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ASSESSMENT OF EMERGENT PHARMACEUTICAL COMPOUNDS IN THE BLACK SEA ECOSYSTEM

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ABSTRACT

The Black Sea, a unique semi-enclosed marine ecosystem, faces increasing environmental challenges due to emerging contaminants, including pharmaceutical compounds. These pollutants, and traditionally monitored substances, contribute to the complex pollution landscape, with potential risks to marine biodiversity and human health.

Pharmaceutical contaminants enter the Black Sea through multiple pathways, including wastewater discharges, agricultural runoff, and various industrial and urban activities. Owing to its limited water exchange with other seas, the Black Sea has a high potential for pollutant accumulation, which may exacerbate ecological and toxicological impacts. Among the most frequently detected pharmaceuticals are antibiotics (e.g., ciprofloxacin, metformin) and endocrine-disrupting compounds, which have been reported in coastal waters. These substances are known to interfere with endocrine functions, potentially affecting the reproductive health and development of marine organisms, while also posing risks to human consumers of contaminated seafood.

The present study aims to establish analytical protocols for the determination of emerging pollutants and to quantify and assess the distribution of pharmaceutical compounds in water and sediment samples from the Romanian Black Sea coast. In addition, it investigates the bioaccumulation of pharmaceuticals in selected pelagic fish species, including *Sprattus sprattus* (European sprat), *Trachurus mediterraneus* (Mediterranean horse mackerel), *Pomatomus saltatrix* (bluefish), and *Alosa tanaica* (Azov shad). The findings provide new insights into the extent of pharmaceutical contamination in the Black Sea environment and contribute to strengthening environmental monitoring strategies and ecological risk assessment frameworks.

Keywords: Black Sea, pharmaceutical compounds, emerging contaminants, marine pollution, bioaccumulation

INTRODUCTION

Emerging pollutants are synthetic chemicals that are not yet routinely monitored or regulated in the marine environment, but which have the potential to cause adverse ecological effects and, ultimately, may also affect the human consumer (Geissen *et al.*, 2015). Their presence in the environment is a direct result of anthropogenic activities, such as poor management of hazardous waste, the overuse of certain chemical substances, and discharges of untreated or insufficiently treated wastewater.

The category of emerging pollutants includes pharmaceutical products for human and veterinary use, disinfectants and biocides, personal care products, plasticizers, food additives, biological toxins, perfluorinated compounds derived from pesticides, fungicides (Yahaya, Abdulrazaq, Abdulkareem *et al*., 2021). Research on the presence of emerging pollutants in the environment has shown that their presence in aquatic ecosystems is influenced by several factors, such as the degree of use, the quantity used, the period of use, as well as their persistence and degradation characteristics (Vystavna *et al.*, 2018), (Chiţescu *et al.*, 2021).

The interest in the occurrence of persistent, water-soluble substances in the marine environment stems largely from concerns about possible toxicological risks to marine species (Zenker *et al.*, 2014), (Straub, 2016), (Mezzelani *et al*., 2018). Descriptor 8 "Contaminant concentrations are at levels that do not generate pollution effects" of the Marine Strategy Framework Directive (Directive 2008/56/EC, 2008) establishes a list of substances of interest at the EU level in areas regulated by European legislation (Tornero, V., Hanke, 2018). This requires member states to monitor substances of potential concern to determine whether there is a risk to the environment.

Pharmaceutical compounds such as diclofenac, 17-β-estradiol, and 17-α-ethinylestradiol were first included on the EU Watch List in 2013 (Directive 2013/39/EU, 2013), with the most recent updated introduced through Decision (EU) 2022/1307 in 2022. The Watch List serves to identify emerging substances that must be monitored across Europe in order to assess potential risks, although no regulatory limits have yet been established for these compounds. At present, only proposals have been issued by the EU Scientific Committee, as outlined in a recent draft document (Scientific Committee on Health, Environmental and Emerging Risks — SCHEER, 2023).

Among these, active pharmaceutical compounds are of particular importance due to their wide range of uses in human and veterinary medicine and aquaculture. Pharmaceutical substances can be introduced into aquatic systems through industrial, agricultural and other wastewater (Patel *et al*., 2019). The widespread presence of pharmaceuticals in marine waters (Mezzelani *et al.*, 2018), (Almeida *et al*., 2021) indicates the lack of effective removal during wastewater treatment. Transported by rivers into the sea, pharmaceuticals spread, usually far from shore, due to favorable hydrodynamic conditions and/or long degradation periods.

