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From Waters to Fish: A Multi-Faceted Analysis of Contaminants' Pollution Sources, Distribution Patterns, and Ecological and Human Health Consequences

Nicoleta Damir *, Valentina Coatu, Diana Danilov, Luminita Lazăr * and Andra Oros

Chemical Oceanography and Marine Pollution Department, National Institute for Marine Research and Development "Grigore Antipa", 300 Mamaia Blvd., 900581 Constanta, Romania; vcoatu@alpha.rmri.ro (V.C.); ddanilov@alpha.rmri.ro (D.D.); aoros@alpha.rmri.ro (A.O.)
* Correspondence: ndamir@alpha.rmri.ro (N.D.); llazar@alpha.rmri.ro (L.L.)

Abstract: This study presents an extensive evaluation of the contamination levels in fish, mollusks, water, and sediments in the Black Sea over eight years, from 2016 to 2023. The primary aim was to determine the concentrations and distribution patterns of heavy metals (HMs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and other persistent organic pollutants (POPs) in fish, water, and sediments of the Black Sea, and their implications for marine ecosystem health and human safety. Data were collected through scientific cruises and the methodology involved systematic sampling across different regions of the Romanian Black Sea, followed by rigorous laboratory analyses to identify and quantify the presence of contaminants. The study also examined the temporal trends of these pollutants, providing insights into their sources, pathways, and persistence in the marine environment. Additionally, the research assessed the bioaccumulation of contaminants in various biota, offering a critical perspective on food safety and potential risks to human consumers. The findings revealed significant spatial insights, highlighting areas of concern that require immediate attention and action. Notably, industrial discharge, agricultural runoff, and historical pollution hotspots were identified as major sources of contamination. This research underscores the need for enhanced monitoring and regulatory frameworks to mitigate pollution sources and safeguard the Black Sea ecosystem, advocating for sustainable practices and effective management strategies to preserve marine resources in the Black Sea.

Keywords: contamination; bioaccumulation; fish and mollusks tissue; ecosystem components; heavy metals; organochlorine pesticides; polychlorinated biphenyls; polycyclic aromatic hydrocarbons

Key Contribution: The key contribution of this study is its holistic approach to understanding the contamination dynamics in the Black Sea, offering insights into pollutant distribution patterns, sources, and impacts on marine and human health. This comprehensive analysis serves informed decision making and the development of targeted environmental management and pollution mitigation strategies.

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1. Introduction

Monitoring the marine environment is crucial for ensuring the security and safety of food, particularly when it comes to fish and shellfish, which are integral parts of a healthy and balanced diet [1]. Marine organisms, like fish and shellfish, accumulate varying amounts of heavy metals (HMs) and organic pollutants (POPs) in their tissues, depending on the species [2]. These pollutants can then be transferred up the food chain, sometimes exceeding the safe limits for human consumption [3,4].

Hazardous substances are widespread in the marine environment. Many, like HMs and polycyclic aromatic hydrocarbons (PAHs), occur naturally in seawater and sediments. However, synthetic hazardous substances such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are not found naturally. The main sources of these contaminants are waste disposal, fossil fuel burning, and industrial activities, including mining and production. Human activities have caused the general mobilization of these hazardous substances in the marine environment, primarily through riverine discharge and atmospheric deposition [5].

Heavy metals pollution in marine environments is a significant global concern due to its adverse effects on marine ecosystems and human health [6]. Various sources contribute to heavy metals pollution, including industrial activities, urban and industrial waste discharge, agricultural runoff, and accidental spills of toxic chemicals. The accumulation of heavy metals in marine organisms varies depending on the pollution sources, elements, and species [6,7]. Studies have highlighted the bioaccumulation of heavy metals in marine organisms, such as edible fish, emphasizing the dangerous threat that these pollutants pose to human health. Monitoring the concentration levels of heavy metals in marine environments is crucial for controlling pollution and protecting water quality [8–12].

Aquatic environments are vulnerable to contamination from both natural and anthropogenic sources. Polycyclic aromatic hydrocarbons (PAHs) can originate naturally from fires, natural gas eruptions, diagenesis under anaerobic conditions, and intense biological activity [13]. Anthropogenic sources of PAHs and persistent organic pollutants (POPs) include industrial activities, agricultural chemicals, water disposal, offshore activities, and maritime traffic. POPs consist mainly of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) [14,15] OCPs, which include chemicals like Hexachlorobenzene (HCB), Lindane, Heptachlor, and DDT, were phased out in the early 1980s due to their toxicity and persistence. These chemicals can remain in the environment and within living organisms for years or even decades [16].

Polycyclic aromatic hydrocarbons (PAHs) represent a class of pollutants of particular concern due to their potential to harm marine life and carcinogenic threat. Monitoring for their presence is a global effort [17]. Out of over 100 PAHs existing in the environment, 16 have been studied the most because they accumulate in living organisms and have harmful effects [13,18]. The European Union has recognized this concern and included these pollutants on the list of priority hazardous substances within the Water Framework Directive 2000/60/EC [19–21].

By analyzing the concentrations of pollutants in different ecosystem components such as water, sediment, and fish, insights into the sources of their emissions can be gained [22]. Fish, in particular, store PAHs and POPs in their fatty tissue because these substances are lipophilic and very chemically stable, making fish good indicators of pollution in coastal waters [23]. Studies have shown that these pollutants can negatively impact marine life, hindering their growth and development and causing deformities in embryos and larvae [24]. Chronic exposure to low levels of organic contaminants can disrupt the hormonal systems in both animals and humans [4], and PAHs found in the environment may become carcinogenic after entering an organism [25,26].

Studying HMs, POPs, and PAHs in fish and mollusk tissues from the Black Sea is important for human health concerns. Despite the well-established health benefits of fish consumption, concerns arise regarding the potential risks associated with frequent polluted fish intake. These risks stem from exposure to chemical pollutants found in fish and shellfish. By analyzing the contaminants in fish and mollusks from the Black Sea, potential health risks associated with eating seafood can be assessed [4].

This study aims to provide a comprehensive analysis of the contamination levels in fish, mollusks, water, and sediments in the Black Sea over eight years, highlighting areas of concern and the need for enhanced monitoring and regulatory frameworks to mitigate pollution sources and safeguard the Black Sea ecosystem. For the first time, preliminary assessments of potential hazards from consuming mussels from the Romanian coast of the Black Sea were conducted, utilizing testing methods used in other Black Sea regions [27]. Health risk indices—estimated daily intake (EDI), target hazard quotient (THQ), total hazard quotient (TTHQ), and carcinogenic risk index (CRI)—were calculated for heavy metals. The results reflect solely the combined impacts of metals in mussels and underscore the need for further research on other contaminants and species.

This paper assesses the concentrations and distributions of heavy metals (HM), persistent organic pollutants (POPs), and polycyclic aromatic hydrocarbons (PAHs) in Black Sea mollusks, fish, water, and sediments. This study aims to explore pollution pathways and their broader implications for the health of marine ecosystems and the safety of human seafood consumption, providing valuable insights into environmental and public health concerns.

2. Materials and Methods

Mollusks (2 species) and fish (13 species), seawater, and sediments were sampled from the Romanian Black Sea sector (25 stations) during expeditions conducted by the National Institute for Marine Research and Development "Grigore Antipa" with the research vessel "Steaua de mare", during 2016–2023, up to a 72 m bottom depth (Table S1). The sampling locations were selected based on variations in ecological conditions and potential human activity impacts. While mollusks were sampled more consistently during monitoring surveys (at least once per year) from 2016 to 2023, fish were not part of this regular monitoring and were only sampled in the 2016 and 2019 campaigns (Table 1).

Table 1. Marine organisms sampling data—Romanian Black Sea, 2016–2023.

Marine Organisms	Type of Marine Organisms	Species	Year of Sampling	Sampling Period	Depth (m)
Mollusks	Bivalve mollusks	*Mytilus galloprovincialis*	2016–2023	Spring, Summer, Autumn, Winter	5–72
	Gastropods	*Rapana venosa*	2016–2021	Spring, Summer, Autumn	15–36
Fish	Pelagic species	*Sprattus sprattus* (sprat)	2019	Summer	54
		Engraulis encrasicolus (anchovy)	2016, 2019	Summer	8–20
		Trachurus mediterraneus (horse mackerel)	2016, 2019	Spring, Summer	20–39
		Chelon auratus (golden gray mullet)	2016	Summer, Autumn	20
		Alosa immaculata (pontic shad)	2016	Summer, Autumn	20–30
		Belone belone (garfish)	2016	Summer	20
		Sarda sarda (atlantic bonito)	2016	Summer	20
		Mullus barbatus ponticus (blunt-snouted mullet)	2019	Spring	43
		Pomatomus saltatrix (bluefish)	2016	Autumn	36
		Alosa tanaica (Black Sea shad)	2016	Autumn	30
	Benthic species	*Neogobius melanostomus* (round goby)	2019	Spring	42
		Scophthalmus maeoticus (turbot)	2019	Spring	20
		Squalus acanthias (picked dogfish)	2019	Spring	20

The stations are included within the marine reporting regions (MRUs) within the Marine Strategy Framework Directive (MSFD):

- BLK_RO_RG_TT03: Northern stations, under the Danube's direct influence, up to a 30 m depth isobath.
- BLK_RO_RG_CT: Stations in the coastal zone, neighboring harbor activities, shipping, tourism, wastewater discharges, up to a 20 m depth isobath.
- BLK_RO_RG_MT01: Stations in shelf waters, including maritime activities, vessel traffic, and industrial activities, from a 30 m depth to 200 m (Figure 1).

