MARINE SCIENCE AND TECHNOLOGY BULLETIN

Volume 13 - Issue 2 - YEAR 2024

e-ISSN: 2147-9666

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MARINE SCIENCE AND TECHNOLOGY BULLETIN

2024 • VOLUME: 13 • ISSUE: 2

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To achieve open access to scholarly journal literature, we recommend two complementary strategies.

I. Self-Archiving: First, scholars need the tools and assistance to deposit their refereed journal articles in open electronic archives, a practice commonly called, self-archiving. When these archives conform to standards created by the Open Archives Initiative, then search engines and other tools can treat the separate archives as one. Users then need not know which archives exist or where they are located in order to find and make use of their contents.
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Open access to peer-reviewed journal literature is the goal. Self-archiving (I.) and a new generation of open-access journals (II.) are the ways to attain this goal. They are not only direct and effective means to this end, they are within the reach of scholars themselves, immediately, and need not wait on changes brought about by markets or legislation. While we endorse the two strategies just outlined, we also encourage experimentation with further ways to make the transition from the present methods of dissemination to open access. Flexibility, experimentation, and adaptation to local circumstances are the best ways to assure that progress in diverse settings will be rapid, secure, and long-lived.
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2. Pre-Evaluation Process

In the pre-evaluation process, the field editors examine the studies, introduction and literature, methods, findings, results, evaluation and discussion sections in detail in terms of journal publication policies, scope and authenticity of study. Study which is not suitable as a result of this examination is returned to the author with the field editor's evaluation report within four weeks at the latest. The studies which are suitable for the journal are passed to the referee process.

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4. Evaluation and discussion: The evaluation report includes the opinion on the subject based on findings, relevance to research questions and hypotheses, generalizability and applicability.

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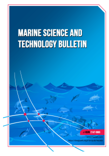
Mar. Sci. Tech. Bull. (2024) 13(2): 111-117
e–ISSN: 2147–9666
info@masteb.com

dergipark.org.tr/en/pub/masteb
www.masteb.com
DOI: 10.33714/masteb.1412927



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RESEARCH ARTICLE

Macroelement and microelement compositions in the liver of smooth-hound *Mustelus mustelus* in fall and spring from Iskenderun Bay, Northeastern Mediterranean Sea

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ARTICLE INFO

Article History:
Received: 01.01.2024
Received in revised form: 09.04.2024
Accepted: 14.05.2024
Available online: 27.05.2024

Keywords:
Common shark
Wet extraction method
Cartilaginous fish
Elements
Mustelus mustelus

ABSTRACT

The shark is an important cartilaginous fish species in the Northeastern Mediterranean and has occupied a wide range of areas. They are landed for different kinds of reasons but mostly as by catch. Sharks have a great proportion of livers that are generally not used. The livers may have potential usage for different materials e.g., fish meal, food ingredients, and fish oil materials. Therefore, they should be used, not wasted. Determining its macro element and microelement composition could be beneficial for any raw material. According to this current study's data, Cd and Pb levels were detected only in Fall. The Cr levels in the livers were not detected all year long. The amounts of the Cu, Mn, and Zn in the livers of common sharks all year long did not exceed 1 mg/kg, 1 mg/kg, and 2.4 mg/kg respectively. The livers contained high levels of Fe which differed from season to season. The difference in Fe amounts was found to be statistically significant between seasons (P>0.05). Even though changes were observed in the levels of microelements in the livers of common sharks in this study, there were no statistically significant changes except for Zn and Fe. There should be more testing to support the result suggested. Results of this study showed that the predominant macro minerals were Na and P for sharks in fall and spring (3968 and 3710 mg/kg, respectively throughout the year).

Please cite this paper as follows:

Özyılmaz, A., Şimşek, E., Demirci, S., & Demirci, A. (2024). Macroelement and microelement compositions in the liver of smooth-hound *Mustelus mustelus* in fall and spring from Iskenderun Bay, Northeastern Mediterranean Sea. *Marine Science and Technology Bulletin*, *13*(2), 111-117. https://doi.org/10.33714/masteb.1412927

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Introduction

Mustelus mustelus (Linnaeus, 1758) is one of the members of the class Chondrichthyes, which includes fish that have skeletons made of cartilage. Sharks are one of the two subclasses of Elasmobranchii e.g., skates and rays. Elasmobranch fish are generally bycatch fish and have larger livers (Lamas & Massa, 2017, 2019; Yığın et al., 2019; Ayas et al., 2019; Gupta et al., 2020; Pagliarini et al., 2020; Kumar et al., 2021; Özyılmaz & Öksüz, 2021; Spada, 2021; Fordham et al., 2022; Yogi et al., 2023; Alvarez et al., 2023). Studies showed that livers have a great amount of crude lipid capacity (Özyılmaz & Öksüz, 2015; Quero-Jiménez et al., 2020; Pagliarini et al., 2020)

Some researchers pointed out in previous reporting that livers of cartilaginous and bycatch fish can be considered as raw materials which can turn into beneficial materials (Kebir et al., 2007; Néchet et al., 2007; Özyılmaz & Öksüz, 2015; Özyılmaz, 2016a; Ayas et al., 2019; Yığın et al., 2019). The materials should be checked for different aspects of their biochemical features. Especially, the lipid they have considered as beneficial for health owing to their fatty acids. Health-promoted fatty acids have many different positive health effects (Šimat et al., 2015; Bagge et al., 2017). However, the raw materials should be safe regarding their nutritional aspects such as heavy metals, microelements, and macro elements.

Even though there are few studies conducted on these fish species (Gökçe et al., 2004; Özyilmaz, 2016b; Küçükgülmez et al., 2018; Šimat et al., 2020), there should be more studies needed in this field. The aim of the study is to search the macro elements and microelements content of the shark to see if it is safe to use them as possible raw materials for people or animals. From this point of view, knowing the macro and micro elements of the liver of the shark biannually may give an idea of whether it is suitable to use as raw materials.

Material and Methods

Study Area and Sample Collection

Sharks (*Mustelus mustelus*, Linnaeus 1758) (n=18 for each season) were caught in a trawling operation in fall and spring in Iskenderun Bay (Northeastern Mediterranean Sea, Türkiye, fall 2010 and spring 2011). Iskenderun Bay is a main sea area in the Northeast Mediterranean, where port management, maritime traffic, industrial facilities, and fishery activities are intense (Demirhan et al., 2020; Yılmaz et al., 2022). A map of the study area is shown in Figure 1. The livers of the fish were taken out and stored at -20°C for the element analysis.

Figure 1. Map of the study area

Extraction and Determination of Trace Elements

In this study, the liver samples were subjected to the wet digestion method. The procedure was performed according to AOAC Method 975.03 with a few minor modifications. The samples (approximately 1 g) were weighed and a total of 3 mL of 60% perchloric acid (Merck, Darmstadt, Germany) was added to the samples in a fume hood. The liver samples were incubated until the dense gas output decreased. This took a while because liver samples contained a high amount of oil. After the gas dense was gone, a total of 7 mL of 65% HNO_3 (Merck, Darmstadt, Germany) was added samples to complete digestion. The next step was to heat the samples on a hot plate for at least 8 hours. The samples were allowed to cool down. The digested materials were filtered through a 15 mL volumetric flask, using ash-free filter paper, and made up to 15 mL with ultra-pure water.

Four macro elements and seven microelements were determined for this study. Calibration curves for each of the individual elements were prepared from ICP Multi-element stocks. The determinations of the micro and macro elements were carried out by using ICP-AES (Inductively Coupled Plasma- Atomic Emission Spectrometry, Varian Model-Liberty series II) in Mustafa Kemal University, Natural Sciences Research and Application Center. ICP multi-element stocks were used for the measurement of elements. Wavelengths used for calcium (Ca, 396.847, λ (nanometer)), magnesium (Mg, 285.213), sodium (Na, 588.995), phosphorus (P, 213.618), cadmium (Cd, 228.802), lead (Pb, 220.353 λ), chromium (Cr, 267.716 λ), copper (Cu, 324.754 λ), iron (Fe, 259.940 λ), manganese (Mn, 257.610 λ), and Zn (zinc, 213.856 λ).

Statistical Analysis

Statistical analysis was performed with SPSS (22.0). Significance was established at $P<0.05$. The data of this study regarding seasons were subjected to a one-way analysis of variance (ANOVA), and a mean comparison was carried out by using the Tukey test. Normality and homogeneity were tested by using Kolmogorov–Smirnov and Levene's tests, respectively.

Results

A total of three heavy metals [cadmium (Cd), chromium (Cr), and lead (Pb)], and eight minerals [four macros; Mg (magnesium), P (phosphorus), Ca (calcium), K (potassium), and four micros; Mn (manganese), Cu (copper), Fe (iron), and Zn (zinc)] were seasonally investigated in shark livers. The levels of heavy metals in the livers of the sharks are shown in Table 1. The levels of the Cd, Pb, and Cr were detected under detection limit or no heavy metals were detected in spring in shark livers. However, the Cd and Pb were detected in fall.

Additionally, the levels of macro minerals in the livers of the sharks are shown in Table 2. Results of this study showed that the predominant macro elements were Na and P all year. The levels of Na and P for sharks throughout the year in the fall and spring were calculated to be 3968 and 3710 mg/kg, respectively. As can be seen from the table, the levels of P and Na, the major macro minerals, changed throughout the year, and the changes were statistically significant ($P<0.05$). The changes in the levels of Mg were also found to be statistically significant ($P<0.05$). The levels of Mg, Na, and P were higher in the spring than they were in the fall, except for the levels of Ca, which were higher in the fall.

The levels of micro minerals in the livers of the sharks are presented in Table 3. The highest macro mineral was measured to be Fe in the livers of the sharks in spring and fall. There were statistically significant changes between seasons regarding the amounts of the Fe ($P<0.05$). The levels of the Zn in livers of the sharks in the fall were found to be higher than those of Zn in the spring ($P<0.05$).

Table 1. The levels of heavy metals in livers of the sharks (mg/kg, wet weight)

Micro Elements	**Seasons**		
	Spring	***Fall***	***In a year***
Cd	0.000±0.000[a]	0.158±0.235[a]	0.079±0.172
Pb	0.000±0.000[a]	0.016±0.028[a]	0.008±0.020
Cr	0.000±0.000[a]	0.000±0.000[a]	0.000±0.000

Note: Values were presented as mean SD (n=3). [a,b] Values within the same row with different superscripts diverge significantly at $P<0.05$.

Table 2. The levels of macro minerals in livers of the sharks (mg/kg, wet weight)

Seasons	**Macro Elements**			
	Ca	***Mg***	***Na***	***P***
Fall	321.73±34.32[a]	345.61±20.82[a]	3533.95±106.49[a]	3051.04±155.66[a]
Spring	155.47±61.65[a]	471.07±171.71[b]	403.88±1427.34[b]	4370.52±1949.02[b]
in a year	238.60±101.41	408.34±129.18	3968.92±1022.98	3710.78±1432.30

Note: Values were presented as mean SD (n=3). [a,b] Values within the same column with different superscripts diverge significantly at $P<0.05$.

Table 3. The levels of micro minerals in livers of the sharks (mg/kg, wet weight)

Micro Elements	**Seasons**		
	Spring	***Fall***	***In a year***
Fe	126.629±99.770[a]	459.399±43.144[b]	293.014±194.799
Zn	1.830±0.161[a]	2.642±0.261[b]	2.236±0.485
Mn	0.149±0.081[a]	0.122±0.062[a]	0.135±0.066
Cu	0.731±0.063[a]	0.626±0.050[a]	0.679±0.076

Note: n=3 for the chemical analysis (Spring n=3; Fall n=3). [a,b] Values within the same row with different superscripts diverge significantly at $P<0.05$.

Discussion

The Cd and Pb in shark livers did not exist or existed under detection limits in the spring. This is a good sign that the fish livers are supposed to be safe for possible usage as raw materials based on the measured heavy metals amounts. They have a certain amount of Cd and Pb in shark livers in the fall. They should be checked before any possible usage. Because there are certain limits for specific heavy metals in foods to decide whether they are safe for consumption.

Özyılmaz & Öksüz (2015) investigated the liver oil of six different cartilaginous fish species including two different shark species and found out the levels of Cd and Pb in the range of 0.02-0.07 mg/kg and 0.15-0.90 mg/kg, respectively. Özyılmaz (2016a) investigated livers of thornback ray in two different regions for males and females and measured their Cd and Pb levels to be in the range of 0 to 0.5 mg/kg in wet weight. The levels of Cd and Pb in shark livers in the fall and spring in this current study are comparable to previous studies.

Cr in the livers of the sharks did not appear throughout the year in this study. Ayas et al. (2019) searched four ray species (*Dasyatis pastinaca, Raja radula, Raja clavata* and *Torpedo marmorata*) caught from Mersin Bay in the Northeastern Mediterranean Sea and found out the Cr levels in muscle and liver in higher than detection limits, which is also higher than those in this study. The levels of Cd and Pb in shark livers in the fall in this current study is similar with previously reported study of Ayas et al. (2019). Having no or very low amounts of these heavy metals can be considered a good sign for a clean environment and safe raw materials.

The levels of Ca, Mg, Na, and P in the livers of the sharks in this study showed that the livers were rich in macro minerals. Ayas et al. (2019) released the data showing that ray species (*D. pastinaca, R. radula, R. clavata* and *T. marmorata*) which are cartilaginous fish species also rich in macro minerals. On the other hand, the amounts of the macro minerals in the liver of cartilaginous fish species have higher amounts of macro minerals than those of many bony fish e.g., bogue, European hake, live sharksucker, wild trout (Öksüz et al., 2010, 2011; Kayım et al., 2011; Ozyılmaz et al., 2017a, 2017b; Ozyılmaz & Miçooğulları, 2020).

The livers contained high levels of Fe, which differed from season to season. The difference in Fe amounts was found to be statistically significant between seasons ($P>0.05$). Iron is known as an important essential micro element which has very important tasks in the human system. One of them is to serve as a carrier of oxygen to tissues from the lungs by red blood cells. Taking enough Fe in diet is recommended to stay away from some health problems (Belitz & Grosch, 2001; Camara et al., 2005). according to the Turkish Standards Institution (TSI, 2000), adequate Fe amount should be less than 10 mg in a kg and exceeding that level of iron is not permitted.

On the other hand, marine systems have the potential possibilities to receive environmental nutrients, residues, pollutants, etc. all territorial activities find a way to reach water (Yilmaz et al., 2018). The lives in this water are quite affected by their environment (Yılmaz et al., 2017). The lives get their bodies needs in the environment mostly through their food chains. The cartilaginous fish used in this current study was a part of this environment. There were a lot of companies that ran their business (e.g., iron and steel facilities, oil pipeline facilities) and a very busy harbor around the environment where cartilaginous fish live. These factors may be part of the reason that the level of Fe is higher in our study.

The amounts of Cu, Mn, and Zn in the livers of common sharks changed throughout the year in this study. According to Ayas et al. (2019) four different ray species have levels of the micro minerals in the following order: Mn<Cu<Zn. This previously reported data regarding the amounts of the Mn, Zn, Cu is like this current study relating their existence in the liver of the shark investigated seasonally.

Conclusion

As a result, this study contains seasonal changes in shark livers heavy metals, macro and micro minerals that could be beneficial, especially for producers who seek good raw materials for their products (such as, fish oil supplements for humans and pets, fish feed, cosmetics, greases, caulking compounds, buffing agents, paints, industrial coatings, pharmaceutical purposes, lubricants, textile auxiliaries, water repellents, soaps, and candles), consumers who care about what they consume, and scholars who intend to study in this very particular area. Because these livers may have potential usage as raw materials if they are safe for any possible usage.

Compliance With Ethical Standards

Authors' Contributions

AO: Conceptualization, Investigation, Methodology, Data curation, Formal analysis, Writing - original draft, Writing-review and editing

EŞ: Investigation, Writing-review and editing

SD: Conceptualization, Investigation, Writing-review and editing

AD: Investigation, Writing-review and editing

All authors read and approved the final manuscript.

Conflict of Interest

The authors declare that there is no conflict of interest.

Ethical Approval

For this type of study, formal consent is not required. All applicable international, national, and/or institutional guidelines for the care and use of animals were followed.

Funding

Not applicable.

Data Availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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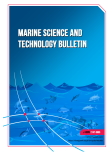
Mar. Sci. Tech. Bull. (2024) 13(2): 118-123
e–ISSN: 2147–9666
info@masteb.com

dergipark.org.tr/en/pub/masteb
www.masteb.com
DOI: 10.33714/masteb.1447530



Marine Science and Technology Bulletin

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RESEARCH ARTICLE

Oil spill modeling of the M/T STI Pimlico and M/V Celestyal Crystal accident on Çanakkale Strait

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ARTICLE INFO

Article History:
Received: 05.03.2024
Received in revised form: 26.04.2024
Accepted: 22.05.2024
Available online: 24.06.2024

Keywords:
ADIOS2
Çanakkale Strait
GNOME™
Modeling
Oil spill

ABSTRACT

Turkish Sea Area is the most important waterway because of its geographical position. According to 2022 statistics of strait passage, 9904 tanker vessels passed through the Strait of Çanakkale. This statistical value shows that the Strait of Çanakkale is at risk due to the tanker vessels' passage. On June 27, 2015, the Celestyal Crystal cruise ship and the STI Pimlico tanker ship collided in the Çanakkale Traffic Separation Scheme, approximately 0.7 nautical miles from the Gelibolu Lighthouse. STI Pimlico suffered an explosion in one of the port wing cargo tanks and listed 15° to port. There were no injuries in the incident, but it was reported that naphtha leaked from the ship into the sea. Directorate General of Coastal Safety teams responded to oil spillage immediately, the leak was taken under control before it spread too much. In this study, the pollution and spread that will occur in case the response of coastal safety teams is delayed has been estimated. The oil spill was determined according to time and place, taking into account the northerly wind direction and strength. Leak simulation was performed with the GNOME™ simulation program. Characteristic of cargo on STI Pimlico was taken from the ADIOS2 program. Results of the simulation showed that the spill reached the coast. 7 kilometers of the coast was polluted by an oil spill.

Please cite this paper as follows:

Taşlı, B. (2024). Oil spill modeling of the M/T STI Pimlico and M/V Celestyal Crystal accident on Çanakkale Strait. *Marine Science and Technology Bulletin*, *13*(2), 118-123. https://doi.org/10.33714/masteb.1447530

Introduction

Approximately more than 10 billion tons of liquid bulk cargo, container and solid cargo are transported annually worldwide by maritime transportation. (Walker et al., 2019). The rapid growth in global trade in recent years has led to an increase in the number, size and voyages of ships in the world fleet. (Branch, 2007). Maritime accidents generally occur in waterways such as canals where there are geographical

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difficulties and traffic density. (Chen et al., 2018; Luo & Shin, 2019).

The Turkish Straits System consists of the Sea of Marmara, Istanbul Strait (Bosporus) and Çanakkale Strait (Dardanelles). Turkish Straits System is one of the very complex and narrow waterways connecting the Black Sea to the Mediterranean. It is a known fact that the Turkish Straits are one of the most difficult and dangerous waterways for ships in the world with their traffic density. The Turkish Straits, which extend from the Black Sea to the Mediterranean, are 164 nautical miles (nm) long and have unique physical, geographical and oceanographic features in the world and the complex navigation conditions prevailing in the region. (Basar, 2010).

According to statistics 8653 tanker ships passed through the İstanbul Strait in 2022 and 9904 tanker ships passed through the Çanakkale Strait in the same year (Ministry of Transport and Infrastructure of the Republic of Türkiye, 2022). In the light of these data, it is concluded that the Turkish Straits are dangerous. A ship must use the straits to pass from the Black Sea to the Istanbul Strait, then continue through the Sea of Marmara and complete its passage to the Aegean Sea via the Çanakkale Strait. Ships passing the Çanakkale Strait make an average of 10 major route changes, and the largest route changes are made in the Nara Return point and Kilitbahir region (Tatlisuluoglu, 2008).

There was a total of 162 maritime accidents in the Çanakkale Strait between 2007 and 2018 (Bayazit et al., 2020). The Celestyal Crystal cruise ship and the STI Pimlico production ship collided at the Çanakkale traffic separation system, approximately 0.7 nautical miles from the Gallipoli Lighthouse, at around 01:26 (UTC+3) on June 27, 2015 (MSIU, Marine Safety Investigation Unit, 2016). Celestyal Crystal suffered extensive damage to her bow above the waterline. Two people were slightly injured. The ship was made ready for voyage with temporary repairs. STI Pimlico suffered damage to port side of her main deck, electrical systems and piping. STI Pimlico's hull plating was punctured above and below the waterline. One tank of the tanker STI Pimlico was punctured and listed 15° on its port side. No one was injured, but it was reported that naphtha leaked into the sea. (MSIU, 2016). General Directorate of Coastal Safety teams intervened quickly and stopped the leak before it spread too much.

Various studies have been carried out with GNOME oil spill simulation. The oil spill that occurred in Point Wells in 2003 was simulated and examined with the GNOME program (Duran et al., 2018). The oil spill incident that occurred in Kota Tinggi, Malaysia is modelled. According to the simulation results, it was determined that a very large coastline was affected (Balogun et al., 2021). Additionally, the impact of possible oil spill events was modeled with the GNOME program. The movement of a 10000-barrel oil spill that may occur on the North-West Coast of India was modeled and found that the spill possibly took 10 hours to reach the Gujarat coast and 15 hours to reach Maharashtra coast (Remyalekshmi & Hegde, 2013). According to the oil spill simulation results conducted on the Bohai Sea, it was determined where it would be beneficial to deploy oil spill response teams (Yu et al., 2016). The pollution caused by the Nassia and Independenta tanker accidents in the Çanakkale Strait was determined using the Oil Spill Simulator program (Usluer et al., 2022). In another study, 4 different scenarios were simulated in 4 areas determined in the Çanakkale Strait and it was determined that greater pollution than expected could occur (Usluer et al., 2020).

In this study, assuming that the delay in intervention to the oil spill and the distribution of 2200 metric tons of cargo of the ST Pimlico (one wing tank totally leaked into the sea) as it leaks the sea, according to the current weather and sea conditions, was determined with the Gnome Oil Spill Simulator. Thus, it is aimed to show how important it is to intervene early in oil spills and how great the consequences of delay will be.

Material and Methods

In the study, GNOME and ADIOS2 simulation programs were used to predict the oil spill. GNOME, developed by the National Oceanic and Atmospheric Administration (NOAA), was used to simulate the temporal and spatial distribution of oil (NOAA, 2001). This software uses wind, tide, and current values to calculate the movement of oil at the sea surface (Beegle-Krause, 1999).

ADIOS2 is an oil spill response program that helps oil pollution response teams and coordinating personnel make decisions about response methods. It integrates a memory of thousands of oils to predict how long the spilled oil product will remain in the sea and to help develop clean-up methods (Al-Mebayedh, 2014). The ADIOS2 oil memory was created in collaboration with many countries and compiled from many sources.

In this study, a scenario was created regarding the leak that occurred as a result of the collision between the M/V Celestyal Crystal and the M/T STI Pimlico in 2015. Information about the accident was taken from the accident report published by MSIU, affiliated with Transport Malta. The amount of leakage was not given in this report, so since STI Pimlico was damaged by the port side, the worst-case scenario was that one of the port tanks leaked into the sea. It means that approximately 2200 metric tons of cargo were leaked into the sea.

Results and Discussion

The Maltese-registered Celestyal Crystal (Figure 1) is a passenger/cruise vessel built in 1980 at Wartsila Ab, Turku, as an Ice Class 1A Ro-Ro1 ferry. She was converted to a cruise ship in 1992. The vessel has a gross tonnage (GT) of 25,611 and is classed by DNV GL (MSIU, 2016). Her length overall is 158.88 m and breadth extreme is 25.2 m.

Figure 1. M/V Celestyal Crystal

STI Pimlico is a chemical/products carrier, double hull, owned by Scorpio Ship Management SAM and managed by Scorpio Commercial Management of Monaco. The vessel was built by Hyundai Mipo Dockyard Co. Ltd., Korea in 2014 and is registered in Marshall Islands and classed by DNV GL (MSIU, 2016). Her DWT is 38,734, length overall is 184 m and her width is 27.4 m.

Weather conditions at the time of the accident was given in Table 1.

Table 1. Weather conditions at the time of the accident

Weather Condition	Status
Wind speed	Beaufort 2
Wind direction	Northeast
Barometric pressure	1012 MB
Sea	Smooth
Visibility	Clear
Current Drift	1,2 kts

According to Accident Report of MSIU, after 12 hours of collision wind speed was 4 Beaufort and the direction was Northeast, after 24 h of collision wind speed was 4 Beaufort and the direction was North, after 36 h of collision wind speed was 3/4 Beaufort and the direction was Northeast (MSIU, 2016).

M/T STI Pimlico was carrying 30,000 tons of naphtha (density (15°C): 0.64 g/cm^3; viscosity (15°C): 0.39 cSt; product type: solvent; flashpoint: > 38°). According to the scenario, it is assumed that 2200 tons of this leaked into the sea during the conflict.

These data were entered into the GNOME simulation program and simulations were run according to 3 hourly currents + hourly wind. Oil spilling situation after the occurrence was given in Table 2.

3 hours after the occurrence 121 mt naphtha leaked. The natural dispersion rate was %0.6, the beached rate was %5.4 and the floating rate was %94.

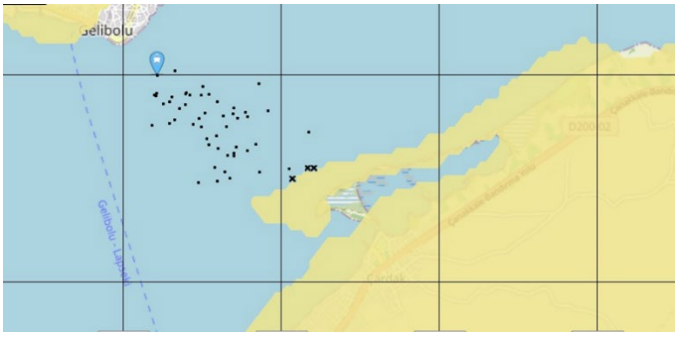

Figure 2. 3 hours after the occurrence

6 hours after the occurrence 244 mt naphtha leaked. The natural dispersion rate was %2.3, the beached rate was %56.4 and the floating rate was %41.3.

12 hours after the occurrence 488 mt naphtha leaked. The natural dispersion rate was %3.6, the sedimentation rate was %0.2, the beached rate was %82.3 and the floating rate was %13.9.

24 hours after the occurrence 977 mt naphtha leaked. The natural dispersion rate was %4.4, the sedimentation rate was %0.2, the beached rate was %82.6 and the floating rate was %12.8.

60 hours after the occurrence 2200 mt naphtha leaked. The natural dispersion rate was %6.0, the sedimentation rate was %0.3, the beached rate was %93.5 and the floating rate was %0.1.