There is little data on the presence of pharmaceutical compounds in the Black Sea ecosystem. Screening for pharmaceutical pollutants carried out within the EMBLAS project (https://emblasproject.org/) for Georgia and Ukraine highlighted the dominance of the antiepileptic drug carbamazepine, with a prevalence of 85% in Black Sea waters and an average concentration of 5.8 ng/L (EMBLAS, 2017). The sum of detected pharmaceutical compounds ranged from 79 ng/L in offshore marine waters to 477 ng/L in the coastal waters of Ukraine. Values of 299 ng/L were measured in the Danube discharge area, and 322 ng/L in coastal waters of the eastern Black Sea (EMBLAS, 2017).

Chițescu *et al*., 2021 highlighted the presence of 23 pharmaceutical compounds in the Danube River, with concentrations ranging from 2.5 to 166 ng/L, the most frequently found being sulfamethoxazole, followed by carbamazepine, trimethoprim, diclofenac and ketoprofen (Chitescu *et al.*, 2015).

A recent study conducted between June and July 2020 investigated the presence of pharmaceutical compounds in the Romanian sector of the Black Sea, based on water samples collected from seven coastal locations. The levels of contamination detected were lower than those reported in freshwater systems, although compounds such as sulfamethoxazole, carbamazepine, diclofenac, and bisphenol A were still present in the marine samples. The values of pharmaceutical compounds varied in the range of 1.04 ng/L (drospirenone) - 132 ng/L (diclofenac) (Ene *et al*., 2025).

Globally, the detection of pharmaceutical compounds in the marine environment is not a recent development; however, their use and occurrence in marine ecosystems continue to increase (Branchet *et al*., 2021). In recent years, both the presence and the effects of these substances in aquatic environments have been intensively studied in order to provide scientific evidence for updating legislation on water protection (Decision EU 2022/1307, 2022).

The present study focuses on quantifying pharmaceutical compounds in both abiotic and biotic components of the Romanian Black Sea environment, with an emphasis on water and sediment samples from the coastal zone, as well as pelagic fish species such as *Sprattus sprattus* (European sprat), *Trachurus mediterraneus* (Mediterranean horse mackerel), *Pomatomus saltatrix* (bluefish), and *Alosa tanaica* (Azov shad).

Despite several regional investigations, comprehensive data on the levels and spatial distribution of pharmaceutical contaminants in both abiotic and biotic compartments of the Romanian Black Sea coast remain limited. This study addresses this knowledge gap by applying validated analytical protocols to quantify pharmaceuticals in coastal waters, sediments, and pelagic fish species, while also evaluating their potential ecological risks.

MATERIALS AND METHODS

Quantification of pharmaceutical compounds, primarily in fish but also in water and marine sediments, represents preliminary data obtained at the National Institute for Marine Research and Development (NIMRD) “Grigore Antipa”.

The analysis of emerging pollutants was carried out on samples collected from the Romanian coastal area during the October 2023 expedition with the research vessel *Steaua de Mare 1*. A total of 18 water samples and 16 sediment samples were obtained from monitoring stations located along the 10, 20, 30, 40, and 50 m isobaths (Fig. 1). Water samples were collected using Niskin bathometers and stored in labeled, screw-capped containers under refrigeration on board the vessel. Containers were filled completely to minimize headspace and prevent the loss of volatile components. Sediment samples were collected using a Van Veen grab sampler (bodengreifer), properly labeled, and immediately refrigerated after collection.

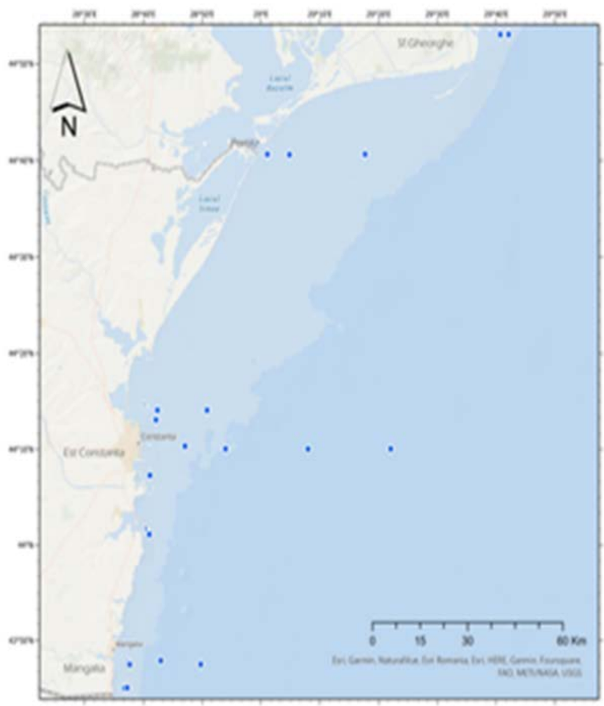

Fig. 1. Map of water and sediment sampling stations on the Romanian Black Sea coast - October 2023

The four species of pelagic fish (Fig. 2., Table 1) were sampled during expeditions carried out by the NIMRD "Grigore Antipa" with the research vessel "Steaua de Mare 1", using a pelagic trawl, during the autumn of 2023 from the Gura Buhaz and Eforie stations.