Pelagic fish in the Black Sea exhibit a wide range of lifespans depending on the species. Some pelagic fish, like anchovy, garfish, and Black Sea shad only live for a few years, while larger species like bluefish and pontic shad can live for a decade or more [28,29]. Factors affecting lifespan include predation, disease, and environmental conditions. Many pelagic fish (like sprat, anchovy, and Black Sea shad) in the Romanian Black Sea are migratory, moving seasonally in search of food and spawning grounds [28–31].

Lifespan varies greatly among benthic fish species. Smaller species like gobies live only a few years, while larger species like *Scophthalmus maeoticus* (turbot) and *Squalus acanthias* (picked dogfish) can reach 20 years or even longer [32]. Some species, like gobies, with specific habitat requirements, might be restricted to a small area with suitable rock formations. The sampling intensity for benthic fish in the Romanian Black Sea varies depending on the species' commercial value, ecological importance, and research focus.

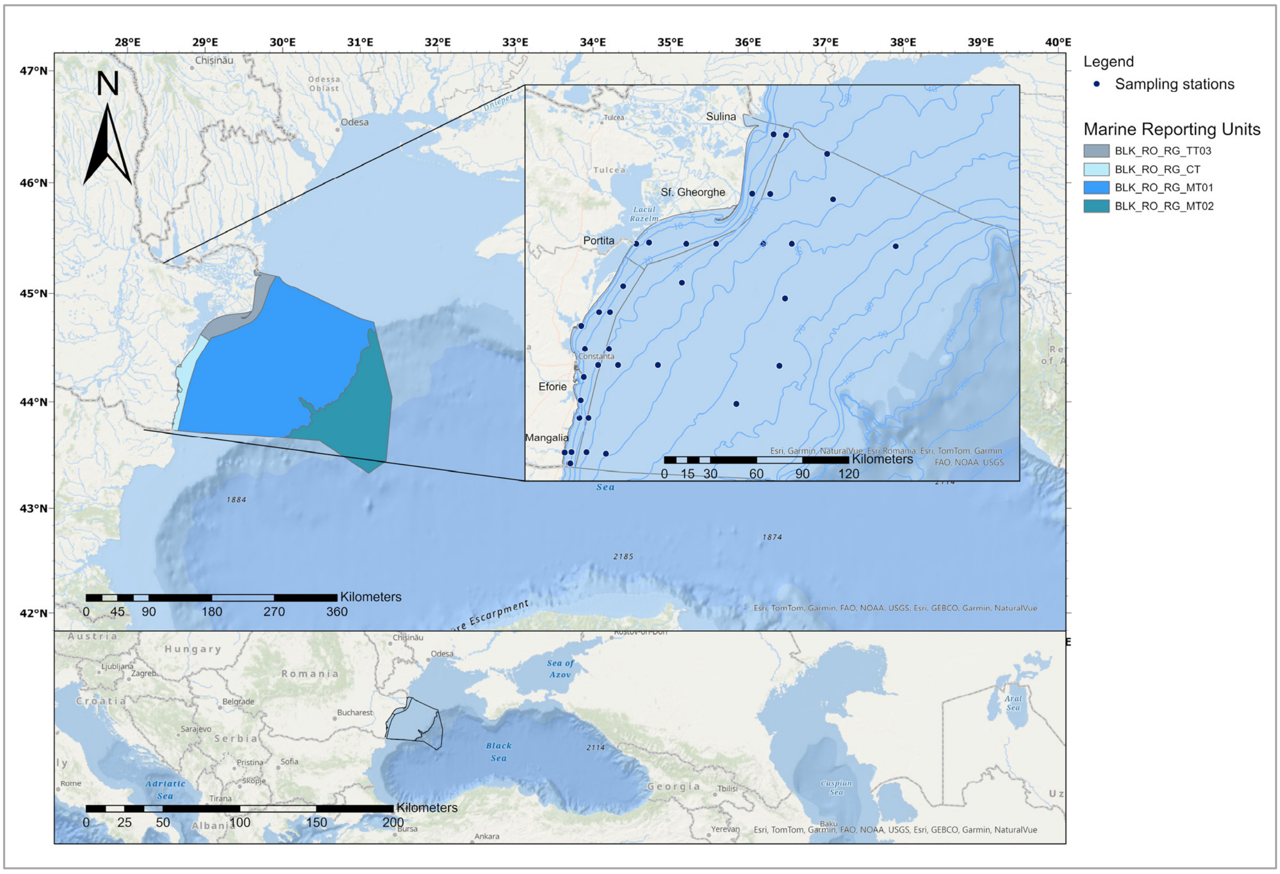

Figure 1. Map of sampling stations at the Romanian Black Sea Sector.

2.1. Sampling and Preliminary Preparation Methods

Seawater samples were collected from the surface layer (1 m below the surface) using Niskin bottles. The seawater samples were stored in a refrigerator (4–8 °C) for further analysis in the laboratory. Sediments were collected with a Van Veen bodengreifer; the thickness of the sampled sediment was 2 cm and was stored at −20 °C. Mollusks were collected using a biological dredge, pelagic fish by pelagic trawl, and benthic fish by bottom trawl. Following sampling, they were stored in freezer boxes and transported to the laboratory. Each sample comprised a composite from 5 to 10 individuals.

Whole mollusk bodies and fish muscle tissues were freeze-dried using a Labconco Freeze Dry System. Finally, the dried tissues were homogenized with an electric grinder.

2.2. Analytical Methods

2.2.1. Heavy Metals in Seawater, Sediments, and Biota

The seawater concentrations of copper (Cu), cadmium (Cd), lead (Pb), nickel (Ni), and chromium (Cr) were determined from unfiltered and acidified water samples (acidified up to pH = 2 with HNO_3 Ultrapure). For heavy metal (Cu, Cd, Pb, Ni, and Cr) analyses in the sediments and tissues, about 0.05–0.5 g of dry material was digested with 10 mL of concentrated HNO_3 in sealed Teflon vessels on an electric hot plate at 120 °C. The solution was made up to 100 mL with deionized water (18.2 MΩ·cm, Millipore, Burlington, MA, USA). Heavy metal (HM) determinations were performed on a High-Resolution Continuum Source Atomic absorption spectrometer (HR-CS ContrAA 800 G equipment, Analytik Jena, Jena, Germany). Calibration was performed with working standards prepared from Merck stock solutions for each element in the following ranges: 0–50 µg/L (Cu), 0–10 µg/L (Cd), 0–25 µg/L (Pb), 0–50 µg/L (Ni), and 0–50 µg/L (Cr). Each sample was measured in three parallel sub-samples, and the average value was reported. The method detection limits for the HMs were, depending on the element, between 0.001 and 0.01 µg/L. To ensure the accuracy of the analytical procedures, standard protocols were used [33,34]. The seawater concentrations of heavy metals are expressed as µg/L, sediments as µg/g dry weight (dws), and tissue concentrations as µg/g tissue wet weight (wwt).

2.2.2. POPs' (OCPs and PCBs) Extraction in Biota

Freeze-dried and crushed samples (approx. 2g) were microwave extracted with acetone/hexane (1/1) mixture. The internal standard 2,4,5-Trichlorobiphenyl was added to the samples for quantifying the overall recovery of the analytical procedures. Lipid removal was performed by adding 10 mL of concentrated H_2SO_4, followed by cleanup with copper and fractionation on a florisil column. Finally, the samples were concentrated using nitrogen flow in a water bath and analyzed by GC-ECD.

2.2.3. PAHs' Extraction in Biota

Unlike OCPs and PCBs, a separate method was used to prepare samples for analyzing the 16 priority polycyclic aromatic hydrocarbons (naphthalene (Na), acenaphthylene (Ac), acenaphthene (Ace), fluorene (Flu), anthracene (An), phenanthrene (Ph), fluoranthene (Fln), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[g,h,i]perylene (BghiP), indeno [1,2,3-cd]pyrene (IP), and dibenzo[a,h]anthracene (DaA)). These compounds were extracted from approx. 2 g of freeze-dried biota samples by the Soxhlet method. The internal standard 9,10-dihydroanthracene was added to the samples for quantifying the overall recovery of the analytical procedures. The samples were Soxhlet extracted for 8 h with 250 mL of methanol. The extracts were then saponified by adding 20 mL of 0.7 M KOH and 30 mL of water and refluxing for 2 h. The fraction containing the PAH fraction was concentrated using a gentle stream of nitrogen to a final volume of 1 mL and analyzed by GC-MS.

2.2.4. POPs' and PAHs' Extraction in Seawater and Sediments

The seawater samples were funnel extracted with a hexane/dichloromethane (3/1) mixture. The sediment samples were processed by freeze-drying, homogenization, and sieving for removing coarse fragments (>0.5 mm), before the extraction of POPs (OCPs and PCBs) and PAHs by the microwave method. The extraction was followed by cleanup with copper and fractionation on a florisil column for OCPs and an alumina/silica column for PAHs. Finally, the samples were concentrated using nitrogen flow in a water bath and analyzed by GC-ECD and GC-MS, respectively. The internal standards 2,4,5-Trichlorobiphenyl for POPs and 9,10-dihydroanthracene for PAHs were added to the samples for quantifying the overall recovery of the analytical procedures [35].

