	**0,005**

I.7. The Results of Seawater Chemical and Bacteriological Analysis Before and After Passing Through Membrane Devices

Tables 19-24 display the findings from the analysis of seawater samples before and after electrodialysis. Based on the experimental results, it is evident that alterations in pH are influenced by the percentage of cations and anions that transition into the concentrate. As the transfer of cations and anions is imbalanced during the initial electrodialysis process, this may result in uneven pH changes - either an increase or decrease.

Through electrodialysis, the decrease in Ca^{2+} and Mg^{2+} ions result in a reduction of water hardness. The electrodialysis process slightly reduces permanganate oxidation as only dissociated ions are transferred to the concentrate. As chemical oxidation is mainly caused by the quantity of organic compounds in water, their number does not significantly change during this process. In addition, the analysis of water pollutants, such as biogenic compounds - NH_4^+ and NO_2- and, SO_4^{2-}, was necessary at the coast near to the port and the Batumi Marine Station (active recreation and swimming zones). This is because the main sources of nitrogen in water are organic compounds, river runoff, and atmospheric sediments. As it is known NH_4^+ ions are formed from indirect regeneration of nitrogen in the surface layers of water, which is a destruction product of complex organic compounds influenced by nitrogen bacteria (ammonifier, nitrifier). NO_2^- ions are intermediate products of the decomposition of nitrogen-containing organic compounds, which are easily oxidized into nitrates under the influence of nitrifying bacteria. As a result of electrodialysis in the selected locations, NH_4^+ was more easily removed than NO_2^-, however, as a result of electrodialysis, the concentration of both ions in seawater samples fell below the MPC, while their content in the initial samples exceeded the MPC.

Our research priority was the seawater purification (rather than desalination), thus all of the water samples taken from the locations were filtered in electrodialysis device. We applied three modes of time: 15 minutes; 10-minute; 5-minute. Out aim was toto determine the time frame required for receiving seawater free from microbes. Filtering of samples through electrodialysis devicewithin15-minute mode, delivered positive results justified by bacteriological analysis of the samples: nocoliform bacteria were found in any of the samples.This led us to make a decision on decreasing time for electrodialysis process to 10 minutes. The results were positive again. Eventually, the time was narrowed down to 5 minutes (this is a minimum time required for stabilisation of the device parameters). These results were positive as well laying precondition for a conclusion that a minimum 5 minute mode is required to water purification as long as it is justified by its cost-effectiveness and required quality of seawater.

Table 19

The Chemical Parameters of Seawater Before and After Filtrationin through the Electrodialysis Device Location – Kitrishi estuary to the sea

№	*parameter, dimension*	*initial sample*	*I dialysate I=1,5A, U=9,5V Spending time - 15 min*	*II dialysate I=1,0A, U=8,0V Spending time - 10min*	*III dialysate I=0,5A, U=5,8V Spending time - 5 min*
1	***pH (MPC 6,5-8,5)***	7,9	8,4	8,3	8,3
2	***Cl^-, mg/l***	10816	9082	10204	10408
3	***NaCl, mg/l***	17846	14985	16836	17173
4	***Ca^{2+}, mg/l***	140,6	116,9	128,8	132,4
5	***Mg^{2+}, mg/l***	448,8	405,5	426,8	432,0
6	***overall hardness, mg.equivalent/l mg/l***	43,9 589,4	39,1 522,4	41,5 553,6	42,1 564,4
7	***permanganate oxidizability mgO_2/l (MPC- not more than 3 mg/l)***	3,5	3,48	3,45	3,45

Table 20

Location – Pichvnari coast (Kobuleti)

№	*parameter, dimension*	*initial sample*	*I dialysate I=1,5A, U=8.0V Spending time - 15 min*	*II dialysate I=1,0A, U=6,5V Spending time - 10min*	*III dialysate I=0,5A, U=5,8V Spending time - 5 min*
1	***pH (MPC 6,5-8,5)***	8,15	8,66	8,5	8,2
2	***Cl^-, mg/l***	11428	8367	8661	10612
3	***NaCl, mg/l***	18857	13721	14290	17509
4	***Ca^{2+}, mg/l***	186,9	150,4	169,8	172,0
5	***Mg^{2+}, mg/l***	705,3	657,0	668,0	680,0
6	***overall hardness,***	67,3 892,4	55,8 737,9	63,0 837,8	64,5 852,0

	mg.equivalent/l ***mg/l***				
7	***permanganate oxidizability mgO_2/l (MPC- not more than 3 mg/l)***	2,9	2,855	2,83	2,78

Table 21

Location – Kvariati beach

№	***parameter, dimension***	***initial sample***	***I dialysate I=1,5A, U=985V Spending time - 15 min***	***II dialysate I=1,0A, U=7,0V Spending time - 10min***	***III dialysate I=0,5A, U=4,5V Spending time - 5 min***
1	***pH (MPC 6,5-8,5)***	8,15	8,75	8,6	8,17
2	***Cl^-, mg/l***	11224	9184	9979	10714
3	***NaCl, mg/l***	18519	15154	16465	17678
4	***Ca^{2+}, mg/l***	180,0	120,0	145,0	160,0
5	***Mg^{2+}, mg/l***	544,5	410,7	498,6	522,9
6	***overall hardness,*** **mg.equivalent/l** ***mg/l***	53,7 724,5	39,7 530,7	48,2 643,6	50,9 682,9
7	***permanganate oxidizability mgO_2/l (MPC- not more than 3 mg/l)***	2,4	2,35	2,28	2,26

Table 22

Location – coastline near port

№	***parameter, dimension***	***initial sample***	***I dialysate I=1,5A, U=7,0V Spending time - 15 min***	***II dialysate I=1,0A, U=5,8V Spending time - 10min***	***III dialysate I=0,5A, U=3,9V Spending time - 5 min***
1	***pH (MPC 6,5-8,5)***	7,11	8,95	8,65	8,2
2	***Cl^-, mg/l***	12250	9773	10234	11660
3	***NaCl, mg/l***	20212	16125	16886	19239
4	***Ca^{2+}, mg/l***	240,8	160,3	180,4	200,4
5	***Mg^{2+}, mg/l***	729,6	607,7	620,0	645,0
6	***overall hardness,*** **mg.equivalent/l** ***mg/l***	72,0 970,4	57,9 768,0	59,9 800,4	63,0 845,4
7	***permanganate oxidizability mgO_2/l***	7,2	7,14	6,95	6,93

	(MPC- not more than 3 mg/l)				
8	***NH_4^+, mg/l (MPC-1,5mg/l)***	2,60	1,33	0,63	–
9	***NO_2^-, mg/l (MPC-3,3 mg/l)***	4,48	3,19	2,67	1,48
10	***SO_4^{2-}, mg/l***	913,0	819,0	805,0	689,0

Table 23

Beach near the Batumi Marine Station (Active recreational and swimming zones)

№	*parameter, dimension*	*initial sample*	*I dialysate I=1,5A, U=6,9V Spending time - 15 min*	*II dialysate I=1,0A, U=5,5V Spending time - 10min*	*III dialysate I=0,5A, U=3,8V Spending time - 5 min*
1	***pH, ზღვ 6,5-8,5***	7,31	8,70	8,55	8,45
2	***Cl^-, მგ/ლ***	11980	9562	10127	11225
3	***NaCl, მგ/ლ***	19767	15777	16709	18521
4	***Ca^{2+}, მგ/ლ***	221,7	147,8	179,0	198,6
5	***Mg^{2+}, მგ/ლ***	644,0	510,7	598,6	622,9
6	***overall hardness,*** **mg.equivalent/l** ***mg/l***	64,0 865,7	49,3 658,5	58,1 777,6	61,1 821,5
7	***permanganate oxidizability mgO_2/l (MPC- not more than 3 mg/l)***	6,1	6,03	5,94	5,90
8	***NH_4^+, mg/l (MPC-1,5mg/l)***	2,11	1,23	0,50	–
9	***NO_2^-, mg/l (MPC-3,3 mg/l)***	3,98	2,50	1,52	0.52
10	***SO_4^{2-}, mg/l***	908,9	802,8	740.3	640,0

Table 24

The total number of coliform bacteria in 100 ml of seawater

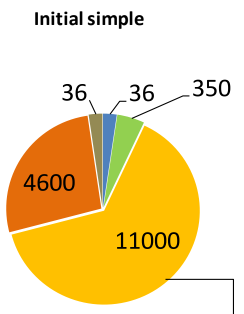
№	**Location**	**initial sample**	**After Filtrationin through Electrodialysis Device**		
			Filtration time-15 min	***Filtration time-10 min***	***Filtration time-5 min***
1	***Pichvnari***	36	___	___	___
2	***Kitrishi estuary to the sea***	350	___	___	___

3	***coastline near port***	>11000	—	—	—
4	***Beach near the Batumi Marine Station***	4600	—	—	—
5	***Kvariati***	36	—	—	—
MPC		**< 1000/100 ml for economic-household purposes** **<500 /100 ml–in swimming areas** **<1000 /100 ml–water sports and settlements**			

We applied microfiltration and ultrafiltration methods to study the seawater filtration process to reveal the method for removal of pollution agents (chemical and bacteriological). Five locations were selected: Kvariati, Pichvnari, the Kintrishi river estuary, coastline near port and beach near the Batumi Marine station. An average size of microfilter pore was 0,02µm (200Å-ს). Seawater primary filtration was carried on microfiltration device to ensure removal of suspended and colloidal particles and filtered through ultrafiltration laboratory device afterwards. Upon completion of those two actions, we made a chemical and bacteriological analysis of filtrate. The results are presented in Tables 25-29. Analysis revealed that total coliform bacteria count in the initial samples exceeded the MPC (>11,000) in the port location. It is 305 times greater than the similar indicators of the water samples from Kvariati and Pichvnari, and it is 31 times greater than the indicator from Kintrishi. On the beach next to the sea station, there were 4600 total coliform bacteria, which was 127 times greater than what Kvariati and Pichvnari indicators and 13 times more than inKintrishi.Elsewhere the parameters mentioned were between 36-350. It was observed that no coliforms were detected in the filtrate of water samples taken at any time after passing through the microfiltration and ultrafiltration devices (Diaram 3, Pictures 18,19). Regarding the chemical analysis of water samples, all samples have reduced amounts of Cl^- ions and NaCl because of micro and ultrafiltration.

Ca^{2+} and Mg^{2+} concentrations are responsible for the decrease in hardness. As a result of the filtration, the oxidation of water influenced by the presence of organic compounds in it was insignificantly fluctuated. The seawater pH changed from 7,11 to 8,95 as a result of the decrease in SO_4^{2-} ion concentration in the port and on the beach near the Marine station (active recreation and swimming zones). At the mentioned areas,

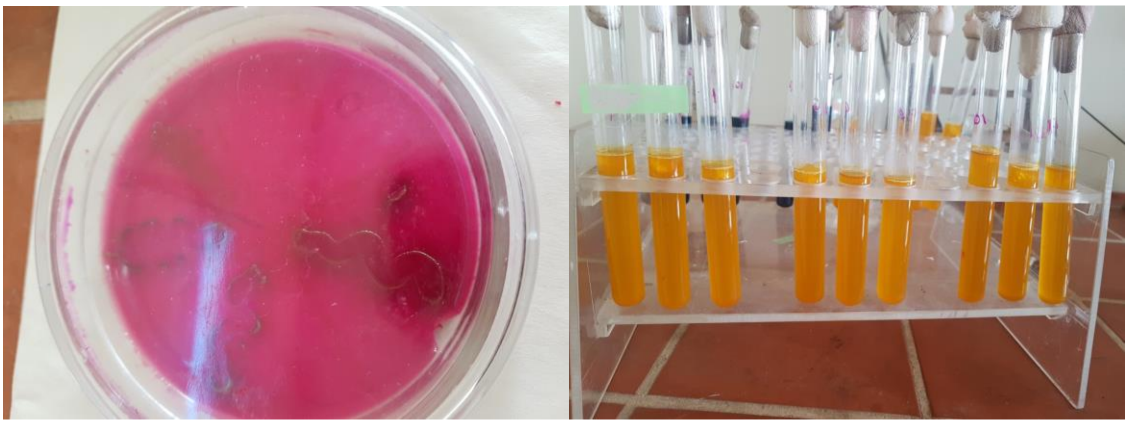
NH_4^+ions were removed more effectively compared to NO_2- ions. The level of both ions at the beach locations close to the port and the sea station was within MPC limits as a result of micro- and ultrafiltration.



Simple	Electrodialysis device 15 minutes; 10 minutes; 5 minutes;	Ultrafiltration device
Pichvnari	0	0
Kintrishi	0	0
Port	0	0
Beach near the port	0	0
Kvariati	0	0

MPC: < 1000/100ml - for household purposes
<500 /100 ml - in bathing areas
<1000 /100 ml - in populated areas

Diaram 3. Number of total coliform bacteria in 100 ml of seawater before purification and after application of purification methods



Picture 18. Determination of total coliform bacteria by applying cultivation method

Picture 19. Membrane and sorption equipment

Table 25

The Chemical and Bacteriological Analysis of Seawater After Passing through Micro- and Ultrafiltration Devices Location - coastline near port

№	*parameter, dimension*	*initial sample*	After micro- and ultrafiltration	*MPC*
1	***pH***	7,11	8,3	**6,5-8,5**
2	***Cl^-, mg/l***	12250	9163	_
3	***NaCl, მგ/ლ***	20212	15118	_
4	***overall hardness, mg.equivalent/l mg/l***	72,0 970,4	59,7 797,8	_
5	***Ca^{2+}, mg/l***	240,8	180,0	_
6	***Mg^{2+}, mg/l***	729,6	617,8	_
7	***permanganate oxidizability mgO_2/l***	7,2	5,8	*not more than 3 mg/l*
8	***NH_4^+, mg/l***	2,60	0,71	**1,5 mg/l**
9	***NO_2^-, mg/l***	4,48	2,15	**3,3 mg/l**
10	***SO_4^{2-}, mg/l***	913,0	850	_
11	***Total number of coliform bacteria***	>11000	___	**< 1000/100 ml for economic-household purposes <500 /100 ml–in swimming areas <1000 /100 ml–water sports and settlements**

Table 26

Beach near the Batumi Marine Station (Active recreational and swimming zones)

№	*parameter, dimension*	*initial sample*	After micro- and ultrafiltration	*MPC*
1	***pH***	7,31	8,82	**6,5-8,5**
2	***Cl^-, mg/l***	11980	8653	_
3	***NaCl, მგ/ლ***	19767	14277	_
4	***overall hardness, mg.equivalent/l mg/l***	64,0 865,7	50,5 673,6	_
5	***Ca^{2+}, mg/l***	221,7	150,3	_
6	***Mg^{2+}, mg/l***	644,0	523,3	_
7	***permanganate oxidizability mgO_2/l***	6,1	4,86	*not more than 3 mg/l*
8	***NH_4^+, mg/l***	2,11	0,42	**1,5 mg/l**

9	***NO_2^-, mg/l***	3,98	0,52	**3,3 mg/l**
10	***SO_4^{2-}, mg/l***	908,9	700,7	**_**
11	***Total number of coliform bacteria***	4600	___	**< 1000/100 ml for economic-household purposes <500 /100 ml–in swimming areas <1000 /100 ml–water sports and settlements**

Table 27

Location – Pichvnari coast (Kobuleti)

№	*parameter, dimension*	*initial sample*	**After micro- and ultrafiltration**	*MPC*
1	***pH***	8,15	8,55	**6,5-8,5**
2	***Cl^-, mg/l***	11428	10612	**_**
3	***NaCl, მგ/ლ***	18857	17510	**_**
4	***overall hardness, mg.equivalent/l mg/l***	67,3 892,2	63,8 839,3	**_**
5	***Ca^{2+}, mg/l***	186,9	160,8	**_**
6	***Mg^{2+}, mg/l***	705,3	678,5	**_**
7	***permanganate oxidizability mgO_2/l***	2,9	2,64	*not more than 3 mg/l*
8	***Total number of coliform bacteria***	36	___	**< 1000/100 ml for economic-household purposes <500 /100 ml–in swimming areas <1000 /100 ml–water sports and settlements**

Table 28

Location – Kitrishi estuary to the sea

№	*parameter, dimension*	*initial sample*	After micro- and ultrafiltration	*MPC*
1	*pH*	7,9	8,1	**6,5-8,5**
2	*Cl^-, mg/l*	10816	9184	_
3	*NaCl, მგ/ლ*	17846	15154	_
4	*overall hardness,* **mg.equivalent/l** *mg/l*	43,9 589,4	40,2 539,1	_
5	*Ca^{2+}, mg/l*	140,6	125,4	_
6	*Mg^{2+}, mg/l*	448,8	413,7	_
7	*permanganate oxidizability mgO_2/l*	3,5	2,78	*not more than 3 mg/l*
11	*Total number of coliform bacteria*	350	___	**< 1000/100 ml for economic-household purposes <500 /100 ml–in swimming areas <1000 /100 ml–water sports and settlements**

Table 29

Location – Kvariati beach

№	*parameter, dimension*	*initial sample*	After micro- and ultrafiltration	*MPC*
1	*pH*	8,15	8,85	**6,5-8,5**
2	*Cl^-, mg/l*	11224	9998	_
3	*NaCl, მგ/ლ*	18519	16496	_
4	*overall hardness,* **mg.equivalent/l** *mg/l*	53,7 724,5	40,6 542,8	_
5	*Ca^{2+}, mg/l*	180,0	124,8	_
6	*Mg^{2+}, mg/l*	544,5	418,0	_
7	*permanganate oxidizability mgO_2/l*	2,4	1,98	*not more than 3 mg/l*
11	*Total number of coliform bacteria*	36	___	**< 1000/100 ml for economic-household purposes <500 /100 ml–in swimming areas <1000 /100 ml–water sports and settlements**

The initial seawater samples taken in the port had a high concentration of soluble oil products amounted to 23 mg/l. This might be because oil leaked into the water as ships were being loaded with oil.