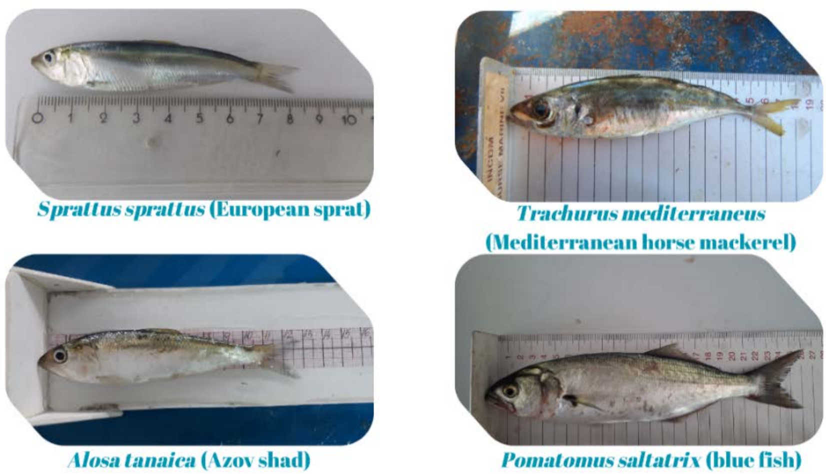

Fig. 2. The four species of pelagic fish sampled in October 2023

Table 1. Data on the fish samples studied

Species	Sampling area	Number of samples	Sample size (no. of individuals)	Length (cm)	Weight (g)	Age (year)
***Sprattus sprattus* (European sprat)**	Gura Buhaz	1	4	7.6-8.5	2.75-4.07	0-1
***Trachurus mediterraneus* (Mediterranean horse mackerel)**	Gura Buhaz	1	3	6.3-18.5	2-59	0-5
***Trachurus mediterraneus* (Mediterranean horse mackerel)**	Gura Buhaz	1	3	11-14.5	15.4-21	1-2
***Pomatomus saltatrix* (blue fish)**	Gura Buhaz	1	5	16-26	41.83-180	1-3
***Alosa tanaica* (Azov shad)**	Eforie	1	3	10-18.5	6.5-47	1-4
***Alosa tanaica* (Azov shad)**	Eforie	1	3	18.1-19.9	42-52	3-4

Sprattus sprattus (European sprat) is a species of high economic value, which lives in numerous schools in the waters of the Black Sea. The sprat prefers lower temperatures between 7 -18 ^oC and feeds on zooplankton, mollusks and marine phytoplankton. The usual length is 8-9 cm with a weight of 10-11 g (Niță *et al.*, 2022).

Trachurus mediterraneus (Mediterranean horse mackerel) is a migratory species that lives also in massive schools in the Sea of Marmara and the Bosphorus area and appears in the Black Sea area between May and October, following the banks of anchovies, sprat and sand smelts on which it feeds. The usual length is 13-15 cm with an average weight in the range of 80-120 g (Niță *et al.*, 2022).

Pomatomus saltatrix (blue fish) is a predatory species, of Mediterranean origin, that prefers water temperatures above 15 ^oC. The bluefish lives in small schools and reproduces and migrates from the Sea of Marmara to the Black Sea during the summer, where it feeds on anchovies, mackerel and horse mackerel. During the winter, specimens from the Black Sea retreat to the warmer waters of the Sea of Marmara. The usual length is 30-40 cm, with an average weight between 2000-3000 g (Niță *et al.*, 2022).

Alosa tanaica (Azov shad) is a Ponto-Caspian relict fish that migrates to the Danube waters for reproduction when the water temperature is 9 - 10 ^oC in the spring and returns to the Black Sea waters in the fall. *Alosa tanaica* feeds on goby, anchovies, horse mackerel, and aterines. Azov shad resembles the Danube shad (Alosa immaculata), but is smaller, around 20 cm. The usual length is 20 cm, with an average weight between 50-130 g (Niță *et al*., 2022).

