

INFLUENCE OF QUARANTINE MEASURES AGAINST THE NEW CORONAVIRUS INFECTION COVID-19 ON THE STATE OF BLACK SEA COASTAL WATERS

Mikael S. Arakelov^{1*}, Dmitry A. Lipilin^{2,3}, Alina V. Dolgova-Shkhalakhova¹

¹Tuapse Branch of Russian State Hydrometeorological University, 4 Morskaya St., Tuapse, 352800, Russia

²Kuban State Agrarian University named after I.T. Trubilin, 13 Kalinina St., Krasnodar, 350044, Russia

³Kuban State University, 149 Stavropolskaya St., Krasnodar, 350040, Russia

*Corresponding author: m.arakelov@rshu.ru

Received: July 31st, 2021 / Accepted: November 9th, 2021 / Published: December 31st, 2021

<https://doi.org/10.24057/2071-9388-2021-089>

ABSTRACT. The Black Sea is one of the main recreational facilities in Russia subject to a high annual anthropogenic stress. Anthropogenic activity led to high coastal sea waters pollution, eutrophy, and endangered the sea's self-purification capabilities. The total quarantine introduced on the Black Sea coast of the Krasnodar territory associated with the new coronavirus infection COVID-19 pandemic led to a decrease in anthropogenic pressure on coastal ecosystems and provided a unique opportunity to trace the dynamics of the most important hydrochemical indicators of coastal waters in the Tuapse district. The study aimed to characterize the impact of quarantine measures against the coronavirus on the state of coastal waters in the eastern part of the Russian Black Sea. For this, we identified and characterized the hydrochemical indicators and determined the effect of quarantine measures on their dynamics. The study used the standardized methods. The results obtained showed that a decrease in the recreational stress led to a proportional decrease in the pollutants supply to coastal sea waters; with the recreational stress resumption the concentrations of mobile pollutants tended to increase; a proportional relationship was established between biochemical oxygen demand (BOD_5) and the ammonium nitrogen (NH_{4+}) concentration; the nitrates' (NO_3) concentration, in the seawater did not depend on the recreational stress degree. In particular, a proportional increase in NH_{4+} concentration and BOD_5 in seawater was detected: in the third quarter of 2019 the concentration of NH_{4+} and BOD_5 amounted to 3.0 mg/dm³ and 8.5 mg/dm³, and 3.8 mg/dm³ and 7.5 mg/dm³ in the fourth quarter, respectively; in the 2020 samples, a decrease in the NH_{4+} concentration to 0.8 mg/dm³ in the third and to 1.2 mg/dm³ in the fourth quarter led to a proportional decrease in BOD_5 4.5 mg/dm³ and 3.9 mg/dm³, respectively. Thus, it was shown that the quarantine measures were shown to have a positive effect on the processes of self-purification of coastal sea waters in recreational zones.

KEYWORDS: COVID-19, quarantine restrictions, sea waters' hydrochemical indicators, pollutants concentration, recreational areas, recreational stress, seawater's self-purification capabilities

CITATION: Mikael S. Arakelov, Dmitry A. Lipilin, Alina V. Dolgova-Shkhalakhova (2021). Influence Of Quarantine Measures Against The New Coronavirus Infection Covid-19 On The State Of Black Sea Coastal Waters. Geography, Environment, Sustainability, Vol.14, No 4, p. 199-204 <https://doi.org/10.24057/2071-9388-2021-089>

ACKNOWLEDGEMENTS: The authors are grateful to Yulia A. Titova, leading researcher in microbiological control laboratory at All-Russian Research Institute of Plant Protection (FSBSE VIZR), PhD in biology, for her invaluable editorial assistance in research styling.

Conflict of interests: The authors reported no potential conflict of interest.

INTRODUCTION

Currently, entering biological and chemical polluting components, including their derivatives, into the general circulation of substances threatens the self-purification capabilities of many water areas. This is due to an increase in the technogenic and anthropogenic recreational stress on the coast, which significantly outstrips the rate of biodestructors increase and distribution (Volkova et al. 2016; Gura et al. 2020). The greatest damage to the Black Sea is caused by pollution of rivers flowing into it. These rivers contain sewage and rainwater, petroleum products, cement dust, and chemicals' residues used in construction (Gogoberidze 2010; Matishov et al. 2015; Aleynikova et al.

