Assessing the Transboundary Water Pollution Possibly Produced By an Armed Conflict

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Abstract. The impact of armed conflicts can be direct and indirect, highlighted by population displacement and casualties, infrastructure destruction, together with social and economic hiatus, but also the movement of air, water and soil pollutants across regional and national borders. There are numerous possible contamination sources of the water bodies and aquatic ecosystems that may appear during armed conflicts, including projectile composition, use of chemical weapons, discharge of untreated wastewater due to damage to sewage lines or wastewater treatment plants, unregulated waste management (improper disposal of industrial, hospital and municipal waste), oil spills, and deliberate poisoning of water resources. Thus, a comprehensive study from a multidisciplinary perspective of the armed conflicts is a sine qua non condition. In accordance, to properly assess the effects of pollution in the study area (Black Sea and coastal area) and to establish further strategies that can hinder the impact, water samples from various points of interest were analyzed to determine the water quality of the aquatic ecosystem and to possibly identify contaminants in the analyzed water bodies. Higher concentration values were observed for Pb in MB3 (27.9 µg/L) and Zn in MB1 (232 µg/L) and MB2 (53.1 µg/L), exceeding the maximum concentration limits set by the national legislation (10 µg/L for Pb and 50 µg/L for Zn).

1 Introduction

Armed conflicts affect the natural ecosystems, causing losses in biodiversity, deforestation, soil, air and water pollution, and territorial shifts. The pollution affects not only the conflict region, but also the territories surrounding it, due to the movement of pollutants across regional and national borders [1-3].

In this context, water, the most precious natural resource, is subjected to frequent pollution typically caused by human activities, such as industry, agriculture and livestock farming, maritime traffic, fuel spillages, deforestation, and also armed conflicts [4, 5]. The

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latter affects the environment by contaminating the ecosystem, disrupting water systems, and exacerbating the climate shift, as natural resources are depleted and environmental factors are polluted [6]. The effects of conflicts on the environment can be direct (physically linked to armed conflicts and short-term occurrence) or indirect (related to the conflict, includes multiple factors, and occurs in the medium to longer-term) [7]. One of the immediate effects of armed conflicts is the destruction of water supply infrastructure, such as blowing up dams (as it occurred in the Dnipro hydroelectric power plant from Ukraine, during World War II), destruction of sewage treatment facilities (as it occurred in the Kuwait during the Gulf War), oil spills in waterways (as it occurred in Chechnya during the war with Russia) [8, 9].

Another direct effect is caused by the exposure of the environment to various pollutants from military ammunition, transport, storage, and living facilities, leading to a significant accumulation of organic pollutants and heavy metals in areas surrounding the battlefields [10, 11]. That was also the case during the Vietnam War, when the US Armed Forces destroyed the forests and crops with a wide variety of herbicides, which poisoned the soil, river systems, lakes, and rice crops allowing the toxic chemical substances to enter the food chain and had a devastating effect on the environment and human health [12, 13].

However, indirect effects include the displacement of people (producing a shortage of personnel in water and electricity delivery networks), lack/destruction of infrastructure, equipment, or machinery, the absence of data, and insufficient funding for environmental protection. Therefore, upholding water service provision is one of the biggest and most essential difficulties in conflict-affected communities [14].

Although there are numerous papers on water as a factor that influences cooperation or conflict over shared resources, the effects of conflict on water systems have been insufficiently studied. In this context, the paper aims to develop complex methods for monitoring the state of water bodies within the territories with permanent residence of the population affected by hostilities, in order to identify future water management priorities.

2 Experimental

2.1 Study area and sampling sites

For this study, seawater samples were collected from five sampling points in the Constanta coastal area (locations are shown in Fig. 1). Water samples were collected in glass bottles, varying the depth (samples MB1, MB2, MB3) and location (samples MB4, MB5, MB6, and MB7).

Different sampling sites were selected in order to evaluate the potential pollution dispersion. Approximatively 2 L of bottom water samples and 200 g sediment sample (denoted Sed) were collected in pre-cleaned polyethylene containers, according to current standards [15-17], and transported to the laboratory under isothermal conditions between 4 and 6 °C for further chemical analysis.

