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Identification and Quantitative Pollutant analysis: A novel approach for environmental assessment in the Romanian Black Sea Coast

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Abstract. This paper presents the main factors affecting the pollution of the Black Sea ecosystem, especially the Romanian coastal zone in the current geopolitical conditions, due to the Russian-Ukrainian conflict, military training activities, various types of spills, microplastics, heavy metals, polyaromatic hydrocarbons (PAHs), emerging substances, shipping, etc. It is well known that pollution of the marine environment and destruction of habitats strongly affect the sustainable use of the seas and influence human health through direct human contact with polluted waters or through the consumption of contaminated marine nutrient sources. Various methods are being researched to prevent and reduce the negative impact of pollution, requiring a regular monitoring and assessment program, with the implementation of corrective measures, following national and international legislation. Our paper aims to demonstrate that in environmental studies, the use of mathematical relationships plays an essential role in calculating the mass value of pollutants, especially in the assessment of pollution levels in marine environments. Hence, through the quantitative analysis of the mass of pollutants present in the environment, it is possible to make a preliminary assessment of the degradation state of the marine environment in the Romanian coastal area. The methodology typically involves the integration of pollutant concentrations, the volume of water, and the area over which the pollutants are distributed. These preliminary theoretical studies will be complemented in our future research by specific in situ as well as laboratory analyses on water, sediment, and bioassay samples from the targeted marine areas.

Key words: pollutants, military operations, quantitative analysis, legislative framework

1. INTRODUCTION

The Black Sea basin is the third largest in Europe, and its isolation from the planetary ocean has given it certain atypical characteristics: low salinity (with variations from 3 ‰ to 21 ‰), counter-clockwise circulation of surface currents (on the western side of the basin), and lack of oxygen at great depths, which has favoured the formation of hydrogen sulphide deposits, due to the presence of anaerobic bacteria. In addition, the vulnerability of the Black Sea is high, as it is considered a "closed" river basin with unique, dynamic, and sensitive ecosystems, which are subject to continental pressures from coastal and maritime activities currently in conflict.

As a result, the prevention of marine pollution has become a desideratum of EU environmental policy, which has established policies and measures for the management of all aquatic ecosystems. Building on the common objective of the European Union (EU) Water Framework Directive 2000/60/EC [1] to achieve "good ecological and chemical status" of waters, it is important that in the

marine environment, there is a unified mechanism to monitor and limit pollution sources by preventing pollution at source. Also, the objectives of the Marine Strategy Framework Directive (2008) set for Europe's seas (to be "productive", "healthy" and "clean") must be linked to the EU's "blue growth" agenda, which is a long-term strategy to support sustainable growth in the marine and maritime sector [1], [2]. Consequently, the European Union has initiated ambitious initiatives aimed at significantly mitigating emissions and pollutants within the forthcoming three decades, on all levels. One notable initiative is the Zero Pollution Action Plan (2022), which aims to mitigate air, water, and soil pollution to levels that are deemed non-hazardous to both human and environmental well-being.

In the Romanian coastal zone, the major threat to the health, productivity, and biodiversity of the marine environment is due to human activities in the coastal zone. Approximately 80% of pollutant discharges come from spills, from residues discharges resulting from economic, industrial, agricultural, tourist, and urban activities [3], [4]. Another source of pollution in the Romanian Black Sea coast area is the Danube River and its affluents. The counterclockwise circulation of currents in the western Black Sea basin contributes to the spread of polluting elements toward the Romanian coastal areas. Due to the current conflict in the northern Black Sea basin responsible for the production of physical (acoustic) and chemical pollution, biomonitoring of the marine environment is more necessary than ever. In addition, we cannot neglect the pollutants caused by the oil and gas extraction activity in the Black Sea continental shelf, the refining and petrochemical industry, and the shipyards in the ports of Constanta and Midia Navodari.

The biomonitoring program will also consider the pollutants caused by military training exercises in the Cap Midia region. Over time, it has been observed that war and military activities produce negative effects on the environment and human habitat with significant effects on climate change through contamination of water sources, deterioration of drinking water supply infrastructure and wastewater disposal, air pollution, soil pollution, etc.