2019). Nitrogen and phosphorus compounds enter the river runoff from household and industrial sources with fertilizers and detergents (Kosyan and Krylenko 2014, 2019). The coastal recreational area is polluted by accidental petroleum products spills occurring in the open part of the water area (Temirov et al. 2019; Antipceva et al. 2019).

Constant monitoring of the Black Sea water area state in the coastal zone conducted at the stations of the Federal Service for Hydrometeorology and Monitoring of the Environment State (Rosgidromet) (Chasovnikov et al. 2019) makes it possible to reveal some hydrochemical markers' indicating the role of the state of seawater and its self-purification capabilities in starting these processes and their dynamics. The stations are located in coastal areas

with a maximum anthropogenic stress. They collect and analyze operational information on the pollution sources in the sea area and river mouths and assess the dynamics of hydrochemical and other parameters both throughout the year and over a long period. The Rosgidromet stations monitor the entire Russian Federation Black Sea coastal area and the largest estuaries on the coast, where industrial and domestic wastewater flows and from where it spreads (Krylenko et al. 2010; Zavyalov et al. 2014; Kostyleva 2015). The main quality indicators of the Black Sea coastal waters include the content of phosphates, nitrates, silicon and iron compounds, ammonium nitrogen, dissolved mercury, petroleum products, and synthetic surfactants (Korshenko 2016; Sergin et al. 2018). Exceeding the maximum concentration limit (MCL) for the above products (established in accordance with the standards of the Interstate Council for Standardization, Metrology, and Certification (ISC) and International Standardization Organization (ISO)), along with changing oxygen concentration in the surface water, cause fluctuations in number of disjunctive organisms and their activity, intensity of the organic substances formation and decomposition processes and, as a consequence, a decrease in the seawater's self-purification capabilities (Mironov et al. 1975; Korshenko 2020).

A decrease in the technogenic and anthropogenic recreational stress should maintain the main MCL indicators for the Black Sea coastal part within acceptable limits and contribute to restoration and acceleration of the seawater's self-purification capabilities (Arakelov et al. 2019). The pandemic of the new coronavirus infection COVID-19, which began at the end of 2019, has become one of the most important factors on a planetary scale, which had an inhibitory effect on the numerous sectors of global economy. The infection forced the people in the whole world to change their way of life. Many countries closed their borders and enterprises, transport traffic dropped sharply, people were called on self-isolation in their homes. Such a change in people's way of life and entire states influenced all life spheres on our planet, changed the environment. Russia was no exception, including the Krasnodar territory, which closed its borders and recreational areas on the coast of the Black Sea on March 31, 2020. Since the Black Sea is one of the main recreational facilities in Russia, the pandemic and the associated restrictive measures had a particularly strong negative impact on the resort and recreational industry state in the region. But in natural and ecological terms, this decreased anthropogenic pressure on coastal ecosystems, in particular, on the Black Sea coastal water area (RuNews24.ru). The introduced total quarantine on the Black Sea coast of the Krasnodar territory lasting from April to July 15, 2020 provided a unique opportunity to trace the hydrochemical indicators dynamics of coastal waters in the Tuapse district.

The research aim was to characterize the impact of quarantine measures against the coronavirus infection on the state dynamics of coastal waters in the Russian Black Sea eastern part within the Krasnodar territory's coast (the case of coastal waters in the Tuapse district). For this, we determined the concentrations of the most important hydrochemical indicators and assessed the impact of quarantine measures on their dynamics.

MATERIALS AND METHODS

The work was performed in the analytical chemical laboratory for environmental monitoring at the Affiliated Branch of the Russian State Hydrometeorological

University (RSU). Analysis of seawater samples and hydrochemical surveys were conducted on a quarterly basis according to the Standards of the Interstate Council for Standardization, Metrology, and Certification (ISC) and International Organization for Standardization (ISO); state standards of the Russian Federation; Management Directives (MD) and Federal Environmental Regulations (FER) of the Russian Federation Ministry for Environment Protection and Natural Resources, Russian Federation State Committee for Environment Protection (Arakelov et al. 2018). Water samples were taken directly in the recreational coastal areas confined to river mouths in the study areas. Hydrochemical indicators did not exceed the maximum concentration limit (MCL) (Korshenko 2020). In 2020, the hydrochemical indicators analysis could be conducted in the Tuapse region only due to the quarantine restrictions – the other Black Sea coastal waters monitoring points did not function.