2.2.5. Gas-Chromatographic Conditions for Organic Pollutants

For OCPs and PCBs, the concentrated extracts were then analyzed using a gas chromatograph Perkin Elmer Clarus 500 equipped with an electron capture detector (ECD). The working conditions for the gas-chromatographic analysis were: Column: 30 m × 0.25 mm × 0.50 µm Elite-5MS; Carrier gas: helium, 1 mL/min; Split/Spitless Injector (S/S), injection made in split mode; split flow 25 mL/min; injector temperature: 330 °C; detector gas: nitrogen; detector temperature, 330 °C. Oven temperature program: 180 °C (0 min); 7 °C/min up to 230 °C (10 min); 15 °C C/min up to 250 °C (2 min).

The quantification of the specific OCPs and PCBs was achieved by comparing the sample peaks areas to those of known standards. Individual standards for 9 OCPs (Hexachlorobenzene, Lindane, Heptachlor, Aldrin, Dieldrin, Endrin, p,p'DDE, p,p'DDD, and p,p'DDT) and 7 PCBs (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 152, and PCB 180), dissolved in methanol with concentrations between 1000 and 5000 µg/mL, were used for the calibration curves for GC-ECD. The values of the retention times, the recovery coefficients, and the maximum admissible limits for OCPs and PCBs are presented in Tables S2 and S3, respectively.

For PAHs, the concentrated extract was then analyzed by GC/MS using a Perkin Elmer Clarus 690 system. The mass spectrometer operated at 70 eV scanning from m/z 47 to 400; the interface temperature was set at 330 °C and the source temperature at 270 °C. The extracts were injected in spitless mode and separated on an Elite 35MS capillary column (5% diphenyl dimethyl polysiloxane; 30 m length × 0.32 mm i.d. × 0.25 lm film thickness). Helium served as the carrier gas, flowing at a constant rate of 1 mL/min, during the sample analysis. Initially injected at 100 °C, the samples were heated in an oven following a two-stage program. In the first stage, the temperature ranged from 100 °C to 250 °C at a rate of 6 °C per min. The second stage increased the temperature further to 330 °C at a faster rate of 10 °C per min. Once at 330 °C, the oven temperature was held constant (isothermally) for 10 min. Data were gathered using the SIR technique, as described in Table S4. The quantification of the specific polycyclic aromatic hydrocarbons (PAHs) was achieved by comparing the retention times of the sample peaks to those of known standards (Table S4). A standard mixture, containing the 16 priority PAHs, dissolved in toluene in individual concentrations of 100 µg/mL, was used to calibrate the GC-MS.

2.3. Human Health Risk Assessment

Health risk indices, including the Estimated Daily Intake (EDI) and the Estimated Weekly Intake (EWI), Target Hazard Quotient (THQ), Total Hazard Quotient (TTHQ), and Carcinogenic Risk Index (CRI), were assessed for heavy metals (Cu, Cd, Pb, Ni, and Cr). Risk evaluations were conducted to determine the potential hazards that may arise because of consuming mussels (*M. galloprovincialis*) from the Romanian Black Sea coast. This was determined by calculating the probability of a health hazard using likely exposure. This study represents the first assessment of the combined impacts of metals in mussels and provides preliminary results that underscore the need for further research on other contaminants and species. The conclusions drawn regarding the risks posed by heavy metals to human health were based solely on mollusks, and fish consumption was not considered in our analysis.

2.3.1. Estimated Daily Intake (EDI) and Estimated Weekly Intake (EWI)

The average daily intake of heavy metals (mg/kg/day) must be considered when calculating risk exposure. The estimated daily intake (EDI) is calculated based on element levels and the amounts of mussels consumed. The following equation was used to calculate the EDI of heavy metals [31,32]:

$$EDI = \frac{C_{metal} \times FIR}{BW}, mg/kg/day$$

where EDI is the estimated daily intake of heavy metals, C_{metal} is the concentration of heavy metals in the mussel samples (whole tissues) (mg/kg, wet wt.), FIR (food ingestion rate) (kg/day) is the daily mean consumption of a food item, and BW is the average body weight (30 kg and 70 kg for children and adults, respectively).

Information on the daily mean consumption of food items (FIRs) was obtained from FAOSTAT [33]. The food supply quantity (kg/capita/year) for the category of "Mollusks, Other" for Romania, during the period of 2010–2021, varied between 0.08 and 0.50 kg/capita/year, respectively, and 0.00022 and 0.00137 kg/day.

The estimated weekly intake (EWI) was found by multiplying the EDI values by 7 [31,32].

Non-carcinogenic hazard (the target hazard quotient (THQ)) and hazardous risk (total hazard quotient (TTHQ)) was also calculated.

The non-carcinogenic risk related to the consumption of mollusks and their associated heavy metals was evaluated using the target hazard quotient (THQ) or hazard index (HI), determined as the ratio of the calculated metal dosage (EDI mg/kg of body weight per day) to the reference dose (Rf. D. mg/kg/day) [34]:

$$THQ = \frac{EDI}{Rf.D.}$$

where Rf. D. is the Chronic Oral Reference Dose (mg/kg/day), which refers to the estimated maximum permissible health risk associated with the daily human consumption of metals in food items (mussels). The Rf. D. values for Cd, Cu, Ni, and Cr are 0.0001, 0.04, 0.02, and 0.003 mg/kg/day, respectively [35]. However, the Rf. D. value for Pb is not given.

If THQ (HI) > 1.0, the EDI of a particular metal exceeds the Rf. D., indicating that the metal is potentially hazardous. This is dependent on both metal levels and the amounts of mussel consumed.

The TTHQ estimates the cumulative risk associated with exposure to multiple heavy metals. Metals can have cumulative or synergistic effects when they impact the same organ. When assessing this risk, if the combined impact (measured by TTHQ) is lower (TTHQ < 1), it typically suggests no potential health risk, because the exposure is within safe limits. Conversely, if the combined impact is higher (TTHQ > 1), it indicates a higher likelihood of health risks due to exceeding safe exposure limits.

2.3.2. Carcinogenic Risk Index (CRI)

The CRI is one metric for measuring the carcinogenic risk. The equation below represents CRI in terms of:

$$CRI = EDI \times CSF$$

The CSF (cancer slope factor) $(mg/kg/day)^{-1}$ establishes the risk associated with a lifetime average contaminant dose. The CSF value is given for Pb, and this value is 0.0085 $(mg/kg/day)^{-1}$ [36].

If the CRI is less than 10^{-6}, it is deemed inconsequential; if the CRI is between 10^{-6} and 10^{-4}, it is acceptable or bearable; and if the CRI is greater than 10^{-4}, it is deemed significant.

3. Results

3.1. Heavy Metals

The statistical parameters provide insights into the distribution and variability of heavy metal concentrations in mussels (*Mytilus galloprovincialis*) (Table 2), gastropods

(*Rapana venosa*) (Table 2), and fish (Table 3) from the Romanian Black Sea investigated during 2016–2023.

Based on Coefficient of Variation (CV) values greater than 100%, suggesting a significant dispersion in the data, the Pb and Cr concentrations in mussels exhibited a high variability, with wide fluctuations around the average value (CV_{Pb} = 196.191%; CV_{Cr} = 119.599%), also indicating outliers or extreme values that contributed to these values. The CV for Ni of 98.097% indicated a moderate variability, while the relative variabilities of the Cu and Cd concentrations in mussels, 56.536% and 71.461%, respectively, were moderate. Positive skewness values suggest that the data for all metals tend to cluster toward the lower end, with a few extreme values pulling the mean to the right. The Cu and Cr concentrations were characterized by a slightly right-skewed distribution, while the Cd, Pb, and Ni skewness values suggested a highly skewed distribution to the right. High positive kurtosis values were observed for Cd, Pb, and Ni, which indicated a heavy tail distribution (more extreme values), while the low kurtosis value of Cr suggested a relatively normal distribution. The negative kurtosis value of Cu indicated a relatively flat distribution (Table 2). We noticed that cadmium extreme values (>1 µg/g wwt) were measured in specimens from the northern sector of the Romanian littoral, under the influence of river discharges.

Table 2. Variability of heavy metal concentrations in mussels (*Mytilus galloprovincialis*)—Romanian Black Sea.

Descriptive Statistics (*Mytilus galloprovincialis*)										
Variable	**N**	**Mean (µg/g ww)**	**Median (µg/g ww)**	**Minimum (µg/g ww)**	**Maximum (µg/g ww)**	**25th Percentile (µg/g ww)**	**75th Percentile (µg/g ww)**	**Coef. Var.**	**Skewness**	**Kurtosis**
Cu	46	2.112	2.154	0.460	5.110	1.038	2.756	56.536	0.540	−0.311
Cd	46	0.520	0.377	0.143	2.018	0.276	0.630	71.461	2.169	5.969
Pb	46	0.149	0.034	0.002	1.587	0.0192	0.102	196.19	3.445	13.486
Ni	46	1.005	0.758	0.143	5.744	0.450	1.140	98.097	3.090	12.160
Cr	46	0.957	0.390	0.080	4.384	0.233	1.169	119.59	1.748	2.091

Table 3 provides insights into the distribution and variability of heavy metal concentrations in *Rapana venosa* from the Romanian Black Sea during 2016–2021: copper and chromium concentrations exhibited a moderate variability (55.47% CV_{Cu}, 81.921% CV_{Cr}), with a distribution shape resembling a normal curve; cadmium concentrations showed a high variability (100.65% CV), a positive skew (longer tail on the right side), and a distribution with pronounced peaks and heavier tails; lead concentrations exhibited an extreme variability (245.91% CV), a highly positive skewness (very long tail on the right side), and a distribution shape emphasizing both peak and tail behavior; and nickel concentrations displayed a substantial variability (85.49% CV), slight positive skewness, and a flatter distribution compared to the others (negative kurtosis value) (Table 3).