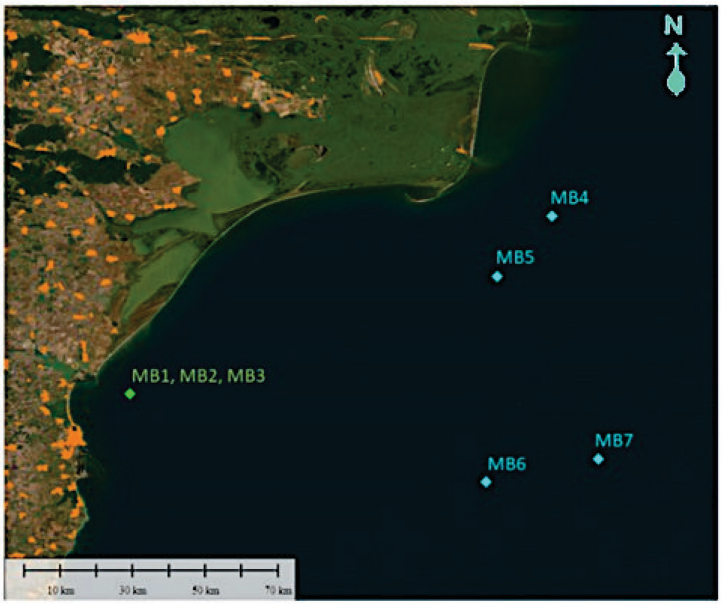

Fig. 1. Location of sampling points along the coast of Romania

2.2 Methods

The physicochemical parameters, the total petroleum hydrocarbons (TPH), and the metal concentration were analyzed for the seawater samples from the Constanta coastal area. Thus, pH was measured with a WTW Multiparameter Benchtop Meter InoLab, while turbidity measurements were carried out with a portable turbidimeter (Velp Scientifica TB1). In addition, ammonium, chlorides, orthophosphates, total phosphorous, nitrate, and nitrite were determined in the laboratory using standard analytical procedures [18-21].

Total petroleum hydrocarbon concentrations in seawater samples were quantified using a JASCO 4100 FT-IR spectrometer. For this determination, 200 mL water samples were extracted with 50 mL carbon tetrachloride, and the organic layer was dried over anhydrous sodium sulfate. The spectra were acquired over the spectral range of 3150–2750 cm^{-1} at a resolution of 4 cm^{-1}, in the absorbance model using a quartz cell of 1.0 cm path length. The total content of petroleum hydrocarbons (TPH) was determined by measuring the absorbance at a wavelength of 2930 cm^{-1}.

For the metal concentrations, a volume of 100 mL from each seawater sample was treated with 5 mL analytically pure HNO_3, and concentrated at high temperature to a volume of 35 mL. After cooling, the water samples were diluted to 100 mL with HNO_3 (0.5%). The concentration of heavy metals from water samples was determined with flame (Ni, Zn, and Pb) and graphite furnace (Cd) atomic absorption methods using an HRCSAAS ContrAA 700 Spectrometer (Analytik Jena, Germany).

3 Results and discussion

The physical and chemical characteristics of seawater from different sites and depths are summarized in Table 1.

Table 1. Physico-chemical properties of the seawater from the different sampling sites

Sample code	pH	Turbidity [NTU]	N-NH_4 [mg N/L]	N-NO_2 [mg N/L]	N-NO_3 [mg N/L]	Chlorides [mg/L]	Orthophosphates [mg P/L]	Total phosphorous [mg P/L]	TPH [mg/L]
MB1	8.1	16.07	0.037	0.015	0.479	8357	0.0405	0.0658	0.272
MB2	8.1	4.37	0.040	0.005	0.094	10166	<0.131* (0.007)	0.0197	0.219
MB3	8.4	2.08	0.239	0.027	0.097	7463	0.0135	0.0329	0.214
MB4	8.2	<1.03* (0.70)	0.035	0.032	0.033	7740	0.0135	0.0263	0.294
MB5	8.4	<1.03* (0.86)	0.032	0.032	0.044	7753	0.0135	0.0395	0.224
MB6	8.3	<1.03* (0.42)	0.026	0.020	0.038	8863	<0.131* (0.007)	0.0263	0.264
MB7	8.2	<1.03* (0.58)	0.012	0.018	0.041	8733	<0.131* (0.007)	0.0460	0.282