The concentration of soluble oil products decreased by 2,5 times after filtration in sawdust, and by 12,7 times - after filtration in polyurethane foam (Table 30, Pictures 20, 21). We applied hybrid approach, which considered processing of seawater in sawdust first and then in foam. This revealed a slight decrease of soluble oil products in the filtrate compared to the processing on foam. We believe that this is caused by the transfer of low molecular weight oil products to the filtrate. The data acquired showed that, in this instance, spending merely on foam was sufficient for the filtration of the initial sample.

Table 30

Determination of Mass Concentration of Oil Products in Seawater by Applying Gravimetric Method

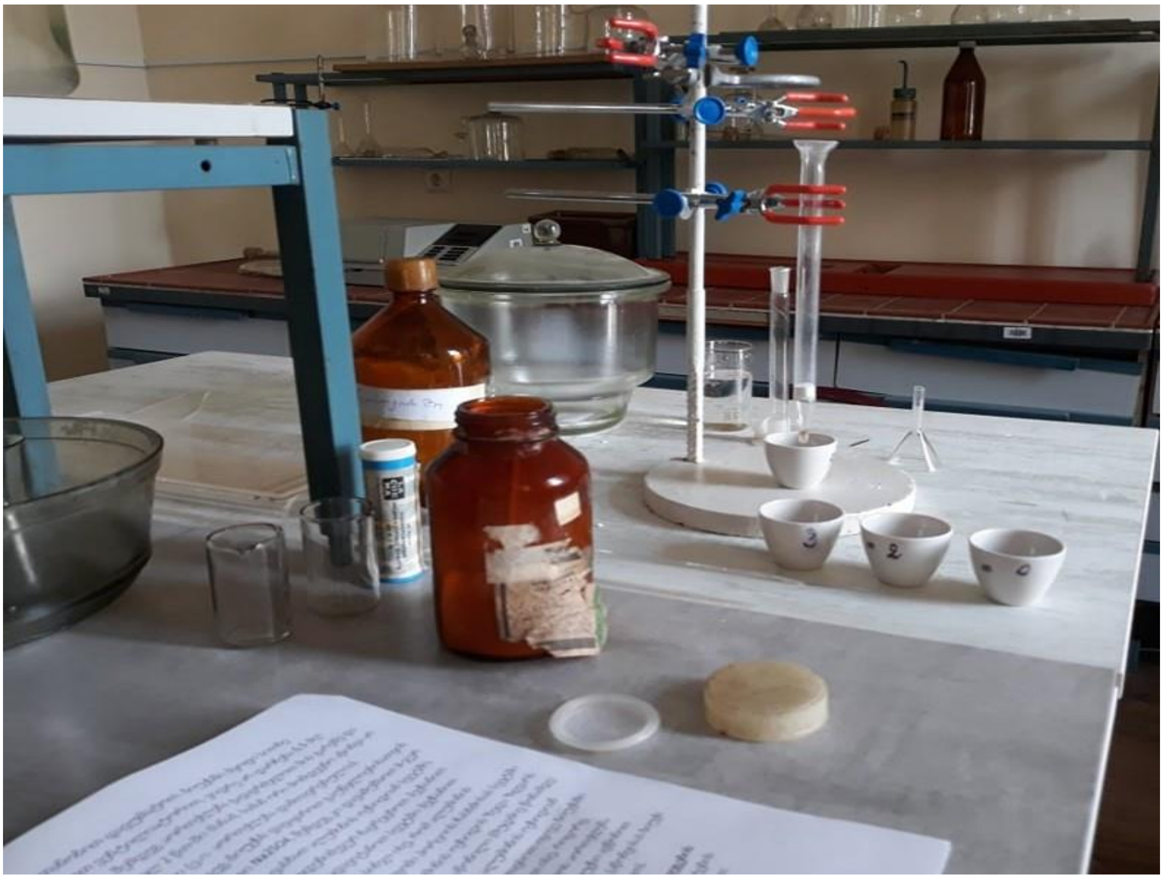
Variant	**Analysis result, mg/l**	
	Coast near port	**Coast near the marine station**
Initial sample	23	7,6
Filtration in sawdust	9,2	7,2
Filtration in polyurethane foam	1,8	1,5
Filtration in sawdust and polyurethane foam	1,6	1,3
Filtration in sawdust, polyurethane foam and microfiltration devices	Not found	Not found
MPC, mg/l	**0,1-0,3**	

We did not achieve the same results with sawdust on the coast near to the Batumi marine station, where the concentration of soluble oil products in the initial sample is almost three times lower than in the port. And we nearly achieved the same outcomes that we did at the port location through filtering in polyurethane foam. We think that this is because the oil that was spilled in the port contains a nearly complete range of oil products (both high and low molecular), which means that sawdust and polyurethane foamcaught high molecular compounds as much as possible, resulting in a decrease in their concentration in the filtrates.

Picture 20. Seawater purification in different sorbents (polyurethane foam - on the left, sawdust - on the right)

The high-molecular oil products in the seawater may have already been separated from the oil slick on the surface and moved to the depths at the beach near the Batumi marine station, whereas the majority of the low-molecular oil products remained on the surface and underwent less sorption on sawdust. The result of filtration on polyurethane foam was almost the same as at the port location. In this instance, the hybrid approach performed worse than polyurethane foam. Consequently, polyurethane foam is more effective than sawdust at capturing oil products.

We do, however, make it clear that in order toclean seawater of oil products, it is preferable to use a combined method rather than using sawdust or polyurethane foam separately. This is because sawdust can be used as a fuel after being used to run on and sorb high molecular mass oil products, and polyurethane foam can be recycled and used once more for sorption.Nevertheless, it should be emphasized, that while the content of oil compounds can be decreased using the aforementioned methods, they cannot be entirely eliminated from the water. Oil products are completely (finally) removed from the seawater by filtration in a microfiltration equipment.



Picture 21. Preparation of sorbent columns and extract filtration process in Al_2O_3 sorbent column, for polar compound sorption: Column length– 20 cm, Al_2O_3 – 4-6cm, n-hexane - 6-10 ml

According to experimental data, baro-membrane methods totally eliminate microorganisms from saltwater. However, depending on the technology, a significant amount of bacteria are concentrated in at least 5% of the concentrate, making its use problematic. Microorganisms are swiftly and totally eliminated during the electrodialysis process (5 minutes),we receive seawater with dead microorganisms in the dialysate; therefore, there is no concentration and no issue with its consumption.We favour electrodialysis for seawater purification in light of the foregoing.

It is preferable to apply combined method (filtered in sawdust and polyurethane foam) rather than sawdust or polyurethane foamseparately to remove oil products from seawater,because sawdust can be used as a fuel after being used to run on and sorb high molecular mass oil products, and polyurethane foam can be recycled and used once more for sorption.The aforementioned methods can only lower the concentration of oilproducts; however, as complete removal of oil products from water is not feasible, microfiltration methods must be used. Nevertheless, the microfiltration method to purify the seawater is not cost-effective due to the enormous volume of seawater. The membranes will need to be totally regenerated in this case, which is not cost-effective. Sorption and membrane technologies are therefore preferable to utilize directly at the sources of pollution before discharging the cleaned water into the ocean.

CONCLUSIONS

1. Georgia's Black Sea coast is distinguished by a developed infrastructure. The coastline of a country is considered to be of the utmost strategic importance because it is the most abundant source of recreational resources (national parks, protected areas, buffer zones of nature reserves), a location for almost all elements found in nature, oil and natural gas natural reserves, as well as ports and terminals.
2. Based on study carried in the Black Sea coastline in Adjara (Kvariati-Pichvnari), it was determined that the organoleptic indicators in the estuary close to the port, the Kintrishi, and the Korolistskali rivers to the sea did not fall within the range of permittable levels. Spring saw the highest water temperatures (16–21°C), the lowest temperature was detected in winter (10–16°C). Seawater pH ranged from 7,28 to 8,20, with the exception of the coast near to the Batumi port, where the pH in the autumn was outside of the MPC permitted range.
3. In all seasons, the concentration of chlorides was lowest near the ports and highest at the sea-river estuary. Salinity was lowest in spring and highest in autumn, according to the season. From autumn to spring, the concentration of Ca^{2+} and Mg^{2+} declined in parallel with the seasonal rise in precipitation.
4. The concentration of dissolved oxygen was at its highest in winter (5,46-10,08 mg/l) and at its lowest in spring (3,95-9,70 mg/l). In Kvariati and Gonio, the water was rich with oxygen in all three seasons (9,10–10,08 mg/l). Oxygen concentration was below MPC in the port. BOD5 was reduced in autumn-winter, and increased in spring, which was associated with the slowdown of microbial activity throughout the cold season. High oxidizability level in the port waters throughout all seasons (4,0-6,05 mg/l), in an indication of pollution. This indicator was the best in Kvariati-Gonio coast (0,98-1,8 mg/l).
5. Dominant elements in seawater: Na; Mg; Ca; K. Concentrations of Al, As, B, Ba - are within MPC limits. Be, Sb, Ti, Tl, V, Li, Se, Mn,

Mo, Fe - were under the limit. Lead concentration was above MPC - in the Kintrishi river estuary -0,0695 mg/l. Phosphorus and Zinc concentration were above MPC - in all locations, except for, Kvariati, Gonio and Pichvnari coasts, while Copper concentration exceeded limit - in port and the Kintrishi river estuary.

6. Total count of coliform bacteria was above MPC in the port (>11000) and the beach near to the Batumi marine station (4600). Micro- and ultrafiltration removed coliform bacteria from the water samples of all locations, it also depicted more effective removal of NH4+ ions, rather than NO2- ions.

RECOMMENDATIONS

We favour electrodialysis for seawater purification (microorganisms' removal), and a combination method for removing soluble oil compounds from seawater (filtration in sawdust and polyurethane foam). Sawdust can be used as fuel, whilepolyurethane foam can be regenerated. As long as it is justified by its cost-effectiveness and the necessary quality of seawater, electrodialysis devices may be used to purify seawater in the minimal time (5 minutes) mode.

After being processed by a microfiltration system, seawater can be completely cleaned of soluble oil compounds. Nevertheless, because there is so much seawater, applying microfiltration for cleaning purposes is not cost-effective. In this case, the membranes will need to be entirely regenerated. Consequently, it is preferable to employ sorption and membrane technologies where the water is directly contaminated and then release the cleansed water into the ocean.

Solving of social-economic and ecological issues of the Black Sea, requires multilateral cooperation to address rational use of its resources.

Chapter II. Chemical and Microbiological Research on Certain Fish Species Inhabiting the Coastal Waters of the Adjara Black Sea Basin

PREFACE

Organoleptic indicators in the Adjara coastline have been evaluated with showcasing its multielement composition; organoleptic, microbiological, and toxic elements (heavy metals) were analysedherring (Clupea harengus) and the Black Sea Jack mackerels (Trachurus mediterraneus) in the research locations. The research materials were collected in an active fishing area in the coastal waters close to the Black Sea and Chorokhi's estuary. According to studies, the smell intensity is stronger on Gonio Beach, where the water is also slightly turbid with an unusual greenish-yellow colour, and floating particles in 0–20 cm deep from the surface. The smell intensity gradually decreases in the water samples taken at 400-500 m deep, the water is transparent without any floating particles. A temperature at the depth decreases to 4°C. pH in seawater is within limits of MPC is within limits (pH 6,5-8,5). Correlation of macroelements in the coastline: Na : Mg : K : Ca = 1 :4 : 9 : 14; at the depth of the sea: Na : Mg : K: Ca =1 : 5 : 11 : 14. A range of decrease in micro elements are presented as follows: B > Fe > Cu > Pb > Zn,Mn > As > Ba,Ni.

Concentration of phosphorus in the coastline is above permittable limit (MPC –0,028mg/l). Concentrations of Cu, Fe, Pbis above MPC in the water samples. The organoleptic characteristics of both fish species (Clupea harengus and Trachurus mediterraneus) are satisfactory. Trachurus mediterraneus has a higher concentration of Zn, As, Cu, and Pb in its muscle tissue compared to Clupea harengus, but a lower concentration of Cd, the metals concentration are also below MPC. Although the presence of Mesophilic aerobic facultative anaerobic microorganisms is slightly higher in Trachurus mediterraneus ($1,5 \cdot 10^2$) than in Clupea harengus ($1,7 \cdot 10^2$), it is still within the allowable limits. None of the pathogenic organisms such as Coliforms, Salmonella, or Staphylococcus Aureus were found in the tissue of either fish species mentioned above.

INTRODUCTION

Water pollution is a crucial ecological issue that has been linked to numerous diseases and rising mortality rates worldwide. Anthropogenic pollution, resulting from the discharge of coastal wastewater and river runoff from the entire watershed, primarily affects coastal water ecosystems. The impact of pollution on coastal waters not only has devastating consequences on water ecosystems but also poses a significant threat to the health of individuals residing in the coastal zone, who rely on sea products for their food, and adversely affects tourism and recreational activities in these areas.

The presence of toxic substances in fish can result in pathological changes in their organs and tissues. Certain xenobiotics exhibit carcinogenic activity. Toxic elements are listed among these substances and are particularly hazardous as they are stable in the water environment and can accumulate in bottom sediments and hydrobionts, such as the organs and tissues of fish. Even in small concentrations, these toxicants can pose a danger to aquatic organisms, causing a range of developmental disorders and impacting animal activity processes. Moreover, the long-lasting activity of these toxicants makes them especially concerning.

Water environments with high levels of pathogenic microorganisms may threat health of humans, who consumer fish, molluscsand seaweeds. These microorganisms, which are prevalent in aquatic ecosystems, can penetrate the gastrointestinal tracts of fish and utilize it as an ecological habitat. Furthermore, the intestinal microflora plays a crucial role in the growth and development of fish. However, the indigenous microorganisms in the fish's intestines pose a risk factor, especially for those with a weakened immune physiological status, as these microorganisms can potentially cause endogenous infections. The ability of bacteria to multiply intensively in the intestines of a weakened individual often leads to bacterial translocation, with the development of systemic bacteraemia.

Assessing the current state of toxic-microbiological indicators in the coastal waters of the Adjara Sea Basin and the fish species inhabiting is crucial in determining the significance of the issue discussed in the study. This examination is necessary to take timely preventive measures.

The research aimed to evaluate the water quality of the Adjara coastline in the Black Sea Basin and analyze the concentration of toxic elements and microbiological indicators in selected fish species living in the area.

The research objectives included assessing the organoleptic indicators and heavy metal levels (including toxic elements) in the waters of the Adjara coastline of the Black Sea Basin;determining the organoleptic, microbiological, and helminthological parameters, as well as the concentration of toxic elements in the tissues of the research subjectsherring (Clupea harengus) and Black Sea mackerel (Trachurus mediterraneus).

The research materials were taken in Adjara the Chorokhi river estuary to the Black Sea, in an active fishing zone. The research focused on analyzing the quality of the Black Sea water and two fish species that inhabit it: herring (Clupea harengus) and Black Sea mackerel (Trachurus mediterraneus).

Laboratory research on the water and fish samples was conducted in the LEPL Laboratory Research Center of the Ministry of Agriculture of Adjara and the Institute of Agrarian and Membrane Technologies of Batumi Shota Rustaveli State University.