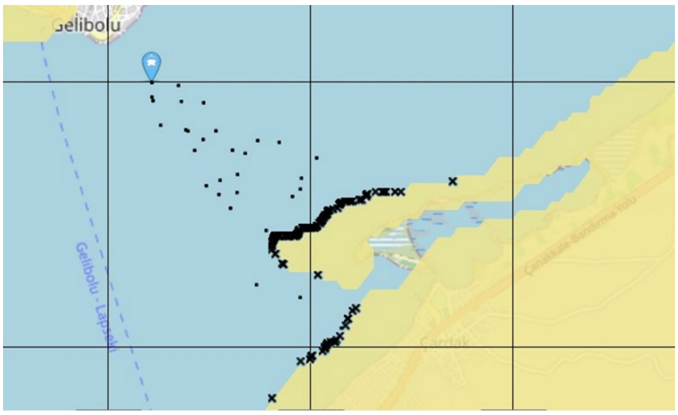

Figure 3. 6 hours after the occurrence

Table 2. Oil spilling situation after the occurrence

Time (hours later)	Amount released (mt)	Natural dispersion (%)	Sedimentation (%)	Beached (%)	Floating (%)
1	39.6	0	0	0	100
6	244	2.3	0	56.4	41.3
12	488	3.6	0.2	82.3	13.9
18	733	4.1	0.2	86.6	9
24	977	4.4	0.2	82.6	10
36	1465	6.6	0.4	85.9	7.1
42	1709	6.2	0.4	88.3	5.2
48	1954	6	0.3	90.3	3.4
60	2200	6	0.3	93.5	0.1

Note: Oil spilling duration was 60 hours. %93.5 of leaked cargo was beached and %6.1 of leakage was natural dispersion.

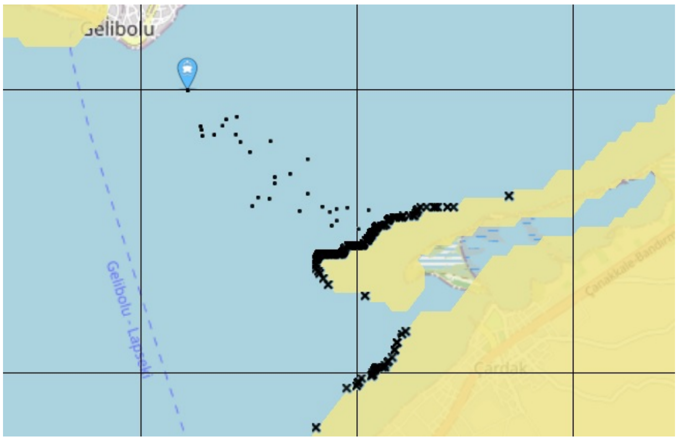

Figure 4. 12 hours after the occurrence

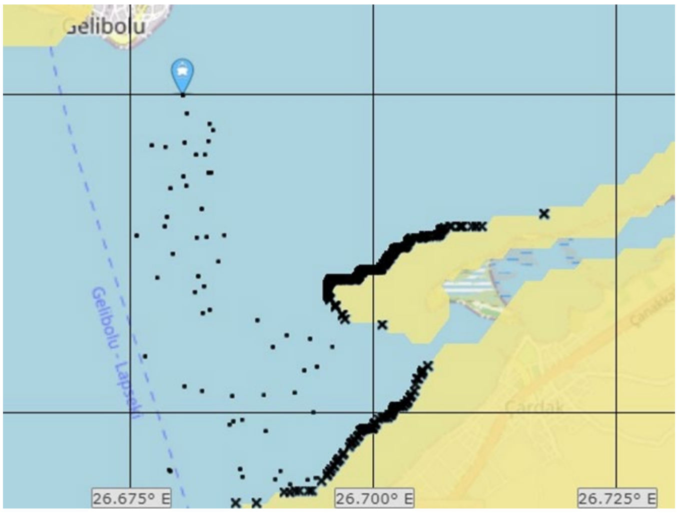

Figure 5. 24 hours after the occurrence

The biggest reason why the naphtha leaked from the ship as a result of the accident spread to such a great distance is that the Strait of Çanakkale has strong winds and currents. In the Independenta tanker accident that occurred in the Strait of Istanbul in 1979, approximately 30,000 tons of crude oil spilled into the sea. By entering the same parameters, the possibility of the Independenta accident occurring off the coast of Gallipoli was also tested in the simulation, and it was observed that the spillage polluted the coastline and sea surface for 22 km.

Figure 6. 60 hours after the occurrence

Conclusion

Sedimentation did not occur 6 hours after the incident, but approximately 66 metric tons of cargo collapsed to the seabed 9 hours later. This is a very dangerous situation for marine creatures. Naphtha contains heavy metal so all marine creatures on the seabed have been affected. The settled oil would have different negative effects on the benthic and pelagic marine life, and the case of cleaning these pollutants would be more time-consuming and expensive.

Oil spill reaches the coast at a high rate and pollution. Approximately 7 km of the coast was polluted by the oil spill. On this coast was a residential area and lots of people lived there. This pollution has been affected to human life.

Quick intervention after the accident occurred prevented the pollution from spreading over a large area. But to prevent such accidents from occurring, tankers and other ships must pass through the Çanakkale Strait in order and without encountering each other.

Compliance With Ethical Standards

Conflict of Interest

The author declares that there is no conflict of interest.

Ethical Approval

For this type of study, formal consent is not required.

Funding

Not applicable.

Data Availability

The data that support the findings of this study are available from the author upon reasonable request.

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Mar. Sci. Tech. Bull. (2024) 13(2): 124-134
e–ISSN: 2147–9666
info@masteb.com

dergipark.org.tr/en/pub/masteb
www.masteb.com
DOI: 10.33714/masteb.1466847

Marine Science and Technology Bulletin

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RESEARCH ARTICLE

The presentation of the risks that oil pollution poses to aquaculture

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ARTICLE INFO

Article History:
Received: 08.04.2024
Received in revised form: 31.05.2024
Accepted: 14.06.2024
Available online: 24.06.2024

Keywords:
Fish farm
Food security
Risk management
Marine pollution

ABSTRACT

Aquaculture has emerged as the most rapidly growing technology for food production on a global scale. The current growth trajectory of aquaculture production surpasses that of all other meat production types and is anticipated to persist in its ascent with the continuous expansion of the agriscience industry. The contribution of aquaculture to food security varies based on species and country, either directly through domestic consumption or indirectly through the stimulation of economic growth via exports. In Türkiye, the share of aquaculture in overall production has increased over the years and has become a significant contributor to the country's economic development through exports. Fish farms concentrated in the Eastern Black Sea and Southern Aegean regions also draw attention due to their proximity to sea areas with intense maritime activities. Potential marine pollution in these regions poses a serious risk to these economically important resources, making it crucial to predict the extent of this risk in advance and take preventive measures. This study aims to simulate, through a scenario, how a possible oil spill in the Southern Aegean region would spread in the sea, how quickly it would reach the fish farms in this region, and how long it would take to impact the fish population to a certain extent. The values derived from this simulation will shed light on intervention plans to be implemented by both local and central authorities, serving as exemplary models for formulating similar plans for all aquaculture resources.

Please cite this paper as follows:

Aşan, C. (2024). The presentation of the risks that oil pollution poses to aquaculture. *Marine Science and Technology Bulletin*, *13*(2), 124-134. https://doi.org/10.33714/masteb.1466847

Introduction

The escalating global population, advancements in technology, and the globalization of fisheries marketing have recently resulted in a significant increase in fishing capacity, which in turn has triggered overfishing pressures on natural resources by expanding fishing fleets in various regions worldwide (Watson et al., 2013). Consequently, since the late 1980s, this has led to the attainment of limits on aquatic product

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reserves, culminating in a decrease in the quantity of catch in the seas. In 2019, the proportion of fish stocks maintained at biologically sustainable levels diminished to 64.6%, marking a decline of 1.2% from 2017. The total output of global capture fisheries in 2020 amounted to 90.3 million tonnes, valued at an estimated USD 141 billion. This total includes 78.8 million tonnes harvested from marine environments and 11.5 million tonnes from freshwater sources, representing a decrease of 4.0% compared to the average yield of the preceding three years. Conversely, global aquaculture production reached an unprecedented level of 122.6 million tons in 2020, encompassing 87.5 million tons of aquatic organisms, which were valued at USD 264.8 billion (FAO, 2022).

According to scientific research, it is anticipated that investment in aquatic products will continue to expand in the coming years. This trend underscores the increasing significance of the world's oceans and inland waters with each passing day. While aquaculture is projected to become a sector with high potential in the future, the sustainability of this growth necessitates implementing environmental measures to protect water resources and ensure their planned utilization.

In Türkiye, as is the case globally, aquaculture is increasingly gaining importance and is experiencing an average annual growth rate of 8%. Over the last decade, total production from aquaculture has surged by 99%, while production through fishing has witnessed an average annual contraction of 2.3%. In 2012, aquatic product production through fishing amounted to 433,000 tons, and aquaculture accounted for 213,000 tons. By 2022, these figures had reversed, with fishing production at 335,000 tons trailing behind aquaculture's output of 515,000 tons (AEPDI, 2023). As of 2022, aquaculture production in Türkiye, accounting for 60.5% of total fisheries production, has predominantly occurred at sea (72%) with the remaining 28% taking place in inland waters. The most significant species cultivated include trout in inland waters, with a production volume of 145,649 tons, and at sea, sea bass and sea bream with productions of 156,602 tons and 152,469 tons, respectively (TUIK, 2023). The key provinces involved in marine aquaculture around Türkiye's coasts are illustrated in Figure 1.

In the marine aquaculture sector, 39% of production takes place in Muğla, with the entirety of this output comprised of sea bass and sea bream (TUIK, 2023).

In line with global trends, aquaculture in Türkiye significantly contributes to economic growth, with its proportion of the Gross Domestic Product (GDP) increasing steadily. This has heightened the sensitivity towards marine pollution, underscoring the need to safeguard this sector. The susceptibility of aquaculture farms to potential marine pollution can be mitigated with the aid of previously established contingency plans and preventive measures.

Figure 1. The major aquaculture regions around the Turkish seas (TUIK, 2023)

In the literature, the focus has predominantly been on the marine pollution generated by the aquaculture industry and its effects on ecological balance. However, Kayhan et al. (2009) examined the potential general health issues, stress, and consequent biological responses in aquatic organisms caused by the accumulation of toxic heavy metals. Tacon (2020) who has analyzed trends in global aquaculture and aquafeed production between 2000–2017 emphasized that future efforts in the aquaculture feed industry, supported by governmental initiatives, should prioritize the utilization of locally sourced, nonfood grade feed resources over the reliance on imported, potentially food-grade inputs. This approach is essential to guarantee the long-term economic viability and ecological sustainability of the aquaculture sector. Subasinghe et al. (2009) explored the role of aquaculture, predominantly driven by small-scale farmers, in promoting sustainable development, alleviating poverty, and enhancing global food security. Hu et al. (2020) provide a comprehensive summary of research advancements over the past two decades, focusing on four key areas: the acquisition and pre-processing of water quality factors, the prediction of water quality factors, the analysis of fish morphological characteristics, and the recognition of fish behavioral characteristics, as well as the mechanisms linking fish behavior to water quality factors. Cai et al. (2010) establish a conceptual model that identifies the links between various threats such as human activities, self-pollution, chemical misuse, and climate changes to the marine aquaculture ecosystem, highlighting these as significant risks. Döndü et al. (2024) emphasize the impact of thermal power plants and aquaculture on the mobility of heavy metals affecting marine life and aquaculture. Offering insights into the redox regulation of fish, Wang et al. (2024) addresses how environmental pollution endangers fish populations and the healthy development of marine aquaculture. By focusing on sustainable marine living resources, Ha (2024) discusses the sustainability of capture fisheries, shellfish aquaculture, and marine aquaculture. To investigate the harmful effects of pesticide pollution on aquaculture, Zhao et al. (2024) look into cypermethrin's comprehensive effects on the aquatic system. Carballeira Braña et al. (2021) delineate the primary ecological concerns associated with marine finfish aquaculture, detailing the interactions between aquaculture practices and environmental health, and underscores the adoption of sustainable methodologies in the sector. They emphasize the importance of rigorous environmental monitoring, strategic siting of aquaculture operations, and the minimization and repurposing of waste and chemicals, as fundamental measures to sustain and expand aquaculture production in an environmentally responsible manner. Green (2016) assesses the effects of conventional and biodegradable microplastics at different concentrations on aquatic ecosystems through outdoor mesocosm experiments that mimic semi-natural conditions. It focuses on whether these microplastics would impact the physiological functions and growth of European flat oysters, alter the diversity and density of macrofauna in oyster habitats, and change the biomass of benthic algae. Emenike et al. (2022) examine the sources, impacts, and remediation strategies for heavy metal pollution in aquaculture, based on literature from academic databases. It underscores the risk posed by enduring heavy metals such as mercury, lead, and cadmium, which build up in the food chain, threatening the viability of aquaculture. The paper explores the use of mitigation methods like adsorption, bio-sorption, and phytoremediation to tackle such contamination.

The purpose of this study is to simulate the impact of an oil spill in the Aegean Sea on aquaculture farms located in the southwestern region of Türkiye, with the intent to determine the time it takes for the pollution to reach these farms and to quantify the rates of fish loss over time as a consequence of this pollution. Considering the fish farms established in the seas surrounding Türkiye, the region around Muğla province stands out for having the highest share of production. Therefore, the sea area chosen as the basis for this study is the marine region located between Güvercinlik and Göltürkbükü in the Bodrum district of Muğla province, as indicated in Figure 2.

For this purpose, the Potential Incident Simulation, Evaluation, and Control System (PISCES-II), a decision support system, is employed to simulate the scenario. This simulation projects the spread of oil and establishes a timeline for their reach at Environmentally Sensitive Areas (ESA) which contain aquaculture sites, assesses the ensuing percentage of all died bions for each species as well as the current number of species bions for the given time. This research provides a framework that allows aquaculture farms, increasingly valuable economically, to develop emergency response plans for marine pollution. Consequently, each aquaculture region can create its contingency plan, tailored to the specific type of product and the dynamics of its marine area.

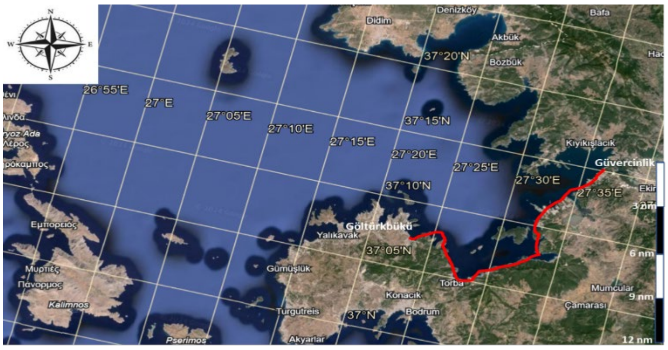

Figure 2. Fish farms region between Güvercinlik and Göltürkbükü (Google Earth, 2024)

Material and Methods

The study aims to reveal how long and to what extent the fish farms located on the coasts of Aydın province in the southeast of the Aegean Sea of Türkiye will be polluted in a possible marine pollution in the framework of a case scenario. For this purpose, the scenario, together with meteorological and oceanographic conditions, was loaded into PISCES-II, an oil spill simulation and decision support system. As a result of the study, it was revealed how the oil will spread within a time period of 60 hours from the beginning of the pollution, how long it will reach the fish production farms and at what rate it will cause fish losses. PISCES-II illustrates both the oil spill's scale and its consequences on fish populations, emphasizing the importance of precise and actionable findings. Given its comprehensive output capabilities, the PISCES-II simulator is ideally suited for this study's objectives. It models the spread of oil, its evaporation, dispersion, sedimentation, and interaction with coastal areas, alongside detailing the deployment of intervention resources like booms, skimmers, and dispersants. In evaluating oil spill models, while wind conditions are considered significant, they are secondary to surface currents, which are the primary determinants for accurate simulations. According to Fingas (2014), surface currents account for 97% of the spill's direction, compared to the wind's 3%. For this study, the winter season was chosen to simulate a worst-case scenario using the PISCES-II simulator, which incorporates both built-in surface current models and additional data from the Turkish State Meteorology Service, highlighting the critical role of morphological changes and currents in affected areas.

Average annual data for weather and seawater temperatures, along with wind conditions, and sea-surface current data, sourced from the Turkish State Meteorology Service (TSMS) and previous studies, were entered into the PISCES II simulator as foundational data. The research modeled the scenario where a 2,500 tons oil spill affected a fish farm that has one million sea bream fish, using these conditions as a basis for the simulation. The initial parameters for the simulation are detailed in Table 1.

Aquaculture and its Role in Global Seafood Production

Notwithstanding notable advancements, the global community is not on pace to eliminate hunger and malnutrition by the year 2030. The deterioration of ecosystems, escalating climate crisis, and the loss of biodiversity are exerting profound impacts on employment, economic stability, and the availability of food across the globe. This predicament highlights the critical necessity for a comprehensive overhaul of agrifood systems to ensure food security, improve nutritional outcomes, and facilitate access to cost-effective, healthy diets, all while preserving employment opportunities and environmental resources. In this context, aquatic foods emerge as pivotal for their contribution to food security and nutrition (FAO, 2022). Aquaculture production exhibits considerable heterogeneity, ranging from small-scale family operations to large-scale multinational enterprises, encompassing a spectrum from rudimentary extensive systems to sophisticated closed production systems, and covering a diverse array of species including algae, bivalves, crustaceans, and finfish. The socio-economic and environmental ramifications of aquaculture are contingent upon these varying factors (Asche et al., 2013; Anderson et al., 2017).

In 1970, the majority of seafood was procured from wild stocks, with aquaculture contributing merely 4% to the total agricultural yield. The late 1980s marked a pivotal shift as the plateauing of wild-fish harvesting signaled limited prospects for significant expansion, prompting a notable growth in aquaculture activities. The practice of aquaculture, which entails the cultivation of aquatic organisms including animals and plants, has since maintained its lead in aquatic food production. Presently, the total output from global aquaculture significantly outstrips that of global capture fisheries by a margin exceeding 100 million tons, a fact illustrated in Figure 3 (FAO, 2018, 2022).

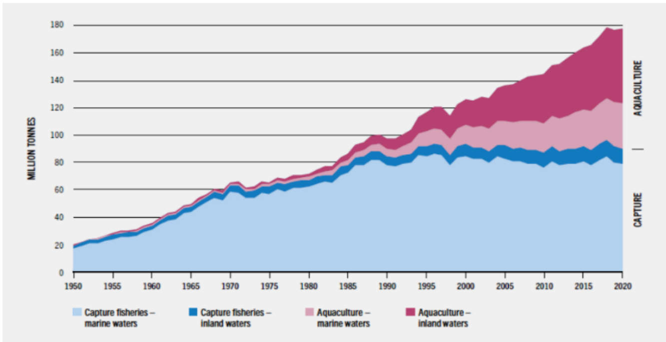

Figure 3. World capture fisheries and aquaculture production (FAO, 2022)

Aquaculture Status in Türkiye

In recent years in Türkiye, significant advancements have been made in aquaculture systems, necessitating the relocation of fish farms to open and deep waters. This shift has mandated the adoption of new techniques suitable for these conditions, leading to improvements that surpass global standards in cage sizes and structures, net, and feeding systems. The production of aquatic products in Türkiye is presented in Table 2, based on an annual basis.

Table 1. Initial settings of simulation (Gürün, 2014; Buyruk, 2019; TSMS, 2022)

Position	Oil type	Wind	Oil spill amount	Air temp.	Water temp.	Wave height	Water density	Name and amount of marine species
37°27′ N 027°03.6′ E	AMULIGAK Group III Viscosity: 15.7 cSt Density: 0.89 g/cm^3	N-NW 5 m/sec	Initial spill: 1000 m^3 Leak spill: 200 m^3/h	15°C	18°C	0.1 mt	1010 kg/m^3	1 million sea bream

Table 2. Aquaculture Statistics in Türkiye (tons) (TUIK, 2023)

Annuals	Capture	Aquaculture	Total
2012	432,442	212,410	644,852
2013	374,121	233,394	607,515
2014	302,212	235,133	537,345
2015	431,907	240,334	672,241
2016	335,320	253,395	588,715
2017	354,318	276,502	630,820
2018	314,094	314,537	628,631
2019	463,168	373,356	836,524
2020	364,400	421,411	785,811
2021	328,165	471,686	799,851
2022	335,003	514,805	849,808

In Türkiye, the production of aquatic products increased by 6% in 2022 compared to the previous year, reaching a total of 849,808 tons. The production from fishing increased by 2% in 2022 compared to the previous year, while aquaculture production saw a 9% increase (TUIK, 2023). The trend of decreasing product quantities from fishing and increasing product quantities from aquaculture indicates a correct orientation of production on a global scale.

Türkiye continues to maintain its position as a net exporter in the trade of aquatic products. In recent years, there has been a significant increase in Türkiye's exports of aquatic products, parallel to the advancements in aquaculture production and processing technologies. The foreign trade statistics of Türkiye's aquatic products, presented annually, are provided in Table 3.

Upon examining the export-import data, it is observed that in 2022, exports exceeded imports by 136,000 tons in quantity and 1.338 billion USD in value. The trade of aquatic products in Türkiye in 2022 showed the largest increase compared to the previous year, with exports growing by 5% and imports by 10%. The aquatic products exports, amounting to 1.651 billion USD in 2022, were distributed to 103 countries, 67% of which are member states of the European Union (AEPDI, 2023).

Ensuring the security of aquaculture against adverse effects is of vital importance for Türkiye, both in terms of food supply security and the increasing share in exports in foreign trade. The subsequent section presents a scenario of the potential impacts of ship-sourced oil pollution, which could pose a threat to sustainability, through a case scenario analysis.

The Effects of Oil Pollution on Marine Life

Marine research indicates the severe impact of oil pollution on seawater, sediment, and marine life. Particularly, polycyclic aromatic hydrocarbons (PAHs), from industrial waste, ship bilge water, and ship accidents, are widespread in marine areas and cause serious toxicity, including tissue buildup and physiological disruptions. Fish absorb heavy metals from aquatic environments mainly through their gills, body surface, and digestive tract. These metals lead to structural and functional disturbances at both cellular and molecular levels in aquatic life, along with a heightened occurrence of DNA damage. (Levesque et al., 2002). As illustrated in Figure 4, during the primary response phase following stress in aquatic organisms, secondary responses develop from the physiological effects of factors released (Kayhan et al., 2009).

Table 3. Türkiye's Foreign Trade in Aquatic Products (TUIK, 2023)

Year	Export		Import	
	Amount (tons)	Value ($)	Amount (tons)	Value ($)
2012	74,006	413,917,190	65,384	176,402,894
2013	101,063	568,207,316	67,530	188,068,388
2014	115,381	675,844,523	77,551	198,273,838
2015	121,053	692,220,595	110,761	250,969,660
2016	145,469	790,303,664	82,074	180,753,629
2017	156,681	854,731,829	100,444	230,111,248
2018	177,500	951,793,070	98,315	188,965,220
2019	200,226	1,025,617,723	90,684	189,438,745
2020	192,462	1,020,673,539	80,525	127,415,564
2021	238,732	1,376,291,922	104,708	217,179,174
2022	251,416	1,651,496,218	115,189	312,980,444

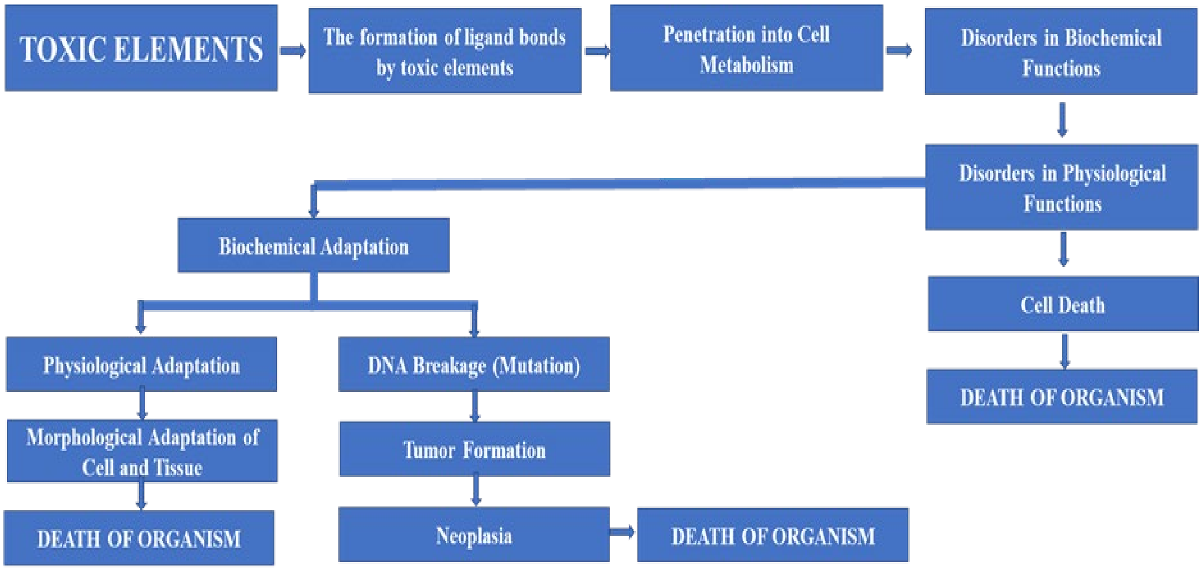

Figure 4. The biological responses and physiological pathways of toxic elements in organisms (Kayhan et al., 2009)

Table 4. Aquatic toxicity of water-soluble fractions of common oils (Fingas, 2014)

Oil Type	Specific Type	Species	Common Name	LC_{50} (mg/L)[1]	Time (hr)
Gasoline		*Daphnia magna*	Water flea	20 to 50	48
		Artemia	Brine shrimp	5 to 15	48
			Rainbow trout larvae	5 to 7	48
Diesel fuel		*Daphnia magna*	Water flea	1 to 7	48
		Artemia	Brine shrimp	1 to 2	48
			Rainbow trout larvae	2 to 3	48
Light crude	Alberta sweet mixed blend	*Daphnia magna*	Water flea	6 to 12	48
		Artemia	Brine shrimp	10 to 20	48
			Rainbow trout	10 to 30	96
			Frog larvae	3	96
	Arabian light	*Daphnia magna*	Water flea	10	48
Medium crude	Cook inlet	*Fundulus*	Fish	50	96
			Scallops	2	96
			Salmon	2	96
			Crab	1	96
Heavy Crude	Arabian heavy	*Daphnia magna*	Water flea	5 to 8	48
Intermediate	IFO-180	*Daphnia magna*	Water flea	1 to 8	48
Fuel oil		*Artemia*	Brine shrimp	0.8 to 4	48
			Rainbow trout larvae	2	96
Bunker C		*Daphnia magna*	Water flea	0.5 to 5	48
		Artemia	Brine shrimp	0.3 to 3	48
			Rainbow trout larvae	2	96

Note: [1] LC_{50} is the lethal toxicity to 50% of the test population at the water concentration, specified in milligrams per liter (mg/L), which is approximately the equivalent of parts per million.

Exposure to toxic substances can result in either fatal or non-fatal outcomes. Fatal exposure is typically quantified by the lethal concentration 50 (LC_{50}), which is the amount of the toxin required to kill 50% of a species' test population within a certain duration. For instance, studies on the impact of various crude oils on the water flea, *Daphnia magna*, indicate that a concentration ranging from 5 to 40 milligrams per liter (mg/L) over 24 hours proves to be fatally toxic. The measurement in mg/L is roughly equal to parts per million (ppm). On the other hand, sublethal exposure adversely affects the test organism without causing immediate death during the observation period. An example of this is observed when Daphnia magna experiences disorientation after being exposed to a 2 ppm concentration of crude oil in water for 48 hours (Fingas, 2014). Crustaceans such as crabs, lobsters, and shrimps, especially species that live buried in the seabed, are the most sensitive to oil pollution. They are affected by petroleum concentrations of 1-10 ppm. Bivalves like mussels and fish species are sensitive to 5-50 ppm, while gastropods and marine plants (algae) are sensitive to concentrations of 10-100 ppm (Tolay, 1998). Table 4 details hydrocarbon concentrations that prove fatal to a range of aquatic life, encompassing both freshwater and marine species.