Our study emphasises the importance of applying mathematical relationships in the preliminary assessment of the degradation status of the Romanian coastal zone (Fig. 1) to protect the environment. By applying these calculations, the main pollutants responsible for the degradation of the marine environment can be quantitatively measured.

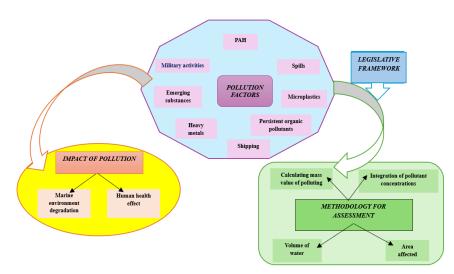


Fig. 1 Interaction between pollutants, their associated impacts, and assessment approaches

2. LEGISLATIVE FRAMEWORK

Nowadays there is an interest of Romania to combine the orientation of the national policy on water management in conformity with the medium and long-term European strategies and policies, which have been imposed by the accession to the European Union.

Therefore, Romania, as a member state of the European Union, must transpose into national legislation and implement the provisions of the European directives in the field of water, mainly the provisions of the Water Framework Directive 2000/60/EC [1] of the European Parliament and the Council establishing a framework for Community action in the field of water policy.

In accordance with the existing Romanian legislation and the international conventions to which Romania is a signatory, the mitigation, decrease, and regulation of marine environmental pollution resulting from activities conducted in inland maritime waters, the territorial sea, the exclusive economic zone, and the atmosphere above them shall be implemented [5]. Safeguarding water and marine resources, as well as protecting their ecological integrity, constitutes a fundamental component of the European Union's environmental strategy. The Water Framework Directive (WFD), introduced in 2000, and the Marine Strategy Framework Directive (MSFD) of 2008 set the framework for the management of all aquatic ecosystems[2]. Their primary goal is to attain a favourable environmental condition for both marine and freshwater resources by employing a method rooted on ecological principles.

On maritime transport, the European Commission presented on 1 June 2023 five legislative proposals to modernise EU rules on maritime safety and sustainability and to prevent water pollution from ships. The objective at the European level regarding ship-source pollution is to harmonise EU legislation with international standards and broaden their applicability to encompass a more extensive array of harmful compounds. Hence, the Commission suggests extending the scope of existing regulations to encompass not only illegal releases of oil and harmful liquid substances, but also the release of harmful substances in packaged form, sewage, waste of any kind, and residues from exhaust gas cleaning systems (scrubbing).

At the international level, the prevention and reduction of marine pollution is regulated by the IMO Conventions, to which Romania is also a party. The International Maritime Organisation (IMO) is a specialized agency of the International Maritime Organisation United Nations in charge of regulating world maritime transport, which plays a role important role in regulating and promoting safe and sustainable shipping practices worldwide. The correlation between Romanian national legislation and international regulations (IMO Conventions) as well as EU Directives on the protection of the marine environment from pollution caused by shipping can be seen in Table 1.

International legislative framework		National legislative framework
	International Convention for the	Law No 6/1993 by which Romania
	Prevention of Pollution from Ships,	acceded to MARPOL 73/78, Annexes I
	1973, as modified by the Protocol of	and II, with the amendments adopted and
	1978 (MARPOL 73/78)	entered into force up to that date, and
		accepted Annex V. Amendments to
		Annexes I and II to MARPOL 73/78,
		adopted after Romania's accession, were
		explicitly accepted by specific Romanian
IMO		normative acts to the 1997 Protocol
Conventions		amending MARPOL 73/78 relating
		thereto, adopted by the Final Act of the
		Conference of the Parties to MARPOL
		73/78, London, 26 September 1997 (for
		Annex VI).
	Annex I - Regulations for the	Law No 6/1993 by which Romania
	prevention of oil pollution	acceded to MARPOL 73/78, Annexes I
	Lee en et en benanen	and II, with the amendments adopted and