II.1. The Geographical and Hydrological Characteristics of the Black Sea

The Black Sea is the most isolated European inland sea from the world ocean and is the largest meromictic water basin where water is permanently stratified.The upper layer receives oxygen from the atmosphere, and the water below 130-150 m is rich in hydrogen sulfide, resulting in 87-90% of the water being deficient in oxygen. The Black Sea catchment basin is five times larger than the area of the sea itself, which means that the rivers contribute the most sediment to the Black Sea.

The catchment basin has a surface area of approximately 435000 km^2, a water mass of 546000 km^3, an average depth of 1235 m, and a maximum depth of 2218 m. Ukraine has the longest coastline of 1628 km, followed by Turkey with 1400 km. Georgia has the shortest coastline of 113 km (Picture 22).

The seabed of the Black Sea comprises different geomorphological structures, namely the shelf, continental shelf, and deep sea basin. The shelf starts from modern coastline and ends at an average depth of 90-

110m, covering 24% of the Black Sea's bottom. Large and small underwater embankments are the typical landforms of the shelf.

The continental shelf, which makes up 40% of the bottom area, is characterized by numerous canyon-like valleys in parts of the Caucasus and Asia Minor. The deep sea basin covers 36% of the sea water area, and it is flat with a slight slope. The coastline of the Black Sea has relatively weak indentation.

The Black Sea is a typical inland sea and lists among the most isolated seas on Earth, without any direct connection with the ocean, making the inflow and outflow of water crucial processes. The sea's primary source of fresh water is from rivers. Amount of water inflow is also influenced by annual precipitation.

The rate of water loss through evaporation is season-dependent and is also affected by wind speed. One of the features of the Black Sea is its water layers, with the upper layer, around 100-140 m thick, being less saline and lighter compared to the water mass below it.

Picture 22. Geographical location of the Black Sea

The Black Sea is characterized by both surface and deep currents, which are particularly strong in the Kerch Strait and the Bosphorus. In these regions, the current system is formed by two opposing currents: less saline surface water flowing from the Black Sea to the Sea of Marmara, and relatively saltier water entering from the Mediterranean Sea. The volume of surface waters is twice more than the deep waters that flow out to the Sea of Marmara annually. Apart from surface and deep currents, the water in the Black Sea circulates both horizontally and vertically. There are two opposite circular currents in the Black Sea that move in opposite directions, allowing for balance distribution of heat, oxygen, minerals, and nutrients in the water, thereby making the Black Sea an attractive habitat for living organisms. Vertical circulation in the Black Sea is relatively weak, with deep and surface waters taking centuries to circulate.

The disruptions caused by daily weak and strong circulations in the Black Sea are usually only a few centimeters, while the more significant disruptions with wave heights reaching 4-6 meters are typically observed in winter (Picture 23).

Picture 23. The disruptions caused by daily weak and strong circulations in the Black Sea

The salinity of the Black Sea is twice that of the Mediterranean Sea due to the inflow of water from rivers.While the Sea of Azov is less salty. The surface water of the Marmara Sea, on the other hand, is saltier than that of the Black Sea. During winter, the surface water temperature of the Black Sea ranges from 1-2°C, while during summer it can reach 30°C. The average annual temperature of the Black Sea basin is around +13°C in the northwest and +16°C in the southeast. However, at 50-140 meters deep, the temperature drops significantly. The temperature at a depth of 500 meters remains constant at 2°C.

The Black Sea water is differentiated into layers: the top layer, which is abundant in oxygen; the bottom layer, which is oxygen-free and contains a high concentration of hydrogen sulfide (H_2S). The amount of hydrogen sulfide can reach up to 13-14 ml/l, depending on the depth, which makes 90% of the Black Sea lifeless. Due to increased anthropogenic load, there has been a noticeable trend of hydrogen sulfide increase in the Black Sea in recent decades. Although anaerobic bacteria are believed to be the only inhabitants of this layer, some roundworms have been found to breathe oxygen from the seafloor sludge. As a result, only 10-13% of the Black Sea can support life. Despite this limitation, the Black Sea has remarkable biodiversity due to its unique natural conditions. The sea is rich in organic matter and is home to 150 relict and 240 endemic species.

The Black Sea has relatively poor biodiversity caused by various reasons, including, low salinity, colder water, less oxygen, and higher hydrogen sulphide (H_2S) concentration. This makes it unsuitable for heat-loving and deep-water species. Nonetheless, the Black Sea is biologically diverse, it is a home for 3774 species of invertebrate and seaweeds. These species come from various sources, such as the remnants of the Pontic Sea, northern species, Mediterranean Sea species, which comprise 80% of the Black Sea's species; freshwater species, and alien species that have settled in the Black Sea from distant ecosystems. Unfortunately, the Black Sea's biodiversity is in danger from human activities and river pollution. Overfishing and pollution have significantly reduced the local populations of hydrobionts. Furthermore, the white-bellied seal has become extinct in the Black Sea due to the invasion of non-native organisms, and the Black Sea dolphins have suffered greatly due to commercial fishing.

The Black Sea has no life below 100-150 meters deep with anaerobic bacteria being the only organisms found there. The surface layer of the water is home to around 350 species of phytoplankton, including 150 species of diatoms, 150 species of peridines, and 280 species of macrophytes, which produce a significant amount of biomass. Phytobenthic organisms, on the other hand, are small and found on the seabed, sand or rocks. The Black Sea is known for its diverse animal life, particularly along the coast of Georgia. The sea is home to approximately 2000 species of animals, including 12 endemic species. Including: 300 - simple organisms, 650 - different worms, 640 - crustaceans, over 200 - mollusks, 186 - fish species, and 150 - other species, from mammals - 4 species of seals and 3 species of dolphins. There are high number of Dolphins in the sea. The most of the fish species in the Black Sea are commercial, including: hops (Huso huso), Russian sturgeon (Acipenser gueldenstaedtii), horse mackerel (Acipenser stellatus), herring (clupea harengus), the European anchovy (Engraulis encrasicholus), European sprat (lat. Sprattus sprattus), the European carp (Cyprinus carpio), Bream (Abramis brama), Taran (Rutilus rutilusheckeli), Mullet, Black Sea mackerel (Trachurus mediterraneus), the Atlantic Mackerel (Scomber scombrus), Black Sea flounder (Psetta maeotica), the Atlantic bonito (Sarda sarda), Tuna (Thunnus thynnus), and others. The Black Sea's ecosystem has been severely threatened by human activities and river pollution, leading to a significant reduction in hydrobiont populations, the extinction of the white-bellied seal, and a decline in the Black Sea dolphin population due to commercial fishing.

The Black Sea's animal kingdom displays a wide variety of forms. It is characterized by coexisting of Mediterranean, freshwater, and relic forms. Mediterranean species dominate the fauna, with 112 of the 180 fish species originating from the Mediterranean, and 31 from freshwater sources. Recently, the Black Sea has welcomed two newcomers, a crab and a native gastropod mollusk, Rapana (Rapana bezoar). Some fish are permanent residents of the Black Sea, while others arrive from the straits. Additionally, numerous Black Sea fish migrate to the Sea of Azov, including the European anchovy, herring, sprats, and mullet. Fish migration also occurs within the sea itself.

The Black Sea's ecosystems are threatened by eutrophication, chemical pollution, overfishing, and invasive species. The primary cause of eutrophication in Georgia's coastal waters, as well as throughout the Black Sea, is the discharge of various types of pollution from rivers and household waste. According to official records, the principal source of pollution from ships in Georgia's territorial waters was agricultural and fecal waste added by unregulated household discharges from the shores. Eutrophication of the Black Sea creates a threat to the upper layer of waterrich in oxygen. Organic pollutants in the water trigger the proliferation of phytoplankton, which, upon dying, consume a substantial amount of oxygen during organic matter oxidation. This process leads to hypoxia in the Black Sea's shelf waters.

The eutrophication of the Black Sea is caused by the interaction of two processes: natural and anthropogenic. Human activity leads to seawater pollution, which promotes the growth of bacteria that produce hydrogen sulfide and methane, resulting in the expansion of oxygen-deprived and hydrogen sulfide-rich dead zones in the Black Sea. The resulting lack of oxygen causes the death of living organisms, further increasing organic pollution and contributing to the formation of more hydrogen sulfide. Overfishing also plays a role in the eutrophication of the

Black Sea, as some industrial species rely on phytoplankton as their food source. A reduction in their numbers is one of the reasons behind the proliferation of phytoplankton.

The long-term monitoring of Georgia's coastal waters revealed the presence of mercury, iron, copper, arsenic, and up to 25 types of pesticides, indicating pollution in the territorial waters. Furthermore, cobalt, lead, nickel, copper, zinc, and bismuth were detected in fish tissues. Since heavy metals have the tendency to settle, it is likely that their concentration is greater on the sea bed.

Oil spills (so called “minor oil spills”) from oil terminals are potential sources of pollution that can cause irreversible damage to biodiversity. The presence of substances (such as polycyclic-aromatic hydrocarbon and benzopyrene) in the water and fish indicate oil pollution in seawater. The highest concentration of carcinogenic benzopyrene was found in benthic flounder (Platichthys flesus), red mullet (Mullus barbatus), Picarel (Spicara smaris), the Black Sea anchovy (Engraulis Encrasicholus), and mackerel (Trachurus mediterraneus ponticus). Mussels had high concentration of benzopyrene. Mussels are an important species for monitoring water conditions due to their ability to filter water and accumulate toxins. However, oil pollution not only increases the accumulation of toxins in the body of mussels, but also degrades the water filtration process. In case of oil pollution, the rate of water filtration by bivalve mollusks is greatly reduced reflected in worsened water quality.

As for the overfishing, under the greatest pressure of fishing, together with theEuropean anchovy (Engraulis encrasicolus), the European sprat (Sprattus sprattus), the merling (Merlangius merlangus), the mackerel (Trachurus mediterraneus ponticus) (Picture 3), the red mullet (Mullus barbatus), Flathead grey mullet (Mugil spp.), spiny dogfish (Squalus acanthias), European flounder (Flatichthys flesus), Pontic shad (Alosa immaculata) and others (Picture 24, 25, 26). In addition to fish, industrial fishing is also allowed for molluskwhelk. It is likely that overfishing is one of the main reasons for the decline of theEuropean anchovy near the coast of Georgia. Overexploitation of fishing grounds and the expansion of fishing throughout the sea, among other threats, have caused significant damage to many species of fish. First of all, this affected the predatory species (for example, Atlantic bonito, mackerel, bluefish, garfish). Then the press intensified on species that feed on plankton - the European sprat (Sprattus sprattus) and theEuropean anchovy (Engraulis encrasicolus).

The decline in the number of commercially valuable fish species in the Black Sea, from 20 to 5 species, is largely due to the use of bottom trawls and the reduction of mesh sizes. Bottom trawling, in particular, is highly destructive to benthic creatures and alters their habitats and community structure. Various studies have demonstrated that this practice leads to a significant reduction in the biomass of animals in benthic communities. Moreover, the long-term use of bottom trawling affects water turbidity and bottom structure. The particles coming up from the bottom can spread over several kilometers, resulting in a sharp reduction in water transparency and the seabed has ploughs for a prolonged time. Therefore, protecting fish species is crucial not only for preserving biodiversity but also for the sustainable development of fisheries.

Picture 24. Mackerel (Trachurus mediterraneus)

Picture 25. Pontic shad (Alosa immaculata)

Picture 26. Anchovy (Engraulis encrasicolus)

In the 19th century, the introduction of non-native species into the Black Sea began, whether by accident or intention, and this has had a significant impact on the Black Sea ecosystem in the XX-XXI centuries. The degradation of this semi-enclosed water body's ecosystem is a result of various factors (eutrophication, chemical pollution, overfishing, invasive species, and climate change). Out of 26 invasive species residing in the Black Sea, six have had a significant impact on its ecosystems. These include the sea walnut (Mnemiopsis leidyi), Harris mud crab

(Rhithopanopeus harrisi), Thomas's whelk (Rapana thomasiana), mollusks (Mya arenaria and Cunearca cornea), and the redlip mullet (Mugil soiuy) (Pictures 27, 28, 29).

The sea walnut (Mnemiopsis leidyi) is one of the most harmful invasive species, as a negative correlation exists between the density of winter spawning fish and the density of the sea walnut. The Thomas's whelk (Rapana thomasiana) is the second invasive species that has had a significant impact on Black Sea ecosystems, greatly reducing the number of bivalve populations. As mussels and other bivalves are water filters, the reduction of their number leads to worsening in water quality, affecting benthic fish, including rare species such as sturgeons, which feed on them. Consequently, the decline of this important food resource leads to a decrease in fish populations

Picture 27. The sea walnut (Mnemiopsis leidyi)

Picture 28. Thomas whelk (Rapana thomasiana)

Picture 29. The redlip mullet (Mugil soiuy)

II.2. The Research Methodology

We took water samples from 0-50 cm deep in the sea in certain points and got average sample by mixing them. Water sampling was conducted both in the coastal zone and 400-500 m away from the coast (Picture 30). We did three parallel tests during each type of analysis. Then we did arithmetic average of the results, if the permissible variation between the parallel tests did not exceed 0,02%. The water samples were analysed on organoleptic parameters – colour, smell, transparency, floating particles according to the GOST 3351-74. At first, we were defining the smell by sniffing it from 0 to 5 degree. To define colouring we were pouring it in the transparent cylinder or glass and were observing on a daylight. The water transparency was assessed using smooth metal disc.

Picture 30. Seawater sampling process in 400-500 m from the coast

The water temperature is crucial factor influencing its physical-chemical and biological processes. An oxygen saturation level of water and self-cleaning intensity depends on temperature. Usually, the water is warmed up in the basins from top to bottom. The basins where water is contaminated from the runoffs, increase of temperature by more than $+5^0C$ from its natural temperature level is not permitted.We were defining the temperature of the water samples right upon taking.

The pH of the analytical waters was determined and evaluated immediately after delivery to the laboratory as this indicator changes rapidly over time (Table 31). To conduct a multi-elemental analysis of waters, we used the plasma atomic emission spectrometry, a device ICPE-9820, SHIMADZU products.

To determine organoleptic, toxic, and microbiological parameters, fish samples were collected according to the norms defined in state standard GOST 31339-2006. To determine heavy metals (including toxic elements), one kilogram of fresh fish was placed in a polyethylene bag, while 0,5 kg was placed in a sterile bag for further laboratory research. Organoleptic indicators such as appearance, consistency, and smell, were assessed in the fish samples taken for analysis, in accordance with GOST 7631-2008.

To assess appearance, several selected samples were placed in a clean container (prewashing of fish is strictly prohibited). The condition of the fish's mucus, scales, skin epidermis, skin color, gills, eye color, and the degree of body deformation were visually evaluated. Consistency was evaluated by pressing a finger on the soft part of the fish's body, and was classified as "dense", "weakened", or "weak". A dense consistency does not leave a mark after finger pressing, a weakened consistency disappears slowly, and a weak consistency does not disappear. The smell undermines any feeling felt through smelling. The sample was required to be at room temperature (18-20°C) during smell determination. Smell was evaluated by inhaling through the nose, holding the breath, and describing the smell. The smell of fresh fish should be characteristic of the given species (for example,seaweed or freshly cut cucumber), while deteriorated fish has a characteristic smell of tainted (Picture 31).

The atomic-absorption spectrophotometer C-115 was utilized to determine toxic elements - Pb, Cd, Zn, Cu, As in fish tissue (Picture 32). This method is based on mineralization of the sample using either the "dry" or "wet" sieving method, followed by the determination of element concentration in the mineralized solution through atomic-absorption. The "dry" mineralization was conducted following the guidelines of GOST 26929-94. Standard solutions of heavy metals (Pb, Cd, Cu, Zn, As) were also prepared.

Picture 31. Assessment of organoleptic parameters in fish samples

Picture 32. The atomic-absorption spectrophotometer - C-115

To create the analysis solution, we ground 0,5 kg of fish in a homogenizer and weighed 2-5 mg of the sample, which was then sit in 10 mg of alcohol for 2-3 hours. After that it was transferred to a porcelain jar and dried in a thermostat at 105^0C for 3 hours. Next, we transferred the dried mass to an electric furnace and added 1 ml (1:1) of diluted HNO_3, carbonizing it until the smoke stopped. Subsequently, we placed the mixture in a muffle furnace at 250^0C, gradually increasing the temperature by 50^0C every 30 minutes until it reached 450^0C.

This process continued until a gray mass was obtained. After cooling the jar, we wetted the crushed mass with 0,5-1,0 ml of HNO_3 solution, and acid drying continued in the electric furnace, followed by heating again in the muffle furnace at 450^0C until the mass turned completely white. If coal particles were present, this process was repeated several times. Once the mineralization was complete, the dry residue was dissolved in diluted 0.1% HCl (1:1), filled to a certain volume, and an aliquot (required volume) was taken for analysis(Picture 33).