Table 3. Variability of heavy metal concentrations in gastropod (*Rapana venosa*)—Romanian Black Sea.

Descriptive Statistics (*Rapana venosa*)										
Variable	**N**	**Mean (µg/g ww)**	**Median (µg/g ww)**	**Minimum (µg/g ww)**	**Maximum (µg/g ww)**	**25th Percentile (µg/g ww)**	**75th Percentile (µg/g ww)**	**Coef. Var.**	**Skewness**	**Kurtosis**
Cu	15	5.994	5.2180	0.93	12.867	4.640	7.672	55.47	0.643	0.450
Cd	15	0.814	0.578	0.111	2.915	0.192	1.199	100.657	1.480	1.827
Pb	15	0.137	0.023	0.001	1.310	0.010	0.065	245.915	3.443	12.292
Ni	15	0.432	0.386	0.010	1.208	0.040	0.744	85.49	0.493	−0.612
Cr	15	0.843	0.5765	0.116	2.376	0.324	1.390	81.921	1.052	0.495

Overall, the heavy metal concentrations in fish from the Romanian Black Sea varied considerably. Lead (Pb) showed the highest variability, followed by nickel (Ni), cadmium

(Cd), copper (Cu), and chromium (Cr). The positive skewness values for most metals indicated that the distribution of concentrations was skewed towards higher values. This suggests that a small number of fish may have high concentrations of heavy metals. Copper (Cu) and cadmium (Cd) still had kurtosis values close to 0, indicating a mesokurtic distribution with normal tails. Lead (Pb), nickel (Ni), and chromium (Cr) all had positive kurtosis values, ranging from 2.736 to 10.949. This indicated a leptokurtic distribution with heavier tails compared to a normal distribution. Heavier tails suggest a higher prevalence of extreme values for these metals in the fish samples compared to a normal distribution (Table 4). For instance, Pb higher values (>0.30 µg/g ww) were measured in some species of pelagic fish (*Engraulis encrasicolus*, *Alosa caspia*, *Trachurus mediterraneus ponticus*, and *Belone belone*).

Table 4. Variability of heavy metal concentrations in pelagic and demersal fish—Romanian Black Sea.

Descriptive Statistics (Fish)										
Variable	**N**	**Mean (µg/g ww)**	**Median (µg/g ww)**	**Minimum (µg/g ww)**	**Maximum (µg/g ww)**	**25th Percentile (µg/g ww)**	**75th Percentile (µg/g ww)**	**Coef. Var.**	**Skewness**	**Kurtosis**
Cu	21	2.990	2.592	0.565	7.907	1.275	4.725	68.518	0.770	−0.263
Cd	21	0.065	0.030	0.007	0.230	0.016	0.075	109.52	1.295	0.323
Pb	21	0.601	0.260	0.002	4.625	0.003	0.520	175.92	3.134	10.949
Ni	21	4.245	3.172	0.092	18.46	0.332	5.808	127.52	1.758	2.736
Cr	21	0.235	0.215	0.028	0.880	0.135	0.277	74.113	2.614	9.363

In seawater, most concentrations of heavy metals determined during 2016–2023 were within normal variability intervals, with the following values of percentile 75th: 10.263 µg/L for Cu, 0.890 µg/L for Cd, 9.370 µg/L for Pb, 7.270 µg/L for Ni, and 4.160 µg/L for Cr. However, depending on the sampling area and season, higher values were occasionally measured, so the overall heavy metals levels varied within wide ranges: 0.790–33.480 µg/L for Cu; 0.001–2.070 µg/L for Cd; 0.001–25.970 µg/L for Pb; 0.010–75.380 µg/L for Ni; and 0.219–47.730 µg/L for Cr. High Coefficient of Variation values, such as those observed for nickel (CV 180.30%),and chromium (CV 152.68%), indicated that the metal concentrations varied significantly, with wide fluctuations around the average values. Positively skewed distributions were observed for all metals in seawater, indicating the occurrence (sporadic) of extremely high values. For copper (Cu), the kurtosis value of 3.495 indicated leptokurtic behavior (heavier tails). This means that extreme copper concentrations occur more frequently than in a normal distribution. With a kurtosis value of 0.637, cadmium's distribution was platykurtic (lighter tails), suggesting fewer extreme values, while lead's kurtosis of 1.028 was close to normal (mesokurtic), indicating a balanced distribution. For nickel (Ni) and chromium (Cr), the extremely high kurtosis values (10.676 and 25.878, respectively) implied very heavy tails, with rare but extreme concentrations (Table S5).

In sediments, most concentrations of heavy metals determined during 2016–2023 were within normal variability intervals, with the following values of percentile 75th: 43.750 µg/g d.w. for Cu, 0.518 µg/g d.w. for Cd, 20.830 µg/g d.w. for Pb, 60.960 µg/g d.w. for Ni, and 47.841 µg/g d.w. for Cr. However, depending on the sampling area, proximity of pollution sources, and sediments' granulometry, higher values were occasionally measured, so the overall heavy metals levels varied within wide ranges: 3.660–123.900 µg/g d.w. for Cu; 0.030–4.345 µg/g d.w. for Cd; 1.350–65.362 µg/g d.w. for Pb; 5.630–160.200 µg/g d.w. for Ni; and 6.290–98.730 µg/g d.w. for Cr. Cadmium had the highest variability in sediments (CV 143.98%). All metals exhibited a positively skewed distribution (longer tail on the right), but chromium had the least pronounced skew. Cadmium distribution stands out with extremely heavy tails (kurtosis 13.883), meaning more extreme values than a normal distribution, followed by copper, while lead and nickel had moderately heavy tails. A kurtosis value of 0.355 indicated that the chromium distribution was closer to a normal distribution (mesokurtic) compared to the other metals (Table S6).

The distribution of heavy metals in the seawater and sediments during 2016–2023 highlighted the influence of localized sources that play crucial roles in shaping the heavy metal levels in marine environments. First, the discharge zone of the Danube River significantly impacts heavy metal concentrations. As the Danube flows into the Black Sea, it carries dissolved and particulate matter, including heavy metals; thus, sediments from the northern sector of the Romanian littoral tend to accumulate higher metal levels. In the southern sector, the Constanta and Mangalia port areas experience intense anthropogenic pressure. Discharges of wastewater, industrial runoff, and shipping activities contribute to metal pollution. Seawater and sediments in and around the port presented elevated heavy metal concentrations. Also, besides land-based sources, offshore activities (oil and gas platforms) can contribute with additional pressures. Increased naval traffic, especially in recent years, can affect metal distribution patterns. Ships release ballast water, which can carry metals from one region to another, and thus, water and sediments in heavily trafficked areas may also reflect this impact. (Figures 2 and 3).

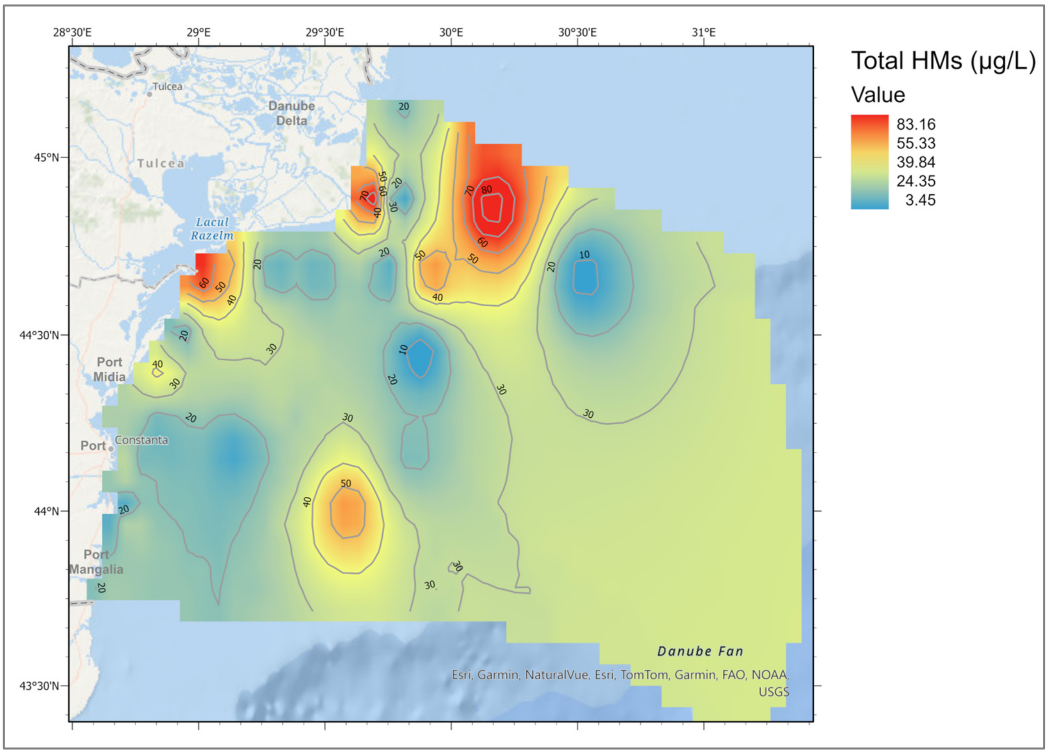

Figure 2. Distribution of total content HMs in seawater—Romanian Black Sea.