The age of *Sprattus sprattus*, *Trachurus mediterraneus*, and *Pomatomus saltatrix* were determined through otolith analysis, in accordance with the regional guidelines provided by Carbonara & Follesa (2019). In contrast, age estimation for *Alosa tanaica* was performed using scale analysis, following the methodology described by Yilmaz & Polat (2002). Biometric parameters (length and weight) were measured according to the standardized procedures outlined by Follesa & Carbonara (2019). After capture, fish specimens were stored under freezing conditions and transported to the laboratory. Each biological sample consisted of a pooled group of 3–5 individuals of the same species, treated as a single analytical unit. Muscle tissues were then freeze-dried with a Labconco system and homogenized using an electric grinder prior to analysis.

Water and sediment samples were transported in refrigerated containers and analyzed at the REXDAN Research Infrastructure, whereas fish samples were processed and examined at the Faculty of Food Science and Engineering, "Dunărea de Jos" University of Galați.

The analyses were performed by applying the protocols for the determination of pharmaceutical compounds in water, sediment and biota using a UHPLC (Ultra-High-Performance Liquid Chromatography) equipment with an HRMS (High Resolution Mass Spectrometer) detector (Thermo Scientific Dionex Ultimate 3000 Series).

Established methods from scientific literature were employed and adapted as necessary to enable the identification of pharmaceutical compounds. The QueChERS extraction and purification protocol was used, followed by instrumental analysis by UHPLC – HRMS (ultra-high performance liquid chromatography coupled with high-resolution mass spectrometry) (Chitescu *et al*., 2012, Gros *et al*., 2012, Abdel Ghani & Hanafi, 2016, Diamanti *et al*., 2020, Kalogeropoulou *et al*., 2021), *De Mastro et al.*, 2022, Ene *et al*., 2025).

The specific steps for the analytical determination of emerging pharmaceutical pollutants from water, sediment and marine biota samples consist of: Filtration (water samples), Extraction, Separation, Detection, Quantification, Identification, Quality Control.

Protocol for the determination of pharmaceutical compounds

Water samples

For water samples, solid phase extraction (SPE) was used as a technique. Preliminary steps – adjusting the pH of seawater to 3 and preconditioning the SPE cartridge.

Add 100 mL of seawater (sample) whose pH has been adjusted to 3 to the preconditioned SPE cartridge. Add 5 mL of methanol/water mixture. Mount the rack with the 2 mL vials in which the pharmaceutical compounds will be eluted with 2 mL of methanol. The collected eluent was concentrated by evaporation under a stream of high purity nitrogen at 40 °C. Methanol and ultrapure water are added, thus preparing the sample for chromatographic analysis.

Sediment and biota samples

The extraction of analytes from sediment and biota was done in a 50 mL centrifuge tube to which 2 g of lyophilized sample is added and homogenized by shaking with 1 mL of ultrapure water and 8 mL of acetonitrile. The first QuEChERS extraction salts kit is added to the resulting mixture. Shake vigorously, then centrifuge at 5000 RPM for 5 minutes. The second QuEChERS extraction kit was added to the extract (4 mL of supernatant) obtained. After shaking vigorously, the sample is centrifuged again at 5000 RPM for 5 minutes. A volume of 2 mL of supernatant was collected in an evaporation tube, after which the solvent is removed in a nitrogen stream at 40°C. The resulting extract is reconstituted with acetonitrile or chromatographic grade methanol and ultrapure water. The sample is filtered through a 0.22 µm hydrophilic Millipore filter into analysis vials, thus being prepared for chromatographic analysis.

The pharmaceutical compounds analyzed in water and sediments samples were substances that are part of frequently used drugs (**Table 2**).

Table 2. The pharmaceutical compounds analyzed in water and sediments samples

Compound category	Compound name
Antibiotic	Ciprofloxacin, enrofloxacin, amoxicillin, clindamycin, trimethoprim, erythromycin, clarithromycin, sulfamethoxazole
Anti-inflammatory	Ketoprofen, diclofenac
Antiepileptic	Carbamazepine
Antidiabetic	Metformin

The pharmaceutical compounds quantified in fish tissues are mentioned in Table 3.

Table 3. The pharmaceutical compounds quantify in fish tissues

Compound category	Compound name
Antibiotic	Trimethoprim, norfloxacin, oxytetracycline, ciprofloxacin, sulfamethoxazole, erythromycin
Anti-inflammatory	Acetaminophen, ibuprofen, ketoprofen, naproxen, diclofenac
Antiepileptic	Carbamazepine
Antidiabetic	Metformin
Antifungal	Clotrimazole, fluconazole, carbendazim, terconazole, tebuconazole, triticonazole, metalaxyl, imazalil
Contraceptive	Drosperinone
Alkaloid	Caffeine

RESULTS AND DISCUSSION

Data regarding the occurrence of emerging pollutants in water and sediment samples collected from the Romanian coastal area are presented below. For the water samples, the concentrations of the targeted pharmaceutical compounds ranged from 0.20 to 131.38 ng/L (Table 4). Antibiotics such as enrofloxacin, amoxicillin, erythromycin, and clarithromycin were not detected in any of the analyzed samples. In contrast, trimethoprim (an antibiotic) and carbamazepine (an antiepileptic drug) were the most prevalent, being identified in 50% and 72% of the samples, respectively.