The susceptibility of fish to hydrocarbons significantly depends on their age, where adult fish generally exhibit lower sensitivity compared to juvenile fish. For instance, research indicates that adult salmon are up to 100 times more resistant to aromatic hydrocarbons than their juvenile counterparts. Additionally, juvenile salmon display 70 times greater resistance than salmon eggs. Numerous investigations have demonstrated that fish larvae or newly hatched fish tend to be more vulnerable than the eggs of fish. Considering that the fish produced in the farms' focus point of this study are still in their growth phase, their sensitivity to oil pollution is significantly heightened. The subsequent section of the study focuses on the vulnerability of sea bream cultivated in fish farms located in the southern Aegean Sea of Türkiye to medium crude oil pollution.

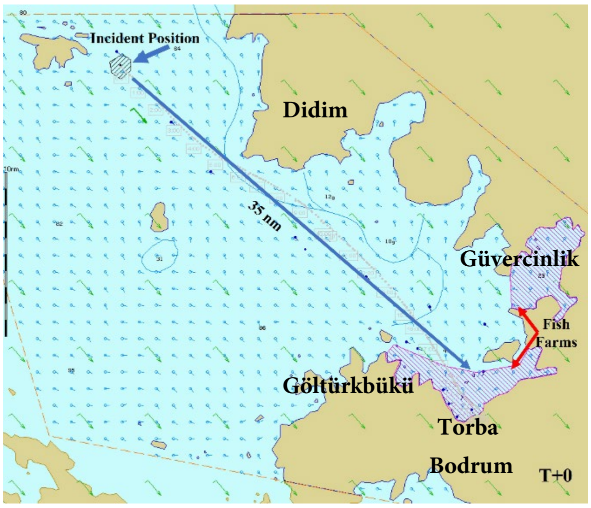

Figure 5. The initial position of the scenario

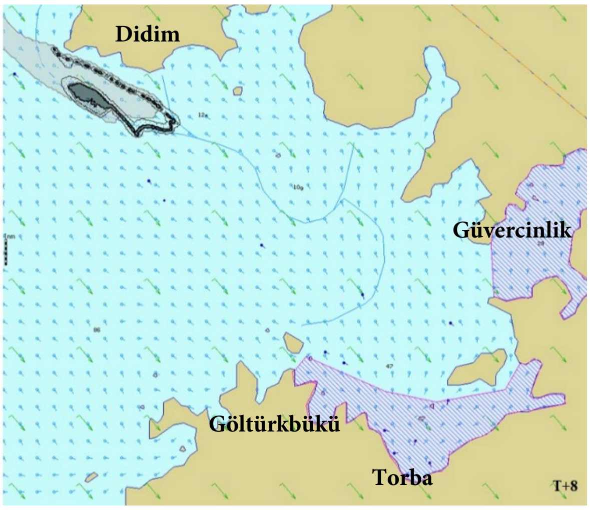

Figure 6. Oil pollution after 8 hours

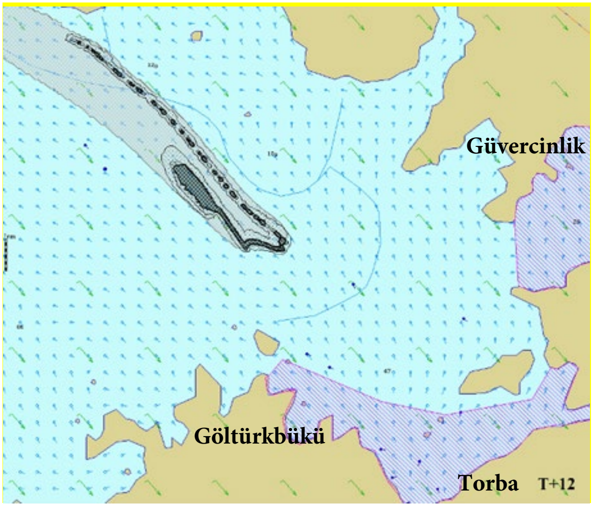

Figure 7. Oil pollution after 12 hours

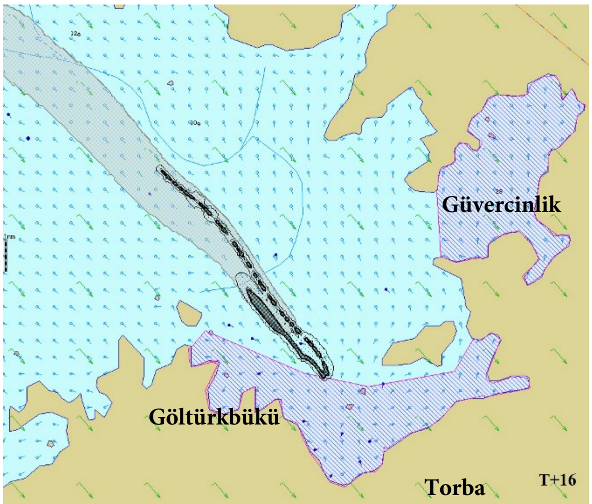

Figure 8. Oil pollution after 16 hours

In this context, the study initially considered adopting the LC_{50} value of 50 mg/L as indicated in Table 4. However, the table provides a general outlook on the sensitivity of marine species to aquatic toxicity without considering aquaculture or wildlife. Considering the aquaculture sea bream will be juvenile, obviously fish will be more sensitive as mentioned before. Therefore, LC_{50} values were set to the simulation as 10 mg/L for 48 hours. Besides, "LC_{50}" and "Time LC_{50}" indicate oil concentration sufficient for the death of half of the bions of the given species, and the time period, in which they die due to the given concentration, which is revealed under test environment conditions. Considering the other effects such as atmospheric and oceanographic variables and the oil weathering process, these values are alterable. Specifically, time and amount of oil dispersion[2] in the fish farm may alter the Time LC50, which is also not a linear proportion.

Results and Discussion

In this section, the primary focus is on an incident that occurred near the aquaculture production farms located along the coast of Aydın province in the southern Aegean Sea of Türkiye, at a position of 37°27′ N-027°03.6′ E, approximately 35 nautical miles away. Initially, a total of 1,000 tons and subsequently 200 tons per hour, culminating in a total of 2,500 tons of crude oil, leaked into the sea. The scenario crafted outlines how the prevailing meteorological and oceanographic conditions facilitated the spread of this oil spill to the sea bream production farms. The scenario was simulated using the PISCES decision support system, illustrating the dissemination of the oil in the sea, and the time it took to reach the fish production farms, as depicted in Figures 5-8.

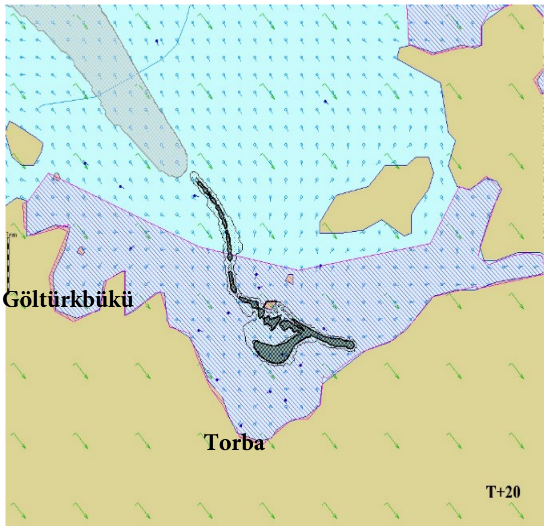

Figure 9. Oil pollution after 20 hours

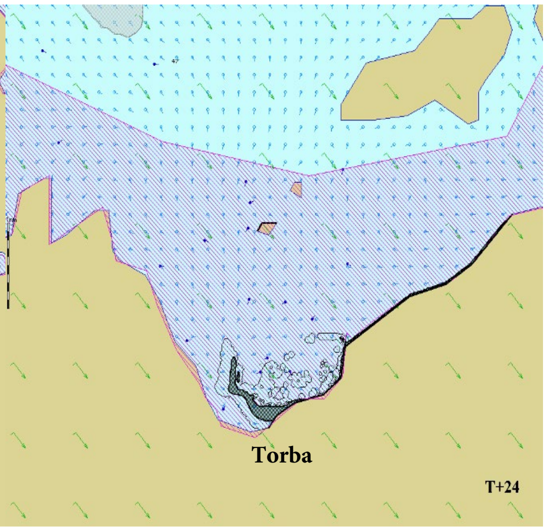

Figure 10. Oil pollution after 24 hours

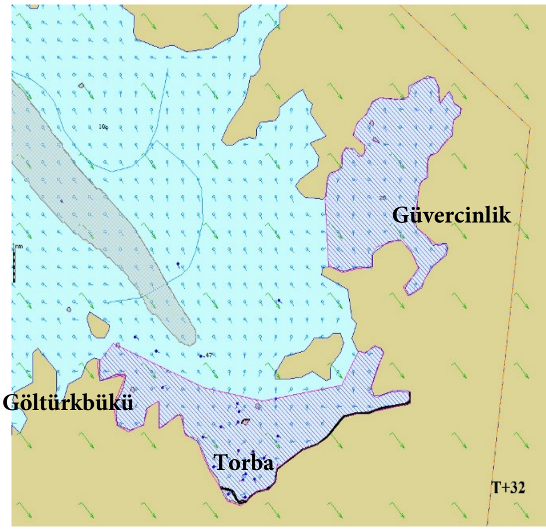

Figure 11. Oil pollution after 32 hours

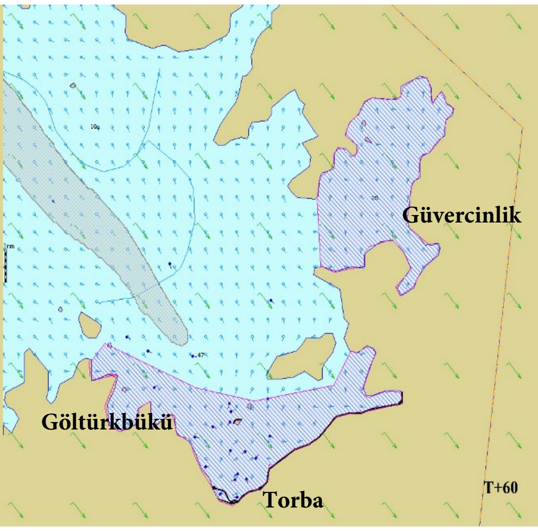

Figure 12. Oil pollution after 60 hours

[2] Natural dispersion is a process of transformation of some part of oil into minute drops as a result of wave motion, these drops remaining in a suspended state in the water column. The speed of natural dispersion depends on the sea state being inversely dependent on oil viscosity.

Table 5. Weathering processes data of the oil during 60 hours

Time	Amount spilled, t	Amount floating, t	Amount evaporated, t	Amount dispersed, t	Amount stranded, t	Amount sunk, t	Max thickness, mm	Slick area, km²	Viscosity, cSt
04:00	1,670	1,502	114	58.1	0	0	7.9	4.5	211
12:00	2,545	2,245	212	92	0	0	4.6	18.7	960
24:00	2,545	2,133	276	98.1	41.7	0.1	177	2.4	1,722
36:00	2,545	2,100	283	98.7	67.3	0.1	769	0.3	1,784
48:00	2,545	2,097	286	98.8	67.7	0.2	741	0.2	1,803
60:00	2,545	2,095	287	98.9	67.9	0.2	750	0.1	1,814

Table 6. Environmentally Sensitive Area (ESA-Fish Farm) status at the end of 60th hour

Report	Time	Date	Duration		
Begin	10:27	02.04.2024	Total time: 60 hours		
End	22:13	04.04.2024			
ESA – 1 Polluted	02:15	03.04.2024	Duration of Pollution of ESA: 44 hours		
Species	**LC_{50} (mg/l)**	**T LC_{50} (h)**	**Dead %**	**Initial amount**	**Current amount**
Sea Bream	10	48	32%	1,000,000 t	680,486 t

As depicted in Figure 8, the oil pollution occurring 35 nautical miles offshore reaches and contaminates the southern fish production farm approximately 16 hours later. Following the arrival of the oil at the farm, the spread within the area and the time it takes to reach the shore are illustrated in Figures 9-12.

From the moment of the incident until the 60th hour, Figure 12 illustrates the final state of the pollution, while Table 5 presents the oil weathering behaviors for this period.

Upon analyzing Table 5, it is observed that approximately 100 tons of the oil were naturally dispersed both on the water surface and within the water column, while 0.2 tons have settled to the seabed. In terms of the oil's viscosity, it is noted that the initial value of 15.7 cSt escalated to 1814 cSt by the end of the 60th hour. In scenarios of potential increases in sea and wind conditions, the natural dispersion of the oil across the sea surface and into the water column, followed by the penetration of water molecules into the oil molecules (emulsification), and the eventual sinking and sedimentation of the oil to the seabed will accelerate. Under these circumstances, the fish mortality rates at the end of the 60th hour provided in Table 6 below are expected to rise further.

Upon examining Table 6, it is revealed that within 44 hours from the 16th hour, when the pollution reached the farm, 32% of the fish in the farm died. As expressed in the preceding paragraph, the alteration of conditions and the progression of time are likely to result in an increase in the fish mortality rate.

Conclusion

This study serves as an illustrative scenario analysis, shedding light on the potential impact and timeline of marine pollution on the aquaculture industry, which is of growing importance for food security not only in Türkiye but also globally. It reveals that production facilities located along Türkiye's southern Aegean coasts, approximately 35 nautical miles away, have a window of about 16 hours to respond to a potential oil spill, under varying atmospheric and oceanographic conditions. It was found that by the end of the 44th hour, 32% of the sea bream species had perished due to contamination at these facilities. The simulation values presented in this work can be adjusted based on different seasonal atmospheric and oceanographic conditions, types of aquaculture species, and pollution scenarios, thereby diversifying situational scenarios.

The critical relationship between environmental factors and marine life vitality is underscored. The presence of hydrocarbons in water, resulting from oil spills, significantly reduces the oxygen levels available to aquatic organisms, leading to hypoxia or even anoxia. Moreover, the increased viscosity of water due to oil contamination can impair fish's ability to move, feed, and further exacerbating the mortality rate. Furthermore, the cumulative effects of prolonged exposure to pollutants can lead to sub-lethal impacts, such as reproductive failures, decreased growth rates, and increased susceptibility to diseases, which may not be immediately apparent but can significantly affect population dynamics over time. Metallic pollutants measured in living organisms as an indicator of environmental pollution can often reach high levels, especially in aquaculture. In this way, toxic substance residues taken with food at low levels continuously affect the environment and human health significantly. Therefore, conducting comprehensive environmental impact assessments following such incidents is essential to devise effective mitigation and restoration strategies that can help minimize long-term ecological damage and promote the resilience of affected marine ecosystems.

Numerous predictions suggest a significant rise in future aquaculture production. This growth is expected to positively impact public health and boost economic opportunities. Farmed seafood plays a crucial role in the global food system and should be regarded as equally important as terrestrial animal and crop production. Although the aquaculture sector has expanded rapidly, it has been somewhat disorganized. To enhance aquaculture's role in food security, better information sharing and improved extension support are essential. Within the framework of these issues, the contribution of the aquaculture industry to both food security and the national economy is increasing in Türkiye as well. Given the increasing economic value of the aquaculture industry within countries' Gross Domestic Products and its significance for food security, it is imperative to consider this industry as a national asset that needs protection. The Eastern Black Sea, where the country's fish farms are concentrated, has the potential to be increasingly exposed to marine pollution through both underwater oil pipelines and East-West axis tanker transport. Similarly, the Aegean Sea and aquaculture production facilities, especially in the southeast, face the risk of pollution due to North-South axis tanker transport and increasing maritime traffic. Previous tanker accidents and resultant marine pollution have led to significant social and economic losses, highlighting the necessity for countries to prepare for such incidents, develop contingency plans, and maintain pollution intervention equipment. Consequently, Türkiye has formulated emergency response plans to protect coastal facilities and ports, against oil pollution. Similarly, the aquaculture industry must have equivalent plans in place. Future research should simulate possible scenarios like the one presented in this study, delineate the pollution spread timeline to aquaculture sites, establish alternative locations for production ponds, and conduct drills to familiarize responsible personnel with the plans, enhancing their readiness and response capabilities.

Compliance With Ethical Standards

Conflict of Interest

The author declares that there is no conflict of interest.

Ethical Approval

For this type of study, formal consent is not required.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data Availability

Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

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Mar. Sci. Tech. Bull. (2024) 13(2): 135-141
e–ISSN: 2147–9666
info@masteb.com

dergipark.org.tr/en/pub/masteb
www.masteb.com
DOI: 10.33714/masteb.1479122

Marine Science and Technology Bulletin

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RESEARCH ARTICLE

Proposal of invader *Pontederia crassipes* as a savior of micro and macro size plastic pollution

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ARTICLE INFO

Article History:
Received: 06.05.2024
Received in revised form: 28.05.2024
Accepted: 28.05.2024
Available online: 24.06.2024

Keywords:
Microplastic
Microplastic adsorption
Macroplastic
Orontes River
Pontederia crassipes

ABSTRACT

This study is the first report evaluating the microplastic (MP) and macroplastics capture potential of *Pontederia crassipes.* Total of 3691 (508 microplastic and 3183 macroplastic) particles were extracted from the roots of 12 examined specimens. Mean macroplastic abundance in the roots was found as 265±44 macroplastic/specimen. Majority of the extracted macroplastics were fragment in shape, blue in color. Mean microplastic abundance was found as 42±23 MPs/specimen. Majority of the extracted microplastics were fragment in shape, blue in color and less than 500 µm in size. Results of this preliminary study showed that this species have significant ability to adsorb micro and macroplastics by the roots which makes them perfect employees for integrated floating systems.

Please cite this paper as follows:

Kılıç, E., & Yücel, N. (2024). Proposal of invader *Pontederia crassipes* as a savior of micro and macro size plastic pollution. *Marine Science and Technology Bulletin*, *13*(2), 135-141. https://doi.org/10.33714/masteb.1479122

Introduction

Microplastics, defined as synthetic polymers less than 5 mm in size (Thompson et al., 2009), are persistent and widespread polluters in aquatic environments. Till the first detection of microplastics in rivers (Moore et al., 2005), only limited efforts were made to understand the distribution, transport, occurrence of microplastics in rivers compared to marine environments (Wagner et al., 2014; Li et al., 2018, Kılıç et al., 2022).

Rivers are more susceptible to any kind of pollution as they are usually surrounded by anthropogenic influences. They usually contain higher amounts of micro and macro size plastic particles and variety of chemicals that alter the biological and chemical dynamics of ecosystem (Scherer et al., 2018). So far, majority of the studies focused on effects of microplastics on microorganisms such as algae, daphnids, mussels, fish (Miloloža et al., 2021), and have been deficient in terms of aquatic plants (Kalčíková et al., 2020; Ceschin et al., 2023). Nevertheless, microplastic exposure might cause inhibition in

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photosynthesis (Yang et al., 2023), limitation in root growth (Ceschin et al., 2023), direct toxicity from contaminated surfaces of MPs (Mammo et al., 2020) in vascular aquatic plants. Besides, MPs can change soil characteristics in sediments (Wang et al., 2020), vary the turnover rate of microbial communities (Wang et al., 2020) and alter the nutrient cycle (Yu et al., 2022). These types of fluctuations in environmental conditions form an indirect impact of microplastics on aquatic plants (Lozano & Rillig, 2020).

Pontederia crassipes is known as the most invasive aquatic plant in freshwater environments (Villamagna & Murphy, 2010). Even though it is originally from Brazil, it is now distributed to the Africa, Asia, Australia, India and North America (Villamagna & Murphy, 2010, Virginia Invasive Species, 2024). It is more widespread in water bodies containing high nutrient concentration (Villamagna & Murphy, 2010). The studied environment, Orontes River, suffered heavily from agricultural runoff, industrial and domestic wastewater discharges (Kılıç & Yücel, 2019) making it an ideal habitat for *P. crassipes.* It was first observed in the eastern part of the Türkiye, Hatay-Altınözü near the border with Syria in August 2010 (Uremis et al., 2014). Since this plant can reproduce both sexually and vegetatively, it doubles its biomass every ten days under favorable conditions. Rapid spread of *P. crassipes* creates a potential problem for the river ecosystem (Uremis et al., 2014). On the other hand, field observations carried out in this study showed that *P. crassipes* is capable of adsorbing plastic debris in the surface water.

This study was undertaken to evaluate whether the invader *P. crassipes* can be solution to urgent plastic pollution in river systems.

Material and Methods

Sampling and Study Area

The specimens were collected from Orontes River, Hatay, Türkiye in November 2022. Randomly selected 12 specimens were collected from the riverbank where macroplastic density is high and water flow is low (Figure 1). Each specimen was collected using a plankton net with an adjustable mouth opening and a pore size of 65 µm.

Macroplastic Extraction

The collected specimens were wrapped in tin foil and transported to the laboratory. Randomly selected one secondary root was examined under microscope to identify the interaction between plastic debris and root structure. The remaining roots of the *P. crassipes* were washed three times with pre-filtered distilled water to wash off the macroplastic density in a glass beaker. After then, average diameter and root length were measured to estimate the root surface area ($Area = \pi \times average\ root\ diameter \times root\ length$).

Figure 1. Sampling site of examined *P. crassipes* specimens from Orontes River (coordinates: 36°15'17" N, 36°12'10" E)

The collected water represented the macroplastic density of each specimen was treated with 50 mL of hydrogen peroxide (30%) and placed on a hot plate at constant temperature of 60°C for 24 h to degrade organic content. Then, mixture was filtered through 5 mm steel sieves. Type and color (blue, black, red, white, yellow, green, brown) of extracted macroplastics were noted.

Microplastic Extraction

The primary roots of each specimen were separated from the main root system and placed in glass beakers. 20 mL of hydrogen peroxide (30%) per gram of roots was added to the beakers in order to remove organic material. Solution was kept on hotplate at 60°C for 24 h to complete degradation process. Next, saturated sodium chloride was added and stirred for 2 minutes to float microplastics in the mixture. Then, samples were allowed to settle for 24 h. Thereafter, the supernatant was filtered through 65 µm pore size mesh filters and filters were placed in glass petri dishes until they were dried. Finally, filters were examined under Olympus SZX7 microscope with an attached Olympus DP to determine accumulated microplastic in the roots. Estimated microplastics were categorized based on their size, shape (fiber, fragment or pellet) and color (blue, black, red, white, yellow, green, brown).

Plankton net which used in collection step was backwashed three times with pre-filtered distilled water and filtrate was processed for microplastic detection. Filtrate was treated with by 20 mL hydrogen peroxide (30%). Then floatation and microscope examination procedure was applied similar to the roots.

FTIR Analysis

Randomly selected 50 macroplastic particles were analyzed by Fourier transform infrared (FTIR) spectrometer. FTIR analysis was carried out on a SHIMADZU QATR10 FTIR spectrophotometer equipped with single reflection attenuated total reflectance (ATR) accessory. The spectrum range was 4000–400 cm^{-1} and a resolution of 4.0 cm^{-1} with 32 scans for each measurement. The polymer type identification was done by comparing absorbance spectra to reference libraries of SHIMADZU library.

Quality Control/Quality Assurance

In the laboratory, serious precautions are undertaken to prevent airborne contamination. First, the authorized personnel always wore cotton lab coats and nitrile gloves. Lab surfaces and laboratory materials (glass beakers, filtration unit, etc.) were rinsed with pre-filtered distilled water for three times before any analysis. Hydrogen peroxide and distilled water were filtered through GF/C filters before being used in the analysis. Mesh filters were checked with the presence of any MPs prior to use. All the used equipment including petri dishes and glass beakers were covered when they were not processing. Finally, at each step of the analysis (degradation, filtration, density separation, microscopic examination etc.) blank filters were replaced to detect contamination. Despite affords 0.3±0.5 MPs were detected in the blank filters which were subtracted from the dataset.

Statistical Analysis

In order to understand whether or not there is relationship between root surface area and microplastic or macroplastic abundance Pearson correlation analysis was used. Graphical representation was done using Florish program, online version.

Results

Results showed that *P. crassipes* have ability to capture microplastics and macro plastics present in the surface waters. Total of 508 microplastic particles were extracted from the roots of *P. crassipes* (Figure 2). Among them, 32% of them were fiber, 69% of them were fragment and 3% of them were pellet. Mean microplastic abundance was found as 42±23 MPs/specimen. Mean length of microplastics was found as 633±628 micrometer. Majority of the MPs were less than 500 µm. Detected MPs were commonly blue (30%), red (24%) and black (16%) in color, respectively (Figure 3).

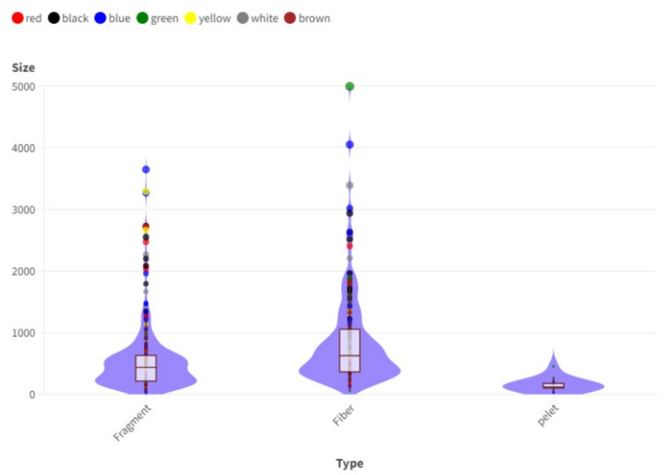

Figure 2. Type, size and color distribution of extracted microplastic from the roots of *Pontederia crassipes*

In terms of macroplastics, 3183 fragmented macroplastic particles were found. Mean macroplastic abundance in the roots was found as 265±44 macroplastic/specimen. Size of macroplastics were varied between 5000 µm and 10500 µm. Blue (22%), black (19%) and red (15%) colored particles form the majority of extracted macroplastics (Figure 3).

FTIR analysis showed that all of the examined macroplastics were high density polyethylene (HDPE).

Statistical analysis showed a strong correlation between root surface area and macroplastic abundance (r=0.07, p<0.01) (Figure 4). On the other hand, no correlation was observed in terms of microplastics (p>0.05) (Figure 5).