Microbiological analysis was performed on four indicators: mesophilic aerobic and facultative anaerobic microorganisms (m.a.f.an.m); intestinal coliform bacteria (i.c.b. coliforms); Enterococcus and Staphylococcus aureus. The classical methods were employed to carry out sanitary-microbiological and sanitary-parasitological analysis on the object. The results were compared to the maximum permissible concentrations (MPC).

To study mesophilic aerobic and facultative anaerobic microorganisms, we took 15 grams of the test material and added it to 135 cm^3 buffered peptone solution. The solution was homogenized, diluted, inoculation mixed with agar, solidified within a minute and dried in a thermostat at 37°C for 72 hours (incubation).

After incubation, the cups were examined. In the case of coliform bacteria, it was revealed in certain number of products.In the case of fresh fish research, coliforms are not allowed in 0,01 gram. For this, a basic dilution of 1:10 was made, where 15 g of the research product was placed in 135 cm^3 of buffered peptone solution, followed by homogenization and dilution. Then, 1 cm^3 of the solution was transferred into 10 cm^3 MacConkey Broth using a sterile pipette and incubated at 37°C for 24 hours (in a thermostat).

Picture 33. Homogenisation and incineration of the fish samples

To determine the presence of Salmonella - enterococcus, we used the material cultured in lactose peptone soil and incubated at 37^0C for 48 hours. After incubation, areas with growth were transferredsectorally to Decoko soil.

To detect Staphylococcus aureus, saline broth was used as the enrichment medium.

The enrichment soil was then cultured on egg salt agar, where lecithinase-positive staphylococci were observed

II.3. The organoleptic and physical-chemical parameters of seawater

The water samples were analysed on organoleptic parameters according to the GOST 3351-74. We compared water samples taken in two different locations. The results revealed that the smell intensity was nearly at the permissible limit of 2 degrees at the Gonio beach location. In this location the water was slightly turbid even during winter (February), with an uncharacteristic greenish-yellow colour. Floating particles were observed at 0-20 cm deep, which is also not allowed by the standard. As for the second sample, it was taken in 400-500 meter distance from the same location in the sea. The smell was slightly noticeable ranging between 0-1 degree.The water was transparent with no foreign coloration or visible particles on the surface. The transparency of natural water is determined by its colour and turbidity. The presence of coarse particles in the water leads to pollution and a reduction in transparency (Table 31).

Table 31

Organoleptic parameters of seawater

№	*Location*	**Smell, points**	**Transparency**	**chromaticity**	**Floating particles**
1.	Gonio coastline (before Adjaristskali confluence to the sea)	2	slightly turbid	greenish-yellow	Observed from the surface at 0-20 cm deep
2.	Gonio, at 400-500m deep from the coast (active fishing zone)	0-1	Transparent	___	___
Norm		***2 points***	***It should be transparent at 0-30 cm***	***Unacceptable Foreign coloration at 0-10 cm***	***There should be no floating particles that are uncharacterized for seawater in the surface and upper layer***

In February, the water temperature along the Gonio coastline was 10°C, and it decreased by 4°C at a distance of 400-500 meters from the coast. The pH of seawater on the content, nature, and state of the dissolved gases and organic compounds in it. High concentrations of soluble molecular CO_2, oil, and organic compounds increase acidity, while the inflow of fresh water decreases it. The pH of seawater at the Gonio coastline was 7,53, indicating that it was nearly neutral. This was likely due to the winter season during which the sampling occurred, where the sea water was neutralized by the excess of sediments and abundant runoff from the Ajaristskali river. In the deeper parts of the sea, where flowing offreshwater masses from the river was slowed down, pH was increased to 8,03 (a weak alkaline medium). Both samples had a pH concentration that was within the acceptable MPC range for seawater (Table 32).

Table 32

Temperature and pH of seawater

№	Location	Autumn	
		T, °C	pH
1	Gonio coastline (before Adjaristskali confluence to the sea)	10	7,53
2	Gonio, at 400-500m deep from the coast (active fishing zone)	6	8,03
MPC			**6,5-8,5**

The results of the multielement analysis of sea water samples taken from two locations (coastal and deep water) revealed that Na, Mg, K, and Ca are the main salinizing ions in the Black Sea water. Among these macroelements, sodium played the leading role as the limiting ion of sea water salinity, with a concentration of 2580-2810 mg/ per litre of water.

The concentration of sodium in the sea water sample taken in 400-500 meters distance from the coast was 1,09 times higher than the sample taken on the coast. In comparison to Na, the content of Mg was almost 5 times lower, K content was 9 times lower, and Ca content was 14 times lower. The same trend was observed in the deep water, where Na >Mg -10 time; Na > K - 11 times; Na > Ca - 14 times. Therefore, the ratio of macro elements on the coast was Na:Mg:K:Ca = 1:4:9:14, and the ratio of macroelements in the deep sea was Na:Mg:K:Ca = 1:5:11:14.

We obtained comprehensive information on the primary macroelements of the Black Sea water in both the recreational zone (coastline) and the active fishing zone (depth) from the data we collected. In particular, the concentrations of Al and Si, two of the macroelements, were within the permissible limits for sea water (Al<1mg/l, Si<10mg/l). However, the concentration of phosphorus in the water sample taken from the coastal zone exceeded the permissible limit (0,028 mg/l), indicating an organic matter pollution issue in that location. Toxic elements such as Be, Cd, Hg, Li, Se, Ti, Tl, and V, as well as Co, Cr, and Mo - were all below the detection limit. The content of As, B, Ba, Mn, Ni, and Zn (including toxic elements) in the analyzed waters in both locations did not exceed the MPC (Table 33).

Table 33

Multielement analysis by plasma atomic emission spectrometry -ICPE – 9820

Macroelements, mg/l

Location	Al	Ca	Mg	Na	P	K	Si
Gonio coastline (before Adjaristskali confluence to the sea)	0.228	201	604	2810	0.0373	297	3.495
Gonio, at 400-500m deep from the coast (active fishing zone)	0.193	178	519	2580	0.0199	235	3.371
MPC, mg/l	**1,0**	**-**	**-**	**-**	**0,028**	**-**	**10,0**

Microelements, mg/l

Location	As	B	Ba	Cu	Fe	Mn	Ni	Pb	Zn
Gonio coastline (before Adjaristskali confluence to the sea)	0.0048	1.82	0,0011	0.063	1.0985	0.0104	0.001	0.0328	0.0105
Gonio, at 400-500m deep from the coast (active fishing zone)	0.0034	1.52	0.0014	0.0077	0.0784	0.0068	0.0009	0.0214	0.0102
MPC, mg/l	**0,05**	**5,0**	**0,1**	**0,005**	**0,05**	**0,05**	**0,8**	**0,01**	**0,05**

The seawater analysis revealed that the concentrations of Cu, Fe, and Pb - exceeded the MPC. The increase in lead content MPC in both the coastal (0,0328 mg/l) and deep-sea zones (0,0214 mg/l) higher than MPC, is particularly concerning. The concentration of this element in both locations was 0,0228-0,0114 mg/l above the MPC. Therefore, the macro elements concentration decreased in the following order: Na>Mg>K>Ca, while microelements decreased in the following order: B >Fe >Cu >Pb>Zn, Mn > As > Ba, Ni.

II.4. The Results of Organoleptic, Physical-Chemical and Microbiological Analysis of the Research Objects (Mackerel and Herring)

The fish samples, herring (Clupea harengus) and Black Sea mackerel (Trachurusmediterraneus), were analyzed for their organoleptic parameters, including appearance, consistency, and smell, according to GOST 7631-2008. The results of the analysis indicate that the organoleptic properties of the fish are within the acceptable limits. To assess the external appearance, multiple samples of both species were selected and placed in a clean dish for visual observation (Pictures 34, 35).

Picture 34. Herring (Clupea harengus)

Picture 35. Black Sea Mackerel (Trachurus mediterraneus)

The condition of the fish mucus, scales, skin epidermis, skin color, gills, eye color, and body deformation were evaluated. No mechanical injuries, signs of disease, or surface parasitism were observed. The gills were reddish-pink, tightly closing the gill cavity, and their eyes were bulging, some slightly sunken, transparent, and undamaged. The surface coating and scales were shiny, and some slightly palewell-attached to the body. The mucus was transparent and had no distinct smell. No cancerous growths were observed on the body, and the skin was of natural color, elastic, and without spots. The fins also had a natural color and were whole. Consistency was determined by pressing the finger on the soft part of the body, on the back muscle. The representatives of both species had well-defined muscle spasms, and the indentation formed when a finger was pressed on the back muscle quickly disappeared. The samples had a dense consistency. For odor determination, the sample was at room temperature (18-20°C). Both species had a characteristic fresh fish smell.

According to the atomic-absorption method applied to determine heavy metals in fish samples, the results indicate that the muscle tissue of fish found in the coastal waters of Adjara did not contain toxic elements beyond the maximum permissible concentrations (Table 34).

Table 34

Concentration of toxic elements in fish of Adjara coastline

Research object	Cd, mg/kg	Pb, mg/kg	Cu, mg/kg	Zn, mg/kg	As, mg/kg
Herring (Clupea harengus)	0,02	0,02	0,05	4,2	0,04
Black Sea Mackerel (Trachurus mediterraneus)	0.01	0,03	0,07	8,9	0,19
MPC , mg/kg	**0,05**	**0.03**	**2,0**	**10.0**	**1,0**

The range of Zinc content in muscle tissue for Black Sea mackerel and herring is from 4,2 mg/kg to 8,9 mg/kg. Black Sea mackerel has a much higher Zinc content (8,9 mg/kg) compared to herring (4,2 mg/kg). The slight variation in Zinc levels in fish tissue appears to be influenced more by endogenous factors rather than exogenous ones. This is supported by several researchers who suggest that Zinc's high biophilicity makes it an unreliable indicator of natural pollution in body tissue.

Copper is another biophilic element concentration of which remains relatively stable in fish tissue. The concentration of Cu in tissue mackerel is higher (0,07 mg/kg) than in herring (0,05 mg/kg). These levels fall within the MPC limit. Zinc and Copper are crucial microelements that aid animal body functions and can have positive effects on fish when within physiological limits. However, being a transition metal, zinc is part of some oxidative enzymes, and its release of electrons can lead to oxidative stress that negatively affects the exchange of nucleic acids, nucleotides, and nucleosides.

The tissue of Black Sea mackerel contains higher levels of Cd, Pb and As than herring, but both fish types have concentrations within permissible limits. Studies show that fish with a less active lifestyle have lower levels of these elements. Cd, Pb, and As are among the most hazardous toxins for hydrobionts. They accumulate in the body and are engaged in metabolism, making it extremely difficult to eliminate them and leading to water body intoxication and pathological changes in organs and tissues. These toxic elements block the functionality of sulfhydryl (SH) groups in proteins, which in turn inhibit enzymes. As a result, the electrolyte balance, biosynthesis of proteins, hormones, and nucleic acids in fish bodies become disrupted.

Mackerel has a higher Lead content (0,03 mg/kg) than herring (0,02 mg/kg), but within the permissible concentrations. Cadmium in herring (0,02 mg/kg) is higher than in mackerel (0,01 mg/kg), but both are below the limit of permissible concentration. Studies show that cadmium concentration in fish tissue and skeleton is lower than in gills, liver, and kidneys. The rate of As content varies among research samples. Mackerel tissue has a higher Arsenic content (0,19 mg/kg) than herring tissue (0,04 mg/kg), but it does not exceed the permissible concentration limits. Arsenic does not accumulate in large amounts in fish tissue, but it can in hydrobionts of extremely polluted areas. This element likely enters fish tissue from the digestive system, where intestinal microorganisms participate in its initial metabolism. Self-cleansing from Arsenic is rapid, it accumulates in liver, kidneys, and digestive system more than in tissue. Microbiological analysis of hydrobionts samples is also interesting because most bacteria that are part of normal microflora belong to the group of conditional-pathogenic microorganisms, which pose a potential threat to the host. The findings show that no pathogenic microorganisms were detected in fish tissue (Table 35).

Mackerel ($1,5 \cdot 10^2$ CFU/g) has a higher amount of mesophilic aerobic facultative anaerobic microorganisms (MAFAnM) compared to herring ($1.,7 \cdot 10^2$ CFU/g), but within permissible concentration in both cases. The concentration of MAFAnM below permissible concentration in both fish species may be attributed to the cold season (in March) during which the fish samples were collected, when the pollution level of coastal waters is usually low due to a decrease in anthropogenic activities. The microflora of hydrobionts can vary depending on the season, fish biology, and environmental pollution. Most bacteria present in hydrobionts' organs and tissues do not exhibit pathogenic properties and can be considered as indigenous microflora, which is a normal bacterial carrier in fish bodies. However, it is important to note that opportunistic pathogens, typically commensals, can become pathogenic under stressful conditions in the living environment.

Table 35

Concentration of microorganisms in certain fish inhabiting coastal waters of Adjara Black Sea Basin

Research object	MAFAnM *	ICB **	Salmonella	Staphylococus Aureus
Herring (Clupea harengus)	$1{,}7\cdot10^2$ **CFU/g *** **	Not observed	Not observed	Not observed
Black Sea Mackerel (Trachurus mediterraneus)	$1{,}5\cdot10^2$ კწე/გ	Not observed	Not observed	Not observed
MPC	$\mathbf{5{,}0\cdot10^2}$	**impermissible**	**impermissible**	**impermissible**

***MAFAnM**-mesophilic aerobic and facultative anaerobic microorganisms
**** ICB -**intestinal coliform bacteria
***** CFU/g-** colony forming unit/gram

The study results revealed that the concentration of toxic elements - Cu, Zn, Pb, As, except for Cd, in mackerel tissue are higher than in herring tissue, while the microbiological indicators are the opposite. These differences can be attributed to the diet and lifestyle of the two species of fish. The low levels of MAFAnM in both species may be due to the low water temperature, which is not optimal for the growth of pathogenic microflora. The experimental studies confirm the absence of pathogenic organisms such as coliforms, Salmonella, and Staphylococcus Aureus in fish tissue. The research led us to conclusion that the chemical and microbiological pollution can be seen as an indicator of the level of anthropogenic impact on the coastal waters of Adjara Black Sea Basin. Therefore, the parameters studied can serve as indicators of animal activity and the state of their environment. These indicators can be useful in monitoring programs, developing criteria for ecological normalization of marine aquaria, and predicting the consequences of anthropogenic impacts.

CONCLUSIONS

1. The assessment of the organoleptic parameters in the Ajara black Sea coastline revealed that the smell intensity was weak of 2 degrees at the Gonio beach, the water was slightly turbid with an uncharacteristic greenish-yellow colour. Floating particles were observed at 0-20 cm deep. In the water sample taken in 400-500 meters from the same location in the

sea, the smell was slightly noticeable ranging between 0-1 degree, the water was transparent with no floating particles. A temperature drops to 4°C in 400-500 meters from the beach. pH concentration was within the MPC limit.

2. The ratio of macro elements on the coast was Na:Mg:K:Ca = 1:4:9:14, and the ratio of macroelements in the deep sea was Na:Mg:K:Ca = 1:5:11:14. The descending order of microelements concentration is: B > Fe > Cu > Pb > Zn ,Mn > As > Ba, Ni. The phosphorus concentration is above the MPC limit in the samples taken in the coast. As for microelements and strong toxic elements, the concentrations of Cu, Fe, and Pb exceeded the MPC. The increase in lead content MPC in both the coastal (0,0328 mg/l) and deep-sea zones (0,0228-0,0114 mg/l higher than MPC).

3. The organoleptic parameters of the fish are within the acceptable limits in both fish species herring (Clupea harengus) and Black Sea mackerel (Trachurus mediterraneus). Black Sea mackerel has a higher concentration of heavy metals Zn, As, Cu, Pb and low concentration of Cd in its tissue than in herring, but in both cases concentrations are below the MPC.

4. Mackerel ($1,5•10^2$CFU/g) has a higher amount of mesophilic aerobic facultative anaerobic microorganisms (MAFAnM) compared to herring ($1,7•10^2$CFU/g), but within permissible concentration in both cases.

Experimental studies indicate that there are not pathogenic organisms, such as coliforms, Salmonella, Staphylococus Aureus in the fish tissue.

RECOMMENDATIONS

Water pollution is a crucial ecological issue that has been linked to numerous diseases and rising mortality rates worldwide. Anthropogenic pollution, resulting from the discharge of coastal wastewater and river runoff from the entire watershed, primarily affects coastal water ecosystems. The impact of pollution on coastal waters not only has devastating consequences on water ecosystems but also poses a significant threat to the health of individuals residing in the coastal zone, who rely on sea products for their food, and adversely affects tourism and recreational activities in these areas.