Table 4. Descriptive statistics of pharmaceutical product concentrations in seawater from the Romanian coastline – October 2023

Variable	N	Mean (ng/L)	Minimum (ng/L)	Maximum (ng/L)	Standard deviation (ng/L)
Metformin	18	0.04	Nd*	0.57	0.14
Trimethoprim	18	0.54	Nd	1.96	0.65
Ciprofloxacin	18	0.02	Nd	0.30	0.07
Enrofloxacin	18	Nd			
Amoxicillin	18	Nd			
Clindamicyn	18	0.98	Nd	9.44	2.50
Carbamazepine	18	13.79	Nd	61.45	15.72
Erythromycin	18	Nd			
Clarithromycin	18	Nd			
Ketoprofen	18	19.39	Nd	131.38	37.02
Sulfamethoxazole	18	1.43	Nd	25.72	6.06
Diclofenac	18	4.26	Nd	20.80	6.79

Not detected

The highest concentration was recorded for ketoprofen at the Mangalia station (40 m), followed by carbamazepine at the Constanța Sud station (20 m), and diclofenac at the Constanța Est station (35 m) (Fig. 3).

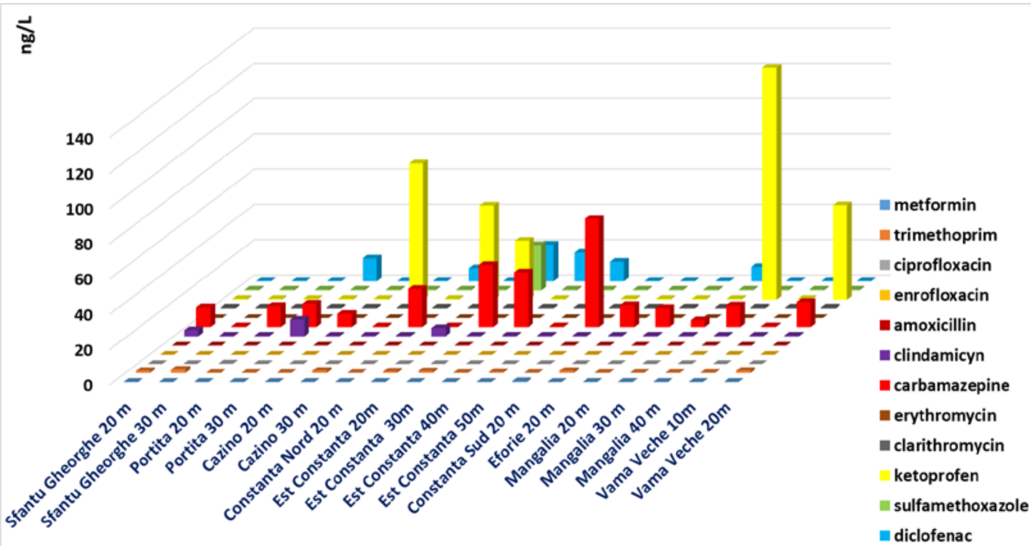

Fig. 3. Concentrations of pharmaceutical compounds in coastal waters of the Black Sea – October 2023

The spatial distribution highlights the presence of the highest concentrations of pharmaceutical substances in the central and southern coastal areas, most likely due to the presence in these areas of the largest urban agglomerations and the related wastewaters treatment plants (WWTP) (Fig. 4.).

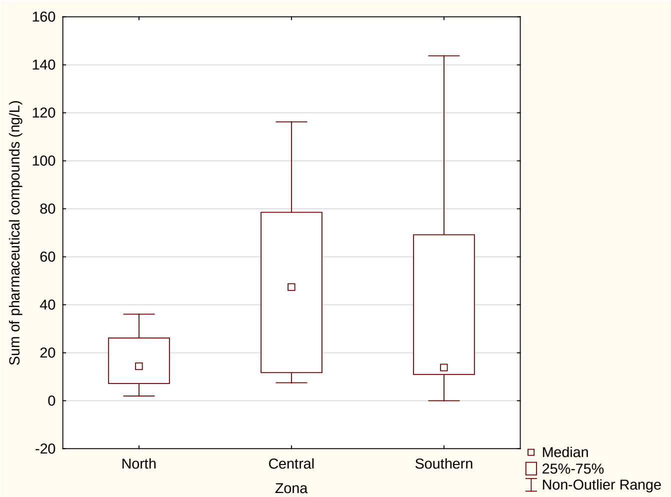

Fig. 4. Distribution of the total content of pharmaceutical compounds in seawater from different areas of the Romanian coastline – October 2023

In sediment, most of the emerging pollutants were undetected, except in coastal areas under the influence of large urban agglomerations. Thus, the only compounds identified were the antidiabetic metformin in the Constanta Est 50 m and Mangalia 30 m and the anti-inflammatory ketoprofen in the Constanta Est 20 m (Fig. 5).