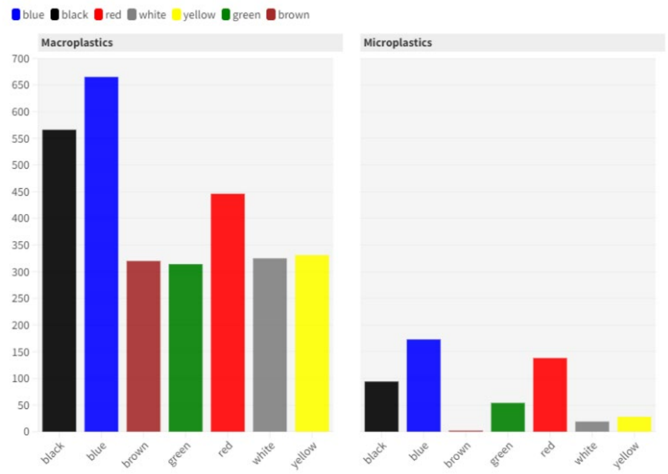

Figure 3. Color distribution of plastic particles extracted from roots of *Pontederia crassipes*

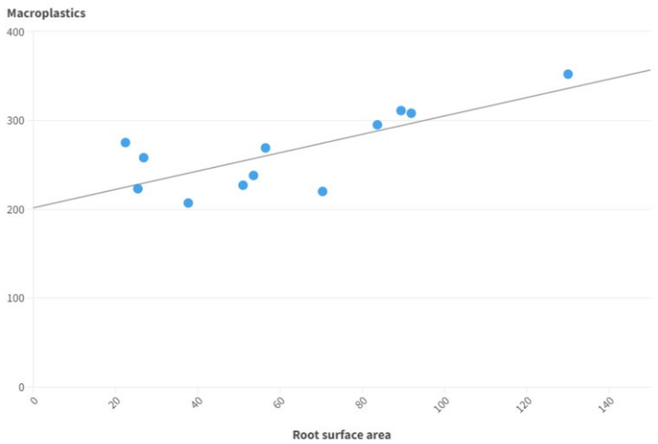

Figure 4. Relationship between root surface area of *Pontederia crassipes* and adsorbed macroplastics

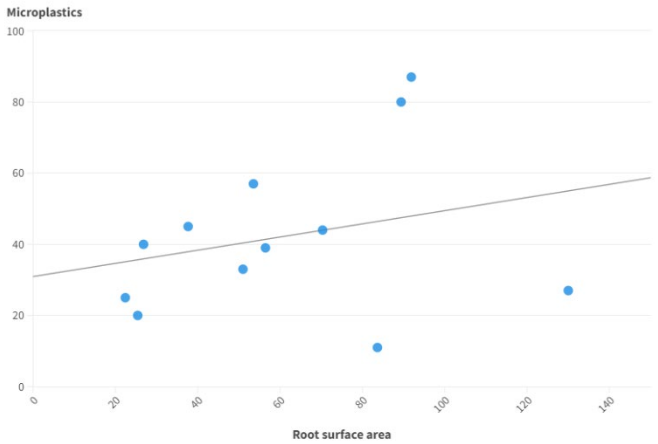

Figure 5. Relationship between root surface area of *Pontederia crassipes* and adsorbed microplastics

Discussion

Concerns regarding the spread of *P. crassipes* are mainly related to its dense malting, which leads to the intertwining of individual plants, reduces the phytoplankton community and reduces the concentration of dissolved oxygen concentrations beneath these malts (Villamagna & Murphy, 2010). On the other hand, previous studies have shown that they can harvest heavy metals in sediment (Greenfield et al., 2007), absorb organic contaminants (Zimmels et al., 2007), nitrogen, phosphate (Rommens et al., 2003) and heavy metals (Tiwari et al., 2007) in the surface water. These contradictory results lead to a debate on the ecological role, potential benefits and harms of *P. crassipes.*

Although this debate is still ongoing, previous studies have shown that *P. crassipes* can be successfully used for the treatment of urban wastewater (Zimmels et al., 2006; Kumari et al., 2014), heavy metals (Eid et al., 2021), ibuprofen and caffeine (de Oliveira et al., 2019). These recent advances have prompted us to think about the potential of *P. crassipes* for the removal of plastic particles in the surface waters. Similarly, Kalčíková et al. (2020) suggested that harvesting of duckweed species at predetermined intervals could reduce plastic litter.

The first characteristic that makes *P. crassipes* a perfect collector of plastic litter is its root structure. The roots are fibrous and unbranched (Penfound & Earle, 1948) and act like a plastic trap (Figure 6). As they tend to create a surface map, the plastic litter on the surface water can easily be caught by the roots. Moreover, the root length decreases when the nutrient concentration in the water increases (Rodríguez et al., 2012). Therefore, in regions where wastewater discharge is a systematic problem, they develop denser, more fibrous root structures that allow us to capture plastic litter discharged into water bodies. Correlation analysis showed that as the root surface area increases, number of adsorbed macroplastic particles increases (Figure 4). This mathematical relationship could be considered as an adsorption kinetics which in light 0f the macro debris harvesting potential of this species.

Figure 6. Microscopic view of macro plastics trapped in the roots of *P. crassipes*

Environmental parameters, especially surface flow rate, seems to be an important parameter for the collection of plastic litter. In this study, specimens were collected from the river bank where plastic litter was trapped (Figure 7) and the water flow was relatively low. *P. crassipes* formed a dense mat on the river surface (Figure 1). From an ecological engineering point of view, these conditions create a natural integrated floating system that allows plastic litter to be collected. For this reason, we are proposing creation of integrated floating systems by using these species to remove plastic litter from water. In a similar sense, this species was employed to remove heavy metals, organic contaminants, dissolved nutrients from freshwater environment (Rommens et al., 2003; Greenfield et al., 2007; Zimmels et al., 2007).

Figure 7. A) Picture of specimen collection point, B) Picture of collected *P. crassipes* specimen, C) Macroplastic debris remaining in the river, D) Picture of the roots of collected *P. crassipes* specimen

More importantly, floating aquatic plants seems not to be affected by micro and macro size plastics. Recent studies showed no impact on plant growth of duckweed species such as *Spirodela polyrhiza* (Dovidat et al., 2020), *Lemna minor* (Mateos-Cárdenas et al., 2019). Ceschin et al. (2023) reported that microplastics can only be adsorbed but not absorbed by the roots of *Lemma minuta*. On the other hand, a current study argued that nanoplastics less than 20 µm can only be absorbed by *P. crassipes*. Therefore, microplastics taken up by the root structure remain in the root structure until harvested, which is consistent with previous reports (Mateos-Cardenas et al., 2019; Dovidat et al., 2020; Kalčíková et al., 2020).

Small size MPs (<1000 µm) can be accidently consumed by aquatic organisms and could pose a significant threat in the food chain. In this study, the majority of microplastics ingested by the roots were smaller than 500 µm. Therefore, this plant appears to be effective in removing microplastics from the aquatic environment.

The macroplastics examined were all HDPE, which is an indicator that plastic has recently been discharged into the river. The results of this preliminary study showed that their complex root system has sufficient surface area (Yang et al., 2023) to capture discharged micro- and macroplastics in the water surface.

Conclusion

This study is the first report investigating the plastic capture potential of *P. crassipes*. The samples were collected from the Orontes River, which is known to have problems with water quality and plastic litter. A total of 3691 micro- and macroplastic particles were extracted from the roots of 12 examined specimens. This preliminary data indicates that *P. crassipes* is a good candidate for the micro and macro size plastic particle removal due to their ability to adsorb micro- and macroplastics through the roots. We proposed that this species can be used as employees for plastic litter removal. Future engineering studies needs to be carried out to understand the operating conditions for the design of floating wetland systems by employing *P. crassipes.*

Compliance With Ethical Standards

Authors' Contributions

EK: Conceptualization, Writing – original draft, Formal analysis, Data curation
NY: Conceptualization, Formal analysis, Data curation
All authors read and approved the final manuscript.

Conflict of Interest

The authors declare that there is no conflict of interest.

Ethical Approval

For this type of study, formal consent is not required.

Funding

Not applicable.

Data Availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Mar. Sci. Tech. Bull. (2024) 13(2): 142-150
e–ISSN: 2147–9666
info@masteb.com

dergipark.org.tr/en/pub/masteb
www.masteb.com
DOI: 10.33714/masteb.1493896

Marine Science and Technology Bulletin

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RESEARCH ARTICLE

Shell composition analysis of European flat oyster (*Ostrea edulis*, Linnaeus 1758) from Marmara Sea, Türkiye: Insights into chemical properties

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ARTICLE INFO

Article History:
Received: 01.06.2024
Received in revised form: 17.06.2024
Accepted: 17.06.2024
Available online: 24.06.2024

Keywords:
Bivalve shells
Calcium carbonate
Ostrea edulis
The zero charge points

ABSTRACT

The chemical structure of *Ostrea edulis* (*O. edulis*) shells was investigated in this work. The study determined zero charge points (PZC) of *Ostrea edulis* shells. The shell surface charge status is indicated by the PZC value. It was found that the shell PZC value was 8.30. The shells were subjected to Energy Dispersive X-Ray Spectroscopy (EDS) analyses and scanning electron microscope (SEM) pictures. The main structure of calcium carbonate ($CaCO_3$) is made up of carbon, oxygen, and calcium atoms, which were found in the largest quantities based on the EDS data. The structure of $CaCO_3$ was supported by Fourier Transform Infrared Spectroscopy (FT-IR) analysis. As part of the study, X-Ray Diffraction (XRD) investigations were conducted, and it was found that the shell structures are primarily composed of an aragonite and $CaCO_3$ mixture. As is well known, $CaCO_3$, which makes up roughly 94% of the shell, is the primary constituent of bivalves' shells. This research offers a thorough examination of the chemical makeup of *O. edulis* shells. This study is thought to serve as the foundation for further research on the biological and chemical characteristics of marine species.

Please cite this paper as follows:

Kızılkaya, B., Yıldız, H., & Vural, P. (2024). Shell composition analysis of European flat oyster (*Ostrea edulis*, Linnaeus 1758) from Marmara Sea, Türkiye: Insights into chemical properties. *Marine Science and Technology Bulletin*, *13*(2), 142-150. https://doi.org/10.33714/masteb.1493896

Introduction

Oyster species are significant organisms of the seas and hold great economic importance. Oysters, which are a fundamental resource for mollusk fishing, are subject to various operations worldwide. These operations encompass activities such as the collection, cultivation, and trade of oysters (Yildiz et al., 2011; Acarli et al., 2011, 2015). Oysters are an integral part of marine ecosystems, serving as a vital food source for many marine organisms (Grabowski et al., 2012). Additionally, they are

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known as a high-value seafood for humans. The proteins, vitamins, and minerals contained within oysters are highly beneficial for human health, and their regular consumption is recommended (Ulagesan et al., 2022). The shells of molluscs, which inhabit the seas, have evolved to protect and support their bodies. These shells not only provide resilience against external forces but also serve as a defense mechanism against predators. Similarly, the shells of bivalves and gastropods fulfill similar protective functions, while the soft tissues of monoplacophorans have also evolved for a similar purpose of providing protection. Belonging to the Mollusca class, these shells are integral to the diverse array of invertebrates found globally, playing crucial roles in marine ecosystems. Beyond safeguarding soft tissues, mollusk shells serve as sustenance and provide defense mechanisms against predators (Yi & Bengtson, 1989; Qian, 1999; Li et al., 2017). All oysters (Mollusca: Bivalvia) exhibit distinctive morphological characteristics, notably the presence of two symmetric calcareous valves interconnected by a calcified structure, which form their shells. This underscores the importance of these organisms as integral components of natural ecosystems. Oysters play a pivotal role in preserving the ecological equilibrium of oceans, seas, and freshwater bodies. Additionally, their economic significance cannot be overstated. Therefore, scientific and economic research on the morphological features and shell structure of bivalve is of paramount importance (Bogan, 2008; Graf, 2013; Chakraborty et al., 2020). The process of early life adaptation to diverse environmental stresses led to the evolution of mollusk shells. The interior organs of the creature are shielded by these shells, which also help in their protection against predators and other dangers (Li et al., 2017). Oysters are classified within the subclass Bivalvia of the mollusk class Mollusca, distinguished by their characteristic shells. These organisms are shielded by two symmetrical calcareous valves comprising their shells. Beyond mere protection from external elements, these shells afford oysters mobility and feeding capabilities. Furthermore, bivalve shells play a crucial role in stabilizing the chemical composition of the surrounding water, thereby fostering the sustainable functioning of the ecosystem (Chakraborty et al., 2020). Shells make up a large percentage (about 56–61%) of bivalves' weight. About 94% of the makeup of a shell is made up of $CaCO_3$. Marine species employ their shells as their hard outer structures for protection and structural support. Numerous creatures, including gastropods and other marine invertebrates, make and use them. Crystals of $CaCO_3$ aggregate to form these shells, which are often protected by a thin organic membrane (Hamester et al., 2012; Ituen, 2015; Mititelu et al., 2022). The primary constituent of shells is commonly $CaCO_3$, yet various small inorganic trace elements are also found in different bivalve species. These trace elements have the potential to impact the physical characteristics of shells and play a significant role in the life cycles of shelled organisms (Chakraborty et al., 2020). Calcite or aragonite crystals are the most common forms of $CaCO_3$ that makes up shells. The shell resilience and hardness are derived from these crystals. Other trace elements found in the shells, nevertheless, are also quite important. Examples of elements that can affect the color and pattern creation of shells are magnesium (Mg), manganese (Mn), iron (Fe), copper (Cu), and zinc (Zn). These substances can also make the shells more resilient and aid in the defense of species with shells against predators (Carroll & Romanek, 2008; Spann et al., 2010; Nakamura et al., 2014; Agbaje et al., 2017, 2018a, 2018b; Chakraborty et al., 2020). The aim of this study was to investigate the chemical structure and composition of *O. edulis* shells. These shells comprise a blend of $CaCO_3$ and organic matrix, crucial for providing strength and durability. The research sought to elucidate how environmental factors such as pH levels, and the chemical composition of *O. edulis* shells. These findings offer insights into how *O. edulis* shells respond to environmental fluctuations, facilitating a deeper understanding of their adaptive mechanisms.

Material and Methods

Study Area and Sampling

One hundred samples of *O. edulis* were collected from the coasts of the Fener Island, Bandırma Gulf in the Marmara Sea. First, the collected shells were run through clean water. These shells were then ground to a homogeneous texture.

Determination of Zero Charge Point (PZC) in Shells

The zero point of charge (PZC) was established through pH assessments conducted on homogenized and ground samples of mollusk shells (Mahmood et al., 2011). Firstly, 100 ml of 0.01 M KNO_3 solutions were made in an Erlenmeyer flask in order to calculate the pH_{PZC}. Using 0.1 M HCl and NaOH, the starting pH values (pH_I) of these solutions were changed from pH 4 to pH 10. These solutions were then supplemented with the altered samples. After that, the mixture was agitated for 48 hours at a steady temperature with a magnetic stirrer. The solution's ultimate pH (pH_F) was tested and noted after 48 hours. Plotting $\Delta pH = pH_I - pH_F$, the difference between the initial and final pH, was done against the initial pH (pH_I). The

PZC was identified as the point where the curve contacts the x-axis.

Chemical Structure Analyzes in O. edulis Shells

Analysis using the SEM-EDS (Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy, model JEOL JSM-7100F) was carried out at Science and Technology Application and Research Center, Çanakkale Onsekiz Mart University. The instrument offers a magnification range spanning from ×40 to 300,000, coupled with an accelerating voltage varying between 0.2 and 30 kV. This was followed by a gold-palladium (80-20%) coating procedure employing a voltage of 10 mA. The resulting coating thickness typically measures approximately 2-3 nm. Secondary electrons were utilized in the SEM apparatus to obtain images. Using a scanning electron microscope (SEM), surface features of the ground shells were analyzed, and discrepancies were found. Additionally, the carbon (C), oxygen (O), nitrogen (N), calcium (Ca), and sulphur (S) contents of the shells were examined using EDS analysis. FT-IR spectra were recorded in the 650–4000 cm^{-1} range on a Perkin-Elmer SpectrumOne instrument. FT-IR investigations of ground and homogenized *Ostrea edulis* shells were conducted. To learn more about the chemical structure of *O. edulis* shell, XRD investigations were also carried out. The PANalytical Empyrean XRD instrument, housed in the Science and Technology Application and Research Center of Çanakkale Onsekiz Mart University, was utilized to conduct the analyses.

Results and Discussion

The zero point of charge (PZC) is a crucial parameter in physicochemistry, particularly concerning adsorption. It signifies the state where the electrical charge on a surface reaches zero. Essentially, PZC corresponds to the pH value at which the net electrical charge on the surface of a solid, immersed in an electrolyte solution, becomes neutral. This concept not only delineates a specific condition of PZC but also holds significant relevance to adsorption processes. PZC represents the pH at which the net electrical charge on the surface of a solid, in contact with an electrolyte, equals zero (Somasundaran & Agar, 1967; Sverjensky, 1994; Babić et al., 1999; Hou et al., 2001; Kosmulski, 2002; Fiol & Villaescusa, 2008; Mahmood et al., 2011). Understanding the significance of the definition provided requires a grasp of the concept of adsorption. Adsorption is the phenomenon where one substance adheres to the surface of another substance. This interaction commonly transpires between solid and liquid or gas phases, with the surface's electrical charge playing a pivotal role in facilitating adsorption. In numerous fields where adsorption processes are investigated, the determination and comprehension of PZC hold paramount importance (Fiol & Villaescusa, 2008; Mahmood et al., 2011). Understanding the pH levels at which a surface is electrically neutral is a crucial first step in comprehending the process of adsorption, and this idea helps with that. Different pH values can be obtained for different surfaces when determining PZC, which is normally done experimentally. The determination and comprehension of PZC are important steps in understanding the adsorption properties of a surface. The variability in PZC across different surfaces, stemming from factors such as chemical composition, structure, and other surface properties, underscores its fundamental importance. This understanding is not only crucial in the realm of physical chemistry but also holds significant relevance across various industrial applications. Especially in materials science, colloid chemistry, environmental engineering, and related fields focusing on surface chemistry and adsorption phenomena, the determination and comprehension of PZC are crucial for material design and application. In conclusion, the PZC is a significant parameter in physical chemistry pertaining to adsorption phenomena, indicating the state where the electrical charge on a surface is zero. Typically, PZC refers to the pH value at which the net electrical charge on a surface submerged in an electrolyte solution equals zero. The PZC of *O. edulis* shell particles was established through analysis of their surface characteristics. The determined PZC value for the shells was 8.30 (Figure 1). Depending on the surface properties of the shells, PZC value may fluctuate based on the capability of groups within the molecule to either gain or lose hydrogen or electrons. The hydroxyl groups in the acidic water draw additional protons, creating a positively charged adsorbent surface on which negative ions are adsorbed. The surface becomes negatively charged and positively charged groups adsorb. The shells' initial pH (pHi) vs ΔpH curves are displayed in Figure 1. Along with the values derived using linear regression, the experimental PZC values acquired at the conclusion of the investigation are also displayed.

Using the X-Ray Diffraction (XRD) method, the shells of *O. edulis* were examined and their crystal structures were compared to those of calcium carbonate ($CaCO_3$) and aragonite. This research, which looks at the atomic and molecular structures of the shells, is based on the X-ray pattern that is specific to each crystal and is produced by the crystalline phase of the structure. The crystal structures of $CaCO_3$ constituting these shells are shaped through biomineralization processes influenced by diverse factors such as species characteristics, growth conditions, and environmental factors. To comprehend the alterations in molecular structures of shells contingent upon crystal formation, it becomes imperative to advance these techniques. Thus, understanding the mechanism by which organic tissue interacts with the mineral phase within tissues becomes crucial. This insight is pivotal for elucidating the intricate processes underlying biomineralization and facilitating advancements in fields such as materials science, biology, and environmental studies (Pokroy et al., 2007). The references employed in this work were aragonite and calcium carbonate, which share the same chemical components but have distinct crystal forms. Aragonite is a carbonate ($-CO_3^{-2}$) mineral that primarily develops naturally in freshwater or marine environments. It differs from calcite (calcium carbonate) in that it has a distinct crystal lattice structure. Figure 2 is a comparison with our samples using XRD information provided by US Geological Survey (USGS, 2001). Every peak in the picture represents the X-rays that a particular atomic plane in a mineral crystal structure diffracted. The peak intensity reflects the quantity of diffracted X-rays, while the peak angle indicates the direction of the diffracted X-rays. Due to their distinct crystal structures, calcite and aragonite exhibit varying peak positions. This image illustrates how XRD enables the determination of a mineral chemical composition and crystal structure. By analyzing peak positions and intensities, valuable insights into the crystalline nature of the material can be gained, facilitating a deeper understanding of its properties and characteristics. After analyzing the spectra presented in Figure 1, it was ascertained that the principal constituents of *O. edulis* shell structures are aragonite and $CaCO_3$. The samples are represented by the blue portion of the spectrum, calcite by the red section, and aragonite by the green component. As a result, recognizing the aragonite and calcium structures in the composition was simpler. An effective method for classifying minerals and analyzing crystal structures is XRD.

SEM-EDS is a microscopy method employed to image surfaces and analyze elemental composition. By directing an electron beam onto the sample surface, this technique visualizes surface topography while also identifying the chemical elements present. SEM-EDS is a prevalent analysis technique utilized across various industrial and scientific domains. Its extensive application derives from its efficacy in scrutinizing both surface characteristics and chemical composition of samples. Another notable aspect of SEM-EDS is its capacity for high-resolution surface imaging. This capability enables the inspection of surface morphology and the observation of microstructures present on the sample surface. Moreover, it facilitates regional elemental analysis, offering valuable information regarding the chemical composition of the sample surface. These capabilities provide intricate insights into the surface properties of the sample, contributing to a comprehensive understanding of its characteristics. Figure 3 displays the shells SEM photos. The ground *O. edulis* shell's tiny structure is depicted in the SEM image. The image shows that $CaCO_3$ crystals make up the majority of the mussel shell. The principal component of the mussel shell, plates of unevenly formed and sized $CaCO_3$ crystals, make up the majority of the image. There could be other elements or organic materials among the tiny particles on the plates. The mechanical characteristics, chemical makeup, and biological activity of the *O. edulis* shells can all be understood by using the important information this image provides on its tiny structure.

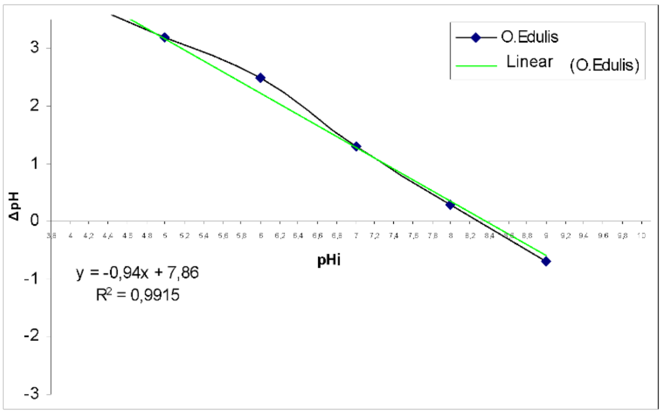

Figure 1. Zero charge point of *O. edulis* shell particles

The salinity values of sea water in the sampling location were measured between 24 and 26 ‰. In addition, temperatures were measured between 6°C and 30°C. The Energy Dispersive X-ray Spectroscopy (EDS) analysis result of *O. edulis* shell is displayed in Figure 4. The method of EDS analysis is used to ascertain a material's chemical makeup. Elements including C, O, Ca, Mg, sodium (Na), and N are clearly visible in the spectrum. The primary structural constituents of $CaCO_3$ are represented by the elements that are most prevalent and fundamental in the spectrum: Ca, C, and O. C is a sign of organic stuff and $CaCO_3$, which is the oyster primary component. Proteins and other organic compounds can be found in oyster shells. The oxygen atoms in $CaCO_3$, a substance found in oyster shells, are the source of oxygen. Ca is derived from $CaCO_3$, the principal constituent of the oyster shell. Magnesium is believed to originate from magnesium carbonate, present in trace amounts within the oyster shell. Na, meanwhile, can be attributed to sodium chloride present in seawater. Most organic compounds, including proteins, contain a sizable amount of nitrogen. Consequently, the presence of proteins or other organic molecules is indicated by the presence of N in the oyster shell. It has been noted that the shell contains N at a 5.8% rate. The elevated N concentration in the oyster shell, compared to other elements, suggests an abundance of proteins or other organic molecules. Potential N sources in the shell encompass proteins from the oyster's diet, proteins secreted by the oyster itself, and bacteria or other microorganisms adhering to the oyster shell. This range of sources offers valuable insights into the chemical composition of the oyster shell. This data aids in assessing the purity of the oyster shell, identifying its elemental composition, and discerning potential impurities. Trace elements in shells typically originate from seawater, which harbors diverse minerals and elements utilized by shell-bearing organisms in shell formation. These components have the potential to alter the chemical structure and physical characteristics of shells. For instance, adding Mg to $CaCO_3$ crystals can increase the shells elasticity and durability. The components that organisms that bear shells acquire from seawater play a crucial role in the formation of their shells. Seawater indeed comprises Ca, Mg, -CO_3^{-2}, phosphate, and various other minerals. These elements serve as the building blocks for shell-bearing organisms in the formation of their shells. $CaCO_3$, in particular, stands out as the primary component of shells, with shell formation facilitated by the uptake of Ca and -CO_3^{-2} ions from seawater. Depending on the ratio of the elements they contain, shells can have different chemical compositions. For instance, the incorporation of Mg can enhance the strength and pliability of $CaCO_3$ crystals. As a result, shell-bearing species' shells can withstand larger environmental stresses. Furthermore, it is thought that additional factors may potentially affect the shells color and texture (Carroll & Romanek, 2008; Nakamura et al., 2014; Chakraborty et al., 2020). Indeed, the elemental composition of shells from shell-bearing organisms can contain traces reflecting geological and climatic variations. Alterations in elemental ratios within seawater can result in discrepancies in shell formation and composition. Consequently, the shells of these organisms serve as valuable archives for deciphering the history of geological and climatic transformations. Scientists are interested in researching the origins of materials found in shells as well as the mechanisms involved in shell creation. It is possible to learn more about the evolutionary processes of creatures that bear shells by comprehending the materials derived from saltwater and their role in the production of shells. In addition, understanding the consequences of environmental changes can be achieved by using the elemental content of shells as an indication (Carroll & Romanek, 2008; Nakamura et al., 2014; Agbaje et al., 2017, 2018a; Chakraborty et al., 2020). In summary, trace elements found in shells primarily derive from seawater and exert a substantial influence on the formation of shells in shell-bearing organisms. The presence of these elements can impact both the chemical composition and physical characteristics of shells. This phenomenon offers valuable insights into the evolutionary dynamics of shell-bearing organisms and their capacity to adapt to environmental changes. For scientists, this is a vital field of study, and knowledge of the past geological and climatic changes can be gained from studying the shells of creatures that carry them.