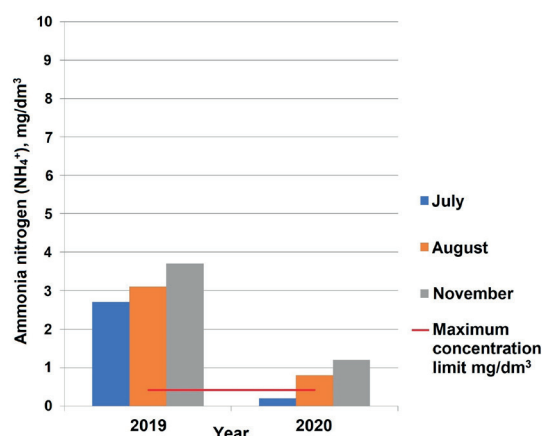
The indicators were analyzed according to ISO 31861–2012: Water. General requirements for sampling and included biological oxygen demand (BOD_5); contents of ammonium nitrogen (NH_4^+), total iron (Fe_{3+}), suspended substances, nitrates (NO_3^-), petroleum hydrocarbons, and synthetic surfactants (Akhsalba and Marandidi 2021). In the work, we used the following methods: gravimetric method for determining suspended substances and total content impurities in water and gravimetric method for measuring their mass concentration (MD 52.24.468–2005), jar method for estimating biochemical oxygen demand (BOD_5) in waters (MD 52.24.420–2006) (Tserenova and Muzalevsky 2015), photometric method for measuring mass concentration of ammonium nitrogen (NH_4^+) in sea waters (MD 52.10.772–2013) (Akhsalba and Ekba 2017), photometric method for measuring indophenol blue NO_3^- , quantitative chemical analysis of waters (ER F 14.1:2.4–95), photometric method for measuring mass concentration of nitrate ions in natural and waste water with salicylic acid and mass concentration of total iron (Fe_{3+}) and 1.10-phenanthroline in waters (MD 52.24.358–2006), extraction-photometric method for measuring mass concentration of synthetic surfactants and anion synthetic surfactants in water (MD 52.24.368–2006), and method for detecting them (LEKI SS2107 spectrophotometer, Republic of Korea), quantitative chemical analysis of waters and fluorometric method for measuring mass concentration of petroleum products in natural, drinking, and waste waters (ER F 14.1:2.4.128–98), and fluorophotometric method for estimating petroleum hydrocarbons content (FLUORAT 02, LUMEX, Russia) (Akhsalba 2018).

RESULTS

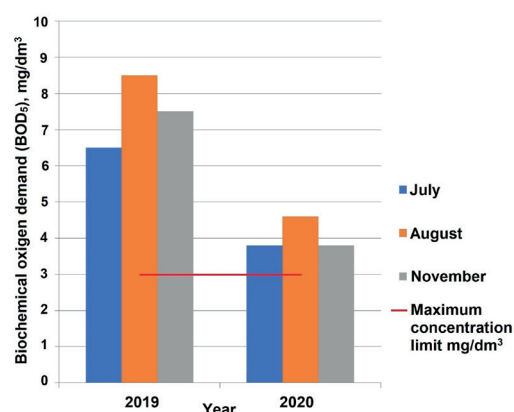
Fig. 1–4 show the assessment of the correspondence of the hydrochemical indicators of the seawater quality to their MCL.

A decrease in the recreational press in the research period of 2020 led to a reduction in the intake of pollutants into coastal sea waters – for all the estimated indicators, the concentrations approached the MCL values. The content of the petroleum derivatives, nitrates (NO_3^-), and suspended solids indicated a decrease in concentrations to a level below the MCL (Fig. 1–4).

Quarantine restrictions imposed on July 15, 2020 and the recreational stress resumption on the coast increased the concentrations of the most mobile pollutants in seawater: petroleum derivatives and ammonium nitrogen (NH_4^+) (Fig. 1a, 2a).