The intestinal microflora plays a crucial role in the growth and development of fish. However, the indigenous microorganisms in the fish's intestines pose a risk factor, especially for those with a weakened immune physiological status, as these microorganisms can potentially cause endogenous infections. The ability of bacteria to multiply intensively in the intestines of a weakened individual often leads to bacterial translocation, with the development of systemic bacteraemia.

Water environments with high levels of pathogenic microorganisms may threat health of humans, who consumer fish, mollusksand seaweeds. These microorganisms, which are prevalent in aquatic ecosystems, can penetrate the gastrointestinal tracts of fish and form endogenic infection source. Assessing the current state of toxic-microbiological indicators in the coastal waters of the Adjara Sea Basin and the fish species inhabiting is crucial in determining the significance of the issue discussed in the study. This examination is necessary to take timely preventive measures.

Chapter III. Assessment of Ecological State in Ardagani and Nuri-Geli Lake Waters

PREFACE

A seasonal study was conducted to evaluate the current ecological condition of two relict lakes in Adjara: Nuri-Geli and Ardagani. Various physical, organoleptic, biochemical, chemical, and microbiological parameters had been outlined for the evaluation purposes. The aim of the study was to assess the current state of the lake water ecosystem and its relevance stems from the irreversible negative impact that human activities can have on the environment.

Results of the study show that the waters of Nuri-Geli and Ardagani lakes have been negatively affected by human activities, resulting in a decline in their sanitary-bacteriological state. The analysis also revealed that many of the limiting parameters in the ecological condition of these lakes exceeded their maximum permissible concentrations. This is due to the anthropogenic negative influence (inflow of fecal waters, various household wastes, and other negative human activities).

It is crucial to conduct regular assessments of the ecological status of the research lakes, given their strategic significance. These vital ecosystems require preventive measures to maintain their quality parameters. Furthermore, both lakes serve as recreational areas for activities such as fishing, water sports and other leisure activities, which highlights importance of the issue.

To tackle the ecological issues of Nuri-Gel and Ardagani lakes, we recommend systematic cleaning works and periodic sanitary-bacteriological and hydrochemical monitoring of their waters. Comprehensive measures need to be implemented to ensure the safe use of these water resources.

INTRODUCTION

There are in total 859 lakes in the territory of Georgia covering an area of 170 km^2. They vary in their geographical location, genesis, configuration, and chemical composition. With around 1 billion m^3 of water, the lakes play a crucial role in the country's strategic development (hydropower, irrigation, fishing, fish farming, peat extraction, healing mud, and tourism). However, any significant changes in the water ecosystems can have adverse effects on the quality indicators of living organisms and the ecological state of these water bodies. Lakes are no exception, and are often negatively impacted by anthropogenic factors, causing their ecological cleanliness parameters to deviate from acceptable norms. These factors include annual increased pollution from industrial and household wastewater, feces, and oil, leading to the accumulation of toxic substances and a decline in water quality.

The importance of the issue is validated by the fact that human activities have jeopardized the functioning of the ecosystems of Nuri-Gel and Ardagani lakes in Adjara, which are crucial for the livelihoods of the people who rely on them. Consequently, these lakes are classified as high-risk areas and require regular monitoring of their ecological parameters to identify the appropriate timing and pace for periodic cleaning activities.

Considering the significant role that these lakes play in the national economy of our country, we aimed to conduct a seasonal study of certain qualitative and sanitary-microbiological indicators of the 2 relict lakes in Adjara - Nuri-Geli and Ardagani - in order to assess their current ecological condition. To achieve this objective, we identified the following tasks:

- evaluate the seasonal changes in the ecological condition of these lakes by determining limiting parameters such as: a) organoleptic parameters (colour, smell, transparency, floating particles); b) Physical-chemical parameters (temperature, pH, dissolved oxygen, BOD_5, Chlorides and salinity, SO_4^{2-}, NH_4^+, Ca^{2+} and Mg^{2+}, HCO_3^- ion concentration, total hardness);
- the multielement water analysis by plasma atomic-emission spectrometer (concentration of chemical elements, including heavy metals and toxic elements);
- Determination of total number of coliform bacteria based on the sanitary-bacteriological analysis of the lake waters.

2 locations were identified for experimental research. We were taking three samples during autumn and winter: 1st location - Nuri-Geli Lake (1 average sample); 2nd location -Ardagani Lake (1 average sample); 3rd location – from the most polluted area in Ardagani Lake (1 sample). The laboratories of analytic chemistry and plasma atomic-emission spectrometry at the Batumi Shota Rustaveli State University’s Agrarian and Membrane Technology Institute provided material and technical research base. The literature utilized in this paper is based on the normative acts under the Georgian legislation, in particular: the Georgian Law on water; a technical regalement on preventing pollution of surface waters in Geogia; sanitary rules and norms for preventing pollution of surface waters, the MPC of pollutants in the basins according to the water consumption category and other.

III.1. The Physical-Geographical and Hydrological Description of Nuri-Geli and Ardagani Lakes

The country of Georgia, covering an area of approximately 70000 km^2, has about 850 lakes with a total surface area of 170 km^2. They vary in their geographical location, genesis, configuration, and chemical composition. They were formed due to factors such as glaciation, tectonic movements, nutrient sources, and underlying rock types. The Georgian lakes are characterized by well-developed resort infrastructure, making them a significant center for human health restoration and recreational resources. The recreational resources around these lakes include National Parks, Reserves, and Reserve Buffer Zones, which are distributed across the landscapes surrounding the lakes. Lakes are almost everywhere to be found in Georgia with around 1 billion m^3 of water. This huge water mass makes it strategically significant for the country's development. Most of these lakes are fresh and have a low mineralization which does not usually exceed 0,1-0,2 g/l, with hydrocarbonate, chloride, or sulfate chemical composition types.

Throughout history, human development has had a significant and frequently irreversible effect on the environment, including lakes. An illustration of this can be found in Western Georgia, where there are three relict lakes. Of these, Nuri-Geli and Ardagani are located on the Kakhaberilowland in Adjara, while the third - Paliastomi - is situated on the Kolkhetilowland in the south of Poti. Adjara is not rich in lakes; most of them are grouped and found in both the coastal and mountainous regions.

ArdaganiLake is a natural formation that remains as a remain from a series of small, narrow, and sparse lakes that existed on the coast of Batumi, which ran along a narrow strip in a southwestern direction from the Black Sea coast. Currently, Ardagani Lake is 520 meters in length and 70-80 meters in width. Initially, the lake was only fed by groundwater, but it was later connected to the city's central drainage collector and became a sort of reservoir. The lake was designed to receive excess surface runoff, sedimentation of suspended particles, and infiltration of water into the sea, which made perfect sense, as this did not disturb the ecological conditions in the lake, and purified water flowed into the sea. This system functioned well,and the lake remained ecologically clean until the 1970s. Unfortunately, residents violated sanitary-ecological norms by connecting their own sewage pipes to the central drainage collector, resulting in the sedimentation and accumulation of a large amount of fecal matter mixed with clay and sand in the lake. Currently, the polluted water from Lake Ardagani flows directly into the sea through a narrow channel. Although the lake requires periodic cleaning, it is associated with technical and material difficulties, and even if the lake is completely cleaned of fecal matter, it will soon become polluted again periodically. Therefore, this problem is closely related to the large volume of work and the difficulty of solving it in the city's sewage system as a whole.

Nuri-Geli Lake, which is located in the May 6 Parkin Batumi at 0,2 m from the sea level, is the largest among the relict lakes on the coast of Adjara. Legend says that the name of the lake is attributed to a tragic event: a child named Nuri who drowned in the lake.His mother was coming everyday to the lake and called him –"Nuri, Geli (I am waiting for you)". The lake has a volume of about 0,24 million^3 and is mostly fed by underground water. It is of lagoonal origin. It has a diverse range of hydrobionts, including Bighead carp, common carp and other fish species. The lake is separated from the Black Sea by a narrow strip of land that is approximately 140-150 meters wide.

It used to be connected to the Black Sea by a channel, but this was later filled in with hard rock and currently there is no direct connection to the sea, however during lack of water the seawater leaks through the river rock. The lake is oval in shape, stretching from east to west, and covers a total area of 5 hectares with a straight coastline. The lake's maximum depth measures approximately 5-6 meters.The lake is fed by water runoff from land and atmospheric precipitation, and is surrounded by vegetation such as sedge, reed, willow, alder, elm, ash-tree, rhododendron, azalea, and camellia. The lake's soil is black mud mixed with sand. Although Nuri-Geli Lake is of marine origin, it has softened in later periods due to the lack of precipitation characterised to Batumi. Unfortunately, sewage pipes have been running near the lake for years and their damage has resulted in fecal matter entering the lake, drastically altering its ecosystem. Periodic cleaning works have been carried out on the lake, the most recent of which occurred in 2003. Human activities and the anthropogenic factor have had a devastating effect on the ecosystems of both lakes. Therefore, in order to address the ecological issues faced by these lakes, it is important to apply complex approach with a focus on the rational use of their resources.

III.2. The Ecological issues of Nuri-Geli and Ardagani Lakes

The water pollution considers a high polluting level in water threatening human health. There are two aspects: 1. natural pollution, which considers intensive piling of organic compounds in the water; 2. anthropogenic pollution refers to a damage caused to the natural resources as a result of human activities. The main anthropogenic factors causing damage to natural resources are: industrial and household waste inflow, which introduces disease carrying bacteria into the water; toxic substances from atmosphere, for example: the car emissions that use ethylated petrol, contamination by heavy metals as a consequence of radioactive and nuclear explosions; disposing of fertilizers and harmful chemicals into water; oil and its by-products are currently the primary pollutants of the water. Oil pollution originates from sources such as river runoffs, port areas, oil refineries and terminals.

Lakes are an important part of the ecosystem and make up a significant portion of the hydrosphere. However, human activities using advanced technology have caused irreversible damage to natural water resources, leading to a decrease in the self-cleaning ability of water bodies. In order to address the issue of pollution, it is crucial to implement timely chemical, biological, and technological measures. Both lakes in Batumi (Ardagani and Nuri-Geli) are owned by the municipality (Pictures 36, 37).

In 2018, the responsibility of maintaining these lakes was transferred to "Batumi Water" LTD, indicating that both lakes already had issues at that time. Consequently, a special service was established to monitor the lakes and perform periodic cleanings of Nuri-Geli lake. However, sporadic laboratory studies conducted by "Batumi Water" LTD cannot accurately reflect the real situation of Lake Nuri-Geli or identify the root causes of the issues.

Picture 36. Nuri-Geli Lake

Picture 37. Ardagani Lake

The biological study conducted on Nuri-Geli Lake concluded that the reproduction of cyanobacteria in its waters caused decrease in oxygen levels and devastation of living organisms, leading to the lake's transformation into a swamp (Picture 38). Although certain recommendations were implemented, the most crucial one - regular and extensive monitoring of the lake - was ignored. Following the implementation of recommendations from specialists in 2017, works were carried out to revive Lake Nuri-Geli. Although the problem could not be fully resolved, the lake showed gradual signs of improvement. Currently, the people of Batumi are actively discussing the underlying causes of the lake's issues. One perspective is that the problem began when the lake became disconnected from the Black Sea preventing inflow of seawater into the lake. Another view is that the construction of multi-storey buildings around May 6 Park in Batumi caused the ground to burn. It hindered the entry of water into the lake in the same amount and as the water is not pressed it finds other exits to outflow. Some suggest that fishermen should avoid fishing until comprehensive laboratory studies are conducted, as the lake is primarily fed by groundwater, with additional input from a fountain and aeration systems. These problems are complex and a subject for discussion in various fields such as geology, chemistry, and bacteriology.

Picture 38. Reproduction of cyanobacteria in Nuri-Geli Lake

The second lake in the city has also become a cause for concern. Ardagani Lake, situated in the new boulevard, is a popular attraction among visitors because of its dancing fountain. Batumi Water LTD carries periodic pumping and cleaning operations. The primary pollution of the lake is the significant volume of household waste discharged from the drainage systems of the surrounding restaurants (Picture 39).

Analyzing the main quality parameters of lake waters provides crucial insights into their current ecological state, including temperature, gas, and salinity levels, as well as the intensity of biological, microbiological, and chemical processes within their waters. Regular monitoring of organoleptic, ecological, microbiological, and toxic parameters of lake water is essential to evaluate its quality and maintain the safety of the population in terms of domestic and sanitary needs. Systematic determination of pollutant concentrations in lake waters is necessary to compare them with the maximum permissible concentrations (MPC).

Picture 39. Pollution of Ardagani Lake with discharges

III.3. The Research Methodology

Water samples were collected from Nuri-Geli and ArdaganiLakes during two seasons, autumn and winter. Multiple points were selected for sampling, and the average sample was obtained by mixing them. Additionally, an extra sample was collected from Lake Ardagani, with its most polluted location being selected for this purpose.

The following parameters were determined in the waters of the studied objects:

1. From organoleptic parameters:

Smell, colour, transparency, floating particles;

2. From physical-chemical parameters:

Temperature, pH, chlorides and salinity, total hardness, Ca^{2+}, Mg^{2+}, NH_4^+, NO_2^-; SO_4^{2-}ions concentration, dissolved oxygen concentration and Biochemical Oxygen Demand during 5 days-nights (BOD_5);

3. Multielement analysis – on plasma atomic emission spectrometry;

4. From microbiological parameters - total number of coliform bacteria.

The samples were taken according to the norms defined by the state standard (GOST 24481-80). The samples were taken in the chemically clean container with a screw cap. The container is exposed to sample water two times, then filled with water and tightly closed by the cap. The volume of the container was 2 litres.The organoleptic indicators (temperature, smell, colour, transparency, floating particles) are inspected right upon taking the sample. During transportation container shall be placed in a package to avoid contamination, damage or excessive shaking.

The samples shall be transported quickly with a special care as it is recommended to do on the same day. Determination of dissolved oxygen and pH required filling up of container, to ensure there is no oxygen under the cap which decreases shaking during container transportation.In the case microbiology analysis, we used 0,5L volume container which was sterilized in autoclave in advance. The samples for wate chemical and microbiological analysis were taken separately. It is necessary to have dark container, to avoid negative exposure of light on the water compounds.

After pouring water into the sample container, it shall be labelled with an indication of sample number, sample description, taking time and place, environmental climate conditions, name of the person taking the sample, the research purpose. It is recommended to take samples on a regular basis, seasonally, which allows for drafting comprehensive image on the water quality. Samples were stored according to the technical regalement, it was frozen for conservation. The analysis started after the sample temperature was dropped to room temperature. We took water samples from 0-50 cm deep in the sea in certain points (Pictures 40, 41).

The water samples were analysed on organoleptic parameters – colour, smell, transparency, floating particles upon taking (GOST 3351-74). The smell was defined by sniffing it from 0 to 5 degree. To define colouring we were pouring it in the transparent cylinder and were observing on a daylight.The water transparency was assessed using smooth metal disc. Usually, the water is warmed up in the basins from top to bottom.We were defining the temperature of the water samples right upon taking.The water pH has been defined on pH meter (Mettler Toledo).

To determine concentration of chlorides in water we applied the method developed by Mohr and Knudsen. To calculate the salinity of water, we multiplied the concentration of chloride ions by a defined coefficient 1,65. Dissolved oxygen in water has been determined by applying iodometric titration method by Winkler. To determine BOD_5 we were keeping one portion of water brought in laboratory in incubator at 20^0C for 5 days. Biochemical oxidation of organic compounds occurred in the water during this process. We were determining free oxygen volume in the samples. By determining difference between initial concentration of free oxygen and oxygen left in water after incubation, we defined Biochemical Oxygen Demand within 5 days. This provided us with an indication of the level of water purity.

Picture 40. The water sampling in Nuri-Geli Lake

Picture 41. The water sampling in Ardagani Lake

Picture 41. The water sampling in Ardagani Lake

We were determining sulphate concentration in the seawater samples on an ultraviolet spectrometer - UV 1800 (cuvette 20 mm, wavelength λ = 364 nm). Mineral nitrogen-containing compounds were defined ultraviolet spectrometer UV 1800. The water hardness and the concentration of Ca^{+2} and Mg^{2+} ions concentration was determined with trilonometric titration. The HCO_3^- ions were determined by titrimetric titration, the principle of which is based on neutralization of HCO_3^- ions by applying hydrochloric acid, with the participation of the methyl orangeindicator. The method allows for calculation of HCO_3^- ions more than 5 grams in the sample. To conduct a multi-elemental analysis of waters, we used the plasma atomic emission spectrometry - ICPE-9820. The water samples were analysed to determine the total number of coliform bacteria (intestinal lactose-positive rods) in accordance with methodological instructions 4.2.2959-11 in 100 ml of water by applying three stage inoculation scheme. Each type of analysis was carried in three parallel trials and further processing of the results (Picture 42).