Previous studies mention that, due to the hydrophilic character of most pharmaceutical compounds, they tend to be present in the water mass, while some of them can undergo specific interactions and accumulate in sediments (Moreno-González *et al*., 2015, Feo *et al.*, 2020). The comparison of water and sediment samples shows that pharmaceuticals are more frequently detected in water than in sediment. This could be due to the higher solubility of these compounds in water, their degradation rates or the dynamics of sedimentation processes. Metformin and ketoprofen were the only pharmaceuticals detected in both water and sediment samples, indicating their persistence in the environment. Pharmaceuticals such as carbamazepine and diclofenac showed high concentrations in water but were not detected in sediment, suggesting that they may degrade or remain dissolved in the water column.

Spatially, concentrations of pharmaceuticals varied from one area to another. Elevated concentrations of several pharmaceutical compounds were observed in water along the Constanța East profile, indicating the Constanta Sud WWTP as a potential hotspot for contamination. Metformin was also detected in both water and sediment in Mangalia, suggesting a localized source of contamination, possibly due to the Mangalia municipal hospital and the Mangalia WWTP in the coastal area.

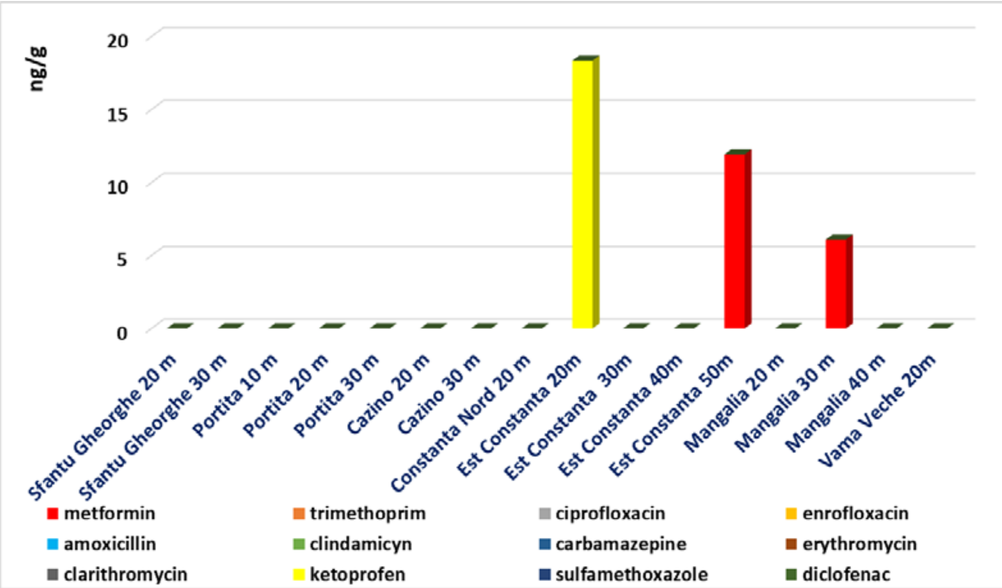

Fig. 5. Concentrations of pharmaceutical compounds in Black Sea sediments - October 2023

Pharmaceutical compounds are emerging pollutants consistently present in wastewater discharged into the marine environment. Studies show that most pharmaceutical compounds are not readily biodegradable, so they persist in the marine environment, affecting the ecosystem in the long term (Mezzelani *et al*., 2018), (Patel *et al*., 2019). Therefore, to protect the marine ecosystem, the development of methods for the biodegradation of pharmaceutical compounds from wastewater, before discharge into the aquatic environment, is being considered (Berkner & Thierbach, 2014), (Barra Caracciolo *et al*., 2015). Recent experimental research on the degradation of some pharmaceutical compounds has demonstrated that these methods are only applicable to certain compounds, and to be successful, the methods must be strictly followed by applying the developed analytical protocols (Nyirenda *et al.*, 2020).