Table 1 Legal framework for the protection of the Romanian marine environment (adapted from [4], [6])

Annex II - Regulations for the control of pollution by noxious liquid substances in bulk

Annex III - Regulations for the prevention of pollution by harmful substances carried by sea in packaged form

Annex IV - Regulations for the prevention of sewage pollution from ships

Annex V (Revised) - Regulations for the prevention of pollution by garbage and cargo residues from ships

Annex VI - Regulations for the prevention of air pollution from ships

Resolution No. 194/2010 'Regulations for the prevention of air pollution from ships', (Official Monitor, Part I No. 790 of 08/11/2011)

Protocol of 1997 to amend the International Convention for the Prevention of Pollution from Ships, entered into force up to that date, and accepted Annex V. Amendments to Annexes I and II to MARPOL 73/78, adopted after Romania's accession, were explicitly accepted by specific legal acts.

Government Order No 38/2001 by which Romania accepted Annex III to MARPOL 73/78, as amended, for the prevention of pollution from ships

Law No 305/2005 by which Romania accepted the revised Annex IV to the International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol done at London on 17 February 1978 (MARPOL 73/78), adopted by the International Maritime Organization (IMO) by Resolution MEPC.115(51) of the Marine Environment Protection Committee in London on 1st April 2004.

Law No 6/1993 by which Romania acceded to MARPOL 73/78, Annexes I and II, with the amendments adopted and entered into force up to that date, and accepted Annex V. Amendments to Annexes I and II to MARPOL 73/78, adopted after Romania's accession, were explicitly accepted by specific legal acts.

Ministerial Order MTI No. 1293/2012 for the publication of the acceptance of the amendments to the Annex to the 1978 Protocol to the International Convention for the Prevention of Pollution from Ships, 1973 (Revised Annex V to MARPOL), adopted by the International Maritime Organization by Resolution MEPC.201(62) of the Marine Environment Protection Committee on 15 July 2011.

Law No 269/2006 by which Romania adheres to the Protocol of 1997 relating to the Amendment of the International Convention for the Prevention of Pollution from Ships, 1973, Annex VI -"Regulations for the Prevention of Air Pollution from Ships", adopted by the Final Act of the Conference of the Parties to MARPOL 73/78, London, 26 September 1997.

Protocol (Version updated on 01/02/2012) to amend the International

1973, as modified by the Protocol of
1978 relating thereto

OPRC International Convention on Oil Pollution Preparedness, Response and Cooperation, 1990

	BUNKERS 2001 International Convention on Civil Liability for Bunker Oil Pollution Damage from Ships	the Regulation on the organisation and functioning of the Operational Command for Marine Pollution Clean-up (CODM). <i>Law No 108/2009</i> for Romania's accession to the 2001 International Convention on Civil Liability for Bunker Oil Pollution Damage from Ships (BUNKERS), adopted in London on 23 March 2001. <i>Government Decision No 1299/2009</i> approving the Rules for the implementation of the 2001 International Convention on Civil Liability for Bunker Oil Pollution Damage from Ships (BUNKERS), adopted in London on 23 March 2001.
Regional agreements	<i>Bucharest Convention, 1992</i> , on the Protection of the Black Sea against Pollution	Law No 98/1992 on the ratification of the Convention on the Protection of the Black Sea against Pollution, signed at Bucharest
	Black Sea Regional Contingency Plan, approved by the Commission for the Protection of the Black Sea against Pollution on 21.11.2006	Signed by Romania on 21.11.2006
European Union Directives	Directive 2005/35/EC on ship- source pollution and on the introduction of criminal penalties	Law no. 102/2008 approving Government Emergency Ordinance (GEO) 130/2007 amending Law 17/1990 on the legal regime of inland maritime

Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 relating thereto.

Law no. 160/2000 on the approval of Governmental Order no.14/2000, for the accession of Romania to the International Convention "OPRC-1990", on preparedness, response and cooperation in case of marine pollution by oil products.