(A)



(B)

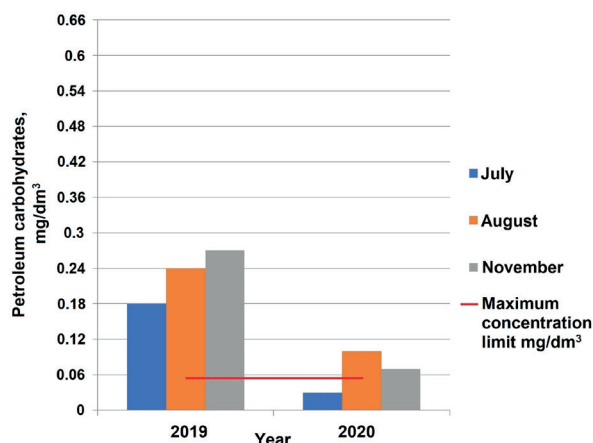
Fig. 1. Concentration dynamics of ammonium nitrogen (NH_4^+) (a) and biochemical oxygen demand (BOD_5) (b) in seawater during periods of medium, minimum, and renewed recreational stress on the Black Sea coastal waters in the Tuapse district of the Krasnodar territory

We revealed a proportional increase in NH_4^+ concentration and BOD_5 in seawater: in the third quarter of 2019 the concentration of ammonia nitrogen and BOD_5 amounted to 3.0 mg/dm^3 and 8.5 mg/dm^3 , and 3.8 mg/dm^3 and 7.5 mg/dm^3 in the fourth quarter, respectively; in the 2020 samples, a decrease in the NH_4^+ concentration to 0.8 mg/dm^3 in the third and to 1.2 mg/dm^3 in the fourth quarter led to a proportional decrease in BOD_5 up to 4.5 mg/dm^3 and 3.9 mg/dm^3 , respectively (Fig. 1).

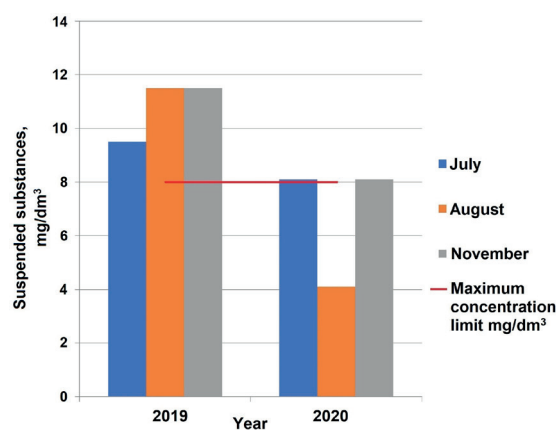
The amount of petroleum derivatives and suspended substances entering the seawater depended on the

recreational stress onto the coast – imposition of quarantine measures coincided with a sharp decrease in the concentrations of the both indicators below the MCL: to 0.03 mg/dm^3 in July 2020 for petroleum derivatives and 4 mg/dm^3 in August 2020 for suspended substances (Fig. 2).

A similar trend was noted in the total iron (Fe_{3+}) and synthetic surfactants concentrations' dynamics: with a decrease in the recreational stress on the coast due to imposing quarantine measures, the above substances concentrations decreased by 2–5 and 2–9 times, respectively (Fig. 3).

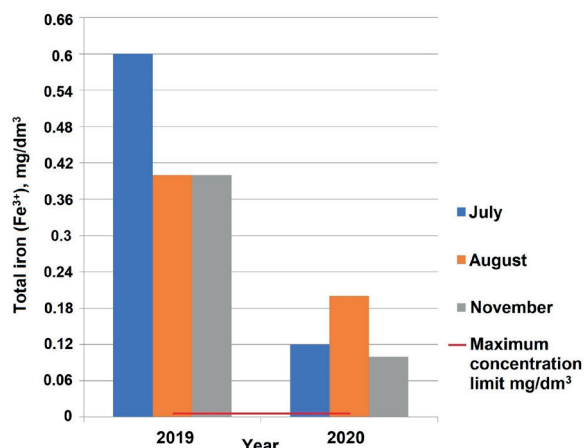


(A)

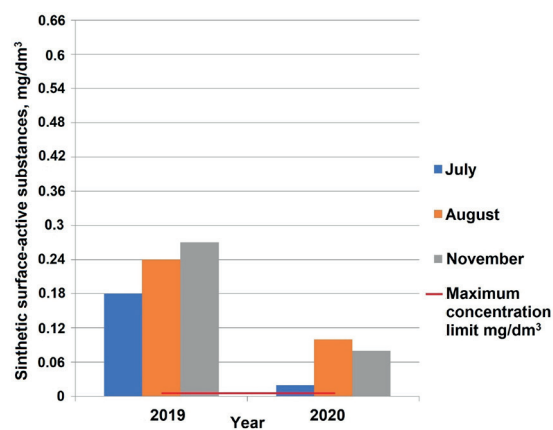


(B)