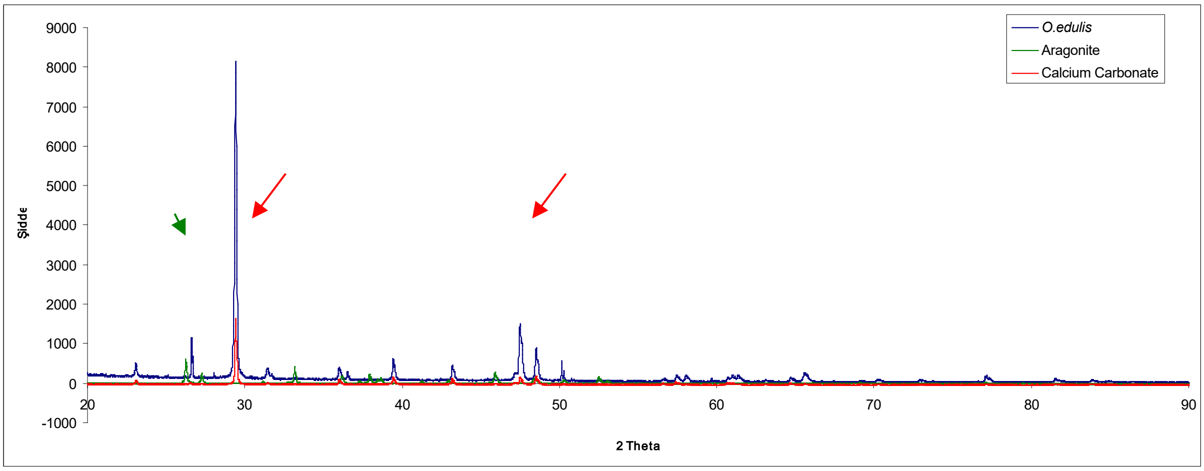

Figure 2. XRD spectrum of calcite, aragonite and *O. edulis* shell using the USGS data (USGS, 2001)

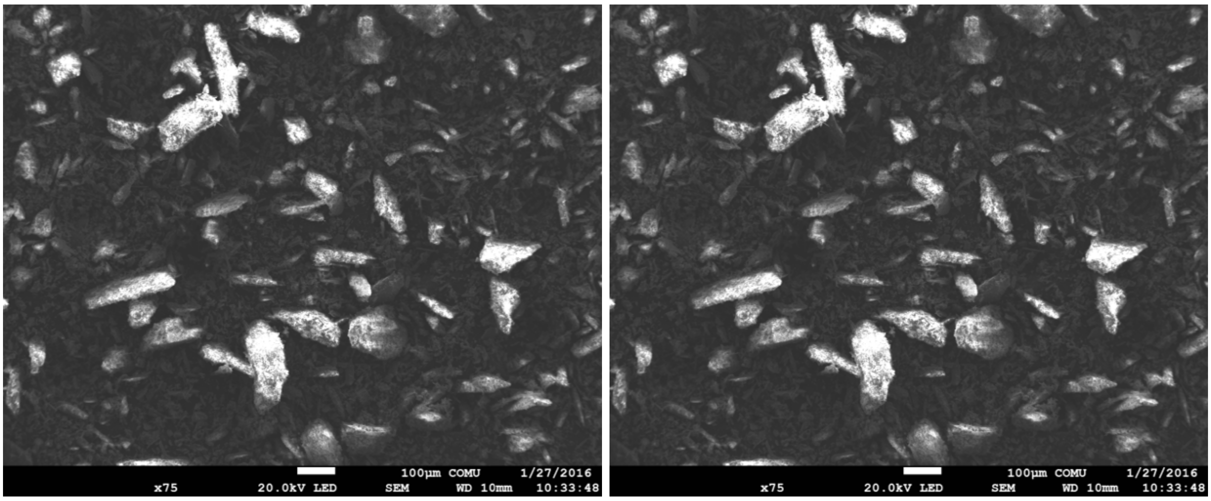

Figure 3. SEM images of *O. edulis* shells

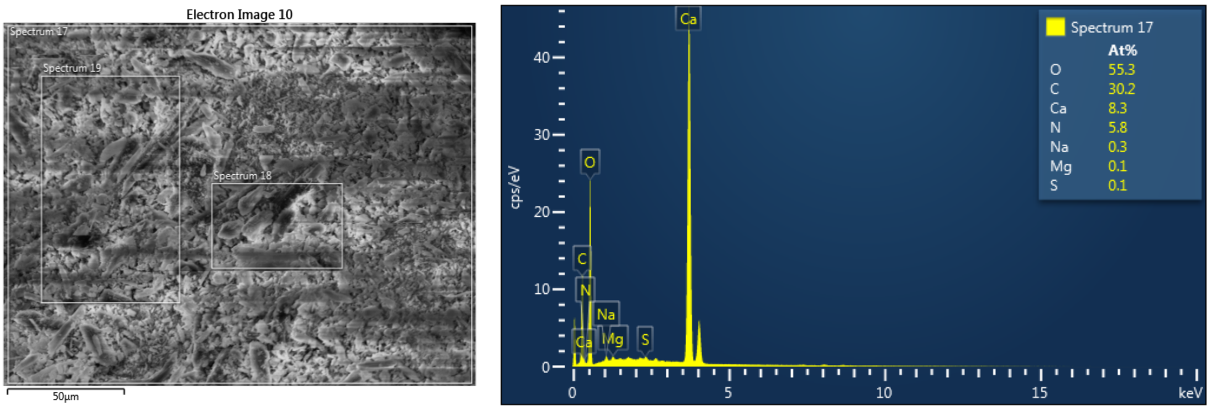

Figure 4. EDS spectrum of *O. edulis* shell

Fourier Transform Infrared Spectroscopy (FT-IR) is a spectroscopic method employed to elucidate the bond structures of molecules. In this technique, infrared light is directed onto a sample, where it interacts with the molecules present. The extent of light absorption by the sample molecules is contingent upon the wavelength of the incident light. The chemical makeup of a sample can be ascertained by measuring the absorption of light at various wavelengths. It is a very useful method for figuring out the molecular structures, functional groups, and chemical bonds of the material being studied. FT-IR spectroscopy is extensively utilized across diverse industries, including biological research, drug development, food analysis, and materials science. Its widespread application stems from its effectiveness in providing molecular-level information. Consequently, the primary objective of FT-IR analysis is to ascertain the structure of the main component present in the shells. The FT-IR spectra of Aragonite (the mineral crystal $CaCO_3$) from spectral data described during the RRUFF Project are given below in Figure 5A (Lafuente et al., 2015). In Figure 5A, the peaks observed at 1420 cm^{-1} correspond to the C-O stretching vibration, while those at 870 and 710 cm^{-1} represent additional C-O stretching vibrations within the $-CO_3^{-2}$ molecule. The FT-IR spectra of *Ostrea edulis* shells are depicted in Figure 5B. FT-IR analysis of the shell data revealed the presence of CO_3^{-2} vibration bands at 1420 cm^{-1}. The $-CO_3^{-2}$ molecule, which makes up the majority of the shell's chemical structure, has an in-plane bending band (V_4) that is moderately intense and appears at 710 cm^{-1}. The presence of the CO_3^{-2} bands, particularly at the observed peaks of 1420, 870, and 710 cm^{-1}, unequivocally indicates that the primary chemical structure of the shells is CO_3^{-2}. Additionally, in the spectrum of the sample, peaks are detected at 3400 (N-H stretching of amides), 1650 (C=O stretching of amides), and 1540 cm^{-1} (N-H bending of amides). Based on the positions of these peaks in the spectrum, it can be inferred that *O. edulis* shells comprises $CaCO_3$ and also contains proteins. This spectrum offers important insights on the chemical makeup of the structure of $CaCO_3$. The purity of the calcium carbonate structure, its crystal form, and the contaminants it contains may all be ascertained using this information. The primary Raman peaks of $-CO_3^{-2}$, which make up the shells of *Ostrea edulis* in this work, and aragonite, which was subjected to FT-IR analysis as part of the RRUFF Project (Lafuente et al., 2015), are complementary to one another.

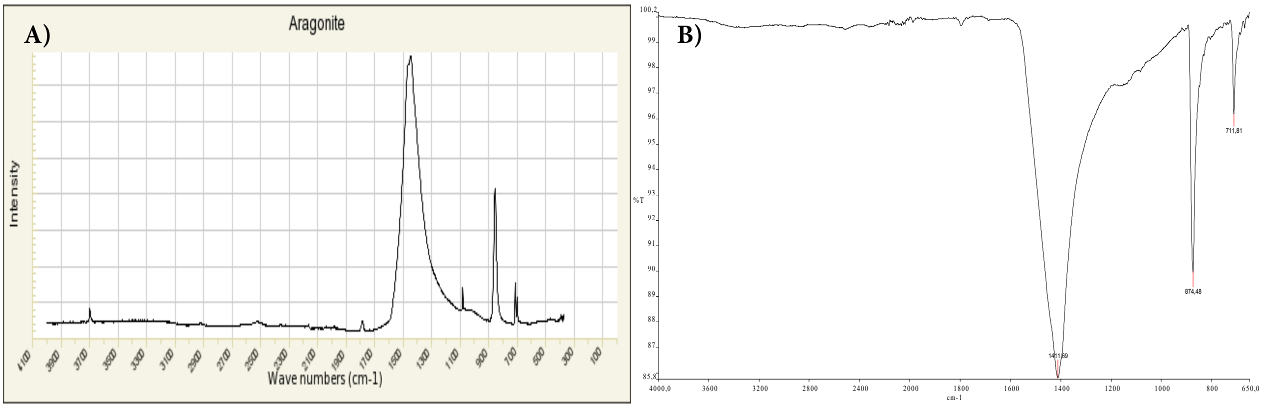

Figure 5. FT-IR spectra of **A)** Aragonite ($CaCO_3$) mineral crystal characterized within the scope of the RRUFF Project (Lafuente et al., 2015) and **B)** *O. edulis* shells

The structures found on shelled organisms are the result of the buildup of minerals like $CaCO_3$. In addition to shielding the organism's body, these shells are impacted by their surroundings. It is well recognized that environmental influences have an impact on the trace elements found in shells. For instance, the chemical makeup and trace element content of the shells can be impacted by the temperature, acidity, and salinity of the saltwater. As a result, changes in the environment can have an impact on the characteristics and makeup of shells in species with shells (Carroll & Romanek, 2008; Spann et al., 2010; Nakamura et al., 2014; Agbaje et al., 2017, 2018a; Chakraborty et al., 2020). The temperature, acidity, and salinity levels of seawater have a direct impact on the survival of shelled organisms. Additionally, these factors play a crucial role in shaping the growth and composition of their shells. For instance, as seawater acidity rises, shelled organisms may reduce their utilization of $CaCO_3$ during shell formation, potentially leading to the production of thinner and more fragile shells. These environmental changes pose significant challenges to the life and sustainability of shelled organism populations within marine ecosystems. Likewise, the salinity level of seawater can impact the composition of shells. Elevated salinity levels have the potential to modify the mineral content of shells, thereby decreasing their durability. Furthermore, environmental factors exert influence on the trace element content of shells in shelled organisms. Trace elements present in seawater significantly contribute to the composition of shells. For example, elements such as strontium, Mg, and Fe can have an impact on how shells develop. The composition of the shells can be affected by variations in the levels of these components due to changes in the surrounding environment. Scientific research has focused on how environmental conditions affect the trace elements found in the shells of organisms that have shells. New discoveries are made in the study of the chemical makeup of saltwater and the impact of environmental changes on shell composition. The findings of these investigations can aid in our comprehension of the life and evolutionary mechanisms of species with shells (Spann et al., 2010; Nakamura et al., 2014; Agbaje et al., 2017, 2018b; Chakraborty et al., 2020). In summary, the shells of shelled organisms are subject to the influence of environmental factors. Variations in seawater temperature, acidity, and salinity levels can directly impact the chemical composition and trace element content of these shells. Consequently, environmental changes have the potential to alter the composition and properties of shelled organism shells. This area remains a focal point of scientific investigation, with profound implications for the evolutionary trajectories of shelled organisms.

Conclusion

$CaCO_3$, the primary constituent of shells, enables marine organisms to construct their shells by utilizing dissolved minerals from the water. The bodies of the organisms expel these minerals, which are then utilized to create shells. A component of the calcium cycle in marine environments is the $CaCO_3$ found in shells. This study offers an in-depth analysis of the chemical composition of shells from *O. edulis* by identifying the zero charge sites (PZC) of the shells, the study examined their surface charge status. The results showed that the shells PZC value is 8.30, which offers important information about the shell characteristics and possible uses. The EDS results revealed that Ca, C, and O atoms, which are characteristic constituents of $CaCO_3$ structures, were present in the highest proportions, suggesting the predominant structure of the shells. The existence of $CaCO_3$ structures was confirmed by FT-IR research. XRD examinations were carried out as part of the study, and the findings showed that the shell formations are mostly composed of an aragonite and $CaCO_3$ mixture. These analyses offer crucial insights into the structural characteristics of the shells. While $CaCO_3$ emerges as the predominant chemical component of the shells, it is recognized that various small inorganic trace elements are often present in different bivalve species. Understanding the presence and impact of these trace elements is paramount in unraveling the complexities of bivalve ecology and shell formation processes. The preservation of marine habitats and the conservation of bivalve organisms are thought to benefit greatly from research in this field.

Acknowledgements

This study was funded by TÜBİTAK, Project number: TOVAG-113O381.

Compliance With Ethical Standards

Authors' Contributions

BK: Investigation, Methodology, Data curation, Formal analysis, Writing - original draft, Writing - review & editing

HY: Investigation, Writing - original draft, Supervision, Funding acquisition

PV: Investigation, Data curation, Formal analysis, Writing - review & editing

All authors read and approved the final manuscript.

Conflict of Interest

The authors declare that there is no conflict of interest.

Ethical Approval

For this type of study, formal consent is not required.

Funding

This study was funded by TUBİTAK, Project number: TOVAG-113O381.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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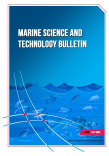
Mar. Sci. Tech. Bull. (2024) 13(2): 151-167
e–ISSN: 2147–9666
info@masteb.com

dergipark.org.tr/en/pub/masteb
www.masteb.com
DOI: 10.33714/masteb.1414048



Marine Science and Technology Bulletin

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RESEARCH ARTICLE

Integrative probabilistic design of river jetties by 3D numerical models of transport phenomena: The case study of Kabakoz River jetties

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ARTICLE INFO

Article History:
Received: 03.01.2024
Received in revised form: 02.04.2024
Accepted: 15.05.2024
Available online: 24.06.2024

Keywords:
Coastal structures
HYDROTAM-3D
Marine engineering
Monte Carlo simulation
Probabilistic design
Wave transformation

ABSTRACT

Various methods are employed to investigate the effects of coastal structures in coastal areas on marine environments and transport phenomena. These methods can be categorized into physical models and numerical simulations. Due to the lack of long-term wave height data in Türkiye, numerical models are utilized to estimate wave heights generated by wind based on long-term measured wind speeds. These wave heights generated in deep sea conditions can be transported to the coast by wave transformation and interactions between coastal structures and waves, turbulence, currents induced by wind and breaking waves, coastal sediment transport rates, and changes in the coastline can be successfully predicted with the assistance of numerical models. In the scope of this study, the new "Integrative Probabilistic Design Approach of River Jetties" was developed. 3D numerical models were used for the optimum design, considering the sediment transport near the jetties and aiming to protect the coastal environment in the long term. 3D numerical modeling has been conducted to investigate the transport phenomena occurring at the outlet of the Kabakoz River in the Şile District of İstanbul Province to acquire the optimum layout and design of the coastal structures. The study presents the "Integrative Probabilistic Design Approach" for coastal protection structures by wind and wave climate, wave transformation, coastal sediment transport, shoreline change, and coastal structure probabilistic design sub-models. Monte Carlo Simulation of Hudson Limit State function conducts probabilistic design for the jetties. The greatest advantage of probabilistic design (Monte Carlo Simulation) is the prediction of uncertainties, such as wave height changes under design conditions. Following the completion of the construction of groins, the effect of probabilistic design on both design and coastal morphology can be evaluated precisely. In conclusion, in the study area, 146,237.55 m^3 of sediment is transported annually from west to east and 221,043.49 m^3 from east to west. In the absence of coastal structures, sediment transport from east to west is approximately 1.5 times greater than from west to east. The annual net coastal sediment transport from east to west is approximately 74,805.94 m^3, while the total transport is estimated to be 367,281.04 m^3. The coastline is expected to reach sediment balance within approximately two years. In this study, the coastal structure of a jetty is designed from an innovative probabilistic design

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perspective. The aim is to ensure the reliability of the structure and, at the same time, protect the morphology of the coastline where the structure will be constructed. The region's wind and wave climate were initially determined using Hydrotam 3D software. Following this procedure, the length of the jetty is predicted considering the closure depth. The model parameters were calibrated from coastline morphology using satellite images and Google Earth over the past twenty years. These parameters are defined to Hydrotam 3D as input data; a trial-and-error model application procedure calibrates the coastline's accumulation and erosion. Finally, the probabilistic design is conducted with Monte Carlo Simulation using the Hudson Equation as the limit state function. Det Norske Veritas developed a design code for marine structures in 1992, where the target reliability is 10-3 for structures with less serious failure consequences. This reliability level validated the Level IV model presented in this paper. The class of failure depends on the possibility of timely warning, and these standards can be revised by the model presented to address the effects of climate change on the design of maritime structures.

Please cite this paper as follows:

Uğurlu, A., & Balas, C. E. (2024). Integrative probabilistic design of river jetties by 3D numerical models of transport phenomena: The case study of Kabakoz River jetties. *Marine Science and Technology Bulletin*, *13*(2), 151-167. https://doi.org/10.33714/masteb.1414048

Introduction

The study area covers the coastal area of Kabakoz Beach, located in Şile District, Istanbul Province, as shown in Figure 1 and Figure 2.

Figure 1. Geographic location of the study area (Google Earth, 2023)

Figure 2. Location of study area (Google Earth, 2023)

Lima et al. (2020) determined the length of the jetty, considering the changes in coastal morphology but ignoring the design procedure of the jetty.

An erosion study conducted by Roebeling et al. (2018) on the central Portuguese coast includes economic design circumstances by focusing on coastal morphology evaluation but not the structure's design. Various coastal structures were compared for their effects on coastal morphology by Franzen et al. (2021) but the design method directly affecting morphology was not considered. The effects of Pranburi Jetties on the coastal area, which take place in Pranburi River Inlet located on the western coast of the Gulf of Thailand, were studied by Phanomphongphaisarn et al. (2020). The one-line model was used to obtain the results by focusing on coastal erosion and ignoring the design methodology and advantages of a 3D model. The shoreline change on North Java Beach with groin protection was investigated by Setyandito et al. (2020), concentrating on morphology effects but ignoring the design conditions of the system. As seen from the studies in the literature, there is a gap for an integrated approach for marine structures fulfilled by this study. This study aims to develop a methodology to revise the design standards by examining the effects of climate change.

Material and Methods

To determine the wind climate of the study area, hourly wind measurements from the Şile Meteorological Station and 6-hour wind forecasts from the ECMWF (European Centre for Medium-Range Weather Forecasts) operational archive at coordinates 41.2°N-29.7°E, representing the project area, were compared and analyzed. The comparisons of wind speeds between the common measurement periods and durations of data sources are presented in Figure 3. All presented wind speed measurements and hindcasts are at a height of 10 meters (U10). After the comparison studies, it was concluded that wind predictions over the sea surface for the coordinates 41.2°N-29.7°E from ECMWF between 2000-2021 are consistent with the data from the Şile Meteorological Station. It was decided that these data over the sea surface could be used to determine the wind climate of the coastal area in the project area. Upon examination of the wind roses provided in Figure 4, it is observed that the wind predominantly blows from the northeast (NE) to the east-northeast (ENE) direction, progressing clockwise from the sea. During the winter and spring seasons, the frequency of southwest (SW) winds blowing from the land is observed, while during the summer and autumn seasons, the frequency of northeast (NE) winds tends to increase.

Monthly average and maximum wind speeds are also presented graphically (Figure 5). The monthly averages of wind speeds were calculated by taking the arithmetic mean of all wind speeds within that month. Monthly maximum values represent the highest, lowest, and average maximum values observed within that month over the same periods (the average of the highest values for each year for any given month).

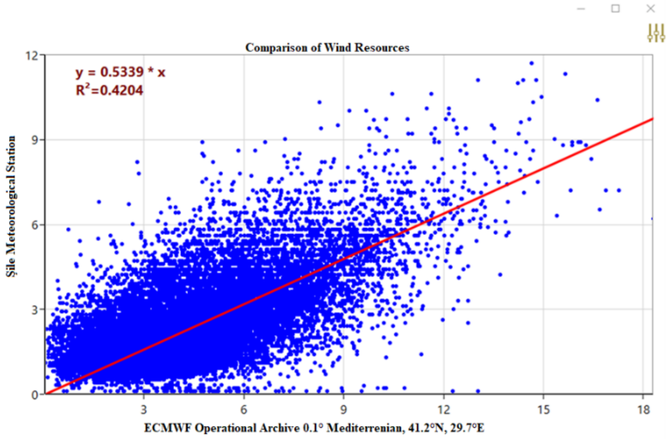


Figure 3. Comparison of wind speeds obtained from Şile Meteorological Station and ECMWF over sea surface Operational Archive at 41.2°N-29.7°E (HYDROTAM-3D, 2023)

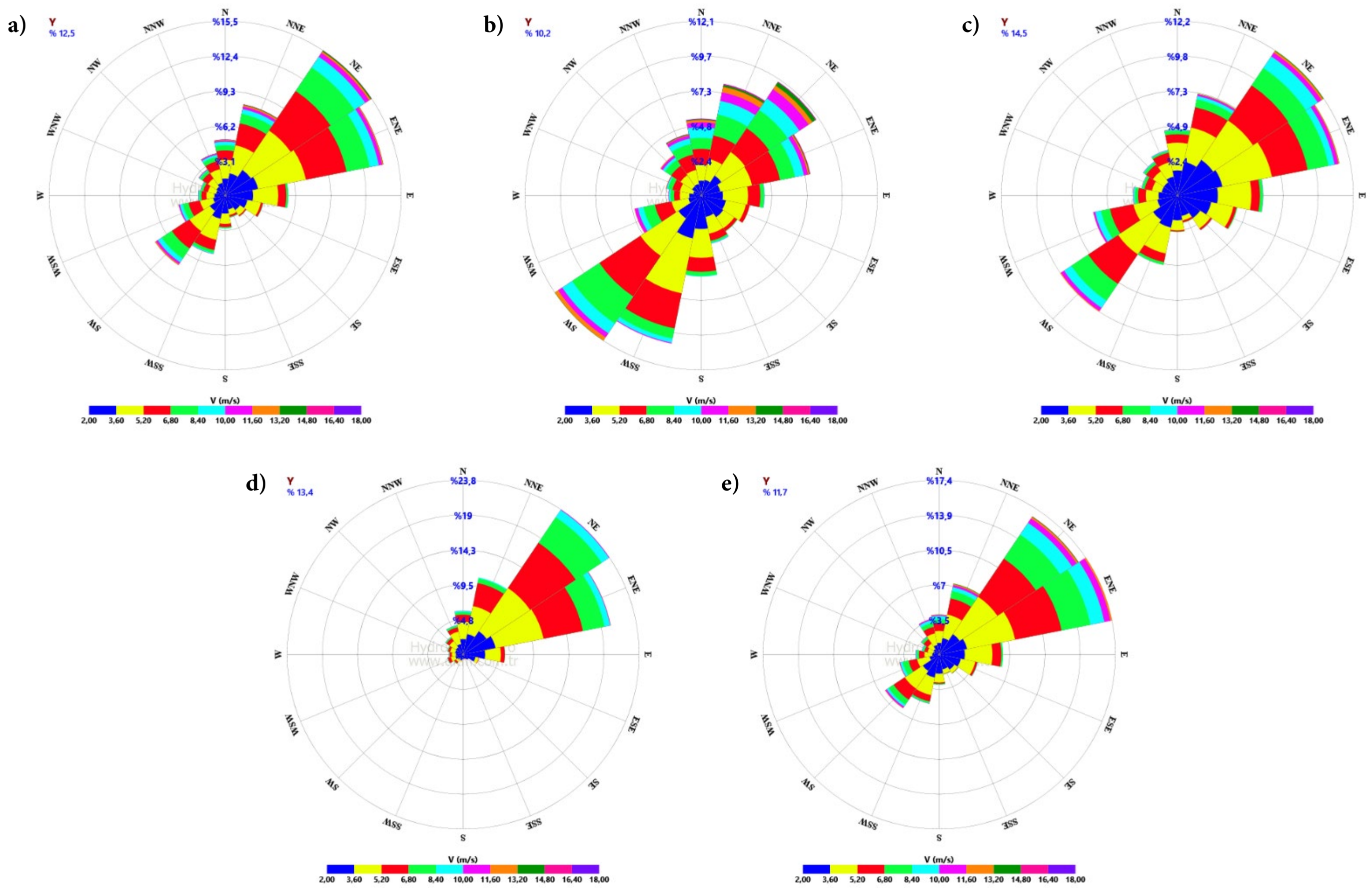


Figure 4. a) Annual and seasonal (b: winter, c: spring, d: summer, e: autumn) wind roses for the ECMWF over the sea surface Operational Archive at coordinates 41.2°N-29.7°E (HYDROTAM-3D, 2023)

The highest wind speeds and prevailing wind directions by year are presented in Figure 6. While the monthly average wind speed ranges from 4 to 5 m/s, the highest maximum wind speeds vary between 12 and 18 m/s. During the study period, the highest wind speed, at 18 m/s, was observed coming from the North (N) direction.

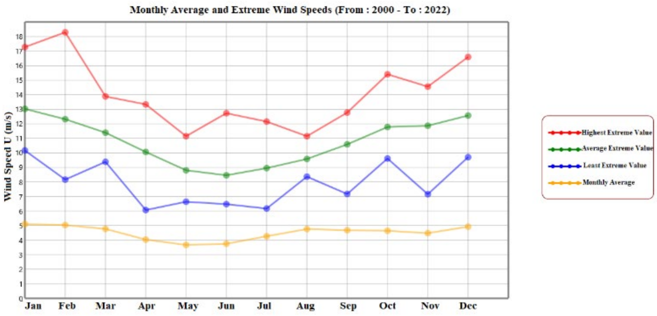


Figure 5. Monthly average and maximum wind speeds based on ECMWF operational archive data at coordinates 41.2°N-29.7°E for 2000-2021 (HYDROTAM-3D, 2023)

In the studied marine area, effective fetch distances ('fetch'; the length of the sea area extending from one coast to another in the wind direction) have been determined in Figure 7 and presented in Table 1. The cosine-averaging method was applied to determine the effective wave fetch length for all directions. Considering the location of the marine area, the wave fetch distances that could cause the most wave actions are in the North-northeast (NNE) – East-northeast (ENE) direction range.

ECMWF conducts meteorological predictions using its atmospheric numerical model and performs wave predictions with a third-generation wave model called the WAM wave prediction model, one of the most widely used models worldwide. Developed collaboratively by researchers and scientists in the WAve Model Development and Implementation (WAMDI) group, this model aims to provide a wave prediction tool based on physical principles (Wamdi Group, 1988).

Table 1. Effective fetch distances ("Fetch") (km)

Direction	Angle (°)	Eff. Fetch (m)
N	0	464930.1
NNE	22.5	581098.8
NE	45	526249
ENE	67.5	674081.9
E	90	72782.8
ESE	112.5	1962.23
SE	135	998.25
SSE	157.5	729.37
S	180	678.33
SSW	202.5	631.11
SW	225	581.32
WSW	247.5	545.65
W	270	17198.6
WNW	292.5	164450.8
NW	315	251326.7
NNW	337.5	320392.6

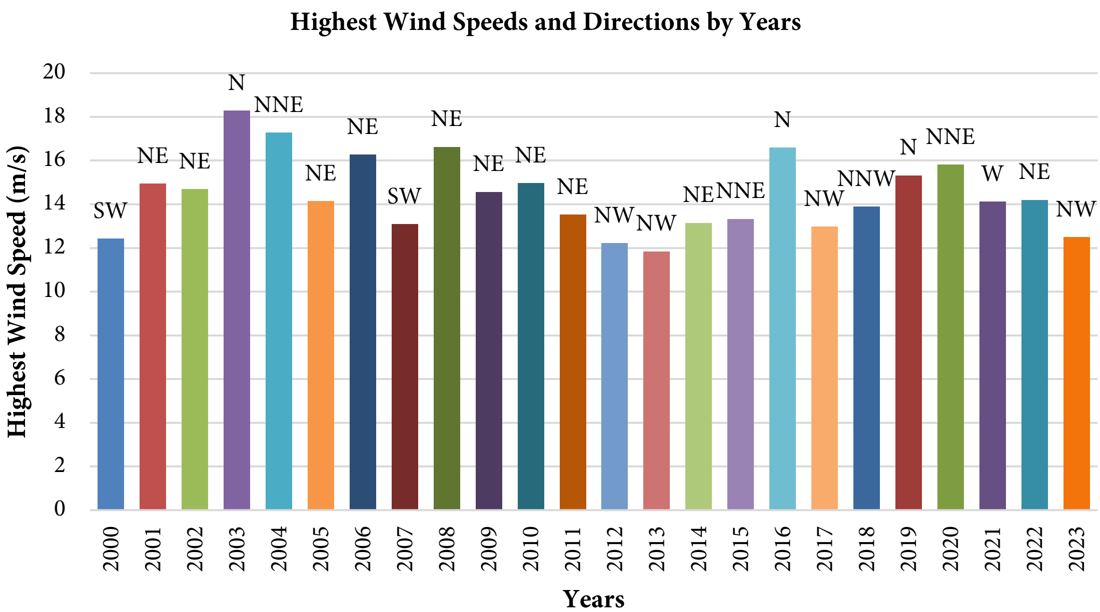


Figure 6. The highest wind speeds and prevailing directions based on ECMWF operational archive data at coordinates 41.2°N-29.7°E for 2000-2021 (HYDROTAM-3D, 2023)

Long-term wave statistics studies were conducted using wave predictions from the ECMWF operational archive for 2000-2022 at the coordinates 41.2°N-29.7°E. The significant wave height (Hs,12) with a 12 hours per year exceedance probability obtained from long-term wave statistics studies falls within the 1.66 m < Hs,12 < 5.47 m. The classification based on wave height in the Coastal Structures Planning and Design Manual of AYGM (2016) corresponds to the effective coastal (E) classification. The model predictions also indicate that the primary directional range is from North (N) to Northeast (NE) in a clockwise direction.