Government Decision No 893/2006 amending Government Decision No 1593/2002 approving the National Plan for preparedness, response and cooperation in the event of marine oil pollution,

Joint Order of Ministry of Environment and Water Management (MEWM), Ministry of Transport, Construction and Tourism (MTCT), Ministry of Administration and Interior (MAI) no.1/217/182, for the approval of the Regulation on the organisation and functioning of the Operational Command for Marine Pollution Clean-up (CODM).

for infringements, amended by Directive 2009/123/EC	waters, the territorial sea, the contiguous zone and the exclusive economic zone of
<i>Directive (EU) 2019/883</i> on ship-generated waste and cargo residues reception facilities	Romania. <i>Government Ordinance 9/2022</i> on port reception facilities for ship- generated waste
Decision No. 2850/2000/EC	Government Decision No 893/2006,
setting up a community framework	amending Government Decision
for cooperation in the field of	1593/2002 on the approval of the
accidental or deliberate pollution.	National Plan for preparedness, response
_	and cooperation in the event of marine oil
	pollution.

The ongoing war between Ukraine and Russia presents a substantial environmental hazard to adjacent nations, such as Romania, which may have ramifications for its maritime territories. Hence, it is crucial to examine the current legislative framework that is accountable for safeguarding Romanian maritime waters against pollution caused by the conflict.

The occurrence of marine pollution in the context of armed conflicts presents substantial risks to ecological systems, livelihoods, and human well-being. As a result, numerous international treaties and agreements have been established to mitigate these hazards and advance environmental conservation. Presented below is a comprehensive analysis of the pertinent legal frameworks:

- The United Nations Convention on the Law of the Sea [7] is a landmark treaty that mandates states to prevent, reduce, and control pollution from various sources, including armed conflict. Articles 192-237 deal specifically with marine pollution, urging states to take the necessary measures to prevent and attenuate pollution during armed conflicts.
- Geneva Conventions (1949) and Additional Protocols (1977): although primarily focused on humanitarian concerns during armed conflict, the Geneva Conventions and their Additional Protocols also address environmental protection. They emphasise the duty of parties to conflict to protect the natural environment, including marine ecosystems, from unnecessary damage [8].
- The Hague Convention IV (1907) is an older treaty that primarily governs the laws and customs of war on land. The principles set out in Hague Convention IV continue to influence international humanitarian law, including provisions related to minimising environmental damage during armed conflict [9].
- Customary International Law has a significant role to play in addressing marine pollution during armed conflicts. States are expected to adhere to customary rules prohibiting unnecessary damage to the environment, including marine ecosystems, even in times of conflict [10].
- International Law Commission of United Nations adopted "Draft Principles on Protection of the Environment in Relation to Armed Conficts" in 2022. Principle 13 of the document prohibited "the use of methods and means of warfare which are intended, or may be expected, to cause widespread, long-term and severe damage to the environment". Furthermore, Principle 14 of the document explicitly declared that "the law of armed conflict, encompassing the principles and regulations regarding differentiation, proportionality, and precautions, shall be implemented in order to protect the environment" [11].
- Regional agreements: Several regional agreements fill in the international frameworks addressing specific challenges related to marine pollution during armed conflicts. For example, the *Barcelona Convention in the Mediterranean region (1976)* addresses marine pollution issues, including those arising from armed conflict [12].

3. MAIN POLLUTING FACTORS IDENTIFICATION

Today, environmental experts are concerned about the effects of pollution and the long-term impact of pollutants on air, land, and water. Urgent issues that need to be addressed today include the growing resource crisis, from natural resources to energy, air quality, reducing harmful emissions into the environment, identifying green energy sources, and recycling materials.

Wastes and substances resulting from many industrial processes must be isolated, transported, and neutralized by specific processes so that they do not reach the ground and from there the water table. Experts estimate that one-third of the planet's soil is already polluted today. Toxic residues, wastes, detergents, oil and oil product spills, industrial cooling water, discharges into running water, pharmaceutical compounds (emerging pollutants), and faulty sewage systems lead to water contamination. The effects are particularly harmful to both flora and fauna and human health [13], [14], [15].