*LOD values; in brackets: detected values, bellow LOD

Each indicator from Table 1 is further analyzed. Thus, an important property of the aquatic environment is pH, as it affects chemical and biochemical processes and its values reflect the productivity and pollution levels [22]. The average pH for seawater ranges between 7.5 and 8.5 [23], depending on human activities, water temperature, and air-sea CO_2 exchange. The pH of the water samples was slightly alkaline, with slight variations, being aligned with the typical pH of the seawater.

Turbidity is a reduction in water clarity because of the presence of suspended particles in water, which include plankton and inanimate organic or inorganic particles. Turbidity measurements are presented in nephelometric turbidity units (NTU), a measure of the amount of light scattered by particles at right angles to an incident beam of white light. The turbidity values ranged from 0.4 to 16.1 NTU, as it can be seen in Table 1, revealing the predominance of low turbidity values, corresponding to the absence of meteorological events during sampling.

Nutrients from seawater were quantified and the recorded values were compared with data reported in previous studies. Nitrate is the main form of dissolved inorganic nitrogen and has a crucial role in water environment management. The minimum and maximum concentrations of nitrates (NO^{3-}) of the investigated samples were 0.033 mg N/L and 0.479 mg N/L, respectively, higher than previously reported values of nitrates in the Black Sea coastal area (between 0.011 mg N/L to 0.3705 mg N/L) [24]. Similarly, the nitrites (NO^{2-}) content in the analyzed sea samples increased from undetectable values to 0.03 mg N/L. These variations of both nitrite and nitrate show an increasing trend and could be explained by a significant level of nitrification activity occurring in the marine environment during the last years.

Phosphorus (P) is a key indicator of the aquatic organism growth and eutrophication and is evaluated as total phosphorous (TP), which represents the sum of the organic and inorganic fractions of phosphorus in seawater, or as PO_4^{3-}, the inorganic form. Results showed that the average concentrations of the total phosphorous and orthophosphates in the investigated water samples were 0.037 mg P/L and 0.007 mg P/L.

Concerning chloride concentrations, all the samples showed a similar level of chloride, around 8000 mg/L, except sample MB2, which exhibits a higher value, of 10000 mg/L. These values are comparable with those obtained by Azdem et al. in seawater samples collected in some sites along the coast of Agadir, Morocco [24].

The total content of petroleum hydrocarbons was evaluated and the results summarized in Table 1 revealed an average value of 0.253 mg/L, which is consistently higher than the results reported by Ţigănuș et al. for 154 seawater samples collected during February - June

2015 [25], due to the sampling location and period. Additional analysis of TPH for the analyzed water samples included FTIR determinations. The spectra of the MB1-MB7 samples (Fig. 2) showed the presence of high-intensity bands associated with the aliphatic hydrocarbons C–H groups, between 2970 cm^{-1} and 2860 cm^{-1} and a low-intensity band around 3820 cm^{-1} ascribed to the aromatic hydrocarbons =C–H deformation. Specifically, the observed peaks can be assigned to the symmetric stretching of $–CH_3$ (2860 cm^{-1}), asymmetric stretching of $–CH_2$ (2930 cm^{-1}) and asymmetric stretching of $–CH_3$ (2970 cm^{-1}), in agreement with other studies [26]. The measured concentrations of TPH in all the samples (MB1-MB7) slightly exceed the allowed limit of 0.200 mg/L, recommended by national legislation (Order No.161/2006 – "Normative classification of surface water quality in order to establish the ecological status of water bodies"). This indicates a certain pollution of seawater, probably explained by the level of urbanization and industrialization of the surrounding land areas.