Picture 42. Water sample analysis and data processing

III.4. The Organoleptic and Basic Quality Indicators of Nuri-Geli and Ardagani Lakes

The seasonal organoleptic indicators of water samples from Nuri-Geli and Ardagani lakes were evaluated by comparing water samples taken at various points in each location. During autumn, the water sample taken from the most polluted location in Ardagani had the strongest smell, which was estimated to be more than 5 degrees. The water was highly turbid with an intense uncharacteristic yellow colour. Floating particles were visible from the surface to a depth of about 0-50 cm, indicating high turbidity and a large number of particles. In the average sample taken from Ardagani, the smell was rated at 4-5 degrees, and the water was turbid with uncharacterized greenish-yellow color. Floating particles were observed from 0-30 cm below the surface, which is also prohibited. In the average sample taken from Nuri-Geli Lake, the smell was rated at 3-4 points. The water was slightly turbid with a greenish-yellow colour, and floating particles were visible from the surface to a depth of about 0-10 cm (Table 36).

Table 36

Organoleptic parameters of water in autumn season

№	*Location*	**Smell, points**	**Transparency**	**Color**	**Floating particles**
3	***Nuri-Geli Lake (average sample)***	3-4	slightly turbid	greenish-yellow	It is observed from the surface to 0-10 cm
4	***Ardagani Lake (average sample)***	4-5	turbid	greenish-yellow	It is observed from the surface to 0-30 cm
5	***Ardagani Lake (Very polluted location)***	>5	very turbid	intensively yellow	It is observed from the surface to 0-50 cm
	Norm	***2 points***	***It should be transparent at 0-30 cm***	***Uncharacteristic colour is prohibited at 0-10 cm deep***	***Uncharacteristic floating particles should not be observed on the water surface or upper layer***

The same tendency was observed during winter: the water sample taken from the most polluted location in Ardagani had the smell that was estimated to be more around 3 degrees. The water was turbid with aslightly yellow colour. Floating particles were visible from the surface to a depth of about 0-30 cm. In the average sample taken from Ardagani, the smell was rated at 4-5 degrees, and the water was turbid with uncharacterized greenish-yellow colour. Floating particles were observed from 0-30 cm below the surface, which is also prohibited. In the average sample taken from Ardagani Lake, the smell was rated at 2-3degree. The water was slightly turbid with a greenish-yellow colour, and floating particles were visible from the surface to a depth of about 0-20 cm. In the average sample taken from Nuri-Geli Lake, the smell was rated at 2 degree. The water was slightly turbid with a greenish-yellow colour, and floating particles were insignificantly visible from the surface to a depth of about 0-10 cm (Table 37).

Table 37

Organoleptic parameters of water in winter season

№	*Location*	**Smell, points**	**Transparency**	**Color**	**Floating particles**
1	***Nuri-Geli Lake (average sample)***	2	slightly turbid	slightly greenish yellow	It is insignificantly observed up to 0-10 cm
2	***Ardagani Lake (average sample)***	2-3	slightly turbid	greenish-yellow	It is observed up to 0-20 cm from the surface
3	***Ardagani Lake (Very polluted location)***	3	turbid	slightly yellow	It is observed up to 0-30 cm from the surface
	Norm	***2 points***	***It should be transparent at 0-30 cm***	***Uncharacteristic colour is prohibited at 0-10 cm deep***	***Uncharacteristic floating particles should not be observed on the water surface or upper layer***

Water temperature was measured right upon taking the sample. Within our observation, the maximum temperature has been detected in the most polluted area of Ardagani lake in autumn - +22°C, and minimal in Nuri-Geli lake during winter - +8°C. Temperature of these lakes is primarily influenced by the distance to the sea, thus in winter the water temperature is above the absolute minimum (+5°C). The water temperature of the lakes in February is 9-10°C more than in September (Table 38).

The surface layer of the lake water has a slightly alkaline pH range of 7,70-8,5, but it decreases to a weak acid range of pH 6,48-5,6 in deeper waters. Seasonal observations showed that the pH of the lake water reached its maximum in winter and minimum in autumn, which may be attributed to the rise in temperature during autumn and the accumulation of organic compounds that cause water acidification. The pH in Nuri-Geli water samples was within the permissible range of 7,74-7,90. However, both samples taken from Ardagani Lake had a minimum pH value of 7,28-7,32. pH concentration was below norm during both seasons in this location.

Table 38

Water temperature and pH

№	Location	Autumn		Winter	
		T, °C	**pH**	**T, °C**	**pH**
1	***Nuri-Geli Lake (average sample)***	18	7,74	8	7,90
2	***Ardagani Lake (average sample)***	21	7,32	11	7,51
3	***Ardagani Lake (Very polluted location)***	22	7,28	12	7,45
Norm			**7,70-8,5**		**7,70-8,5**

The concentration of chloride ions is an indicator of the salinity of lake water. The chloride concentration in the water samples of Nuri-Geli Lake was within the standard range, measuring at 140,0 mg/l - in autumn and 113,1 mg/l - in winter. In both seasons, Ardagani Lake had the highest chloride concentration, with results by 1,05-1,7 times higher than the MPC. This indicates a severe level of water pollution in Ardagani Lake. Therefore, the NaCl content (the salinity of lakes) has a direct correlation with the concentration of chloride ions. Salinity decreased in winter due to the abundant rainfall (Table 39, Diagram 4).

Table 39

Cl^--ions and salinity (concentration of NaCl)

Locastion	Autumn		Winter	
	Cl^-, mg/l	**NaCl, mg/l**	**Cl^-, mg/l**	**NaCl, mg/l**
Nuri-Geli Lake (average sample)	140,0	231,0	113,1	186,6
Ardagani Lake (average sample)	567,1	935,7	369,0	608,85
Ardagani Lake (Very polluted location)	605,3	998,7	392,3	647,3
Norm, mg/l	**Not more than 350**		**Not more than 350**	

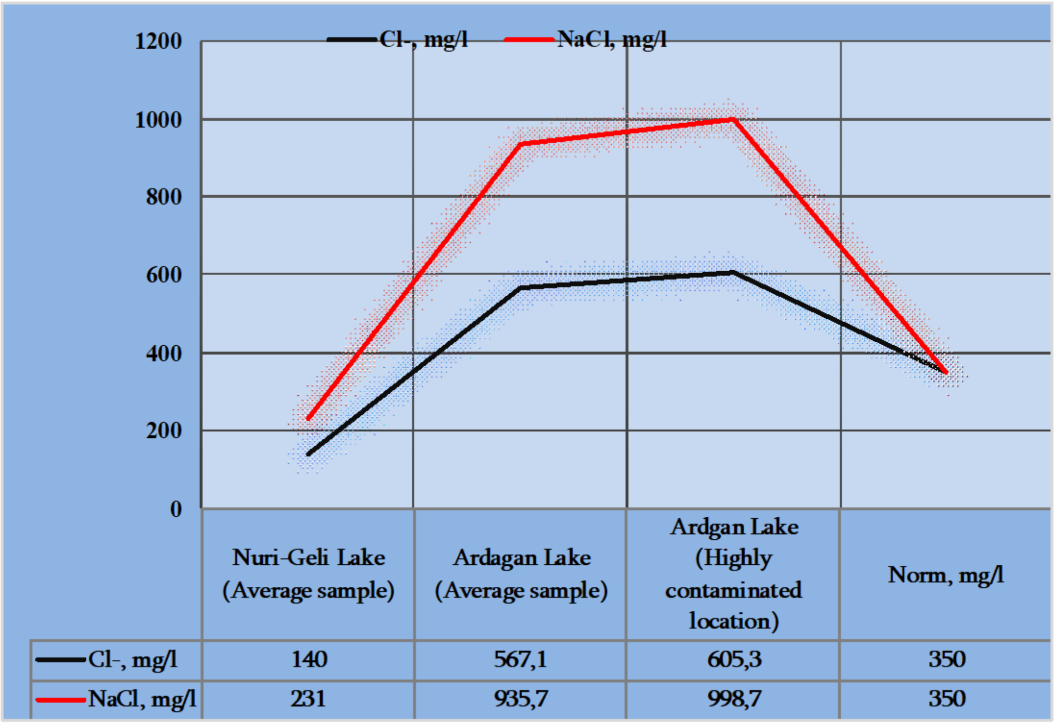


Diagram 4. Cl^- ions concentration and salinity in the waters of Nuri-Geli and Ardagani lakes

The seasonal decrease of Ca^{2+} and Mg^{2+} ions happens from autumn to winter, which may be attributed to the increased precipitation in winter. This leads to a higher influx of fresh water into the lakes, causing a reduction in water hardness. The concentration of these ions is directly related to the hardness of the lake water. The lowest amount of Mg^{2+} ions was found in Nuri-Geli lake, measuring at 9,7-10,2mg/l. A similar trend was observed in the content of hydrocarbons (Table 40).

Table 40

Concentration of Ca^{2+}, Mg^{2+}, HCO_3^- ions, total hardness

Location	**Autumn**				**Winter**			
	Ca^{+2}	Mg^{+2}	**hardness**	HCO_3^-	Ca^{+2}	Mg^{+2}	**hardness**	HCO_3^-
Nuri-Geli Lake (average sample)	45,8	10,2	56,0	170,8	31,1	9,7	40,8	128,1
Ardagani Lake (average sample)	62,0	37,7	99,7	250,6	52,2	35,6	87,8	137,9
Ardagani Lake (Very polluted location)	**67,4**	**42,9**	**110,3**	**256,2**	**54,1**	**38,3**	**92,3**	**146,4**

The minimum level of dissolved oxygen required for the survival of aquatic organisms is 5 mg/l, and anything below 2 mg/l can result in the death of hydrobionts. In all seasons, the concentration of dissolved oxygen in water samples collected before noon should not drop below 4-6 mg/l. According to the research data on dissolved oxygen concentration in the water samples, this parameter was higher in winter (4,5-5,5 mg/l) than in autumn (4,20-4,47 mg/l). The increased solubility of gases in water during winter is the reason for this. During the autumn season, the lowest level of dissolved oxygen (4,20 mg/l) was found in the polluted area of Ardagani Lake. In both seasons and all locations, the concentration of dissolved O_2 in water was below the MPC (Table 41).

The degree of water pollution with organic compounds is determined by the parameter called Biochemical Oxygen Demand for 5 days and nights (BOD_5), with the MPC of no more than 3 mg/l in surface waters. The experimental results of determining the BOD_5 confirmed the depletion of oxygen in the researched waters: according to the dissolved oxygen concentration,at all locations, the BOD_5 exceeded the MPC and measured at 3,85-4,1 mg/l - in autumn and 3,6-4,0 mg/l - in winter. As for seasonal dynamics, tis parameter regularly decreased during winter and increased in autumn, which is attributed to seasonal temperature changes that result in a reduced activity of microorganisms in the cold winter period.

Table 41

Dissolved O_2 and BOD_5, mg/l

Location	dissolved O_2 , მგ/ლ				BOD_5, mg/l	
	Autumn		Winter		Autumn	Winter
	X_1	X_2	X_1	X_2		
Nuri-Geli Lake (average sample)	4,47	0,62	5,5	1,9	3,85	3,6
Ardagani Lake (average sample)	4,31	0,23	4,5	0,6	4,08	3,9
Ardagani Lake (Very polluted location)	4,20	0,10	4,5	0,5	4,1	4,0
MPC	**Not more less 5 mg/l**				**Not more less 3 mg/l**	

The reason for determining NH^{4+} ions is to identify the sources of nitrogen accumulation in water, which include organic compounds, feces, and atmospheric precipitation. Thus, it was of interest to observe the accumulation of organic compounds in both locations. NH^{4+} ions are known to be formed during the transformation of nitrogenous substances in the surface layers of water as a result of the destruction of complex organic compounds. This process involves nitrogen bacteria (ammonifiers and nitrifiers).

The study results revealed that the sulfate content in the water of Ardagani Lake is higher than that of Nuri-Geli Lake. However, the concentration of this parameter is within the permissible limit, indicating that the two lakes are not sulfate pharmaceutical lakes. As for the concentration of ammonium nitrogen, it is much higher than the MPC in both seasons: in autumn, Nuri-Geli lake recorded 1,8 times higher content while in Ardagani lake the content was 4,2-4,6 times higher; in the winter season, Nuri-Geli Lake had a 1,2 times higher content while in Ardagani Lake the content was 3,2-3,6 times higher. This indicates the progressive eutrophication of lake waters (Table 42).

Table 42

Concentration of NH_4^+ and SO_4^2 ions in lake waters

Location	Autumn		Winter	
	NH_4^+ mg/l	**SO_4^2 mg/l**	**NH_4^+ mg/l**	**SO_4^2 mg/l**
Nuri-Geli Lake (average sample)	0,70	14,5	0,45	8,2
Ardagani Lake (average sample)	1,63	38,5	1,26	26,8
Ardagani Lake (Very polluted location)	1,80	47,1	1,40	33,14
MPC, mg/l	**0,39**	**100,0**	**0,39**	**100,0**

The results of the total coliform bacteria concentration indicated a decline in the sanitary and bacteriological condition of the lakes in both seasons. Specifically, in the autumn season, Nuri-Geli Lake had 4600 coliform bacteria, which is 4,6 times higher than the MPC, while in winter, it had 1600, which is 1,6 times higher than the MPC. In the case of Ardagani Lake, the total number of coliform bacteria in both samples was over 11000 - in the autumn season, which reduced to 2100-2900 - in winter, although it was still 2,1-2,9 times higher than the MPC during this season (Table 43).

Table 43

Total number of Coliform bacteria (intestinal coliform bacteria) in 100 ml seawater

№	Location	Total number of coliform bacteria	
		Autumn	**Winter**
1	***Nuri-Geli Lake (average sample)***	4600	1600
2	***Ardagani Lake (average sample)***	>11000	2100
3	***Ardagani Lake (Very polluted location)***	>11000	2900
MPC		**< 1000/100 ml - for economic-household purposes <500 /100 ml – in swimming areas <1000 /100 ml – water sports and settlements**	

III.5.The Multi-element Analysis of the Lake Waters

The analysis of water samples from different locations in Nuri-Geli and Ardagani lakes revealed that macroelements play a dominant role: Na (214-427mg/l), Ca (47,1-610 mg/l), Mg (14,3-44,2 mg/l), and K (13,8-20,3 mg/l). Their concentration decreased in the following order: Na>Ca>Mg>K. It is worth noting that the concentration of phosphorus in all three samples was above the MPC, indicating the accumulation of organic matter in the lakes. Microelements, including toxic elements such as Boron, Barium, Cadmium, Cobalt, Nickel, and Manganese, did not exceed the MPC in the water samples (Table 44, Diagram 5).

The multi-element analysis revealed that certain microelements (including highly toxic elements) were above the MPC in all three samples: As, Cr, Cu, Fe and Pb.