It is well known that plastics are the most damaging materials, both for soil and water. It is estimated that it takes between 10 and 1000 years for a plastic bag to degrade naturally, depending on the material. [16], [17]. Human's impact on nature after industrialization has taken off is devastating in the long term. The planet can be restored by reducing energy consumption, and fossil fuels, taking action on hazardous waste, recycling, protecting nature in various ways, especially through afforestation, and improving the quality of the marine environment by implementing corrective measures in regular monitoring programs.

Air quality is a priority these days. Manufacturing, transport, and other industries use fossil fuels that release carbon dioxide, carbon, nitrogen, sulfur compounds, and other greenhouse gases into the environment causing an imbalance in air quality and composition. Many air pollutants thin the ozone layer and expose the Earth to harmful radiation emitted by the Sun [18].

The biotope and biosystem of the Black Sea are a semi-enclosed ecosystem, favorable to the persistence and accumulation of pollutants. The ecosystem of the marine environment is modified through the alteration of the life of fish and marine mammals due to noise and vibrations generated by land activities in coastal areas (traffic, tourism, wastewater), various maritime works (dredging, port construction), drilling (construction and extraction), naval transport, etc. Taking the Port of Constanta area as a reference, the noise level is 60 dB during the day and 55 dB at night. Port railway noise can be taken into account as an important environmental pollutant. It leads to noise pollution along the railway and marshaling yards due to the braking regimes of the freight wagons' brake shoes. These problems also affect the health of the population by causing hearing loss or pathological effects. The discomfort caused by these factors can impair attention, communication, concentration, relaxation, and sleep [19]. Also, by causing chronic nervousness and stress; can influence cardiovascular arterial or mental diseases. For example, sounds with an amplitude of 3-5 Hz can cause anxiety, headaches, and pain in the spine because the sounds of this sound spectrum coincide with the resonance frequency of the human body. Increased noise can cause insomnia, rapid fatigue, aggression, impaired reproductive function, and contribute to serious mental disorders. Depending on the level of noise intensity, there are categories of effects that are harmful to humans, namely: auditory fatigue, noise trauma, acute hyperacusis occupational deafness, and impairment of the nervous system often with negative influences on visual function [20].

However, it is important to acknowledge that military training operations have detrimental effects on the marine environment, mostly owing to noise pollution and the release of toxic compounds arising from explosions.

4. CONSEQUENCES ANALYSIS OF THE RUSSIAN-UKRAINIAN CONFLICT ON THE ROMANIAN BLACK SEA COAST

Literature data have shown that in general, military activity and armed conflict contribute significantly to environmental pollution and thus affect human health [21]. Significant damage is done to the environment as a result of military and war activities, as well as the recreational use of hunting weapons.

According to the Shukla et al. (2023) study, military operations are responsible for the release of carcinogenic and toxic persistent organic pollutants into the aquatic environment, such as polyaromatic

hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), hexachlorocyclohexane (HCH), dichlorodiphenyltrichloroethane (DDT), and hexachlorobenzene (HCB).

Firing small arms results in gaseous chemical and particulate matter (PM) emissions into the environment. The creation of smoke during firing is due to primer and propellant ignition and the frictional interaction between the bullet and the barrel of the weapon [22]. The type of ammunition used should be considered when the environment is contaminated with heavy metals (Pb, Cd, Hg, As, Sb, Sr, Sr, Cu, Zn, W). One example encompasses the resulting shots from steel-core NM229s, responsible for the significant release of Cu and Zn into the environment, while SS109 cartridges release a significant amount of Pb particles [23],[24]. Significant emissions of soot and particles loaded with Cu, Zn and Fe are observed in Pb-free small calibre ammunition [24], [25]. Also, explosives are responsible for releasing significant amounts of heavy metals into the environment. For example, Pb and Cu can also be released from firing shells or gun barrels [24], [26]. According to Weber *et al.*, (2020) study, flash bang grenades have been identified as a notable contributor to elevated levels of lead (Pb) concentrations [24], [27].