Fig. 2. Concentrations dynamics of petroleum products (a) and suspended solids (b) in seawater during periods of medium, minimum, and renewed recreational stress on the Black Sea coastal waters in the Tuapse district of the Krasnodar territory



(A)



(B)

Fig. 3. Concentrations dynamics of total iron (Fe_{3+}) (a) and synthetic surfactants (b) in seawater during periods of medium, minimum, and renewed recreational stress on the Black Sea coastal waters in the Tuapse district of the Krasnodar territory

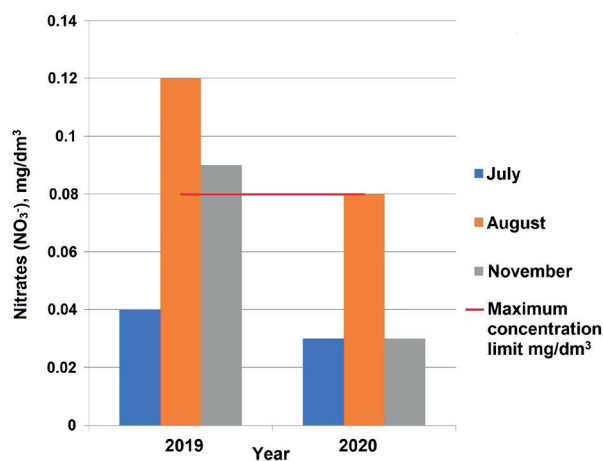


Fig. 4. Concentrations dynamics of nitrates (NO_3^-) in seawater during periods of medium, minimum, and renewed recreational stress on the Black Sea coastal waters in the Tuapse district of the Krasnodar territory

In contrast to the abovementioned hydrochemical indicators, the quarantine measures did not have such a significant impact to the nitrates (NO_3^-), although there is a tendency to decrease it (Fig. 4).

DISCUSSION

The seawater's self-purification capabilities is an important indicator of its state sustainability. Identifying the factors that determine such a state and its dynamics makes it possible to assess the Black Sea coastal water area self-purification capabilities (Ostroumova 2008; Baskakova et al. 2012). The hydrochemical indicators investigated during the periods of maximum, minimum, and renewed recreational stress of the Black Sea coastal waters in the Tuapse district of the Krasnodar territory revealed tendencies in the biodegradants development from eutrophy ($\text{BOD}_5 = 3 \text{ MCL}$) to restoring seawater's self-purification capabilities ($\text{BOD}_5 = \text{MCL}$). Establishing a proportional relationship between biochemical oxygen demand (BOD_5) and the ammonium nitrogen (NH_4^+) mobile forms concentration revealed the indicator function of these jointly considered parameters in assessing the possibilities of seawater's self-purification capabilities and the risks of developing its eutrophy (Dolgova-Shkhalakhova et al. 2020). We established a positive effect of quarantine measures on the sea coast state, since compared to the hydrochemical indicators of the most unfavourable 2019 year, the ecological state of the Black Sea coastal waters in the Tuapse region has improved (Gitsba and Ekba 2019; Dolgova-Shkhalakhova et al. 2020). We established that

the coastal recreational stress contributes to the seawater pollution with petroleum products. Despite the fact that the petroleum refineries in the Tuapse city worked at full capacity during periods of medium, maximum, minimum, and renewed recreational stress, imposition of the quarantine measures coincided with a sharp drop in the petroleum derivatives concentration in the test samples. When the quarantine measures were cancelled, the petroleum derivatives began to increase (Temirov et al. 2019; Arakelov et al. 2020).

CONCLUSIONS

Based on the results of the hydrochemical analysis conducted in 2020 and their comparison with the results of 2019, it was established that:

1. a decrease in the recreational stress led to a proportional decrease in the pollutants supply to coastal sea waters, which concentration reached the MCL level and below;
2. with the recreational stress resumption on the coast, the concentrations of the most mobile polluting components in seawater (petroleum derivatives and ammonium nitrogen) tended to increase;
3. a proportional relationship has been established between biochemical oxygen demand (BOD_5) and the ammonium nitrogen (NH_4^+) mobile forms concentration;
4. the amount of petroleum derivatives and suspended solids entering the seawater is proportional to the recreational stress on the coast;
5. the nitrates' (NO_3^-) concentration in seawater does not depend on the recreational stress on the coast. ■

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