Emerging pollutants present in fish tissues

Emerging contaminants were measured in four pelagic fish species: *Sprattus sprattus*, *Trachurus mediterraneus*, *Pomatomus saltatrix* (bluefish), and *Alosa tanaica*. The concentrations of the analytes ranged from below the detection limit to a maximum of 10.54 ng/g dry tissue. Among the investigated compounds, caffeine showed the highest concentration and was consistently detected in all sampled individuals (Fig. 6). Due to its widespread global consumption (Temple *et al*., 2017; Quadra *et al*., 2020), caffeine is frequently introduced into both freshwater and marine ecosystems, where it may cause sublethal and ecotoxicological effects on aquatic organisms (Dafouz *et al*., 2018).

The biodegradation of caffeine in marine ecosystems is possible and is influenced by multiple factors, including microbial activity, temperature, trophic conditions, and water depth (Buerge *et al.*, 2003; Dafouz *et al.*, 2018). According to the study conducted by Kelly Ann Peeler, the half-life of caffeine ranged between 71.5 and 177.7 days; however, controlling such parameters under natural environmental conditions remains challenging (Peeler, 2024).

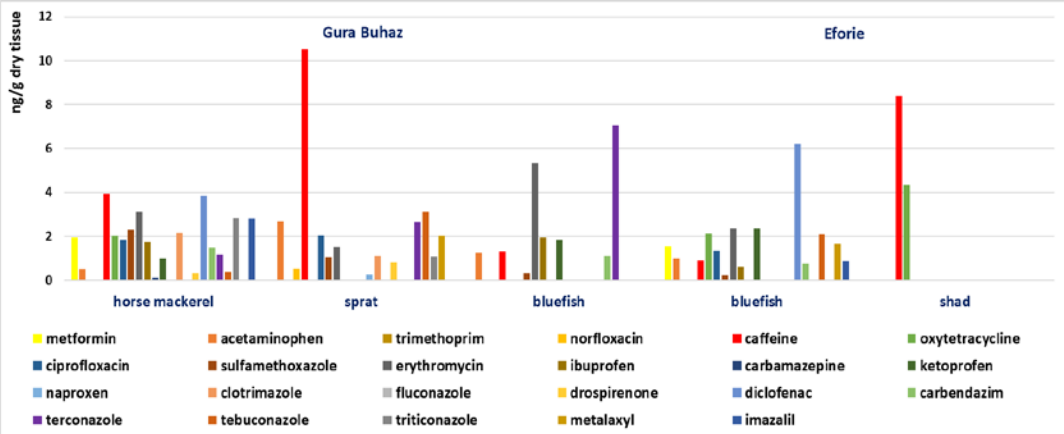

Fig. 6. Concentrations of emerging pollutants in Black Sea pelagic fish at Gura Buhaz and Eforie stations – October 2023

Neither trimethoprim (antibiotic) nor fluconazole (antifungal) were detected in any of the analyzed specimens, remaining undetectable.

Within the class of antibiotics, erythromycin was detected at the highest concentration (5.32 ng/g dry tissue), followed by oxytetracycline (4.37 ng/g dry tissue) and sulfamethoxazole (2.32 ng/g dry tissue).

When compared with results from previous research, erythromycin was found to be rapidly eliminated from aquatic organisms. For example, in Oncorhynchus tshawytscha (Chinook salmon), the compound became undetectable within 21 days after treatment (Fairgrieve et al., 2005). In contrast, oxytetracycline has shown a greater potential for transfer through aquatic food webs. One study reported its efficient accumulation first in aquatic plants (Wolffia globosa), followed by secondary uptake in the carp species Probarbus jullieni, indicating that dietary exposure may play a more important role than direct absorption from water (Boonsaner & Hawker, 2013). Nevertheless, bioaccumulation in fish was measurable but relatively low (Boonsaner&Hawker, 2013). For sulfamethoxazole, Song *et al.* (2021) reported considerable persistence in aquatic environments. Although the bacterium *Sphingobacterium mizutaii* was capable of degrading sulfamethoxazole, complete mineralization did not occur, and some the resulting transformation products were identified as potentially posing ecological risks (Song *et al.*, 2021).

Among nonsteroidal anti-inflammatory drugs, diclofenac exhibited the greatest accumulation (6.21 ng/g dry tissue), with acetaminophen and ketoprofen quantified at 2.67 ng/g dry tissue and 2.35 ng/g dry tissue, respectively.

Regarding anti-inflammatory agents, one of the most widely used examples—diclofenac— is not a naturally persistent compound; it can persist in the aquatic environment due to continuous release and the formation of more persistent and toxic degradation products. The study by Hernández-Zamora *et al*. (2025) reported the toxic effects of diclofenac across different trophic levels, beginning with the microalga *Pseudokirchneriella subcapitata*, followed by the zooplankton *Daphnia curvirostris*, and finally the fish Danio rerio, highlighting the transfer in the food chain (Hernández-Zamora *et al*., 2025).