The levels of heavy metals in both seawater and sediments significantly impact the bioaccumulation of these elements in mollusks and fish. Heavy metals exist in seawater in dissolved and particulate forms, and the bioavailability of these metals depends on their concentration and chemical speciation. Over time, metals can accumulate in the tissues of marine organisms. Sediments act as sinks for heavy metals associated with particles and benthic organisms (mollusks and fish), which accumulate metals from sediments through their diet and direct contact. Under certain conditions (e.g., low oxygen), sediments release previously sorbed metals back into the water column, making them available in the pelagic habitat. Mollusks and fish are part of food webs, and they transfer accumulated metals to higher trophic levels (e.g., predators). Humans consume seafood, including mollusks and fish, as part of their diet. Elevated metal concentrations in contaminated seafood pose health risks to humans, especially when consumed over extended periods.

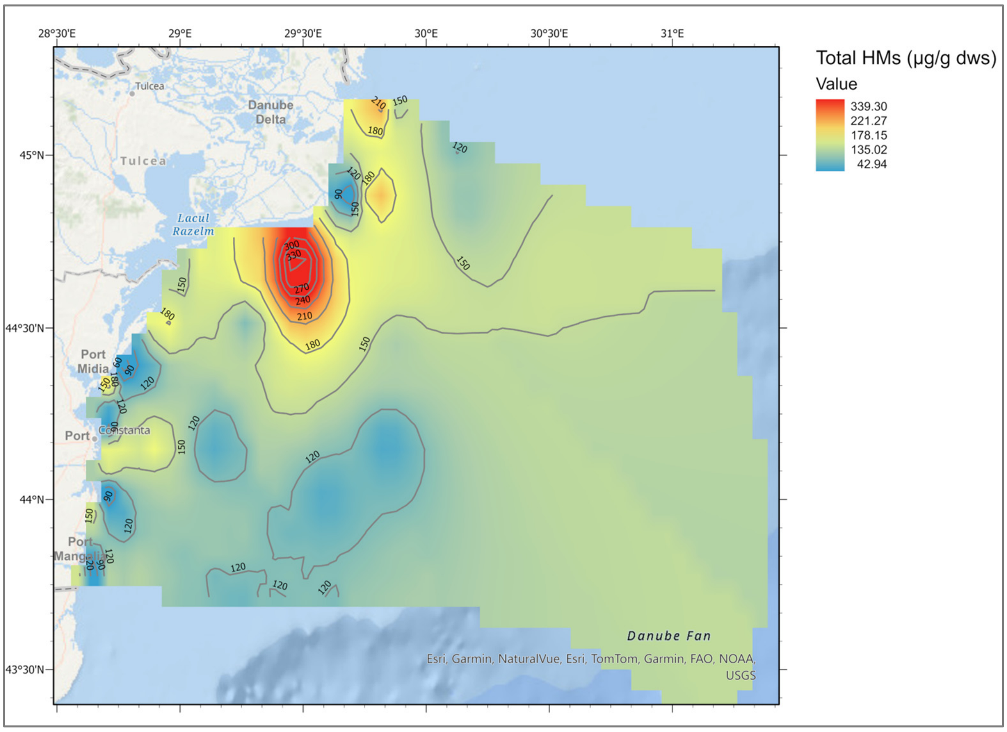

Figure 3. Distribution of total content HMs in sediments—Romanian Black Sea.

3.2. Human Health Risk Assessment

The heavy metal (Cd and Pb) values measured in the mussels and fish were compared to the concentrations permitted by European Commission Regulation (EU) 2023/915 [26] for consumed seafood. In mollusks, the maximum admissible concentrations (MACs) of 1 µg/g ww Cd were surpassed in 6% of mussels and in 30% of gastropods, respectively, with most of the contaminated samples being found in the area under the influence of Danube discharge (Figure S1). The number of Pb values surpassing the MAC of 1.50 µg/g ww Pb was insignificant in mollusks (below 0.3% of samples). In summary, while some Cd contamination was observed in both mussels and gastropods, the Pb levels remained well below the established limits. Monitoring and managing contamination sources, especially near the Danube discharge area or various hot spots, are essential to ensure the safety of consumed seafood.

In pelagic and demersal fish, the MAC for Cd of 0.05 µg/g ww was surpassed in 35% of samples, whereas the MAC for Pb of 0.30 µg/g ww was surpassed in 48% of samples. These findings highlight the importance of monitoring the heavy metal levels in fish to ensure the safety of seafood consumption (Figure 4).

The present study investigated the estimated daily intake (EDI), Target Hazard Quotients (THQs), Total Hazard Quotient (TTHQ), and Carcinogenic Risk Index (CRI) of heavy metals in two distinct groups (children and adults) consuming mussels (*M. galloprovincialis*) harvested from the Romanian coast of the Black Sea.

Our findings are summarized in Table 4. Notably, the EDI rates for the heavy metals in mussels were consistently below the Chronic Oral Reference Dose (Rf. D.) for both children and adults, suggesting safe consumption levels.

The calculated exposure values by food item (mussels) (EDIs) were also compared and found to be below the health-based guidance values provided by the European Food Safety Authority (EFSA) (Table 4). For Pb, the benchmark dose level (BMDL10) of 6.3×10^{-4} mg/kg/day is considered to be a health-based guidance value (HBGV) by the EFSA Panel on Contaminants in the Food Chain (CONTAM Panel), a value confirmed by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) as well [37]. For Ni, a tolerable daily intake (TDI) of 1.3×10^{-2} mg/kg/day was established by a recent decision by the EFSA CONTAM Panel after the European Commission asked EFSA to update its previous opinion on nickel in food and drinking water, considering new occurrence data [38]. For Cd, a tolerable daily intake (TDI) of 3.6×10^{-4} mg/kg/day is recommended by the CONTAM Panel [39].

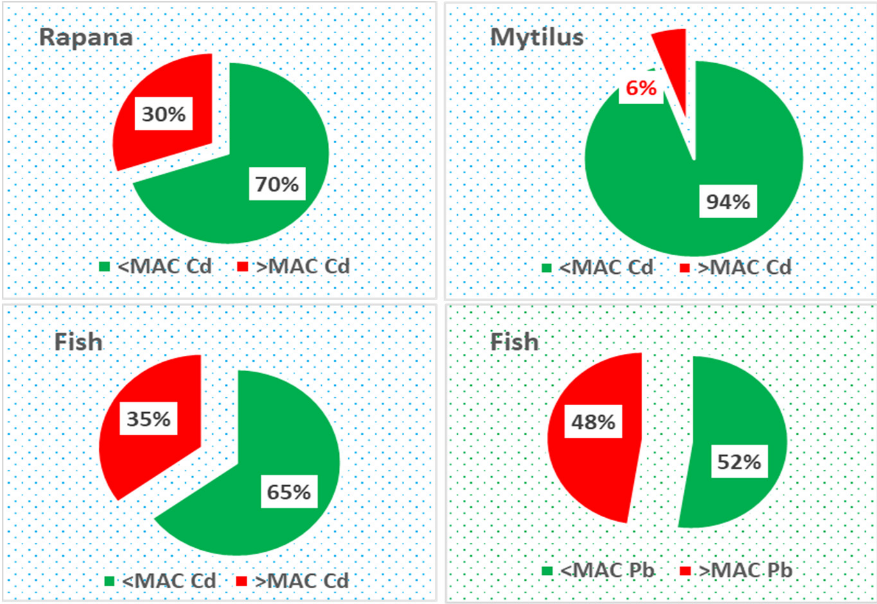

Figure 4. Heavy metals (Cd and Pb) values measured in mollusks (*Rapana venosa* and *Mytilus galloprovincialis*) and pelagic and demersal fish, compared to the values permitted by European Commission Regulation (EU) 2023/915 for consumed seafood.

Table 5 also provides the Target Hazard Quotients (THQs) and Total Hazard Quotient (TTHQ) values for copper (Cu), cadmium (Cd), chromium (Cr), and nickel (Ni) in mussels consumed by both children and adults. If the THQ exceeds 1.0, it indicates that the estimated daily intake (EDI) of a specific metal surpasses the Chronic Oral Reference Dose (Rf. D.), [40] suggesting potential health hazards. Based on our preliminary findings, based solely on four heavy metals, mussel consumption poses no risks to consumers, considering that the calculated Target Hazard Quotients (THQs) for Cu, Cd, Ni, and Cr indicated values below concern (THQ < 1).

In our study, the TTHQ values for the combined impact of metals found in mussels along the Romanian coast of the Black Sea were consistently lower than 1. This result indicated that there are no adverse effects for consumers associated with heavy metals (Cu, Cd, Ni, and Cr) exposure from consuming mussels. Furthermore, the calculated Carcinogenic Risk Index (CRI) [41–44] associated with lead (Pb) exposure was found to be negligible, being less than 10^{-6} (Table 4).

Given that other chemicals (PAHs and POPs) were also detected in the mollusks and fish, it is crucial to further conduct comprehensive studies encompassing a broader range of contaminants and species. These preliminary results obtained for heavy metals in mussels provide a foundation for future research aimed at delivering a more accurate assessment of the risks posed by hazardous chemicals to human health.