Table 44

Multielement analysis by plasma atomic emission spectrometry (ICPE 9820)

Macroelements, mg/l

Location	Al	Ca	Mg	Na	P	K
Nuri-Geli Lake (average sample)	6.0067	47,1	14,3	214	0.0368	13.8
Ardagani Lake (average sample)	1.0224	55,7	38,6	395	0.0446	19.7
Ardagani Lake (Very polluted location)	2.0306	61,0	44,2	427	0.0667	20.3
MPC, mg/l	**1,0**	**-**	**-**	**-**	**0,028**	**-**

Microelements, mg/l

Location	As	B	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb
Nuri-Geli Lake (average sample)	0.042	0.0602	0.0299	0.0033	0.0028	0.0063	0.082	0.973	0.0011	0.0008	0.018
Ardagani Lake (average sample)	0.061	0.0171	0.0357	0.0035	0.0038	0.007	0.278	1.069	0.00653	0.0012	0.0282
Ardagani Lake (Very polluted location)	0.065	0.0165	0.02	0.0037	0.0046	0.0073	0.324	1.773	0.00793	0.0012	0.0339
MPC, mg/l	**0,05**	**5,0**	**0,1**	**0,005**	**0,005**	**0,001**	**0,005**	**0,05**	**0,05**	**0,8**	**0,01**

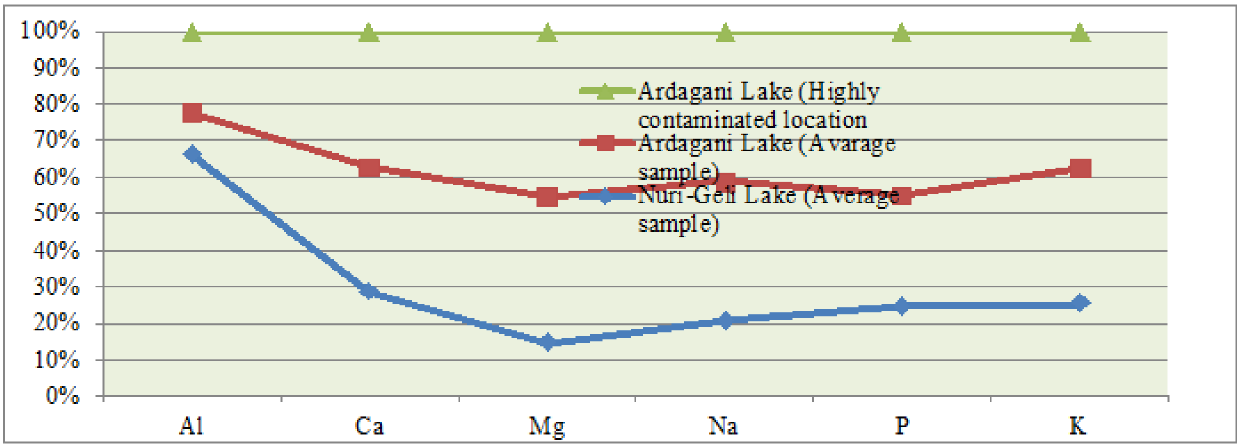


Diagram 5. Concentration of macro elements in Nuri-Geli and Ardagani lake waters

CONCLUSION

1. Any change in the ecosystems may have negative influence over quality parameters of living organisms, objects, ecosystems. The same applies to the lakeswhich serve as recreational areas for activities such as fishing, water sports and other leisure activities and is of vital importance for its human inhabitants.

2. The organoleptic parameters of Nuri-Geli and Ardagani lakes, such as smell, transparency, colour, and floating particles, do not meet the natural standards during the autumn and winter seasons. Despite being in a cold season, the temperature of the lakes remains higher than the absolute

minimum (+5°C) due to the influence of warm currents from the Black Sea.

3. pH in Nuri-Geli water was within the MPC (7,7-8,5) with a range of 7.74-7.90. The two samples from Ardagani Lake had minimal pH concentration 7,28–7,32. pH concentration was below the standard during both seasons.

4. In both seasons, the highest level of chlorides was observed in Ardagani Lake, with results being 1,05-1,7 times more than the MPC. The concentration of chlorine ions has a direct correlation with the salinity of the lakes. Salinity decreased in winter, likely due to the abundance of precipitation.

5. The concentration of Ca^{2+} and Mg^{2+} ions was decreased form autumn to winter, caused by increased precipitation in winter and accordingly, reduction of water hardness.

6. The lowest amount of dissolved O_2 was detected in the most polluted area Ardagani Lake - in the autumn (4,20 mg/l). In both seasons, the concentration of dissolved O_2 was below the MPC. Consequently, the BOD_5 exceeded the MPC with values ranging from 3,85-4,1 mg/l - in autumn and 3,6-4,0 mg/l - in winter. According to the seasonal dynamics, this parameter decreased in winter and increased in autumn.

7. The determination of NH_4^+ and SO_4^2 ions revealed that the concentration of sulfates in Ardagani Lake is higher than that in Nuri-Geli Lake. Moreover, the level of NH_4^+ in both lakes is above the MPC in both seasons. Specifically, in the autumn season, the concentration of NH_4^+ in Nuri-Gel Lake was 1,8 times higher than the MPC, while in Ardagani Lake it was 4,2-4,6 times higher; in the winter, NH_4^+concentration in Nuri-Geli Lake was 1,2 times higher than the MPC, and in Ardagani Lake, it was 3,2-3,6 times higher. These findings suggest that the lakes are experiencing progressive eutrophication.

8. Current sanitary-bacteriological condition in both seasons has declined as confirmed by the total coliform bacteria count, which is 1,6-4,6 times higher than the MPC - in Nuri-Geli Lake. In Ardagani Lake coliform bacteria exceeds 11000 - in the autumn season, even it decreases to 2100-2900 - in winter, but still is 2,1-2,9 times higher than the MPC.

RECOMMENDATIONS

The study of Nuri-Geli and Ardagani lakes indicates that several ecological indicators assessing their quality are outside the limits of the MPC due to the factors with anthropogenic origin. Considering the strategic importance of these lakes, we thinkit is necessary to implement regular cleaning works and periodic sanitary-bacteriological and hydrochemical monitoring on the lake waters.

Chapter IV. Treatment of Wastewater in Anaerobic Digesters and Processing Dynamics of Biogenic Matters

PREFACE

The treatment and discharge of wastewater into surface waters is a crucial environmental process. Unlike natural wastewater, treated water undergoes physical, chemical, and biological changes. Discharging untreated wastewater into natural waters can have a negative impact on the natural water balance.

In Georgia, there is a water purification system that meets European standards, which has been operating in the territory near Batumi since 2012. The water treatment process includes both mechanical and biological filtration, resulting in the removal and stabilization of sediment.

The laboratory research on the Batumi water purification system revealed that the quality parameters of runoffs, such as COD (Chemical oxygen demand), BOD (Bochemical oxygen demand) and suspended particles is below the permissible limit. This is likely due to the fact that the river water is diluted with external and natural water sources.

Furthermore, an examination of water parameters (COD, BOD and suspended particles) in anaerobic ponds demonstrates a correlation between suspended particles in the inflow waters and the decrease in COD and BOD_5 parameters in anaerobic ponds. The higher the concentration of suspended particles in the wastewater, the greater the reduction in COD and BOD_5. Conversely, low loads of biogenic substances result in lower cleaning quality.

INTRODUCTION

The treatment of wastewater and disposal of purified water into surface waters is a crucial environmental process. The wastewater differs from its natural state as it undergoes physical, chemical, and biological changes. Discharging untreated wastewater into natural waters has negative effect on the natural water balance. Meeting the normative requirements for the concentration of wastewater within permissible concentration in cities and populated areas is of great importance to clean and discharge it into water bodies (seas, rivers, lakes, etc.). Thus, constructing treatment plants and treating wastewater is a legal requirement in economically developed countries, while for developing countries it still remains as a challenge.

There is a wastewater treatment plant in Adjara, Georgia that meets European standards and has been operating since 2012. This facility, located near Batumi, is unique in the Transcaucasia region in terms of compliance with European standards for wastewater treatment, which includes both mechanical and biological purification processes. Therefore, studying the process of wastewater treatment and the dynamics of biogenic substance processing is important.

The objective of this research was to examine the mechanical purification stages of wastewater at the Adlia wastewater treatment plant, assess the efficacy of water purification in anaerobic ponds, and analyze the impact of pollutant loading in inflow water on anaerobic pond processes. The study focused on the wastewater flowing to the Adlia wastewater treatment plant.

The research aimed to achieve several tasks, including examining the primary mechanical cleaning processes (flooding, sand, and grease capture); evaluating the quality of water purification in anaerobic ponds by laboratory analysis of parameters such as Chemical Oxygen Demand, Biochemical Oxygen Demand, suspended particles, pH, and temperature; determining the Chemical Oxygen Demand of water outflowing from anaerobic ponds. Additionally, laboratory analysis was conducted to determine the Biological Oxygen Demand, suspended particles, pH, and temperature, while the dynamics of biogenic substance recycling were also studied.

IV.1. The General Mechanism for Treatment of Wastewaters

The treatment of wastewater and disposal of purified water into surface waters is a crucial environmental process. The wastewater differs from its natural state as it undergoes physical, chemical, and biological changes. Discharging untreated wastewater into natural waters has negative effect on the natural water balance. Meeting the normative requirements for the concentration of wastewater within permissible concentration in cities and populated areas is of great importance to clean and discharge it into water bodies (seas, rivers, lakes, etc.). Thus, constructing treatment plants and treating wastewater is a legal requirement in economically developed countries, while for developing countries it still remains as a challenge.

Wastewater refers to water utilized for domestic, industrial, agricultural or other purposes, which is changed in quality and gets mixed with foreign and rainwater collected into the sewage system. The purpose of the water (sewage) system is to collect wastewater from buildings' sanitary facilities and transport it out of the inhabited area through an external self-powered network for treatment, where the water is cleaned within permissible concentration limits according to norms, and then discharged into the basin.

The types of wastewaters are:

- Domestic wastewater refers to water coming from households and small enterprises;
- Commercial-industrial waters come from industrial and commercial plants, production of various products, such as milk, beer, meat, fish, and leather. These waters contain organic and mineral substances, have extreme pH levels, or high temperatures;
- Agricultural waters, that can be generated during the production of animal feed or from dairy waste and silage. These waters are polluted with organic matter;
- Foreign water. This includes groundwater that gets into damaged sewage systems, drainage water that drains from deep basements, as well as water from wells and fountains;
- Rainwater is formed during precipitation, snow melting, hail, and enters the sewage system from streets, yards, and gardens. These waters have high levels of mineral pollution;

- Mixed water is formed when the drain and sewer systems are combined, resulting in mixed wastewater that flows to the wastewater treatment plant.

The treatment of urban and residential wastewater involves a combination of methods that gradually remove large impurities (paper, cloth, and kitchen waste), heavy impurities (sand, slag), colloidal and soluble organic pollutants, and pathogenic microflora. The inflow water is treated in several phases. At the Adlia treatment plant, about 60000 m^3 of water is processed every day. The purified water is then discharged into the sea. The laboratory at the Adlia wastewater treatment plant conducts daily monitoring of the purified water in accordance with the European Union standard for the permissible concentration of discharged purified water into the sea.

The Adlia wastewater treatment plant plays a vital role in safeguarding th sea ecosystem and preserving the cleanliness of Adjara's coastline. According to the studies by the treatment plant's laboratory Black Sea Monitoring Center, the Black Sea pollution has been significantly improved significant since 2007. The treatment process involves multiple stages: initially, wastewater undergoes primary mechanical cleaning from sand, grease, and waste, followed by collection and stabilization of sludge; in the biological purification stage, ammonium is transformed into nitrate through nitrification, while fats, proteins, and carbohydrates are reduced; finally, secondary mechanical treatment separates the secondary sludge from the water in the final settlement tanks.

Wastewater carries various types of pollution in solid, also, colloidal, sediment and dissolved forms, which require different technologies and methods for treatment. To understand the overall mechanism of wastewater treatment, we can examine the general scheme of the Adlia treatment plant. The wastewater complete purification involves multiple stages. The plant is equipped with various equipment and basins for the purification process. The Batumi wastewater treatment plant comprises 4 anaerobic basins, 4 biofilters, and 4 final settlement tanks (Picture 43).

In the initial stage of the treatment process, mechanical cleaning is carried out to remove large wastes, sand, grease and sediment particles, known as sludge. The water is first mechanically cleaned ina separator, following which sand and grease are separated from it and directed to the four anaerobic basins (Picture 44).

Picture 43. The Adlia wastewater treatment plant in Batumi

Picture 44. Primary mechanical treatment of wastewater

In the anaerobic basins, sludge undergoes cool, anaerobic stabilization, pumping, dehydration and solar drying. Each anaerobic basin supplies water to four biofilters where biological purification begins, removing dissolved and suspended substances. The biological treatment process is crucial in wastewater treatment and involves nitrification and denitrification processes, reduction ofchemical and biological oxygen demand. Bacteria, fungi, and single-cell organisms transform organic substances in water and sludge and break down into simple and stable compounds. Those processes are also ongoing in the natural water bodies, but in lower scale, because compared to wastewater the natural ware bodies are low in concentration or are completely clean unless polluted by anthropogenic influence. The water is enriched with oxygen and undergoes nitrification and the processing of fats, proteins, and carbohydrates. Each biofilter flows into four final settlement tanks, and the biomass from the biofilter is settled to remove secondary sludge through a secondary mechanical cleaning process.

There are certain substances dissolved in water that can be removed only through chemical precipitation, which is requires additional coagulants are added induce precipitation. The settled sludge is regularly pumped to the anaerobic ponds, thereby circulating the biomass in the treatment plant. The purified water from the final settlement tank is pumped into the sea through a pumping station a 1 km and 100 meters away, at a depth of 40 meters. The laboratory at the Adlia wastewater treatment plant conducts daily monitoring of purified water in compliance with the European Union standard that sets the maximum permissible levels for purified water released into the sea. The Adlia wastewater treatment plant plays a vital role in protecting the marine ecosystem and maintaining the cleanliness of the Adjara coastline. The laboratory of the treatment facility and the latest research from the Black Sea Monitoring Center indicate that the degree of pollution of the Black Sea has significantly reduced since 2007.

The subsequent recycling of the sludge is a crucial step in the wastewater treatment process and involves a multistage process that must be implemented at all treatment facilities. Sludge treatment employs physical, mechanical, and chemical processes. Due to its high-water content, sludge has a large volume that must be reduced through stabilization, settling, dehydration, drying, and volume reduction. Bacteria are used to reduce the organic matter in the sludge, a process referred to as stabilization.

IV.2. The Mechanical Treatment of Wastewaters

The initial stage in wastewater treatment is mechanical treatment, which involves preparing the water for further cleaning (biological or chemical). The process of mechanical cleaning separates coarse-dispersed impurities of both mineral and organic origin that are undissolved in the wastewater. These impurities follow the laws of gravity, with heavier materials sinking and lighter materials floating.

The Adlia treatment plant implements a two-stage mechanical cleaning process for wastewater. In the first stage: the separation, sand and grease capture, and primary sludge sedimentation in anaerobic ponds. The second stage involves secondary sludge sedimentation in final settlement tanks. The initial mechanical purification of the water entering the facility occurs through two 6 mm diameter automatic grates that remove any coarse impurities (Picture 45).

Picture 45. Automatic grates

The following stage is the removal of sand and grease from the watercarried out in two combined basins. The sand removal unit functions anaerobically. Two compressors blow air continuously into the basin to facilitate the forced sedimentation of sand. A collection system is installed at the basin's base, which operates continuously, drawing the sedimented sand into the conical shaft of the basin where the pump is placed. The pump automatically pumps the sand into the classifier, where the sand and water separate, with the sand gathering in a container while the water flows into the inlet channel.

The sand and grease basins are divided by wooden plates with openings between them. The grease trap is not aerated, which enables the grease to collect on the water surface. From the aerated sand compartment, the grease flows in a calm setting between the openings and floats on the surface of the water. The collected grease is then pumped into the grease shaft and removed from the building along with the sand waste. Once these processes have been completed, the water is transported to the primary settlement tanks - the anaerobic ponds - where the water-insoluble residues settle. Our study aims to evaluate the quality of mechanical water purification in anaerobic ponds, as well as the impact of the incoming water's pollutant load on the processes occurring in the anaerobic ponds.

After the primary mechanical cleaning in the wastewater treatment plant, sludge is settled in the primary settlement tanks. These sediments include organic and inorganic substances that are adsorbed on the suspended particles. The primary settlement tanks at the Adlia wastewater treatment carry a functionality of anaerobic stabilisation, the reason they are called anaerobic ponds.

As sludge settles in anaerobic ponds, various water quality parameters decrease, including: suspended particles, Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD). The degree to which these indicators decrease depends on the type of primary settlement tanks used at the treatment plant and the amount of biogenic substances present in the wastewater.

Anaerobic ponds have the primary function of removing mechanical impurities from water in the form of sludge to provide biologically treated water to the biological compartment. In the event when a large amount of biogenic substances are removed through mechanical cleaning, the bacteria and simple organisms in the biological unit will lack nutrients, which will lead to a starvation phase and hinder their ability to metabolize.

The wastewater incoming to the treatment plant should contain a certain amount of biogenic substances. Based on studies, to ensure the biological cleaning process operates efficiently. It is well-documented that in order to maintain high efficiency in biological cleaning, the pollution levels in the wastewater must fall within the limits presented in Table 45.

Table 45

The wastewater loadwith to ensure cleaning efficiency

Parameter	Chemical oxygen demand (COD)	Biochemical oxygen demand BOD_5	NH_4	Total phosphorus	Total nitrogen
mg/l	400–600	200–400	20-50	8–12,5	20–50

The values listed in the table are not universally found in all treatment plants. The amount of wastewater with biogenic content can vary depending on the volume of external water entering the sewage system. In cases where the number of external sources is high, the organic and biogenic load of the wastewater will be lower.

The water load is particularly crucial in the treatment plant for the effectiveness of the biological treatment process, as biogenic substances serve as a food source for bacteria and other microorganisms. A lack of these substances can hinder the biological treatment process.