At present, the North-Northwestern areas of the Black Sea basin are under very high pressure due to the current geopolitical situation. Thus, due to the explosives used in the current conflict, and destroyed military equipment, very large quantities of toxic substances such as heavy metals and persistent organic pollutants are released into the atmosphere and water with toxic effects on aquatic organisms, plants, and not least the civilian population. In addition, there are chemical, and wastewater spills due to the bombing of civilian land-based facilities (refineries, storage, and water plants) [28]. For example, the destruction of the Nova Kahovka dam on the Dnieper River in southern Ukraine has caused flooding over an area of 2,000 square kilometers, and the environmental consequences are long-term. Large quantities of fertilizers used on flooded farmland have been washed into the water and will be a real environmental threat due to organophosphorus compounds responsible for water quality deterioration. In addition to chemical pollution, noise, and bacteriological pollution should not be neglected [29], [30].

The chemistry of their explosives used in the Russo-Ukrainian war involves rapid oxidationreduction reactions. The detonation wave in high explosives induces rapid decomposition of the explosive molecules, resulting in the release of gases under conditions of elevated temperature and pressure. The explosion produces a shock wave, which is the force of destruction. In fuels, the controlled burning of the material generates gas rapidly but without a detonation wave, propelling objects forward. In the context of the Ukraine-Russia war, the specific compositions and innovations of explosive materials are likely to be evolving as both sides adapt to the tactical and strategic requirements of the conflict. The development and deployment of new types of explosives or the modification of existing formulations for increased efficiency or to circumvent defenses are ongoing aspects of modern warfare, with adverse impact on the aquatic environment, the land and especially the civilian population.

Marine organisms and the marine biological environment are adversely impacted in the aquatic ecosystem by the accumulated presence of pollutants generated by the war. The majority of heavy metals have little solubility and are easily assimilated by marine flora and fauna, so significantly impacting their viability in coastal regions and impeding the progress of the fishing sector. As exemplified by the 1956 Minamata illness episode in Japan, mercury has the capacity to amass in seawater, sediment, and fish, thereby inducing sickness within the food chain. The ingestion of cadmium by the human body is not possible, and prolonged eating of fish or algae polluted with cadmium can result in the development of "Itai-itai disease." This disease manifests as major bone abnormalities, which cause extreme discomfort, reduced height, and brittle bones. A particular risk to human health is the release of radioactive contaminants into the aquatic environment, which enter the human body through the food chain by easily accumulating in the sediment layer on the seabed [31].

5. APPLIED MATHEMATICAL INSTRUMENTS IN THE ENVIRONMENTAL ASSESSMENT APPROACH

Severe marine pollution is regarded as a serious threat with irreversible implications for human health, economic prosperity and the aquatic environment of the affected coastal zone. For good stewardship of

the marine environment from the point of view of protection, there must be a plan that includes prevention, surveillance, and rapid response. Innovative strategies and solutions also complement this approach.

As a result, calculating the mass value of pollutants responsible for contaminating the marine environment is an innovative prevention solution. The pollutants with the highest environmental risk can be identified by correlating the values obtained from the calculation of the mass of pollutants present in the water with the relative toxicity coefficients. This perspective will lead to the development of mitigation methods focused on reducing the most harmful pollutants. On the Romanian Black Sea coastal zone, this approach is necessary for protecting marine biodiversity and improving ecosystem sustainability. By understanding the mathematical and toxicological relationships, policymakers can implement more effective environmental regulations and conservation efforts, aimed at preserving the ecological integrity of this vital marine habitat.

In recent years, in order to prevent and estimate preliminary pollution, new mathematical diffusion models for different categories of pollutants have been developed to improve observation and calculation conditions.

Calculating the mass of pollutants in marine environments involves various equations and models, depending on the type of pollutant, its behavior in water, and the specific conditions of the marine environment. Generally, the mass of a pollutant in a marine environment can be estimated using principles from environmental chemistry and fluid dynamics.