Table 5. The EDIs and EWIs for all heavy metals, THQs and TTHQ for Cu, Cd, Cr, and Ni, and carcinogenic risk index (CRIs) for Pb in two groups consuming mussels (*M. galloprovincialis*) from Romanian coast of the Black Sea.

Metal	EDIs (mg/kg/day)		EWIs (mg/kg/week)		THQs		CRIs		Health-Based GUIDANCE Values (EFSA) (mg/kg/day)
	Children	Adults	Children	Adults	Children	Adults	Children	Adults	
Copper (Cu)	8.27×10^{-5}	3.54×10^{-5}	5.79×10^{-4}	2.48×10^{-4}	2.07×10^{-3}	8.86×10^{-4}			
Cadmium (Cd)	1.89×10^{-5}	8.09×10^{-6}	1.32×10^{-4}	5.66×10^{-5}	1.89×10^{-1}	8.09×10^{-2}			3.6×10^{-4}
Chromium (Cr)	3.88×10^{-5}	1.66×10^{-5}	2.72×10^{-4}	1.17×10^{-4}	1.29×10^{-2}	5.55×10^{-3}			
Nickel (Ni)	4.12×10^{-5}	1.77×10^{-5}	2.88×10^{-4}	1.24×10^{-4}	2.06×10^{-3}	8.83×10^{-4}			1.3×10^{-2}
Lead (Pb)	1.05×10^{-5}	4.52×10^{-6}	7.38×10^{-5}	3.16×10^{-5}			8.96×10^{-8}	3.84×10^{-8}	6.3×10^{-4}
TTHQ					2.06×10^{-1}	8.81×10^{-2}			

EDI: Estimated daily intake; EWI: Estimated weekly intake; Target hazard quotient: THQ; Total hazard quotient: TTHQ; and Carcinogenic Risk Index: CRI.

3.3. Persistent Organic Pollutants—POPs (PCBs and OCPs)—In Biota, Seawater, and Sediments

The statistical parameters provide insights into the variability of POPs concentrations in mussels *(M. galloprovincialis)* (Tables 6 and 7), gastropods *(Rapana venosa)* (Tables 8 and 9), and fish (Tables 10 and 11) from the Romanian Black Sea investigated during 2016–2023.

Table 6. Variability of OCPs concentrations in mussels (*M. galloprovincialis*)—Romanian Black Sea.

Descriptive Statistics (*M. galloprovincialis*)								
Variable	**N**	**Mean (μg/g ww)**	**Median (μg/g ww)**	**Minimum (μg/g ww)**	**Maximum (μg/g ww)**	**25th Percentile (μg/g ww)**	**75th Percentile (μg/g ww)**	**Coef. Var.**
HCB	46	0.0335	0.00021	0.00008	0.4505	0.00008	0.0176	0.0858
Lindane	46	0.3312	0.00324	0.00006	7.3458	0.00006	0.1041	1.2112
Heptachlor	46	0.4533	0.00005	0.00005	9.0988	0.00005	0.0415	1.5225
Aldrin	46	0.0050	0.00005	0.00005	0.0577	0.00005	0.0019	0.0121
Dieldrin	46	0.0827	0.00032	0.00005	1.4328	0.00003	0.0137	0.2893
Endrin	46	0.0857	0.00212	0.00006	0.7117	0.00006	0.0893	0.1721
p,p′ DDE	46	0.0589	0.00041	0.00003	1.1550	0.00003	0.0103	0.2073
p,p′ DDD	46	0.5189	0.00089	0.00003	15.1661	0.00003	0.0553	2.2678
p,p′ DDT	46	0.1560	0.00003	0.00003	5.3864	0.00003	0.0025	0.8001

Table 7. Variability of PCBs concentrations in mussels *(M. galloprovincialis*)—Romanian Black Sea.

Descriptive Statistics (*M. galloprovincialis*)								
Variable	**N**	**Mean (μg/g ww)**	**Median (μg/g ww)**	**Minimum (μg/g ww)**	**Maximum (μg/g ww)**	**25th Percentile (μg/g ww)**	**75th Percentile (μg/g ww)**	**Coef. Var.**
PCB28	46	0.0497	0.0001	0.00006	1.3773	0.00006	0.0011	0.2139
PCB52	46	0.0555	0.0003	0.00005	0.9289	0.00005	0.0540	0.1515
PCB101	46	0.0195	0.0004	0.00009	0.1863	0.00009	0.0091	0.0458
PCB118	46	0.0188	0.0005	0.00006	0.1260	0.00006	0.0296	0.0310
PCB153	46	0.0068	0.0001	0.00009	0.0688	0.00009	0.0010	0.0182
PCB138	46	0.0856	0.0001	0.00011	2.1570	0.00011	0.0047	0.3439
PCB180	46	0.0045	0.0002	0.00005	0.0547	0.00005	0.0048	0.0102

Table 8. Variability of OCPs concentrations in gastropods (*Rapana venosa*)—Romanian Black Sea.

Descriptive Statistics (*Rapana venosa*, 2016–2021)								
Variable	**N**	**Mean (μg/g ww)**	**Median (μg/g ww)**	**Minimum (μg/g ww)**	**Maximum (μg/g ww)**	**25th Percentile (μg/g ww)**	**75th Percentile (μg/g ww)**	**Coef. Var.**
HCB	15	0.0084	0.0037	0.0001	0.0323	0.0003	0.0161	0.0105
Lindane	15	0.0596	0.0044	0.0001	0.3320	0.0003	0.1252	0.1009
Heptachlor	15	0.2029	0.0062	0.0001	1.2954	0.0009	0.0977	0.4271
Aldrin	15	0.1592	0.0020	0.0001	1.2146	0.0001	0.0925	0.3744
Dieldrin	15	0.3487	0.0238	0.0001	1.9202	0.0001	0.3265	0.6307
Endrin	15	0.2421	0.0168	0.0001	1.3636	0.0077	0.2814	0.4306
p,p′ DDE	15	0.0029	0.0001	0.0001	0.0185	0.0001	0.0026	0.0057
p,p′ DDD	15	1.2885	0.0020	0.0001	10.6067	0.0001	0.6253	2.9083
p,p′ DDT	15	0.4965	0.0289	0.0001	3.7823	0.0001	0.0983	1.1062

The OCPs′ mean concentrations in the mussels ranged from 0.005 to 0.5189 μg/g ww. Most of the compounds had levels below 1 μg/g ww. The dominant compounds were p,p′ DDD, Heptachlor, and Lindane, with the highest overall concentrations among the studied pollutants (p,p′ DDD—15.1661 μg/g ww, Heptachlor—9.0988 μg/g ww, and

Lindane—7.3458 µg/g ww). HCB had the lowest coefficient of variation, indicating more consistent concentrations across samples, whereas p, p′ DDD showed a high variability (Table 5).

Table 9. Variability of PCBs concentrations in gastropods (*Rapana venosa*)—Romanian Black Sea.

Descriptive Statistics (*Rapana venosa*)								
Variable	**N**	**Mean (µg/g ww)**	**Median (µg/g ww)**	**Minimum (µg/g ww)**	**Maximum (µg/g ww)**	**25th Percentile (µg/g ww)**	**75th Percentile (µg/g ww)**	**Coef. Var.**
PCB28	15	0.0043	0.0005	0.0001	0.0290	0.0001	0.0016	0.0100
PCB52	15	0.0204	0.0063	0.0001	0.1169	0.0012	0.0417	0.0330
PCB101	15	0.0055	0.0005	0.0002	0.0383	0.0002	0.0061	0.0111
PCB118	15	0.0044	0.0001	0.0001	0.0300	0.0001	0.0023	0.0099
PCB153	15	0.0074	0.0002	0.0002	0.0549	0.0002	0.0017	0.0164
PCB138	15	0.0084	0.0002	0.0002	0.0545	0.0002	0.0044	0.0177
PCB180	15	0.0090	0.0002	0.0001	0.0692	0.0001	0.0069	0.0189

Table 10. Variability of OCPs concentrations in pelagic and demersal fish—Romanian Black Sea.

Descriptive Statistics (Fish)								
Variable	**N**	**Mean (µg/g ww)**	**Median (µg/g ww)**	**Minimum (µg/g ww)**	**Maximum (µg/g ww)**	**25th Percentile (µg/g ww)**	**75th Percentile (µg/g ww)**	**Coef. Var.**
HCB	21	0.0315	0.0197	0.0001	0.2223	0.0001	0.0285	0.0537
Lindane	21	0.0100	0.0001	0.0001	0.0875	0.0001	0.0049	0.0210
Heptachlor	21	0.0251	0.0020	0.0001	0.1974	0.0001	0.0271	0.0483
Aldrin	21	0.0089	0.0001	0.0001	0.0844	0.0001	0.0020	0.0205
Dieldrin	21	0.0536	0.0101	0.0001	0.5735	0.0001	0.0283	0.1333
Endrin	21	0.0326	0.0040	0.0001	0.2291	0.0001	0.0107	0.0663
p,p′ DDE	21	0.0155	0.0033	0.0001	0.1288	0.0019	0.0096	0.0312
p,p′ DDD	21	0.0688	0.0053	0.0001	0.4481	0.0031	0.0406	0.1272
p,p′ DDT	21	0.0309	0.0028	0.0001	0.2195	0.0008	0.0081	0.0659

Table 11. Variability of PCBs concentrations in pelagic and demersal fish—Romanian Black Sea.