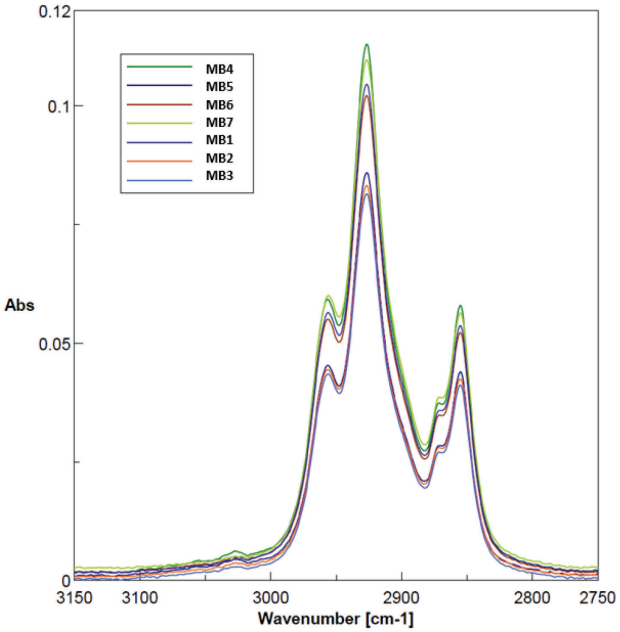

Fig. 2. FTIR spectra of the water samples (MB1-MB7)

Also, the metal concentrations of the water and sediment samples were determined through AAS investigations. The concentrations of Cd, Ni, Pb, and Zn in seawater and sediment samples have been summarized in Table 2. For the water samples, the metal levels decreased in the following order: Zn > Pb > Ni > Cd. The maximum concentration limits set by the national regulations for coastal marine water are as follows: 50 µg/L for Zn, 10 µg/L for Pb, 100 µg/L for Ni, and 5 µg/L for Cd. The high concentration of Zn at MB1 can be attributed to the activity of the refinery and petrochemical plant located nearby. The values of Cd and Ni in marine coastal water exhibited a regular distribution across the 7 sampling stations, below the maximum allowable thresholds. Similarly, the concentration of Pb ranged between 4.7 µg/L and 8.7 µg/L and was significantly higher in the MB3 sample, which can be related to an increase of the terrestrial input such as riverine, domestic, and industrial inputs before sampling.

Table 2. Heavy metals concentration in seawater samples collected along the Coast of Constanta, Romania

Sample name	Cd (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)
MB1	0.080	2.86	4.7	232
MB2	0.330	3.33	6.4	53.1
MB3	0.140	0.57	27.9	35.2
MB4	0.130	2.50	8.75	7.25
MB5	0.167	2.48	6.29	2.57
MB6	0.146	1.62	3.52	0.76
MB7	0.037	0.38	6.29	4.29
Sed	0.32*)	53.35*)	37.32*)	102.65*)

*) The concentrations are presented using units in the form of mg/kg dry weight

Regarding the heavy metals content in the sediment sample, the values obtained for Zn, Pb, and Cd are below the maximum permissible values as defined by the Romanian national regulation (Order no. 161/2006), which are as follows: 150 mg/kg for Zn, 85 mg/kg for Pb and 0.8 mg/kg for Cd. The detected value of Ni in the Sed sample exceeds the maximum limit allowed (35 mg/kg), indicating a certain contamination, which can be associated with intensive commercial and industrial activities around the sampling site.

4 Conclusions

The sampling regime of the present study aimed to evaluate the physico-chemical properties in different locations and at various depths of the marine environment, in the Romanian Black Sea Sector in the context of armed conflicts occurring in the vicinity. The results showed that overall, the values are below the maximum allowed limits set by national legislation. The higher values observed in Pb and Zn cannot be directly linked to pollution due to armed conflicts.

Therefore, future investigations should refer to frequent in situ measurements and expansion of the sampling location, correlation between the heavy metal bioaccumulation and the heavy metal concentrations in seawater, evaluation of the impact of anthropogenic conditions in seawater versus natural phenomena on the seasonal fluctuations of physical and chemical properties.

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