According to study of Wania&Mackay (1999), the basic formula to calculate the mass of a pollutant (eq. 1) is based on its concentration in the water [32]:

$$\mathbf{M} = \boldsymbol{C} \times \boldsymbol{V} \tag{1}$$

where:

- M is the mass of the pollutant (usually in grams or kilograms).
- C is the concentration of the pollutant in the water (usually in mg/L or kg/m³).
- V is the volume of the water body or segment being considered (usually in liters or cubic meters).

In order to comprehend the dispersion or dilution of contaminants in marine environments, one can utilise models such as the Gaussian plume model or Fick's second law of diffusion [33], [34]. These models facilitate the estimation of pollutant concentration at diverse locations and time intervals, taking into account elements such as water currents, depth, temperature, and the properties of the pollutant.

The bioaccumulation factor (BAF) or the biomagnification factor (BMF) can be applied to determine the concentration of contaminants in marine animals [35] by comparing it to the concentration in the water (eq 2):

$$C = BMF(BAF) \times Caq \tag{2}$$

where:

C is concentration of contaminants in marine animals (expressed in mg/L),

BMF is Biomagnification Factor (expressed in units of mass of chemical per kg of the organism), Caq is concentration in the water.

As per the Stockholm Convention on Persistent Organic Pollutants established by the United Nations, substances are classified as bio accumulative when they exhibit the following characteristics [36]:

- ➤ The BCF or the BAF is greater than 5,000 L/kg wet weight or, in the absence of such data that log KOW ≥ 5.
- Various indications suggest a chemical poses additional concerns, such as significant bioaccumulation in other species, severe toxicity, or ecotoxicity.
- > The analysis of biota data reveals that the chemical possesses a bioaccumulation potential that is substantial enough to warrant its inclusion within the purview of this convention.

The strategies used in examining environmental safety issues are currently being substantially advanced. The study by Grigorieva *et al.*, (2021) demonstrated that comprehensive monitoring and detailed examination of polluted waters, together with unification of various parameters and methods of ensuring their purification from pollution, are essential for identification of the environmental situation and development of pollution prevention and response measures. At the same time, this approach proposes the construction of mathematical computer models to accurately determine the degree of pollution [37].

According to a study of Velikova *et al.*, (2017) [38], the total value of the effective mass of pollutants discharged, M_x is calculated as the sum of individual values of the effective mass of each of the pollutants discharged into water body, using the (eq. 3):

$$M_{\chi} = K_{rs} \cdot \sum_{i=1}^{n} M_i \tag{3}$$

where,

i = 1, ...n

n is the number of pollutants and represents the i-th pollutant,

 K_{rs} , is a dimensionless coefficient; and for point sources, $K_{rs} = 1$.

For annual rainfall-runoff, the annual mass of pollution, (M_i) , is calculated by the (eq 4):

$$M_i = C_i \cdot Q \tag{4}$$

where,

 C_i is the pollutant concentration, (mg/L);

Q is the annual rainfall-runoff (m³/year), which is calculated by the (eq 5):

$$Q = 10 \cdot F \cdot (\varphi_r \cdot H_r + \varphi_s \cdot H_s) \tag{5}$$

where φ_r, φ_s are the run-off coefficients for rainfall and snow-melt waters;

F is the catchment area of the territory (expressed in ha);

 H_r , H_s , are the average annual precipitation depth for warm and cold periods, respectively (expressed in mm).

The assumed values of the coefficient, denoted as φ_r are 0.3-0.4 for small towns and urban settlements, and 0.6-0.8 for major cities.

The coefficients of φ_s are considered ranging from 0.5 to 0.714

The calculation of the localized effects of pollutant emissions on the aquatic environment, taking into account the dispersion of wastewater through surface water bodies like rivers, lakes, or seawater, is determined using the subsequent equation (eq 6):

$$f_x = \frac{K_{rs}}{N_L} \cdot \sum_{i=1}^{P_x} C_{ix} / MAC_i \tag{6}$$

where:

 C_{ix} s denoted as the concentration of the i-th substance in the wastewater of the x-th source of pollution, mg/dm³;

 N_L represents the reciprocal dilution of wastewater at a distance of L = 50 m from its discharge, during the most worst weather conditions;

 P_x represents the total count of all substances released into the wastewater from the x-t polluting source;

 K_{rs} , is undefined coefficient and for point sources K_{rs} is equal to 1.