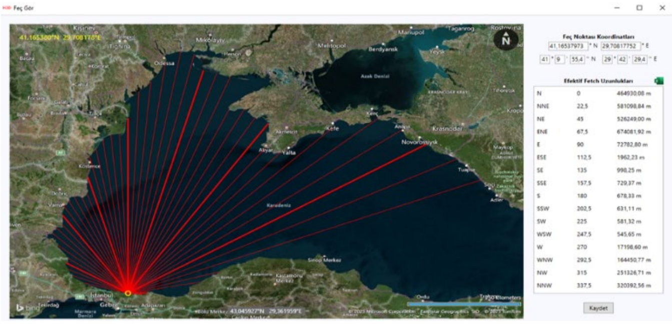


Figure 7. Fetch distances by directions (HYDROTAM-3D, 2023)

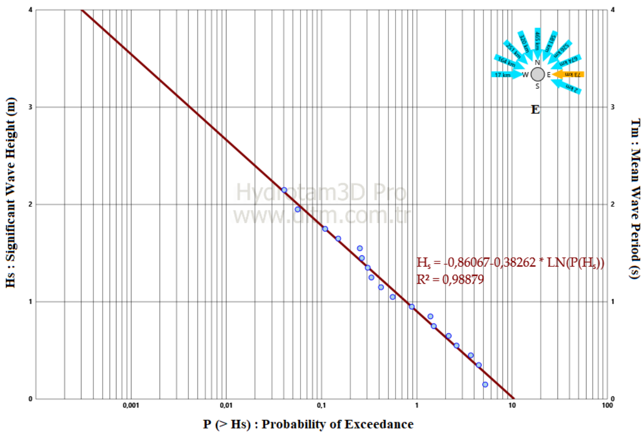


Figure 8. Long-term significant wave statistics for the East (E) direction

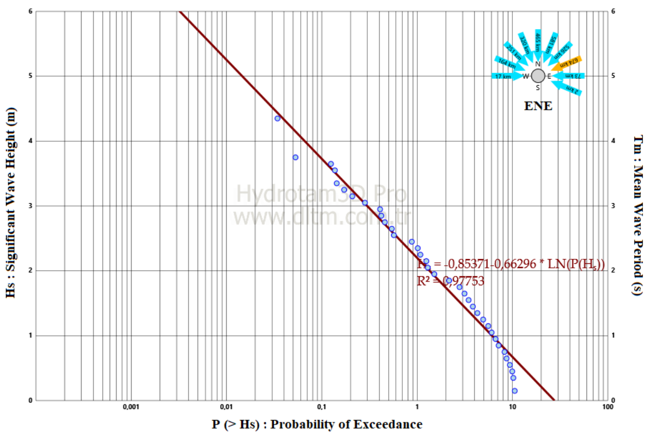


Figure 9. Long-term significant wave statistics for the East-northeast (ENE) direction

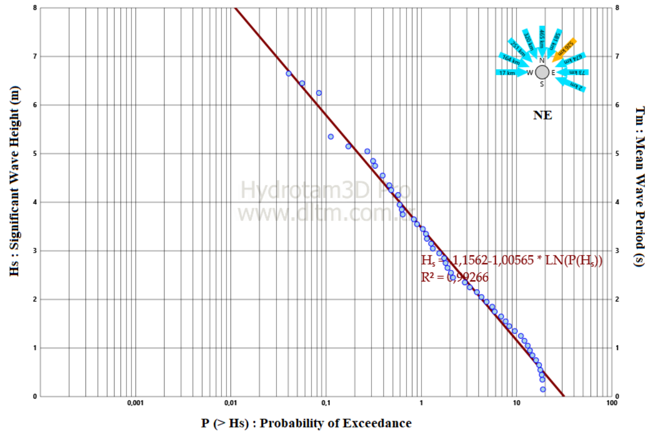


Figure 10. Long-term significant wave statistics for the Northeast (NE) direction

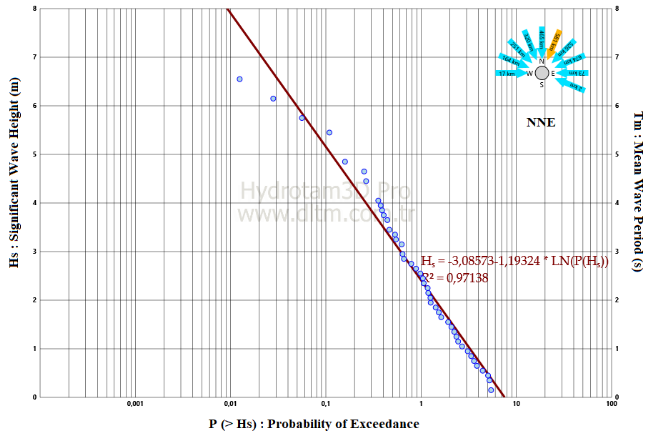


Figure 11. Long-term significant wave statistics for the North-northeast (NNE) direction

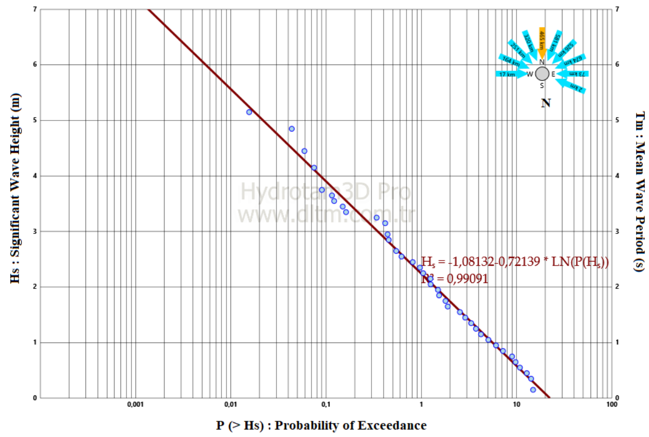


Figure 12. Long-term significant wave statistics for the North (N) direction

The results of the long-term wave statistics are presented in Figures 8-12. As part of the long-term wave statistics studies, the relationship between significant wave height (Hs) and mean wave period (Tm) for all directions is shown in Figure 13.

Table 2. The deep-sea significant wave height, mean wave period, breaking height, breaking depth, and breaking wavelengths for waves approaching the marine area

Approach Direction	Deep-sea significant wave height H_o (m)	Wave Period T(sec)	Deep Sea Wavelength L_o(m)	Breaking Wave Height H_b (m)	Wave Breaking Depth d_b (m)	Breaking Wavelength L_b(m)
NNW	5.45	7.53	88.37	5.04	6.37	54.99
NW	4.55	7.98	99.26	3.71	4.46	50.29
WNW	4.15	7.63	90.82	2,52	2.12	36.52

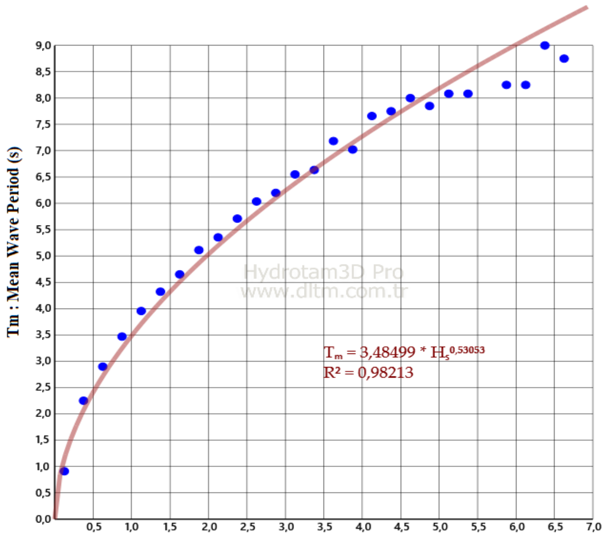


Figure 13. Long-term wave statistics: the relationship between significant wave height and mean wave period (Hs - Tm) (HYDROTAM-3D, 2023)

Annual and seasonal wave roses are presented in Figure 14, and monthly average and maximum significant wave heights are shown in Figure 15. When examining the long-term log-linear wave statistics studies, it is observed that the prevailing waves originate from the North (N) and East-northeast (ENE) directional ranges in the clockwise direction. The predominant directions are North (N) and Northeast (NE) in the winter and spring. The dominant wave direction during the summer is northeast (NE). In the autumn season, the dominant wave directions are Northeast (NE) and East-northeast (ENE) (Figure 14). While the monthly average wave height is at its highest, reaching 1 meter, the maximum significant wave heights vary in the 2.50-6.50 meters (Figure 15). In the long-term statistics, wind data from the ECMWF Operational Archive were utilized for the offshore point of the port. Figure 16 provides extreme (maximum) design wave values and non-exceedance probabilities obtained for specific recurrence periods for deep-sea highest wave heights over the years. As seen in Figure 16, for a 50-year return period (Rp=50 years return period), the significant deep-sea wave height (with a 90% confidence interval) is Hs=8.03 meters, and the average wave period is Tm=11.33 seconds (HYDROTAM-3D, 2023).

The accuracy of HYDROTAM-3D has been assessed through comprehensive verification and validation studies, and the model has been applied to a wide range of applications in the last 20 years (Balas & Balas, 2023). Research has shown that HYDROTAM-3D has proved successful for a wide range of applications in real-life scenarios around the coast of Türkiye.

The HYDROTAM-3D is supported by Geographic Information Systems (GIS) and cloud computing, which facilitates processes such as data entry and output and remote access to all functions through a graphical user interface controlled by a menu structure. The model has a relational database for Turkish coastal waters that includes bathymetries of all Turkish coasts, hourly wind data since establishing Turkish Meteorological Stations (MS), and measured physicochemical data at the sites.

Based on long-term wave statistics in the marine area, the deep-sea significant wave height, mean wave period, breaking height, breaking depth, and breaking wavelengths for waves approaching from different directions are provided in Table 2.

In the marine area, the approximate depth of the wave-breaking zone is between the water depth of d = –6.37 meters and the shoreline.

The process of determining the height, period, and direction values of waves coming from deep-sea conditions, considering bathymetry and boundary conditions (islands, bays, capes), as well as the influence of coastal orientation, for sizing the structure to be designed is referred to as wave transformation. Wave transformation, or the process of obtaining the wave in front of the structure (wave transformation), was carried out to design the jetties planned at the mouth of Kabakoz Stream using the wave propagation module of the HYDROTAM 3D software (Balas & Balas, 2023) For the analysis, the bathymetry of the study area was initially loaded into the model (Figure 17).

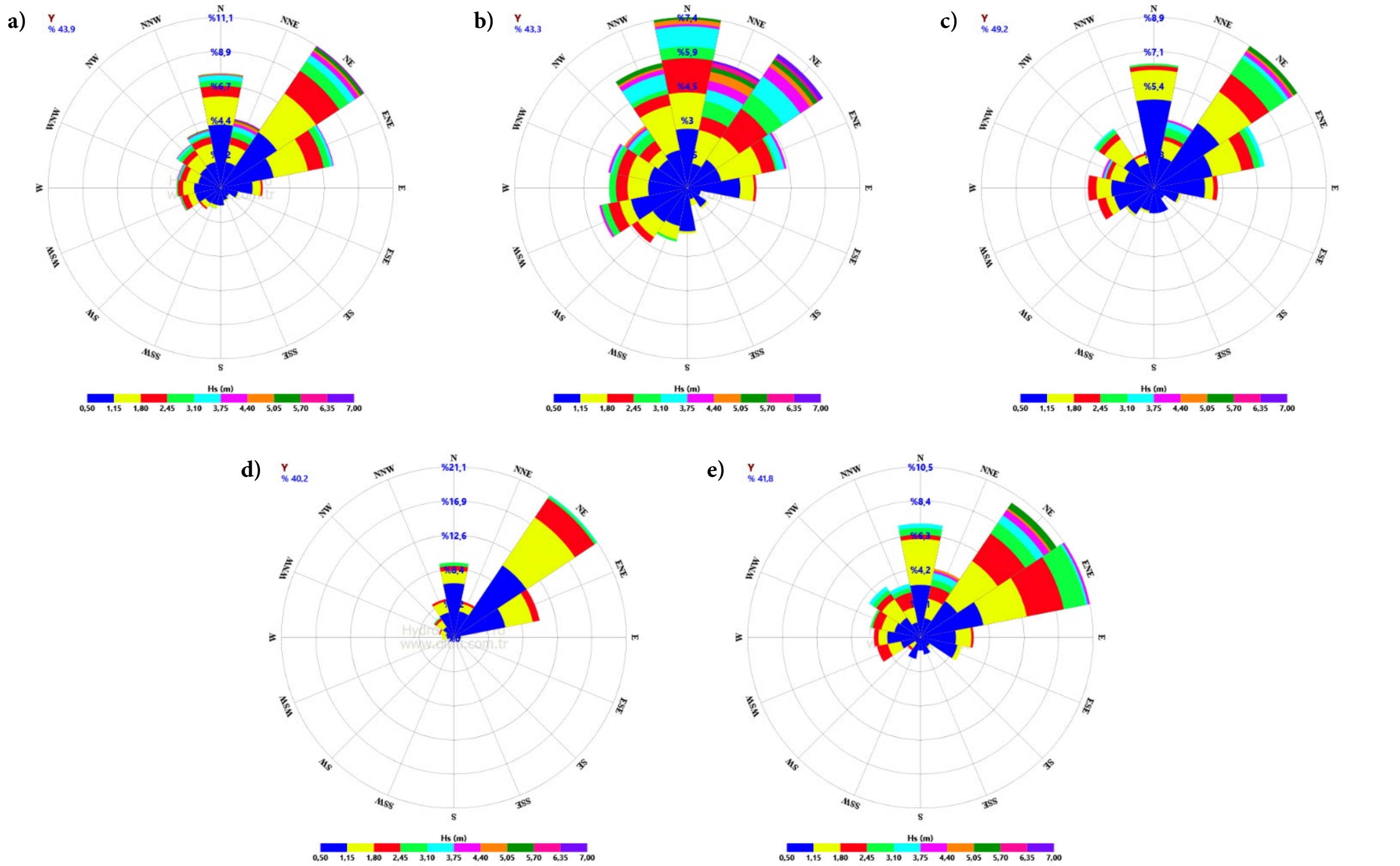


Figure 14. The project area's a) annual and seasonal (b: winter, c: spring, d: summer, e: autumn) wave roses (HYDROTAM-3D, 2023)

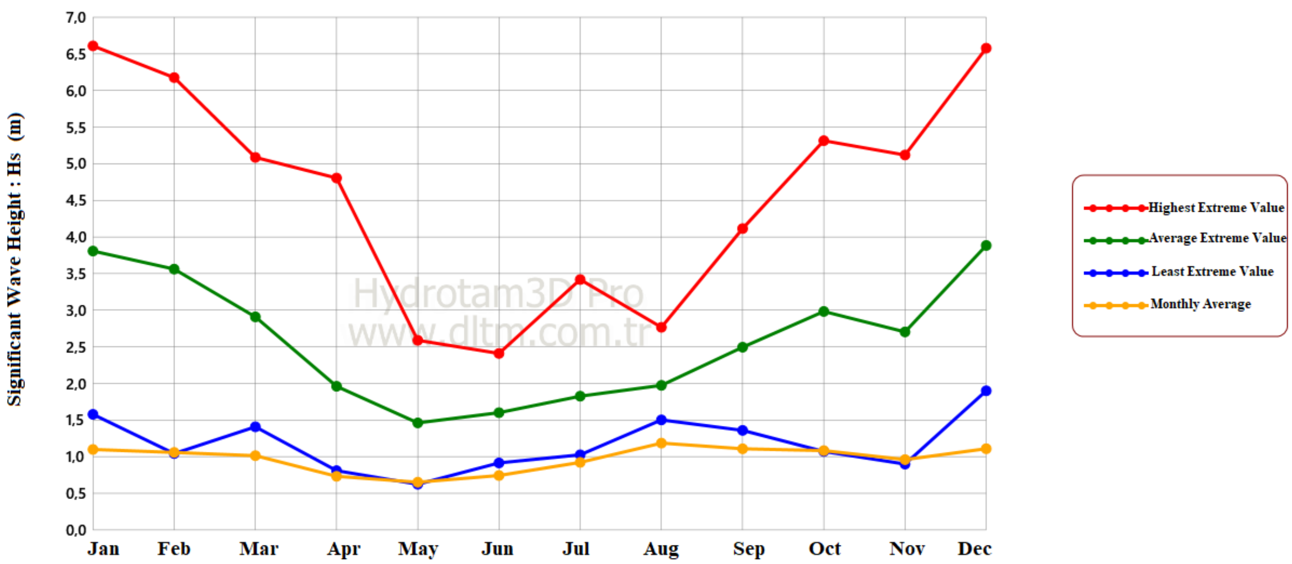


Figure 15. Monthly average and maximum significant wave heights (HYDROTAM-3D, 2023)

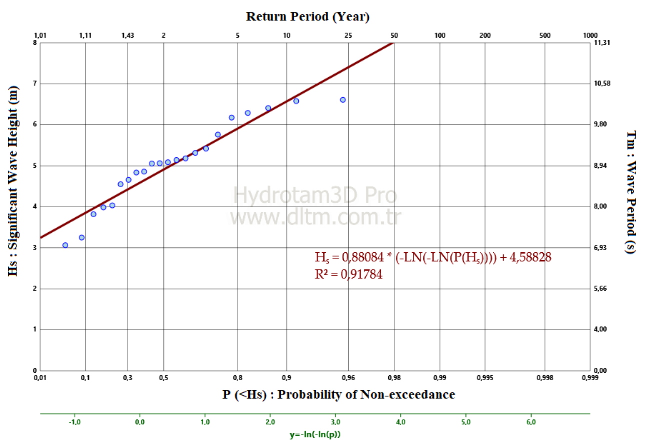


Figure 16. Extreme wave statistics (Gumbel Distribution) (HYDROTAM-3D, 2023)

The significant deep-water design wave height having a return period of Rp=50 years was obtained from the HYDROTAM3D wave climate module (Balas et al., 2023) with a 90% confidence interval as Hs=8.03 meters and an average wave period of Tm=11.33 seconds. The wave values obtained regionally because of the analysis are presented in Figure 16. The wave in front of the structure (design wave) was obtained using the HYDROTAM3D wave propagation module. The wave value at the structure's outermost point (crest), which should be formed at -2m according to the closure depth, was obtained as a model result. Solving the shallow-water slope equations with the HYDROTAM3D model transforms the predicted wave heights in open waters into coastal areas under bathymetry and topography (Balas et al., 2023). Effects such as shoaling, refraction, diffraction, friction, breaking, and wave setup are calculated during wave propagation. Spatial or pointwise distribution maps of wave heights or temporal change graphs can be accessed. As a result, the Design Significant Wave Height in front of the structure was determined as Hs=1.60 meters, and the average wave period Tm=4.65 seconds (Figure 18).

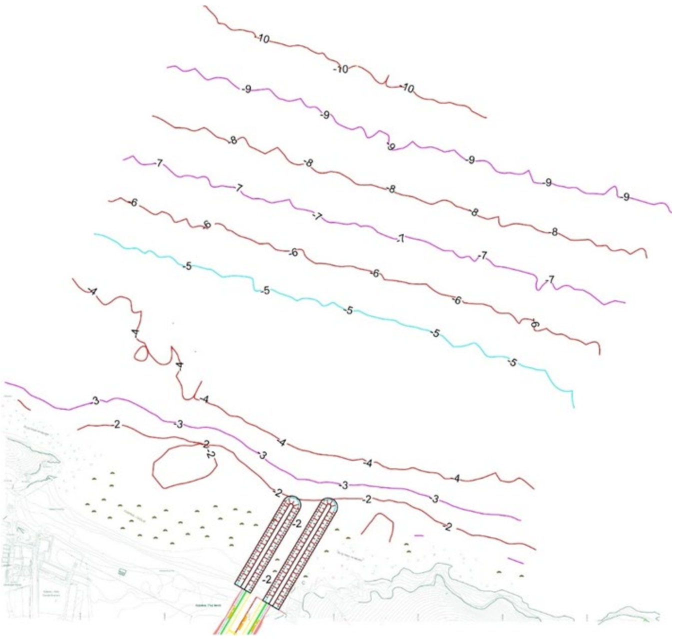


Figure 17. The bathymetry of the project area

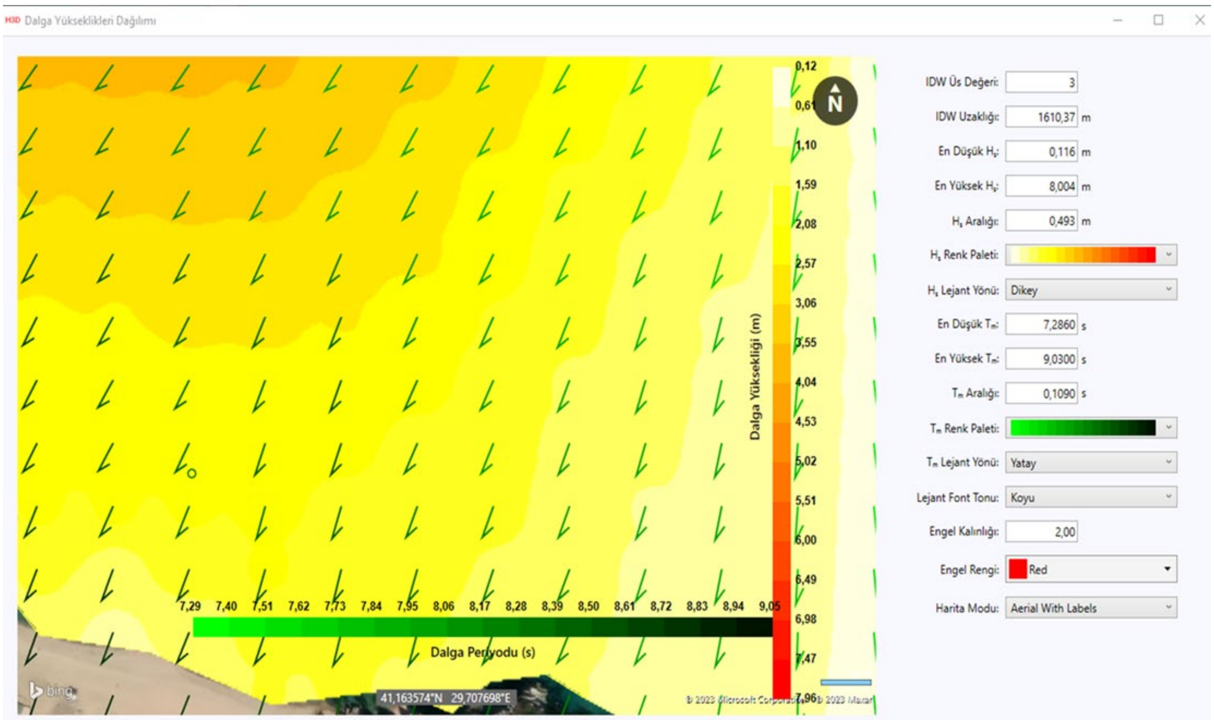


Figure 18. The study area's wave height (Hs) distributions (HYDROTAM-3D, 2023)

The closure depth was investigated to determine the distance from the outlet of the Kabakoz River jetty to the coastline. The closure depth is a theoretical depth along the beach profile where sediment transport does not occur, depending on wave height, period, and sediment grain size. Two equations by (Birkemeier, 1985; Hallermeier, 1981) are used to investigate the closure depth. Both equations use the significant wave height with a 12-hour annual exceedance probability.

Hallermeier closure depth equation (Hallermeier, 1981):

$$DoC = 2.28 * H_{\frac{12h}{y}} - 68.5\left(\frac{H^2_{\frac{12h}{y}}}{g * T^2_{\frac{12h}{y}}}\right) \quad (1)$$

Birkemeier closure depth equation (Birkemeier, 1985):

$$DoC = 1.75 * H_{\frac{12h}{y}} - 57.9\left(\frac{H^2_{\frac{12h}{y}}}{g * T^2_{\frac{12h}{y}}}\right) \quad (2)$$

The closure depths were investigated using the east (E) direction, which has the lowest wave height among the directions shown in Figure 8, and depths of -2.92 m according to the (Hallermeier, 1981) equation and -2.17 m according to the Birkemeier formula were obtained. The closure depth was determined based on these two formulas, and a value giving a shallower depth (Birkemeier) was selected to stay on the safe side. The deepest point of the structure was approximately set at -2.00 m, behind the closure depth as a result of these studies. In the event of a storm, the basin where the structure is seated, including the lower part, must be scanned to -2.00 m from the coast to the structure's end to eliminate the effect of stream-sea interaction and prevent sediment accumulation at the jetty mouth. This way, rebound effects will be prevented, and the risk of flooding will be mitigated. Following the modeling studies, jetty structures are proposed for the Kabakoz Stream in Figure 19, which will not affect the shoreline change. Closure depth is a theoretical depth along the beach profile where sediment transport does not occur, depending on wave height, period, and sediment grain size. The closure depth is the most important criterion in designing a structure that will not harm the coastal morphology. The hydraulic structure designed based on this value is presented in Figure 19.

The circulation in coastal water bodies is generally irregular and turbulent. The model connects turbulent and mean motion through vertical and horizontal eddy viscosities and mass exchange caused by vertical and horizontal eddy diffusions. In coastal waters where the surface area of the water body, such as a gulf, is large compared to its depth, the turbulence intensity of the motion significantly varies in both horizontal and vertical directions. This difference in vertical and horizontal lengths creates a non-isotropic condition, making it crucial to use different eddy viscosity values in the model for both horizontal and vertical directions in simulations. By utilizing eddy viscosity values calculated with the isotropic k-ε model in the vertical direction, horizontal eddy viscosity values have been computed in the direction that compensates for this difference using a sub-turbulence model with a length scale in the horizontal direction. The seawater temperature, salinity, and density have been assumed to be constant spatially and throughout the depth.

Figure 19. Designed jetty structure

A modeling study was conducted to determine the current pattern in the study's coastal area. 6-hour wind data was obtained from the ECMWF operational archive at coordinates 41.2°N–29.7°E for 2000-2022; 6-hourly annual current pattern time series were obtained. The current profile along the depth, obtained at the point where the depth of the jetty is approximately -2 m in the modeling area, is presented in Figure 20.

Coastal sediment transport analysis was conducted for the Kabakoz Beach segment based on the depth of breakwaters. Annual net and gross sediment volumes transported in different directions (m^3/year) are presented in Figure 21. The annual sediment transport for Kabakoz Beach, which is approximately 300 meters long and bounded by rocky headlands from both east and west, is 367,821 m^3/year. Due to the small and sheltered nature of the study area from both directions, the annual gross sediment transport does not reach high figures. This situation is crucial for the construction of perpendicular structures along the coast.