Descriptive Statistics (Fish)								
Variable	**N**	**Mean (µg/g ww)**	**Median (µg/g ww)**	**Minimum (µg/g ww)**	**Maximum (µg/g ww)**	**25th Percentile (µg/g ww)**	**75th Percentile (µg/g ww)**	**Coef. Var.**
PCB28	21	0.0108	0.0008	0.0001	0.0516	0.0001	0.0164	0.0163
PCB52	21	0.0147	0.0014	0.0001	0.1636	0.0001	0.0074	0.0370
PCB101	21	0.0260	0.0006	0.0002	0.2390	0.0004	0.0138	0.0649
PCB118	21	0.0342	0.0008	0.0001	0.1939	0.0001	0.0822	0.0579
PCB153	21	0.0265	0.0003	0.0002	0.2220	0.0002	0.0052	0.0558
PCB138	21	0.0205	0.0002	0.0002	0.1126	0.0002	0.0485	0.0335
PCB180	21	0.0082	0.0005	0.0001	0.1262	0.0001	0.0025	0.0274

Although the PCBs' mean concentrations in mussels (*M. galloprovincialis*) were lower than those of the OCPs, ranging from 0.0045 to 0.0856 µg/g ww, they also represent a possible threat to marine life. PCB 28, PCB 52, and PCB 138 had the highest overall mean concentrations (0.0497, 0.0555, and 0.0856 µg/g ww) and the greatest coefficients of variation. The least encountered was PCB 180, which recorded the lowest values (mean concentration—0.0045 µg/g ww, maximum concentration—0.0547 µg/g ww) (Table 6). The detection of PCBs in mussels warrants further investigation due to their potential for bioaccumulation within the food chain.

The highest mean values and coefficients of variation in the *Rapana venosa* were recorded for p,p′ DDD (1.2885 µg/g ww), p,p′ DDT (0.4965 µg/g ww), and Dieldrin (0.3487 µg/g ww). Oppositely, p,p′ DDE had the lowest values (mean concentration—0.0029 µg/g ww, maximum concentration—0.0185 µg/g ww) (Table 8).

The PCBs′ concentrations in gastropods ranged from 0.0001 to 0.1169 µg/g ww, with the highest average concentration (0.0204 µg/g ww) and the most extensive range (from 0.0001 µg/g ww to 0.1169 µg/g ww) recorded for PCB 52. PCB 118 and PCB 138 had the lowest average concentrations (around 0.004 µg/g ww) and very low maximum concentrations (around 0.003 µg/g ww) (Table 9).

Overall, the POP concentrations in fish from the Romanian Black Sea varied considerably. Most pesticides showed very high coefficients of variation, indicating a significant variability in pesticide concentrations across the fish samples (Table 10).

Table 11 summarizes the levels of seven polychlorinated biphenyls (PCBs) found in the fish samples. Most PCBs showed very high coefficients of variation, indicating significant variability in the PCB concentrations across the fish samples.

The OCP values exceed the maximum admissible levels for human consumption stipulated by national legislation (Order 147/2004) [45], and were recorded mostly in mollusks (for HCB, Lindane, Dieldrin, Endrin, Heptachlor, and Total DDT), but also in fish (for HCB and Dieldrin).

The study found that the maximum admissible concentrations (MACs) for various contaminants were exceeded in mussels, as follows: HCB (5%), Lindane (19%), Dieldrin (11%), Endrin (22%), Heptachlor (27%), and Total DDT (30%) (Figure 5). The MACs in gastropods were exceeded as follows: Heptachlor (21%), Aldrin (14%), Dieldrin (29%), Endrin (21%), and Total DDT (29%) (Figure 6).

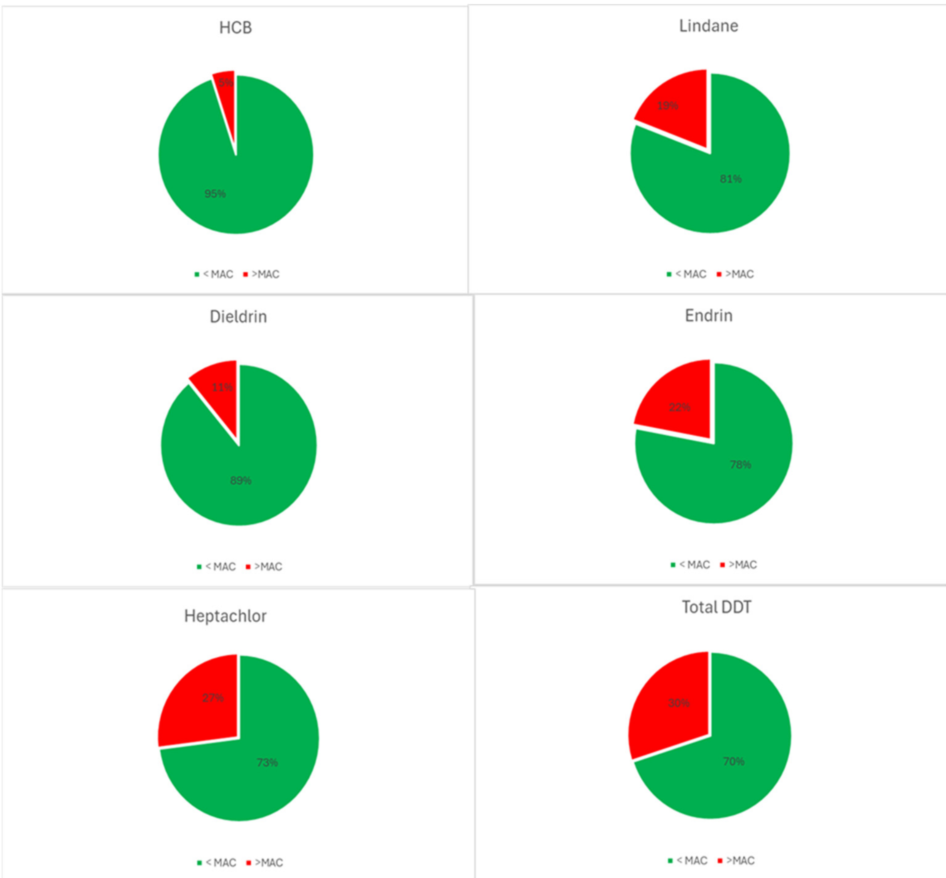

Figure 5. OCP (HCB, Lindane, Dieldrin, Endrin, Heptachlor, and Total DDT) values measured in mussels compared to the values permitted in Order 147/2004.

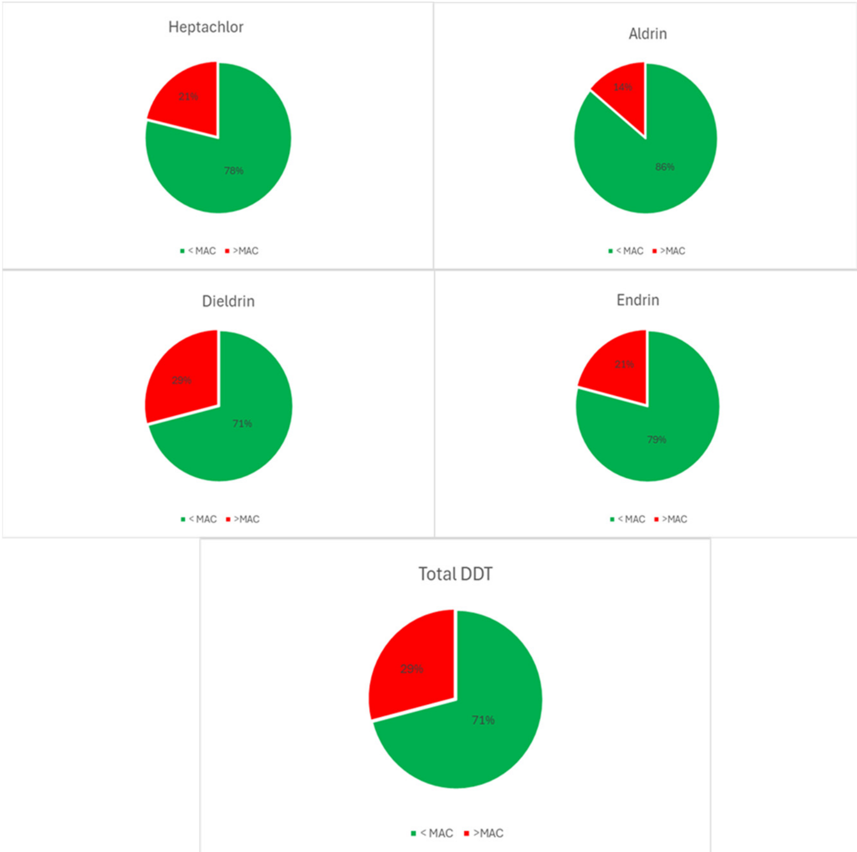

Figure 6. OCP (Heptachlor, Aldrin, Dieldrin, Endrin, and Total DDT) values measured in gastropods compared to the values permitted in Order 147/2004.

The PCB concentrations measured in mussels, gastropods, and fish and were compared to the values (sum of six PCBs) stipulated by the European Commission Regulation (EU) 2023/915 for consumed seafood [26]. The MAC of 0.075 µg/g ww for the sum of six PCBs was surpassed in 27% of mussels, 29% in gastropods, and mostly in fish (43%) (Figure 7).