The reciprocal dilution of waste water at a distance of L 50 m away from the discharge point under the most unfavourable weather conditions can be calculated approximately using the following algorithm (eq 7):

$$N_L = \frac{\Phi(z_1)}{y_0 z_2}$$
(7)

where:

$$z_1 = \frac{L + x_0}{x^* + x_0} \tag{8}$$

$$z_2 = \frac{q}{u \times H^2} \sqrt{\frac{D_v}{D_h}} \tag{9}$$

$$\Phi(z_1) = \begin{cases} z_1, \text{ for } z_1 \le 1; \\ \sqrt{z_1}, \text{ for } z_1 > 1; \end{cases}$$
(10)

$$x_{0} = \begin{cases} \frac{q}{4\pi} \cdot \sqrt{\frac{D_{\nu}}{D_{h}}}, & \text{if } z_{2} \leq 1; \\ \frac{q^{2}}{4\pi \cdot H^{2} u D_{h}}, & \text{if } z_{2} > 1; \end{cases}$$
(11)

$$\chi^* = \frac{uH^2}{4\pi D_v} \tag{12}$$

q is the waste waters volume (m^3/s) ,

L is the spatial separation between the point of release and the closest monitoring section, expressed in metres (m), (L=50 m),

 x_0, x^* are the intermediate calculated parameters (m),

u the water flow velocity in the receiving water body (m/s),

 x^* is the parameter of the interface of the section of two-dimensional diffusion with the section of three-dimensional diffusion (m),

 D_v , and D_h are the coefficients of vertical and horizontal turbulent diffusion (m²/s),

H represents the mean depth at the point of release (in metres),

 y_0 is the parameter taking into account the effect of shore on reciprocal main dilution; ($y_0 = 2$, if wastewater (WW) discharge is carried out directly to the sea not far from the shoreline; $y_0 = 1$, if WW discharge is realized far from the shoreline,

 l_0 represents the distance from the discharge to the coastline, expressed in metres.

The coefficient of horizontal turbulent diffusion, are determined from the (eq 13):

$$D_h = 0.032 + 21.84u^2 \tag{13}$$

The coefficient of vertical turbulent diffusion is calculated using the eq 14:

$$D_{\nu} = C_0 + C_1 u + C_2 H + C_3 u^2 + C_4 H^2 + C_5 u H + C_6 u^2 H + C_7 u H^2$$
(14)

where $C_0 \dots C_7$ are constants.

In our future research, we will complement these initial theoretical models by conducting detailed *in situ* and laboratory analyses of water, sediment, and bioassay samples collected from the targeted marine locations.

CONCLUSIONS

Environmental protection means prevention, conservation and rapid intervention to mitigate potential hazards. By establishing environmental policies and measures for the management of aquatic ecosystems, the EU has set itself the important goal of preventing marine pollution for the coming decades.

The aquatic environment present on the Black Sea coast is under continuous threat of pollution due to the local geopolitical situation, military and other urban, tourism and industrial activities. The military tensions between Ukraine and Russia challenge the Romanian legislative context, which needs to be updated to protect ecosystems from pollution from the conflict in another Black Sea region. A feasible approach could be to adhere to other agreements, conventions and norms already present at the international level.

The close correlation between determining the content of pollutants and their effect on the environment is directly linked to assessing environmental hazards. Environmental protection specialists will have to be involved in the development of standardized classifications that analyse the pollutants with the highest risk. The risk index can be based on determining the mass of pollutants in water and comparing it with relative toxicity coefficients. In this way, strategies can be devised to decrease the risk of pollution by lowering the levels of hazardous pollutants.

One of the most important perspectives for future research for good monitoring is the need to correlate *in situ* testing with laboratory analysis of sediment, water, and biota samples in the areas adjacent to the conflict-prone areas of the Black Sea.

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