The primary settlement tanks generally achieve a 30-40% water purification rate. The degree of cleaning quality depends on the form of primary settlement tank. If sludge stabilization occurs in the primary settlement tanks, as is the case at the Batumi wastewater treatment plant, the processing quality is higher compared to primary settlement tanks where sludge is not stabilized and is pumped out daily.

To evaluate the effectiveness of wastewater treatment at the Adlia plant, we conducted laboratory tests on the pH, temperature, Chemical Oxygen Demand, Biological Oxygen Demand, and suspended particles of both inflow and outflow water from the anaerobic ponds.

Chemical Oxygen Demand (COD) indicates the presence of organic and inorganic compounds with recovery capability (sulphites, nitrates, nitrites, iron salts, manganese and other) in the water. COD measures the amount of oxygen, in milligrams, consumed per liter of water to oxidize organic and inorganic compounds.

Biochemical Oxygen Demand (BOD) is an indicator of the amount of organic matter present in water. It measures the amount of oxygen, in mg/L, required for the oxidation of impurities in water during biochemical processes. Typically, BOD is 50% of COD.

The number of suspended particles is a crucial indicator of the loading of incoming water. The effectiveness of sedimentation of suspended particles in water depends on: the initial concentration of the particles; the degree of dispersion of particles; their tendency to agglomerate (compact and thicken).

The pH level plays a crucial role in the wastewater treatment process as it has a significant impact on the chemical and biological processes occurring in the water. Anaerobic biological treatment of wastewater is effective when the pH falls within the range of 7-8. Temperature also plays a vital role in maintaining the quality of the treated wastewater, usually ranging between 10-22°C.

The quality of biological purification and oxygen saturation level also depends on temperature. Oxygen in the primary condition for biological purification. For successful nitrification, the wastewater should be saturated with 8-10mg/l of oxygen. However, if the temperature falls below 12°C, the biological treatment process of the wastewater is hindered.

IV.3. The Research Methodology

The statistical analysis of changes in water quality indicators was carried out in the laboratory of the wastewater treatment facility. Determination of Chemical Oxygen Demand (COD) according to ISO 15705, in photometer DR 6000 with cuvette test method (Picture 46). Chemical Oxygen Demand was determined by the respirometric method.

The Hach HQ40d multi-probes were utilized to measure the pH, temperature, and dissolved oxygen in the wastewater sample. The respirometric method, DIN 38409 H 52, was used to determine BOD_5. Before determining the volume and range of the sample to be analyzed, it is necessary to determine the BOD.

The analysis process: before starting the analysis, we mixed the sample with a laboratory mixer for 2-3 minutes. We placed magnetic stirrer into BOD_5 bottles corresponding to the COD concentration and filled these bottles with the mixed samples (filling up before spilling). We added 5-9 drops of nitrification blocking liquid ($C_4H_8N_2S$) to the sample based on the volume.

Picture 46. Photometer DR 6000

A rubber stopper was attached to the neck of the bottle, in which one tablet of sodium alkali was placed, and the cap was closed with a special monitor. The monitor was drained, and the bottle was placed in a thermostat at a temperature of 20°C for 5 days, while continuously mixing the sample with a magnetic stirrer. After 5 days, we read the result on the cap monitor, multiplied it by the dilution factor. The result data represented the Biological Oxygen Demand in 5 days. This method is specifically intended for use in treatment facility laboratories.

The Hach HQ40d multi-probes are used to measure pH, temperature, and dissolved oxygen in the wastewater sample. The sample is transferred to a test tube and the pH, temperature, and dissolved oxygen are determined immediately using the equipment.

The results are displayed on a monitor and can be re-evaluated to check for accuracy. The equipment is portable, powered by an electric battery, and the probes are stored in a special liquid to prevent them from drying out. The pH probe is calibrated using buffer solutions with pH values of 4,01 and 7,00.

IV.4. The Laboratory Analysis of Chemical Oxygen Demand, Biological Oxygen Demand, Suspended Particles, pH and Temperature in Waters of Anaerobic Basins

During the period from January to April, the dynamics of Chemical Oxygen Demand, Biological Oxygen Demand, suspended particles, pH, and temperature were analyzed in the anaerobic ponds at the Adlia treatment plant (Table 46). The table displays the concentrations of fixed chemical and biological oxygen demand in mechanically treated water (water in aerobic ponds).

The results indicate that the water is diluted with external and drainage water, resulting in low pollutant loads. An increase in the concentrations of COD and BOD_5 was observed in April, which is likely due to a decrease in precipitation and drainage water flow. The data also show that the number of suspended particles in the incoming water is interrelated with the values of COD and BOD_5. The pH values were found to be within limits, while the average temperature was also within the acceptable range.

Table 46

Dynamics of certain parameters in the water incoming to anaerobic ponds

Month	*COD, mg/l*	*BOD_5, mg/l*	*suspended particles, mg/l*	*pH*	*T °C*
January	248	155	250	7,7	10
February	219	125	161	7,4	10,5
March	248	145	178	7,6	15,8
April	307	165	220	7,6	11,4
The average	***255***	***147***	***202***	***7,5***	***11,6***

The change dynamics of Chemical Oxygen Demand, Biological Oxygen Demand, suspended particles, pH, and temperature in the water exiting the anaerobic ponds at the treatment plant during January to April, the quality parameters, such as Chemical Oxygen Demand, Biological Oxygen Demand, suspended particles, pH, and temperature of water exiting the anaerobic ponds at the treatment plant showed a decrease tendency due to sludge sedimentation. Additionally, pH and temperature values were within the normal range during this period (Table 47).

According to research findings, the concentration of parameters in wastewater at the Batumi wastewater treatment plant, such as COD, BOD, suspended particles, is low, which could be attributed to the dilution of wastewater with foreign and drainage water. The processing dynamics of substances in the wastewater entering and exiting the anaerobic ponds were analysed.

Table 47

The change dynamics of certain parameters in water exiting the anaerobic ponds at the treatment plant

Month	*COD, mg/l*	*BOD_5, mg/l*	*suspended particles, mg/l*	*pH*	*T °C*
January	190	95	178	7,1	12
February	147	60	122	7	11
March	199	95	160	7,1	16,4
April	199	100	203	7,1	19,3
The average	183	87	165	7,0	14,6

COD and BOD_5 are the most important parameters for assessing the wastewater load. They are regularly monitored at all treatment plants, both in incoming water and throughout the treatment process. The data on the dynamics of COD and BOD_5 changes in incoming water in anaerobic ponds indicate that the wastewater is diluted with foreign water, resulting in a low pollutant load (Diagram 6). The increase in COD and BOD_5 concentrations is detected from April, the reason could be attributed to a decrease in precipitation and the subsequent low discharge of drainage water. Diagram 6 also reveals that the change in COD and BOD_5in the anaerobic ponds is relatively small and remains within narrow limits.

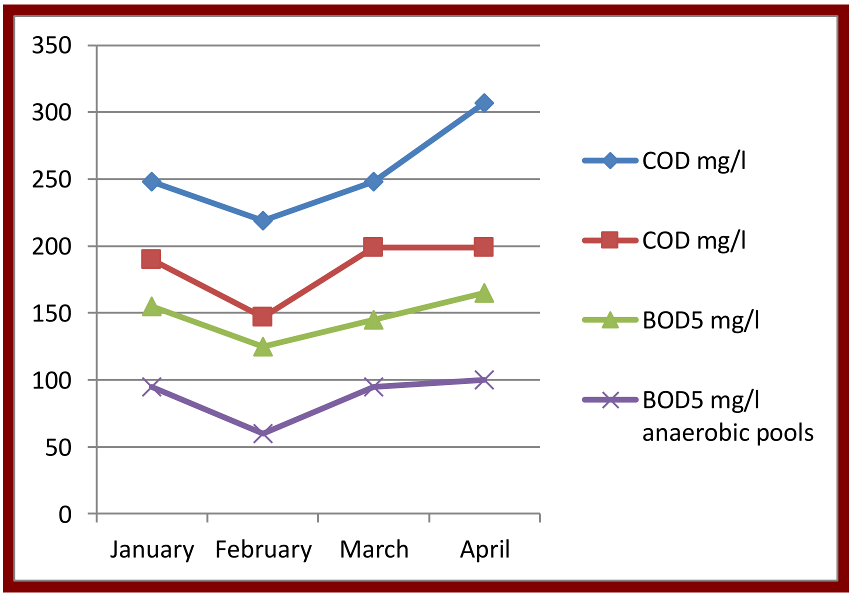


Diagram 6. The change dynamics of COD and BOD_5 in incoming water and anaerobic ponds at the Batumi wastewater treatment plant

The quantity of suspended particles in incoming water is a significant factor in determining the level of loading. The greater the concentration of suspended particles in wastewater, the more significant the reduction in volume in anaerobic ponds. When the load is low, the efficiency of the treatment process also decreases. The changes in the concentration of BOD_5 follow a pattern similar to that of suspended particles. The highest concentration of suspended particles, which is 250 mg/l, was observed in January, leading to an increase in sedimentation in the anaerobic ponds (Diagram 7).

Based on the analysis of the diagrams, the following conclusion can be drawn: the reduction of COD and BOD_5 is a result of the sedimentation of the suspended particles, which are the primary source of food for methane bacteria and the basis of sludge stabilization. A significant change is observed in January, which coincides with an increase in organic mass load in the wastewater. This is attributed to excess precipitation, which leads to flushing of the sewage system and a high amount of settled waste in the form of suspended particles, resulting in an increase in the concentrations of COD and BOD_5.

pH is a critical parameter in wastewater treatment since it significantly affects the biological and chemical processes in water. Based on the analysis of the pH changes in the incoming water and anaerobic ponds, it can be concluded that at the Batumi wastewater treatment plant, the pH in incoming water fluctuates between 7,4-7,7, and in anaerobic ponds, it remains between 7,0-7,1. It never transforms to acid or alkaline environment.

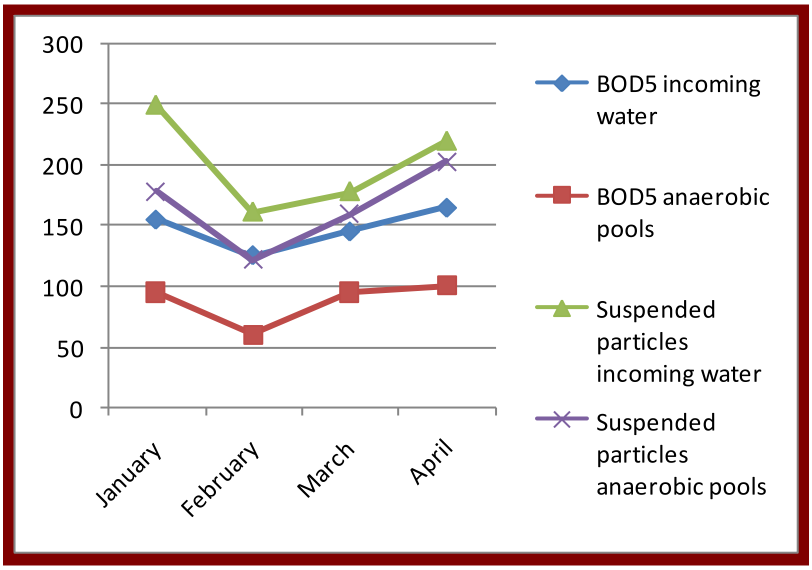


Diagram 7. Dynamics of concentration in BOD_5 and suspended particles

This neutral condition of water can be attributed to the fact that the Batumi wastewater plant mainly treats municipal wastewater, which facilitates plant operation and avoids additional challenges in the water treatment process (Diagram 8).

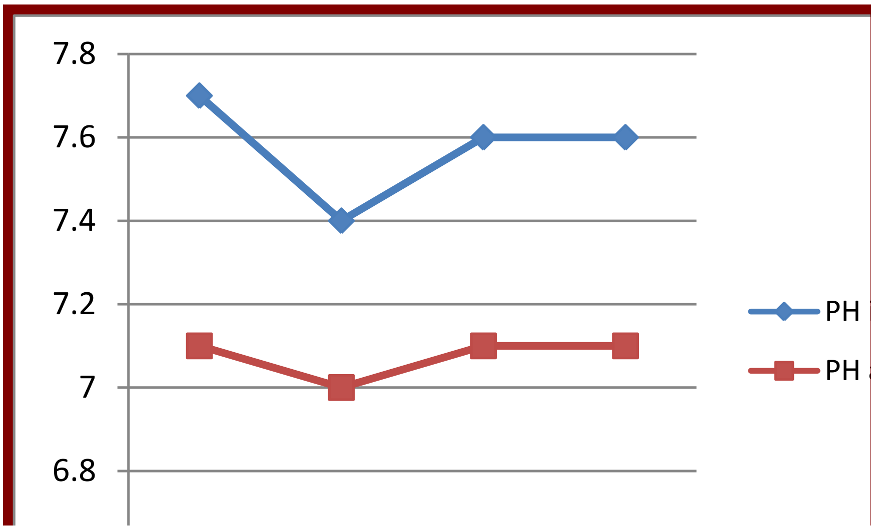


Diagram 8. pH change dynamics in incoming water and anaerobic ponds

The temperature is a crucial factor in maintaining the quality of wastewater treatment. It affects the degree of biological purification and oxygen saturation in water. If the temperature of the wastewater is below 12°C, it can hinder the biological processing of the wastewater. Based on the dynamics of temperature change observed in the incoming water and anaerobic ponds, it can be concluded that fluctuations in temperature do not have a significant impact on the quality of water purification. This is due to the presence of methanotrophic bacteria in the anaerobic ponds, which can stabilize the sludge in a cold environment and are not sensitive to temperature changes and the sedimentation of suspended particles is also not affected by temperature (Diagram 9).

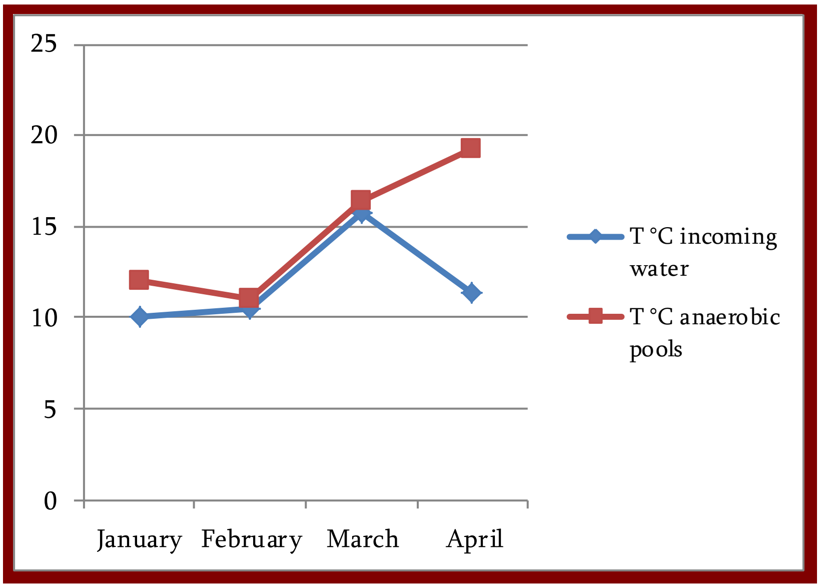


Diagram 9. Temperature change dynamics in incoming water and anaerobic ponds

CONCLUSION

1. The research has shown that the concentration of COD, BOD and suspended particles in the wastewater at the Batumi wastewater treatment plant is below the limit, possibly due to the wastewater being somewhat diluted with foreign and drainage water.

2. The data analysis reveals a correlation between the amount of suspended particles present in the incoming water and the corresponding decrease in the values of COD and BOD_5 in the anaerobic ponds. As the amount of suspended particles in the wastewater increases, there is a greater reduction in the volume BOD and BOD_5. The quality of cleaning is decreased during low.

3. The pH concentration in the anaerobic ponds is lower than that in the incoming water, however, the water remains in a stable neutral environment without transforming to acidic or alkaline state.

4. The quality of water purification is not affected by changes in water temperature, as the methanotrophic bacteria residing in the anaerobic ponds can stabilize the sludge even in cold environments. Additionally, the sedimentation of suspended particles is not influenced by temperature.

AFTERWORD

The Black Sea, particularly its coastline, is a highly vulnerable area that demands constant attention from humans as every action they take, whether living or working in its waters, has a direct impact on the upper living layer of the sea. Thus, it is crucial to give special attention to the cleanliness of the Adjara coastline and its internal waters and wastewater content during monitoring studies. This area is of utmost importance as it serves as a strategic destination, port, and tourist attraction. Thus, to assess the current state of this vital ecosystem and take timely preventive measures, it is essential to conduct periodic and comprehensive monitoring of water quality and chemical composition, creating a data "bank".

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