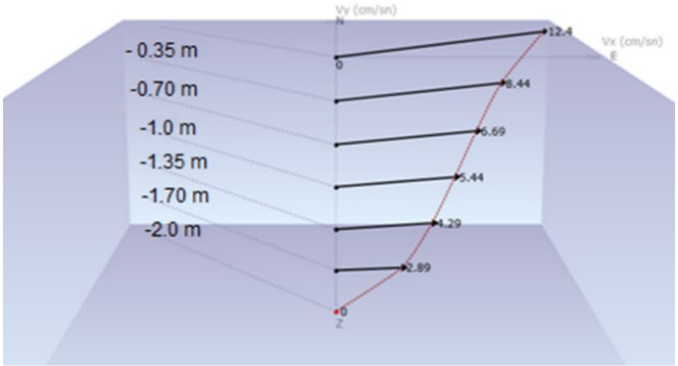


Figure 20. Current profile along the depth of 2.0 m at the jetty outlet under the influence of NNW direction winds at a speed of 10 m/s (HYDROTAM-3D, 2023)

This study included all uncertainties that occur in nature during the design process of coastal structures. Hence, this methodology eliminates the limitations of other methodologies, such as deterministic methods, where the variation in sea levels due to climate change cannot be involved in the design as a standard procedure. The effects of climate and environmental changes can be considered in future regulation alterations using the methodology suggested in this paper, which is the main advantage of this method. The methodology developed in this paper can be used to modify design standards for the near climate change era.

All the wind and wave data used within the study were collected from ECMWF, the regulative body for meteorology in the EU, as the data source, giving reliable results in the design procedure. Probabilistic design is a method that considers all the uncertainties, gives precise results for the design, and considers the challenges the structures will embrace during their lifetime. The assumption of HYDROTAM-3D is that it uses the implicit baroclinic three-dimensional unsteady Navier-Stokes Equations with the Boussinesq assumption. The limitation of the model is that it numerically simulates hydrodynamic transport, turbulence, and water quality, and calibrating the model is necessary for initial and boundary conditions using measured data.

Results

The three-dimensional Hydrodynamic Transport Model, HYDROTAM-3D (Balas & Balas, 2023), was used to obtain wind and wave climate in the study area. The coastal direction in the marine study area approximately extends from West (W) to East (E) (Figure 21). Directions lying to the east of the normal to the coastline (N, NNE, NE, ENE, E) contribute to sediment transport from east to west, while directions lying to the west of the normal to the coastline (NNW, NW, WNW, W) cause sediment transport from west to east. The net sediment transport quantity is the difference between the two transports, and the total (gross) sediment transport quantity is the sum of the two transports. Due to the east-west (E-W) direction of transport, erosion will occur in the impact area of the western breakwater.

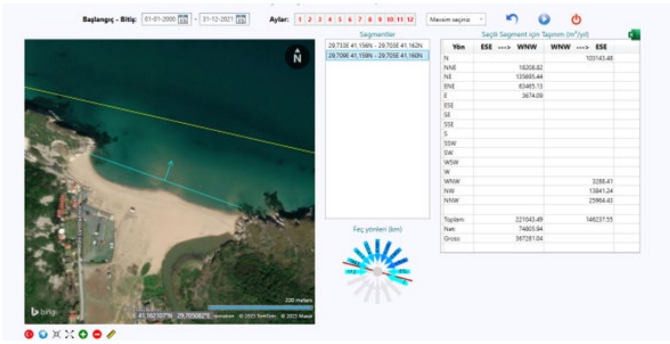


Figure 21. Coastline orientation and sediment transport directions

Since the eastern breakwater will be in the region where the rocky area begins, it will not affect sediment transport. The breakwater lengths are approximately the same as the two rocky headlands that bound Kabakoz Beach. According to the model results, the coastline of Kabakoz Beach, which is already quite sheltered between two rocky headlands, is within a sediment movement of about 300 m of coastline. According to the model results, the coastline reaches sediment equilibrium within approximately two years. Sediment transport, influenced by many parameters such as the depth of breakwaters, bathymetry, coastal sediment grain size, structure location, and dimensions, closure depth, predicts a maximum erosion of 3 m west of the western breakwater and a maximum accumulation of 3 m east of the eastern breakwater. The locations of the newly constructed jetties and the direction of the coastline extension are presented in Figure 22. The change in the coastal line from 2003 to 2021 has been examined for the calibration of the model, as shown in Figure 23 and Figure 24.

As observed from these drawings, the coastal sediments move along the coast (longshore) within Kabakoz Beach (approximately 300 m), given that the coastline is bordered by headlands in both directions. In this case, the coast is in equilibrium, meaning the sediment budget shows minimal changes. Furthermore, constructing jetties at the easternmost part of the coast, where rocky headlands end, will have a limited impact on coastal morphology.

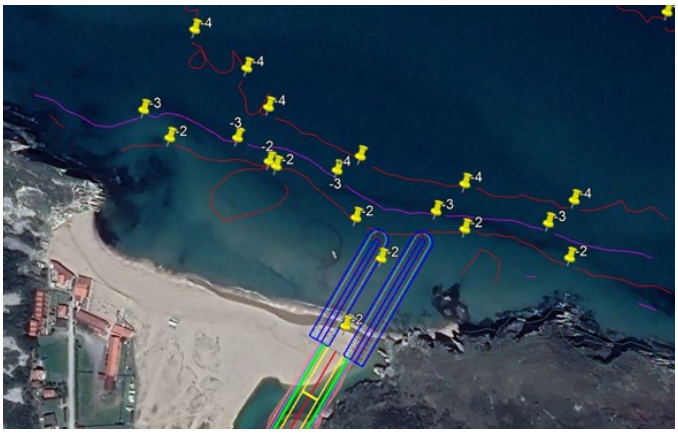


Figure 22. The locations of the newly constructed jetties and the direction of the coastline extension

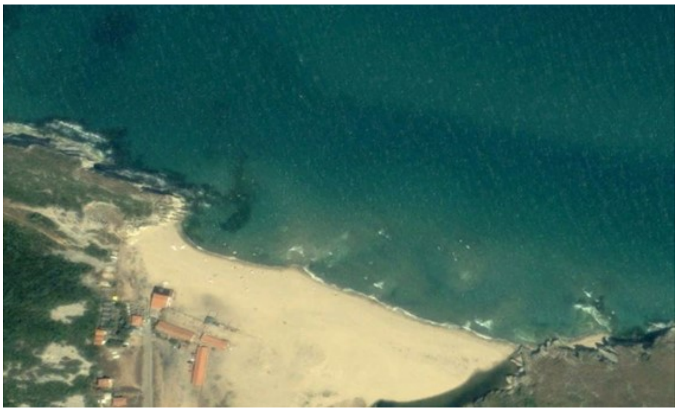


Figure 23. Satellite image of the jetty area's coastal morphology in 2003 (Google Earth, 2023)

Figure 24. Satellite image of the coastal morphology for the jetty area in the year 2021 (Google Earth, 2023)

The influence zone of the jetties has been determined to be approximately 60-80 m, as obtained from model analyses. After the completion of the construction of coastal structures, there is a limited change in coastal morphology due to the cessation of sediment transport in the E-W direction (Figure 25).

The HYDROTAM-3D model calculated directional wind waves based on long-term directional exceedance probabilities for coastal sediment transport quantities. The annual net coastal sediment transport quantity, Q_{net}, provides information about the direction and amount of material accumulation or erosion along the coast. The total sediment quantity transported in one year, Q_{gross}, is used in studies to determine the effects of shoaling in navigation channels. The calculated net and total sediment quantities are provided in Table 3.

Table 3. Annual coastal sediment transport volume. Q (m^3/year)

Direction	ESE → WNW	WNW → ESE
N		103143.48
NNE	18208.82	
NE	135695.44	
ENE	63465.13	
E	3674.09	
ESE		
SE		
SSE		
S		
SSW		
SW		
WSW		
W		
WNW		3288.41
NW		13841.24
NNW		25964.43
Total	221043.49	146237.55
Net	74805.94	
Gross	367281.04	

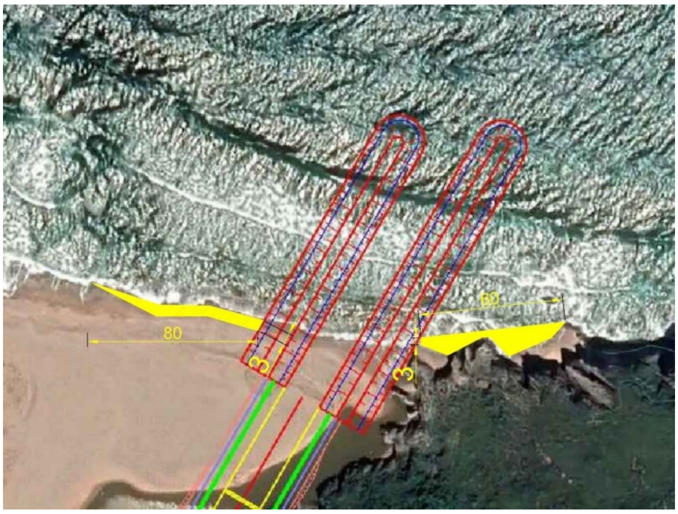


Figure 25. The changes in coastal morphology occurred within two years based on the proposed coastal structure (HYDROTAM-3D, 2023)

In the study area, 146,237.55 m^3 of sediment is annually transported from west to east, and 221,043.49 m^3 is transported from east to west. In the absence of coastal structures, the sediment transport from east to west is approximately 1.5 times greater than the transport from west to east.

The annual net coastal sediment transport from east to west is estimated to be approximately 74,805.94 m^3, while the total transport is estimated to be 367,281.04 m^3. The expected changes in coastal morphology within two years, based on the proposed coastal structure modeled by HYDROTAM 3D, are presented in Figure 25.

The model predicts a maximum excavation of 3 m on the west side of the breakwater and a maximum accumulation of 3 m on the east side. According to the model results, the coast is expected to regain its sediment balance within approximately two years. Artificial nourishment with suitable granulometry material is recommended to counteract the changes occurring on the west side of the breakwater. The material used for nourishment should be compatible with the natural gradation of the shoreline. Crushed sand from a quarry can be used for this purpose. This way, nourishment with sand of appropriate granulometry can be transported to the excavation area, minimizing the impact of the structure on the coastline.

The Hudson formula based on the wave height obtained with the HYDROTAM3D software determined the armor layer stone category. A slope of 1/1.5 was chosen to align with the approved slope of the Kabakoz River reclamation project.

$$W_{50} = \frac{\gamma s * (H + \Delta\text{MWL})^3 * tan\alpha}{(Sr-1)^3 * KD} \qquad (3)$$

W_{50}: Nominal armor weight (tons)

D_{n50}: Nominal median armor diameter $= \sqrt[3]{\frac{W_{50}}{\gamma_s}}$ (m)

γ_s: Unit weight of rock = 2.65 t/m^3

γ_w: Unit weight of seawater = 1.025 t/ m^3

tan α: Slope of the structure = 1/1.5

H_d: Design significant wave height of 1.60 m

$K_{D,\ breaking}$: Stability coefficient of Hudson for wave breaking condition= 1.9

S_r: Specific weight of armor= (γ_s / γ_w - 1) = 1.58

The HYDROTAM-3D modeling results indicate the highest and lowest water level changes according to RCP8.5, expected to occur above the TUDES average water level (MWL). The RCP8.5 Sea Level Rise (ΔMWL) expected in 100 years is estimated to be 87 cm. The cumulative scenario value includes wind setup, tidal effect, and wave setup. The nominal stone diameter was determined as D_{n50}= 0.70 m, and the protective layer thickness was selected as 2-4 t. The thickness of the layer, which will be constructed in two rows, is 2.00 m. A single layer of 0.4 - 2 tons will be used as the filter layer. The layer thickness for a single row is 0.75 m. It is deemed suitable for design and construction to use material weighing 0 - 0.4 tons at an elevation of +0.50 for the core layer. It is designed with a width of 3.50 m at its narrowest point to allow for construction. The cross-section of the jetty type is presented in Figure 26, and the designed coastal structure at the river mouth is shown in Figure 27.

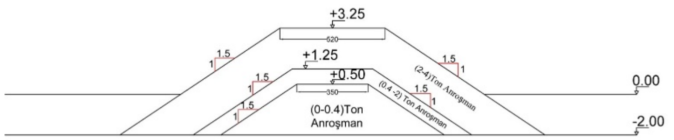


Figure 26. Cross-section of jetty

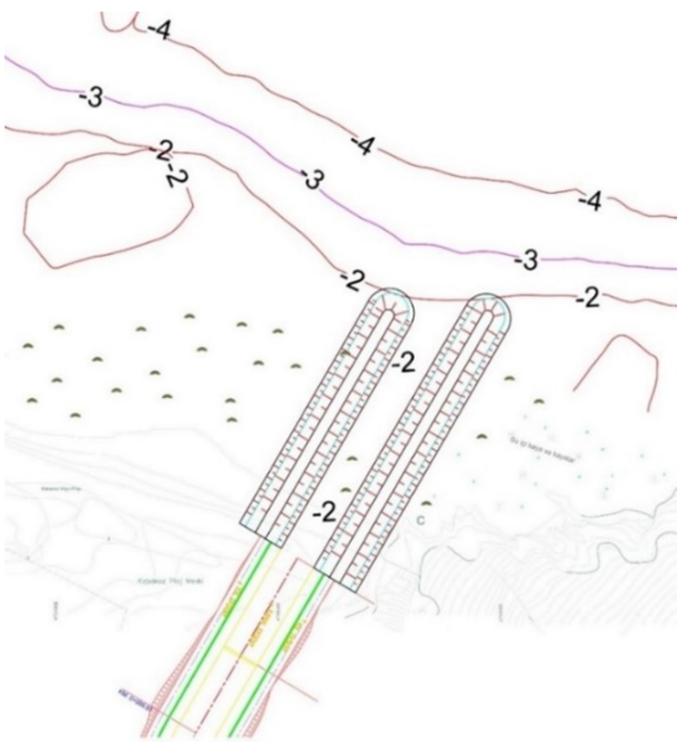
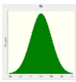
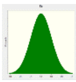
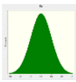


Figure 27. Designed jetty

Monte Carlo simulation is applied to model the probability of different outcomes in design that cannot easily be predicted due to the intervention of random variables (Balas, 2023). Monte Carlo simulation is used to understand the effects of risk and uncertainty on environmental parameters (Durap et al., 2023). Hence, the Monte Carlo simulation will ultimately be fruitful for the probabilistic design of coastal structures. Predicting uncertainties such as wave height is the most crucial part of coastal structure design. In the scope of this paper, a probabilistic design is also conducted for the jetty, which will be constructed on the outlet of the Kabakoz River, and the results are compared with a deterministic design. The Hudson equation is the limit state function, and random variables are modeled by various probability distributions in Monte Carlo Simulation, as seen in Table 4. 30000 simulations are conducted for randomly generated samples.

Table 4. The variations of design parameters and probability distributions modeled in MCS (SD: Standard deviation)

Variable	Definition	Minimum	Average	Maximum	SD	Distribution type	Distribution
W50	Median Armor Weight (tons)	0.40	0.7	1.50	0.20	Simulated	
H_d	Design Wave Height	1.30	1.60	1.90	0.10	Normal	
ΔMWL	Mean Sea Level Rise	0.71	0.87	1.12	0.05	Normal	
ɣs	Unit weight of Armor	2.50	2.65	2.80	0.05	Normal	
ɣw	Unit Weight of water	1.01	1.025	1.04	0.01	Normal	

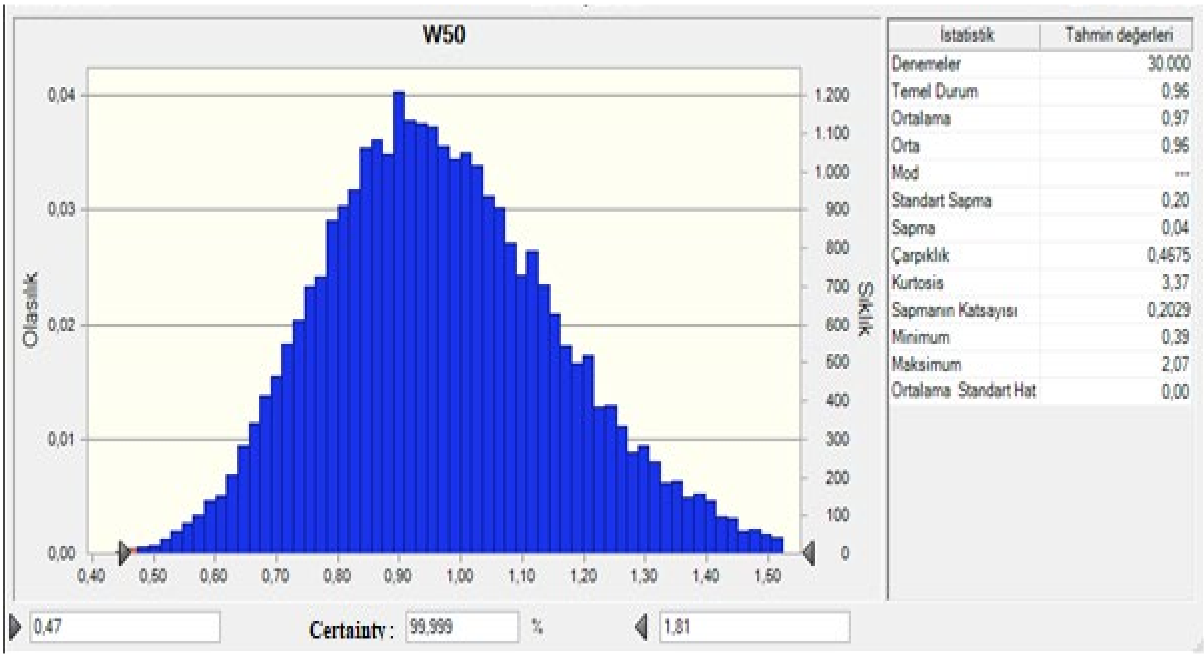


Figure 28. Hudson limit state function (W50) of the structure failure in its lifetime

The result of the Monte Carlo Simulation for Hudson limit state function (W_{50}) indicates the structure's failure in its lifetime of 50 years, as shown in Figure 28. As can be seen from the figure, the lifetime failure probability of the coastal structure is 10^{-3} when considering all the environmental risk parameters, such as climate change and sea level changes.

Following the completion of simulations, design parameters of paramount importance were identified through a sensitivity analysis, as seen in Figure 29. It is seen in the figure that H_{design} has the greatest contribution to the determination of structural stability concerning MCS. The sensitivity analysis is applied to analyze the contribution of random design variables in the Monte Carlo simulation (MCS).

One of the goals of this study is to determine the correlation between various design variables. The scatter diagrams in Figure 30 show that the coastal structure's stability is positively or negatively correlated with design variables. The design significant wave height (H_d) affects the limit state function with a maximum correlation of ρ=0.918, indicating the limit state function is highly sensitive to the deviations and uncertainties in design wave height. The unit weight of seawater ($ɣ_w$) has a moderately low effect on stability with a correlation of ρ=0.1052. Unit weight of rock has a negative effect over stability with ρ=-0.35.

The results of this study show the precision of probabilistic design while it takes environmental risk parameters such as climate change and sea level changes. The deterministic method does not consider environmental effects; thus, the general approach for designing coastal structures is insufficient. The first investment costs of coastal structures are high and hard to construct. For this reason, the probabilistic method should become an indispensable part of coastal structures design.

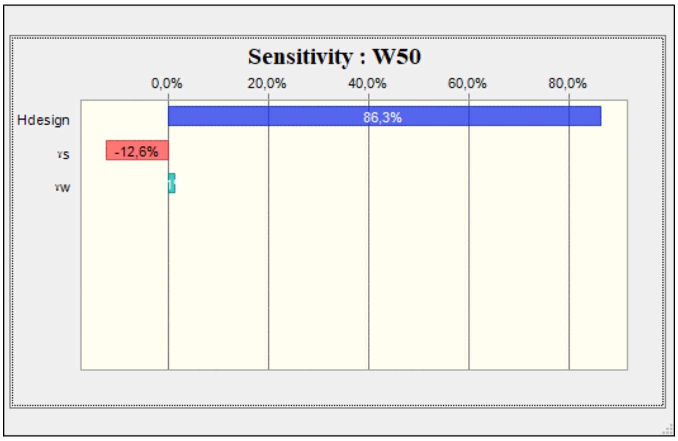


Figure 29. The sensitivity analysis of Hudson limit state function conducted by MCS

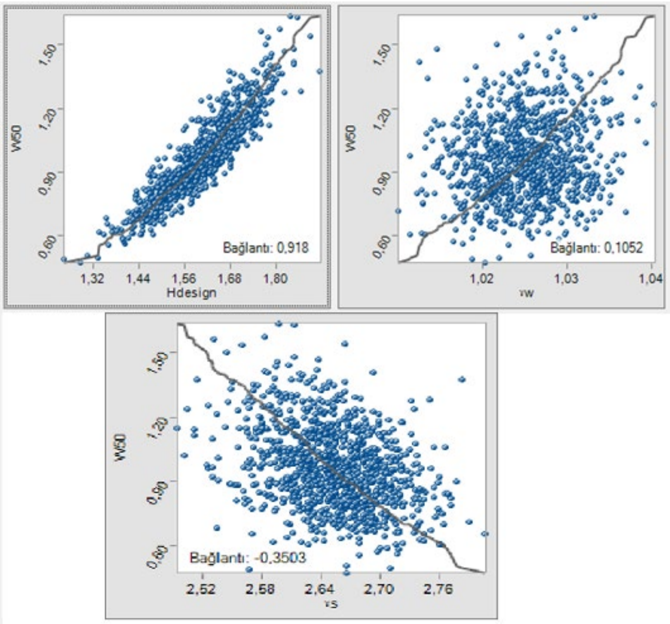


Figure 30. Scatter diagrams of design parameters

Discussion

Hourly wind measurements from the Şile Meteorological Station and 6-hour wind forecasts from the ECMWF operational archive at 41.2°N-29.7°E, representing the study area, were compared and examined. Comparisons of wind speeds for common measurement periods and durations of the data sources are presented in Figure 3. All presented wind speed measurements and forecasts are at a height of 10 m (U_{10}). After the comparison studies, it was decided that ECMWF wind forecasts over the sea for the coordinates 41.2°N-29.7°E between 2000-2021 can be safely used to determine the wind climate of the coastal area in the study region. The wind rose for ECMWF coordinates 41.2°N-29.7°E is presented in Figure 4.

When examining the wind rose study, it is observed that the wind blows from the northeast (NE) to the east-east (ENE) direction in the clockwise direction from the sea. An increase in the frequency of Southwest (SW) winds blowing from the land is observed in the winter and spring seasons, while in the summer and autumn seasons, the frequency of Northeast (NE) winds increases. Monthly average and maximum wind speeds are also presented graphically (see Figure 5). Monthly average wind speeds are calculated by taking the arithmetic average of all wind speeds within that month. The monthly maximum values represent the highest, lowest, and average maximum values observed during the same periods within that month (the average of the highest values for each year for any given month). The highest wind speeds and directions by year are presented in Figure 6. The monthly average wind speed ranges between 4-5 m/s, while the highest maximum wind speeds vary between 12-18 m/s. Throughout the study period, the highest wind speed was observed at 18 m/s, blowing from the North (N) direction. The long-term wind statistics follow the Weibull probability distribution for dominant wind directions.

From the extreme value (Gumbel Distribution) wind statistics, the wind speed with a recurrence period of twenty-five hours per year is obtained as Vs=18.718 m/s with a 90% confidence interval of ±0.172 m/s.

Long-term wave statistics studies were conducted using wave predictions from the ECMWF operational archive for the coordinates 41.2°N - 29.7°E from 2000-2022. The significant wave height ($Hs_{,12}$) obtained from long-term wave statistics studies has a range of 1.66 m < $Hs_{,12}$ < 5.47 m, with a 12-hour-per-year exceedance probability. According to the Coastal Structures Planning and Design Technical Principles of the Ministry of Transport and Infrastructure (2016) document, it falls under the effective coast (E) classification based on wave height. Model predictions also indicate that the primary wave direction is clockwise from North (N) to Northeast (NE). The results of long-term wave statistics are presented in Figure 7.

As part of the long-term wave statistics studies, the relationship between significant wave height (Hs) and mean wave period (Tm) for all directions is shown in Figure 13. Annual and seasonal wave roses are presented in Figure 14, and monthly average and maximum significant wave heights are provided in Figure 15. When examining long-term log-linear wave statistics, it is observed that the dominant waves come from the North (N) and East-Northeast (ENE) directions in a clockwise direction. The dominant directions are North (N) and Northeast (NE) in the winter and spring. The prevailing wave direction in the summer is Northeast (NE). In the autumn season, the dominant wave directions are Northeast (NE) and East-Northeast (ENE) (Figure 14). The monthly average wave height is 1 m, while the highest significant wave heights vary between 2.50 and 6.50 m (Figure 15). In the long-term statistics, ECMWF Operational Archive wind data were used for the point offshore of the jetty. Figure 16 provides extreme (maximum value) design wave values and non-exceedance probabilities obtained for certain return periods from deep-sea highest wave heights by years. As seen in Figure 16, for a return period of 50 years (Rp=50 years recurrence interval), the significant deep-sea wave height (at a 90% confidence level) is Hs=8.03 m, and the average wave period is Tm=11.33 seconds. The process of determining the height, period, and direction values of waves coming from deep-sea conditions, reaching the structure front due to bathymetry and boundary conditions (islands, bays, headlands), and the effect of coastline orientation is obtained as a result of the wave transformation model.

Wave transformation (obtaining the structure front wave) for the jetties design planned at the Kabakoz Stream sea outlet was conducted using the wave propagation module of the HYDROTAM3D software. For the analysis, the bathymetry of the project area was first loaded into the model. The wave in front of the structure (design wave) was obtained using the HYDROTAM3D wave propagation module. The wave value at the outermost point (toe) of the structure, which should be formed at a closure depth of -2m, was obtained from the model results. The HYDROTAM3D model (HYDROTAM-3D, 2023) solves the shallow water equations to transfer the predicted wave heights in the open sea to coastal areas under the influence of bathymetry and topography. Wave progression involves calculations of shoaling, refraction, diffraction, friction, breaking, and wave setup effects. Spatial or pointwise distribution maps of wave heights and temporal variation graphs can be accessed. Regionally obtained wave values are presented in Figure 18. As a result, the design's significant wave height, Hs=1.60 m, and average wave period, Tm=4.65 seconds, are obtained in the structure front, considering the water depth. The breaking index is approximately 0.8, close to the 0.78 breaking index, confirming the model result. As a result of these studies, the deepest point of the structure has been placed at a depth of approximately 2.00 meters, ensuring that it remains below the closure depth. In storms, to eliminate the effect of stream-sea interaction and prevent sediment accumulation at the mouth of the jetty, the basin where the structure is placed, including the lower section, needs to be dredged to -2.00 meters from the coast to the structure's end. The dredging will prevent backflows and mitigate the risk of flooding.