For antifungal compounds, terconazole was predominant, with a maximal concentration of 7.05 ng/g dry tissue, followed by tebuconazole (3.13 ng/g dry tissue) and triticonazole (2.85 ng/g dry tissue).

Carbamazepine, a widely prescribed antiepileptic drug characterized by high persistence in the environment, was quantified at a maximum concentration of 0.12 ng/g dry tissue. Comparative assessments with literature values indicate notably higher concentrations in other aquatic organisms: 51.9 ng/g dry tissue in ascidians (Navon *et al.*, 2020); 63 ng/g dry tissue in mullet muscle, and 2.6 ng/g dry tissue in mullet liver tissue (Moreno-González *et al.*, 2016). Additionally, in pelagic fish species from the Sea of Marmara, carbamazepine concentrations ranged between 7.6 and 222 ng/g dry tissue (Korkmaz *et al.*, 2023). Due to the high resistance of carbamazepine to biodegradation, conventional wastewater treatment processes are generally ineffective for its removal. However, advanced treatment methods, such as reverse osmosis membranes, nanofiltration, ozonation, and Fenton processes, have been reported to be most effective when applied in combination (Hai *et al*., 2018).

In summary, of the 12 pharmaceutical compounds analyzed in seawater and sediment, 7 were detected in water samples, with the highest concentrations observed for ketoprofen (131.38 ng/L), carbamazepine (61.45 ng/L), and sulfamethoxazole (25.72 ng/L). Only metformin and ketoprofen were detected in sediments, primarily in areas impacted by urban discharge. Analysis of fish tissues for 23 pharmaceutical compounds showed measurable residues in all four pelagic species, with caffeine, erythromycin, terconazole, and diclofenac displaying the highest concentrations. These results underscore the spatial variability and persistence of pharmaceutical contaminants in the Romanian Black Sea ecosystem, particularly near major urban centers and wastewater sources.

The presence of pharmaceutical residues in both water and biota underscores the urgent need for continuous environmental monitoring and the development of targeted mitigation strategies to reduce ecological risks. The limited occurrence of these compounds in sediment samples suggests that their primary transport and distribution occur within the water column, with sediments playing a comparatively minor role.

Further in-depth research is essential to fully elucidate the long-term ecological consequences and potential risks to human health associated with the persistent presence of pharmaceutical contaminants in marine ecosystems. Such investigations should focus on their environmental persistence, bioaccumulation potential, trophic transfer through marine food webs, and possible sublethal effects on aquatic organisms. Insights gained from these studies will be critical for evidence-based environmental policies and for the integration of emerging pollutants into national and regional marine monitoring frameworks.

The detection of multiple pharmaceutical compounds in coastal waters and fish, along with the detection of selected substances in sediments, highlights the ongoing vulnerability of the Black Sea to contamination by emerging pollutants. These findings indicate that current wastewater treatment technologies and regulatory measures are insufficient to fully prevent pharmaceutical residues from entering the marine environment.

CONCLUSIONS

This study provides novel baseline data on the occurrence and distribution of emerging pharmaceutical compounds in the Romanian Black Sea environment. Analytical protocols were developed for seawater, sediments, and biota, employing extraction procedures and instrumental analyses adapted from methodologies originally designed for freshwater systems.

Most of the investigated pharmaceutical compounds were detected in seawater and in the four pelagic fish species, whereas sediment samples contained only metformin (an antidiabetic) and ketoprofen (a nonsteroidal anti-inflammatory drug) at low concentrations. In seawater, trimethoprim and carbamazepine were the most frequently detected compounds, with the highest concentrations observed for ketoprofen, diclofenac, and carbamazepine. In fish tissues, caffeine was consistently present, while the highest concentrations were recorded for erythromycin (an antibiotic), terconazole (an antifungal), and diclofenac (an anti-inflammatory drug).

Spatial analysis revealed elevated concentrations of pharmaceutical contaminants in coastal areas influenced by large urban centers and wastewater discharges. The limited occurrence of these compounds in sediments suggests that their transport and persistence predominantly occur in the water column rather than in benthic environments.

Recommendations

The findings highlight the urgent need for continuous environmental monitoring of pharmaceutical compounds in the Black Sea and their integration into regular monitoring programs under MSFD Descriptor 8. Upgrading wastewater treatment technologies to enhance removal efficiency is also essential. Further research on persistence, bioaccumulation, trophic transfer, and ecological impacts of these compounds is necessary to inform evidence-based management strategies. The implementation of these measures is critical for safeguarding marine biodiversity, ensuring seafood safety, and minimizing ecological risks associated with emerging contaminants.

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