In conclusion, in the study area, 146,237.55 m^3 of sediment is transported annually from west to east and 221,043.49 m^3 from east to west. In the absence of coastal structures, sediment transport from east to west is approximately 1.5 times greater than from west to east. The annual net coastal sediment transport from east to west is approximately 74,805.94 m^3, while the total transport is estimated to be 367,281.04 m^3. The expected changes in coastal morphology within two years, based on the proposed coastal structure modeled by HYDROTAM 3D, are presented in Figure 25. The lengths of the jetties are approximately the same as the rocky headlands in Kabakoz Beach, which is bounded by two rocky headlands. Kabakoz Beach, located between the rocky headlands, is a well-protected beach with sediment movement along approximately a 300 m coastal stretch, as indicated by the model results. The coastline is expected to reach sediment balance within approximately two years.

The sediment transport, influenced by parameters such as breaking depth, bathymetry, coastal sediment grain size, structure location and dimensions, and closure depth, is predicted to have a maximum erosion of 3 m on the west side of the jetty and a maximum accumulation of 3 m on the east side, according to the model results. The influence area of the jetties is obtained to be approximately within the range of 60-80 m after model analyses. Using artificial nourishment with suitable granulometry in the expected eroded shore sections is recommended. The material used in nourishment should be compatible with the natural gradation of the shore. Crushed sand obtained from a quarry can be used for this purpose. Thus, by transporting sand with the appropriate grain size to the eroded area, the impact of the structure on the coastline can be minimized.

The most crucial part of this study is its difference from conventional methods, as the developed methodology can include the future environmental changes due to global warming. This aspect provides researchers or designers with the most reliable design of coastal structures such as rubble mounds or piles, allowing the alteration of design codes considering the changes in future environmental parameters.

Conclusion

Using the Integrative Probabilistic Design Approach of River Jetties introduced in this paper, 3D numerical models were used for the design considering the sediment transport near the jetties. As a result, the optimum layout and design of jetty structures were obtained by the proposed "Integrative Probabilistic Design Approach" and are presented in Figure 19 for the Kabakoz River. This optimum layout and design will not interfere with the coastline long-term, balancing the environmental effects.

Closure depth is a theoretical depth along the beach profile where sediment transport does not occur, depending on wave height, period, and sediment grain size. Closure depth is the most important criterion in designing a structure that will not damage coastal morphology. The hydraulic structure designed based on this value is presented in Figure 27. Due to the east-southeast to west-northwest (ESE-WNW) direction of sediment transport, erosion will occur in the influence area of the western jetty. Since the eastern jetty is planned to be constructed in the region where the rocky area begins, it will not effectively impact long-term sediment transport.

Additionally, the lengths of the jetties are approximately the same as the rocky headlands in Kabakoz Beach, which is bounded by two rocky headlands. Kabakoz Beach is a well-protected beach between the rocky headlands, with sediment moving along approximately a 300 m coastal stretch. According to the model results, the coastline is expected to reach a sediment balance within approximately two years. After the completion of the construction of coastal structures, limited changes in coastal morphology are expected due to the termination of E-W sediment transport, as shown in Figure 25. The calibration of the model was examined for the change in the old-new coastline from 2003 to 2021, as shown in s 26. As evident from the figures, the coastline is in balance within itself. The proposed jetties will be constructed at the easternmost part of the coast, at the end of the rocky headland, so the impact of the jetties on coastal morphology will be extremely limited in the long term.

In conclusion, Monte Carlo Simulation (MCS) is applied to model the probability of different outcomes in a process that cannot be easily predicted due to the intervention of random variables. Thirty thousand simulations were conducted for randomly generated samples, as seen in Table 4. MCS gave the lifetime failure probability of the coastal structure as $10^{-3,}$ which means the structure is reliable under the effect of risk parameters such as sea level increase due to climate change changes when the design standards are considered.

The consequences of failure give the target reliability as in (British Standards, 2005), where values are conferred for the target reliability. (Det Norske Veritas (DNV), 1992) developed a more specific code for marine structures in 1992, where the target reliability is 10^{-3} for structures with less serious failure consequences, and this validated the model developed in this paper. The class of failure depends on the possibility of timely warning as the development of failure. These codes and standards are used as a first estimate and guidance for the design of maritime structures. The precise design can be performed using the methodology developed in this paper. The reliability of the structure is evaluated by the model and compared with the target reliability suggested by the standards. These standards do not consider the effects of climate change yet.

This study has powerful outcomes in designing robust coastal structures and precisely predicting shoreline change while providing the basis for design codes such as Det Norske Veritas. The probabilistic design presented in this paper's scope is the most reliable way to achieve this success. This method can be used to alter the regulations to reduce costs and design robust structures.

Recommendation for Future Research

For future studies, it is recommended to develop the following items to improve the model presented in this paper:

1. It is recommended that the low-resolution outputs of the climate models included in the IPCC's CMIP6 protocol be obtained by dynamically reducing them to grid points with a resolution of approximately 1 km, creating the initial and boundary conditions required for the hydrodynamic modeling.
2. The combined effect of climate change and sea level rise is expected to be much greater for marine structures when the structural risks are incorporated into the reliability model.
3. It is possible in the model to modify the risk iteratively according to its environmental consequences based on the scenario by considering the hazard to the marine environment. Hence, the probability of earthquakes and tsunamis can be added to the structural reliability model.

Acknowledgements

The authors would like to thank Dr. Saleh Abdalla from the Reading (UK) headquarters of ECMWF (European Centre for Medium-Range Weather Forecasts) and DLTM Software Technologies at the Gazi University Technopark for their permissions granted in the application of HYDROTAM-3D in modeling and the database that supports the findings of this study. This research received no specific grant from any funding agency.

Compliance With Ethical Standards

Authors' Contributions

AU: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing—Original Draft

CEB: Writing—Review & Editing, Supervision, Visualization

All authors read and approved the final manuscript.

Conflict of Interest

The authors declare that there is no conflict of interest.

Ethical Approval

For this type of study, formal consent is not required.

Funding

Not applicable.

Data Availability

The data supporting this study's findings are available from HYDROTAM-3D. However, restrictions apply to the availability of these data, which were used under license for the current study and are not publicly available. Data are, however, available from the authors upon reasonable request and with permission of HYDROTAM-3D (http://www.hydrotam.com/) and ECMWF (https://www.ecmwf.int/)

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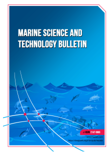
Mar. Sci. Tech. Bull. (2024) 13(2): 168-174
e–ISSN: 2147–9666
info@masteb.com

dergipark.org.tr/en/pub/masteb
www.masteb.com
DOI: 10.33714/masteb.1443969



Marine Science and Technology Bulletin

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RESEARCH ARTICLE

Growth, lipid, and pigment properties of locally isolated (Kastamonu, Türkiye) *Chlorella* sp.

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ARTICLE INFO

Article History:
Received: 28.02.2024
Received in revised form: 13.06.2024
Accepted: 14.06.2024
Available online: 25.06.2024

Keywords:
Chlorella sp.
Isolation
Culture
Biochemical composition

ABSTRACT

Chlorella has become one of the most studied and produced microalgae, with *Spirulina* among the hundreds of species since the beginning of microalgal biotechnology. The growth performance of microalgae and the biochemical composition of the biomass may also vary significantly by strain. Therefore, it is thought that searching for new strains from aquatic environments is important in providing the most suitable microalgae for production. An isolated strain from Daday Stream was cultured in the laboratory at Kastamonu University. BG-11 was used as a medium, and CO_2 from the air was used as a carbon source in the experiments. The initial cell number was arranged to 1.0×10^6 cells $mL^{-1,}$ and the highest cell number was found on the 17th day as 40.52×10^6 cells mL^{-1}. Chlorophyll *a* and carotenoids were determined at the end of the experiment and were found as 3.48±0.08 µg mL^{-1} and 1.16±0.02 µg mL^{-1}, respectively. Total lipid amount and fatty acid composition analysis were also conducted at the end of the study. According to the analyses, the lipid content of *Chlorella* sp. was found to be 15.37±0.00% (w/w). ∑SFA (saturated fatty acid), ∑MUFA (monounsaturated fatty acid), and ∑PUFA (polyunsaturated fatty acid) ratios were calculated to be 31.30±1.21%, 4.99±0.34% and 63.71±2.65%, respectively.

Please cite this paper as follows:

Elp, M., Durmaz, Y., & Erbil, G. Ç. (2024). Growth, lipid, and pigment properties of locally isolated (Kastamonu, Türkiye) *Chlorella* sp. *Marine Science and Technology Bulletin*, *13*(2), 168-174. https://doi.org/10.33714/masteb.1443969

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Introduction

Natural sources have decreased considerably since the increase in human population and industrial production. Water resources provide an excellent habitat for microalgae growth and proliferation. However, studies on the taxonomy and diversity of these group of microorganisms are still limited. Microalgae stand out with their large-scale producibility and usability in different industrial fields such as aquaculture, nutrition, pharmaceuticals, and even energy (Shah et al., 2018; Durmaz et al., 2020; Mehariya et al., 2021).

Chlorella has become one of the most studied and produced microalgae, with *Spirulina* among the hundreds of species since the beginning of microalgal biotechnology (Sugiharto, 2020). Lutein production, used as a food additive, biodiesel-oriented studies, and environmental applications constitute the main topics of this species (Farooq et al., 2015; McClure et al., 2019; Asadi et al., 2019; Konar et al., 2022).

Alteration of the biochemical composition of microalgae by culture conditions is already known for decades (Renaud et al., 1991; Ram et al., 2019). New studies are carried out every day for this purpose. Searching for more efficient production of microalgae to obtain target metabolites at higher concentrations causes these efforts. However, this is not the only way to achieve the desired production biochemical composition. The growth performance of microalgae and the biochemical composition of the biomass may also vary significantly by strain. Therefore, it is thought that searching for new strains from aquatic environments is crucial in providing the most suitable microalgae for production. This study was aimed to examine isolate and biochemical composition of new strain from the Daday Stream.

Material and Methods

The water sample was collected from the Daday Stream (41°27’18.4” N 33°42’15.2” E) in Kastamonu, Türkiye. The Autoclaved (121°C, 15 mins) falcon tubes were used for that purpose. First, the samples were inoculated into petri dishes on the same day. After several repeats of the inoculation process, an isolated microalgae strain was obtained. The strain was inoculated to the tubes and flasks to secure appropriate stock.

The culture growth performance and lipid content of the isolated strain were investigated and, for this purpose BG-11 was used as a medium, and cultures were mixed with air. 0.2 µm syringe filters were used in aeration to avoid contamination. The temperature was 21°C during the experiment period. Cultures were illuminated with 40 $\mu mol.m^{-2}.s^{-1}$ fluorescent lamps (Apogee MQ-620). Taxonomic identification was made according to Vuuren et al. (2006) and Bellinger & Sigee (2010).

Growth

The experiment and the analysis were completed in triplicate. Cell numbers were counted under the light microscope daily. The specific growth rate (µ) was calculated according to the formula given in the Eq. (1): (*X*: cell number; *t*: time).

$$\mu = \frac{\ln X_2 - \ln X_1}{t_2 - t_1} \quad (1)$$

Cell size was also measured. Cell size measurement was conducted with ImageJ (National Institutes of Health, USA) software by using digital images of microalgae samples on a Neubauer hemocytometer (Figure 1).

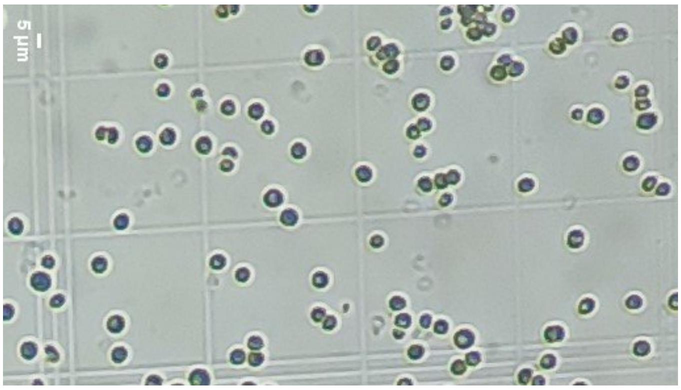

Figure 1. *Chlorella* sp. (Daday Stream) cell size on Neubauer hemocytometer

Dry weights were determined at the end of the experiment. 0.45 µ Whatman filters were weighed after drying at 105°C for 2 h. Then, 5 mL samples from each culture were filtered and dried at the same temperature until the weights became constant and were weighted.

Pigments

Chlorophyll *a* and carotenoids were determined spectrophotometrically. 5 mL samples were centrifuged, and supernatants were discarded. After adding 5 mL methanol, samples were mixed by vortex and placed in ultrasound for 15 mins. Lastly, samples were centrifuged again, and supernatants were used to determine absorbance values. Pigment amounts were calculated using the formulas below (1-2).

(i) Chlorophyll a ($\mu g\ mL^{-1}$) = 13.9 A_{665} (Macías-Sánchez et al., 2005)

(ii) Carotenoids ($\mu g\ mL^{-1}$) = 4.5 A_{470} (Zou & Richmond, 2000)

Lipids

SPV (sulfo-phospho-vanillin) method (Mishra et al., 2014) was used to determine the lipid content in addition that, fatty acids analysis was conducted according to the direct transesterification method (Chu et al., 2015).

Results

After the isolation process, the obtained strain was examined under the microscope. The size of the cells varied between 4.42-8.32 μm, and the average cell size was calculated as 5.90±1.00 μm. Cells were single and non-motile. Also, single-cell formation was observed without flagella. According to the visual identification, the strain was determined to be *Chlorella* sp. (Vuuren et al., 2006; Bellinger & Sigee, 2010).

Growth

Cell numbers were counted daily for 18 days of the experiment period. The initial cell number was arranged to 1.0×10^6 cells mL^{-1}; the highest cell number was found on the 17th day as 40.52×10^6 cells mL^{-1} (Figure 2). The specific growth rate reached the highest point at the beginning of the experiment (4th day) and was calculated as 1.08±0.06. When specific growth was turned negative at the 18th day, the experiment was terminated. Dry weight analysis was conducted on the 18th day of the experiment and found 2.47±0.15 g L^{-1}. According to the cell number of the day, cellular weight was calculated as 60.15±3.83 pg cell^{-1}.

Pigments & Lipid

Chlorophyll *a* and carotenoids were determined at the end of the experiment and were found as 3.48±0.08 μg mL^{-1} and 1.16±0.02 μg mL^{-1}, respectively. Total lipid amount and fatty acid composition analysis were also made at the end of the study. According to the results, the lipid content of *Chlorella* sp. (Daday Stream) was found to be 15.37±0.00% (w/w).

The direct transesterification method was chosen to determine the local strain's fatty acid composition. ΣSFA (saturated fatty acid), ΣMUFA (monounsaturated fatty acid), and ΣPUFA (polyunsaturated fatty acid) ratios were found to be 31.30±1.21%, 4.99±0.34% and 63.71±2.65%, respectively (Table 1).

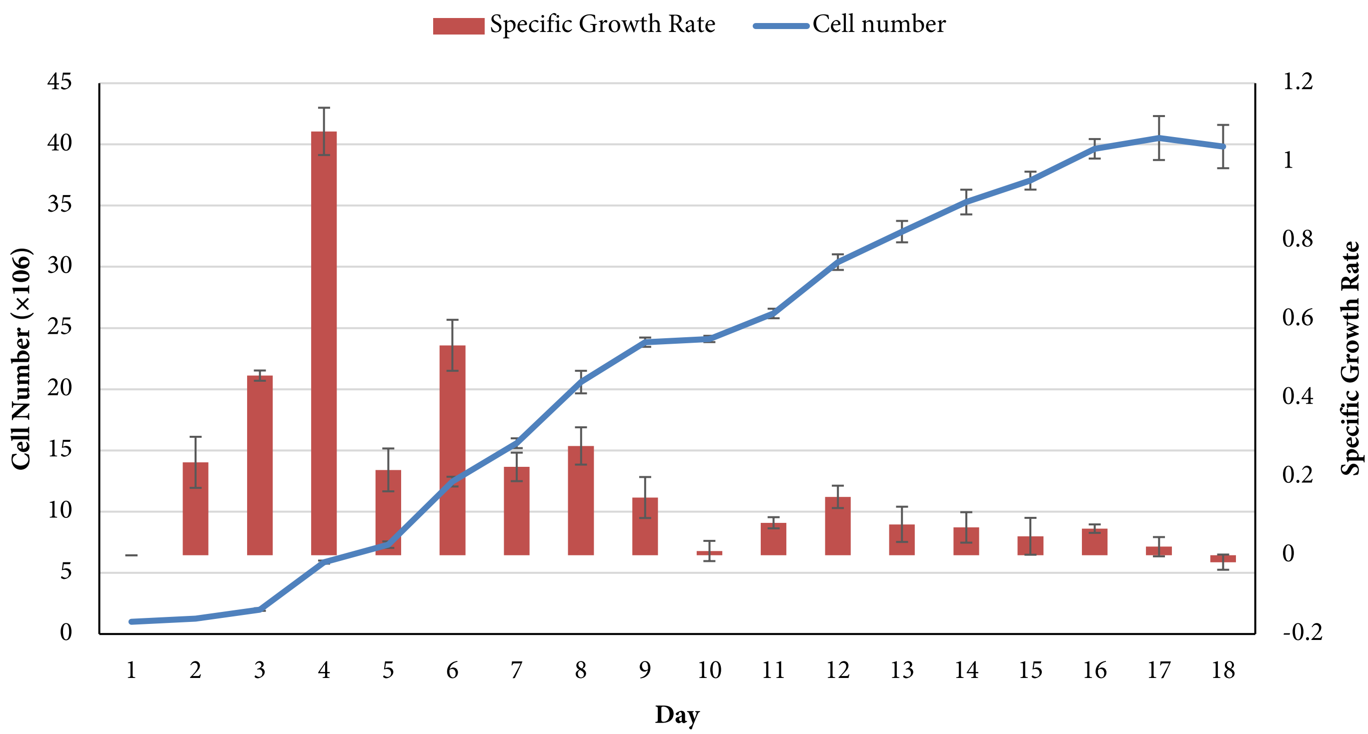

Figure 2. Growth parameters of *Chlorella* sp. (Daday)

Table 1. Fatty acid composition of *Chlorella* sp. (Daday Stream)

Fatty Acids	Composition (%)
Octanoic acid (C8:0)	0.00±0.00
Decanoic acid (C10:0)	0.00±0.00
Dodecanoic acid (C12:0)	0.12±0.04
Tridecanoic acid (C13:0)	0.00±0.00
Tetradecanoic acid (C14:0)	0.74±0.02
Palmitic acid (C16:0)	29.03±0.96
Palmitoleic acid (C16:1)	0.12±0.03
Stearic acid (C18:0)	0.69±0.02
Oleic acid (C18:1)	4.87±0.31
Linoleic acid (C18:2)	52.89±1.78
Eicosanoic acid (C20:0)	0.17±0.05
α-linolenic acid (C18:3)	10.71±0.84
cis-11-Eicosenoic acid (C20:1)	0.00±0.00
Heneicosanoic acid (C21:0)	0.14±0.04
Docosanoic acid (C22:0)	0.16±0.04
11,14,17-Eicosatrienoic acid (C20:3)	0.12±0.03
Arachidonic acid (C20:4)	0.00±0.00
Tricosanoic acid (C23:0)	0.25±0.04
ΣSFA	**31.30±1.21**
ΣMUFA	**4.99±0.34**
ΣPUFA	**63.71±2.65**

Note: SFA; saturated fatty acids, MUFA; monounsaturated fatty acids, PUFA; polyunsaturated fatty acids.

Discussion

Chlorella is one of the most common species found in freshwater. As stated above, the current strain isolated from the Daday Stream was cultured under laboratory conditions. 2.47±0.15 g L^{-1} dry weight was obtained in this study with 60.15±3.83 pg $cell^{-1}$ cellular weight. The cell weight of *Chlorella vulgaris* is given as 6-18 pg $cell^{-1}$ in the study on the effect of different culture media on growth (Chia et al., 2013). Even if it is stated that cellular weight is alterable by culture nutrient composition, *Chlorella* sp. (Daday Stream) cell weight is higher than that. In another study, *Chlorella vulgaris* culture with modified BG-11 provided 0.9±0.001 g L^{-1} biomass after 12 days (Wong et al., 2017). Results of the study on 5 different *Chlorella* strains and their biomass production with 4 different culture media show that both the strain and the culture medium are effective in growth performance (Sharma et al., 2016). Since the dry weights varied between 0.9-1.7 g L^{-1} in the mentioned studies, it can be stated that the *Chlorella* sp. (Daday Stream) strain exhibited higher growth performance.

Chlorella is known as a source of chlorophylls, lutein, astaxanthin, and a few other carotenoids with a 1-2% (w/w) pigment ratio of total (Safi et al., 2014). In this study, chlorophyll *a* and carotenoids of *Chlorella* sp. were found as 3.48±0.08 µg mL^{-1} and 1.16 µg mL^{-1}, respectively. It was reported that *Chlorella* strains isolated from Nigeria contain similar amounts of chlorophyll *a* and carotenoids varied 1-3.5 µg mL^{-1} and 0.4-1.2 µg mL^{-1}, respectively (Idenyi et al., 2021). However, much higher pigment contents are also reported in several studies. For instance, 2.8% total pigments for *Chlorella* sp. (Erbil et al., 2021), 6.04% of pigment concentration for *Chlorella vulgaris* (Mastropetros et al., 2022), and 9.33% pigment concentration for another *Chlorella vulgaris* strain (Soto-Ramirez et al., 2021) are indicated.

The lipid ratio and fatty acid composition of microalgae are also alterable by culture medium and strain. For instance, it is indicated that *Chlorella* sp. 1 strain's lipid accumulation varied between 14-16% depending on the medium. Also, lipid accumulation of another strain (*Chlorella* sp. 2) was given between 8-10% in the same study (Sharma et al., 2016). *Chlorella* sp. T4 can accumulate 25.87% lipid, another strain from South Africa. This result is higher than the lipid ratio of *Chlorella* sp. (Daday sample). However, the T4 strain with 0.77 g L^{-1} biomass production is three times lower than *Chlorella* sp. (Daday sample), which leads to lower lipid production (Gumbi et al., 2022).

In the study, dominant fatty acids of *Chlorella* sp. were palmitic acid (29.03%), linoleic acid (52.89%), and α-linolenic acid (10.71%). Palmitic acid, around 30%, is a widespread result for *Chlorella* species (Sharma et al., 2016; Dahiya et al., 2021; Gumbi et al., 2022). Previous studies conducted with *Chlorella* show that linoleic acid is highly variable and can be found between 13.6 and 42.54% (Tang et al., 2011; Ördög et al., 2016; Gumbi et al., 2022). *Chlorella* sp. (Daday sample) was determined as one of the richest linoleic acid sources among the *Chlorella* strains. α-linolenic acid is another fatty acid found in *Chlorella* with different ratios. For instance, studies on *Chlorella vulgaris* differ with the α-linolenic acid ratio, which varies between 8.3-27.5% (Yusof et al., 2011; Park et al., 2014). We found that *Chlorella* sp. contains 10.71% α-linolenic acid. This ratio can be accepted as an average value considering various strains from previous studies (Zhu et al., 2015; Krzeminska et al., 2015; Ördög et al., 2016; Anto et al., 2019).

Conclusion

According to the result of this study, the locally isolated *Chlorella* sp. strain showed promising growth performance. Lipid and pigment accumulation ratios were also acceptable if it was considered that any optimization or stress conditions were not applied. Further investigations may help to improve the growth and desired biochemical composition of the *Chlorella* sp. strain.

Compliance With Ethical Standards

Authors' Contributions

ME: Project administration, Methodology, Funding acquisition, Writing – review & editing

YD: Investigation, Methodology, Formal analysis, Writing – original draft, Writing – review & editing

GÇE: Investigation, Methodology, Formal analysis, Data curation

All authors read and approved the final manuscript.

Conflict of Interest

The authors declare that there is no conflict of interest.

Ethical Approval

For this type of study, formal consent is not required.

Funding

This research has been supported by Kastamonu University Scientific Research Projects Coordination Department. Project Number: KÜ-BAP01/2021-49.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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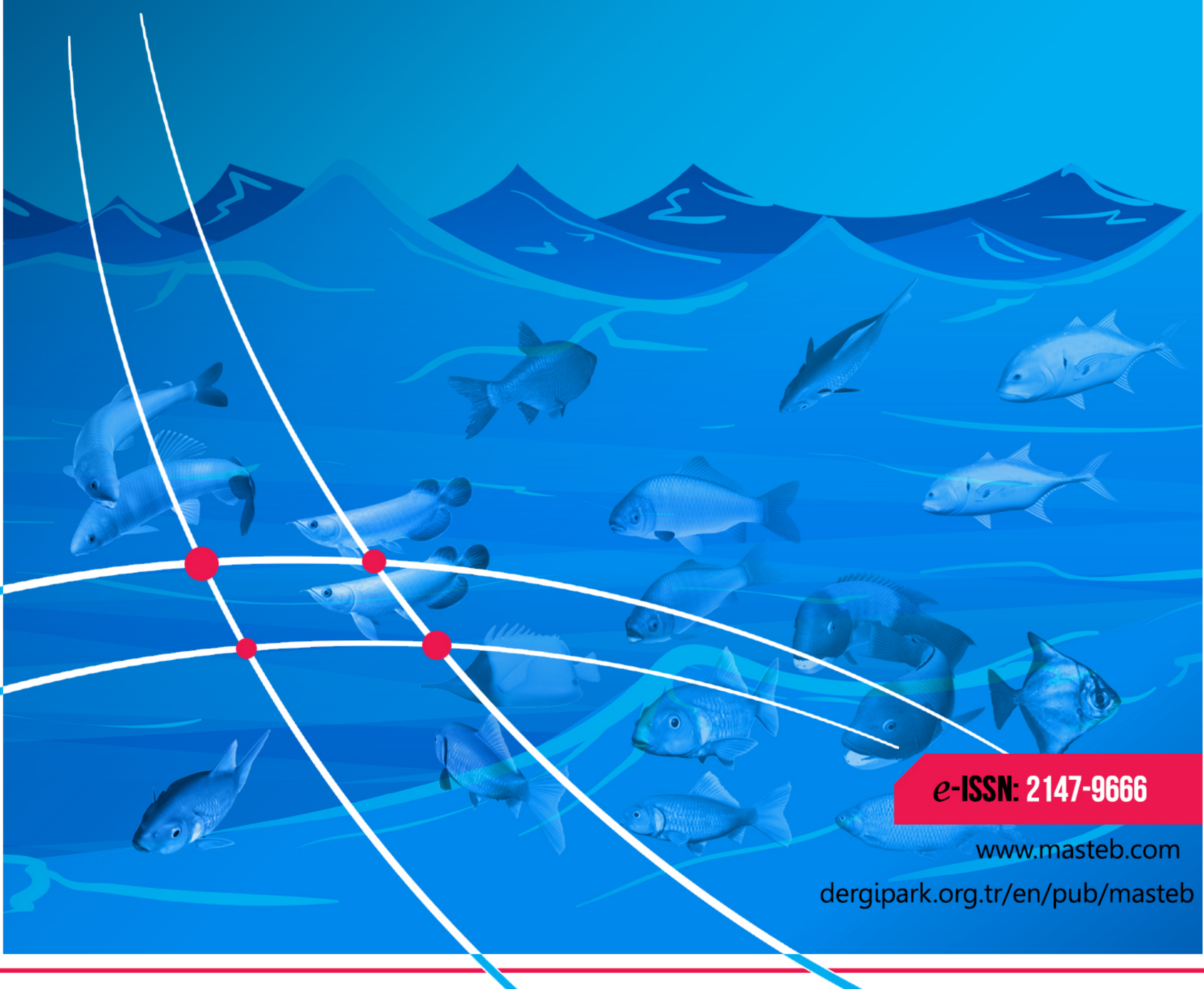

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