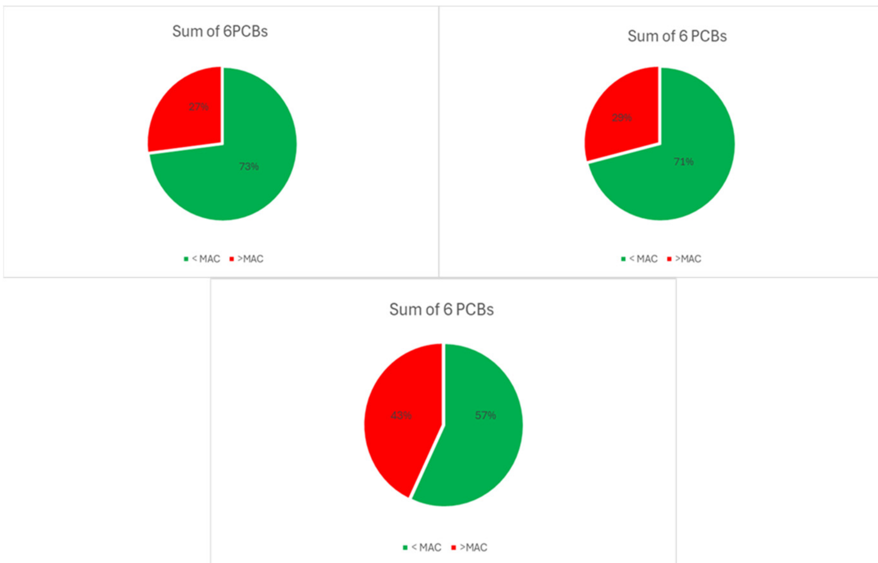

Figure 7. PCB (sum of 6 PCBs) values measured in mussels, gastropods, and fish, compared to the values permitted by European Commission Regulation (EU) 2023/915 for consumed seafood.

These findings highlight the importance of monitoring POPs' (OCP and PCBs) levels in seafood to ensure its safety of consumption.

High concentrations of DDT and metabolites were detected in biota from the Constanta and Mangalia areas, indicating significant local contamination (Figure 8). These elevated levels in aquatic organisms suggest a persistent presence of DDT in these port regions, likely due to historical usage and ongoing inputs from maritime activities. The port of Constanta is a cereal hub in the Black Sea, while both Constanta and Mangalia are major hubs for maritime transport and industrial activities, which can contribute to the introduction and persistence of such contaminants in the local marine environment.

In contrast, biota from the broader shelf area exhibited moderate DDT concentrations. This indicates a more diffuse but widespread contamination across the shelf. The moderate levels suggest that DDT is present throughout the shelf region. The entire shelf area is influenced by various activities, including maritime transport and possibly atmospheric deposition, all contributing to the observed DDT levels in marine organisms. The presence of DDT in biota across these regions is concerning due to its persistence, bioaccumulative nature, and potential to cause adverse effects on wildlife and human health. DDT, despite being banned or restricted in many countries, continues to persist in the environment and bioaccumulate in the food web, leading to higher concentrations in higher trophic levels.

High concentrations of PCBs were detected in biota from shelf waters under the influence of rivers from the northwestern part of the Black Sea (Danube, Dnieper, and Dniester) and Mangalia area, indicating local contamination (Figure 9), probably due to industrial activities related to Mangalia harbor.

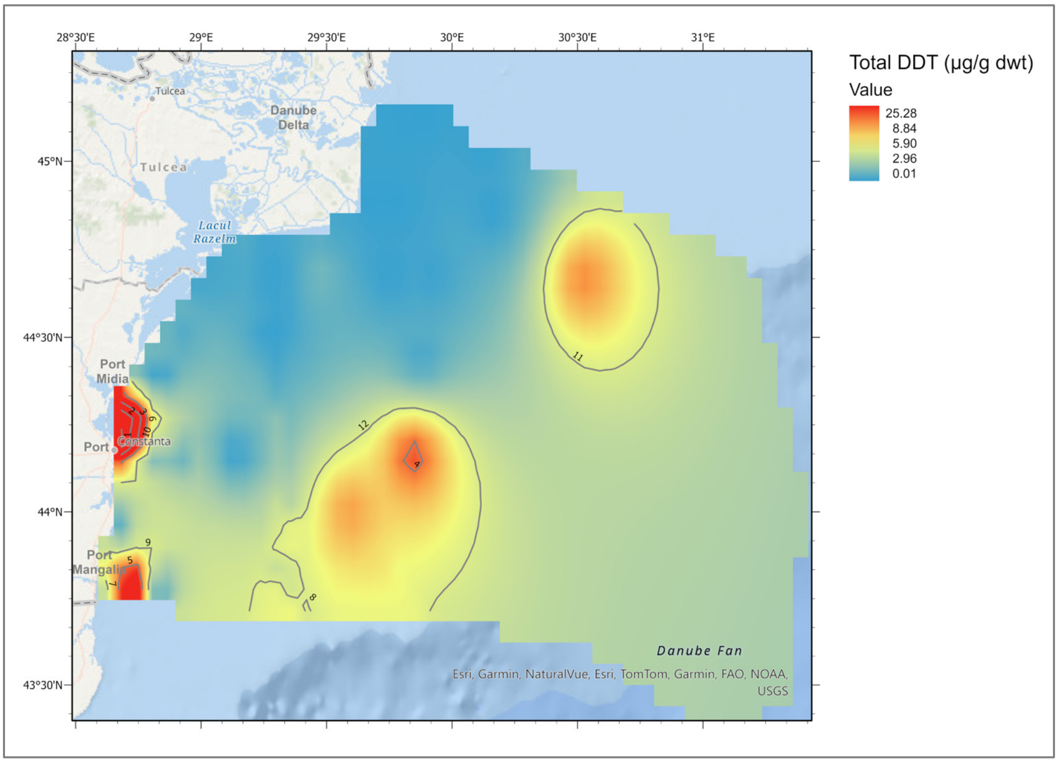

Figure 8. Total DDT content in biota—Romanian Black Sea.

The analysis of organochlorine pesticides (OCPs) in seawater revealed two primary sources of contamination. The first source was identified in the Sfântu Gheorghe arm (Figure 10) of the Danube, located near an important agricultural area, Dunavat-Murighiol (2.538 ha) [46]. This proximity to intensive farming activities suggests that agricultural runoff is a significant contributor to the presence of OCPs in this part of the water system, even though their use is forbidden in the Danube Delta. The use of pesticides in crop cultivation likely leads to their leaching and washing into the river, especially during rainfall or irrigation events, resulting in elevated concentrations in the water (Table S7).

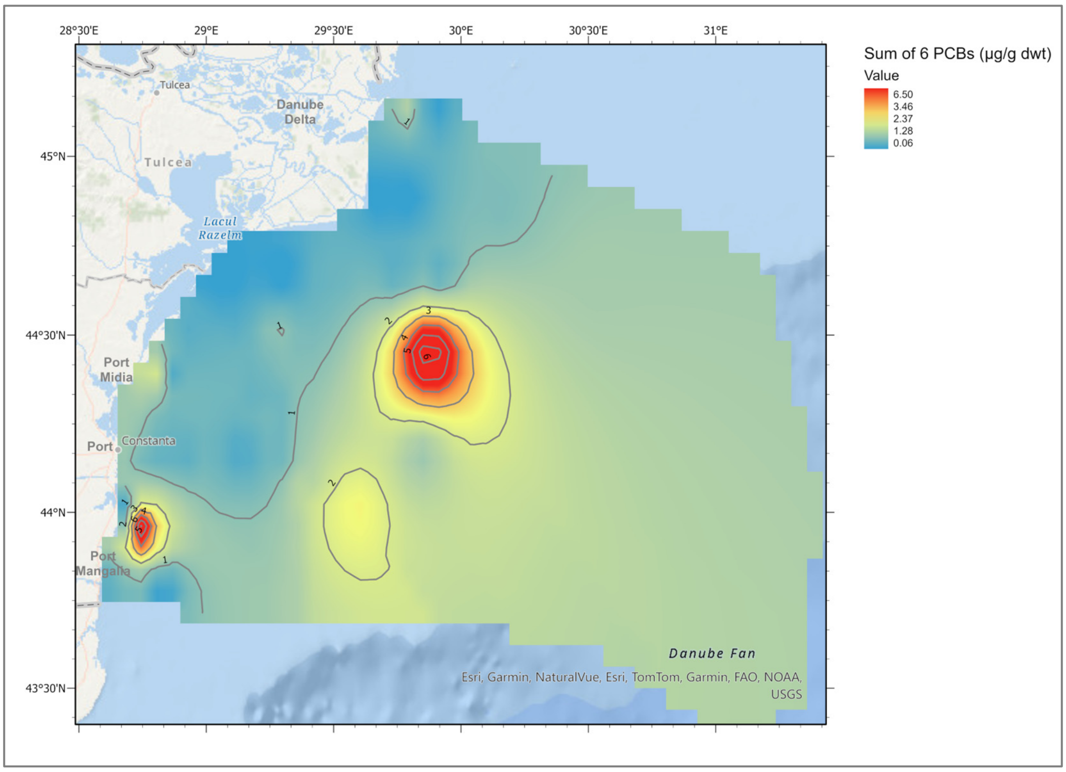

Figure 9. The sum of 6 PCBs in biota, Romanian Black Sea.

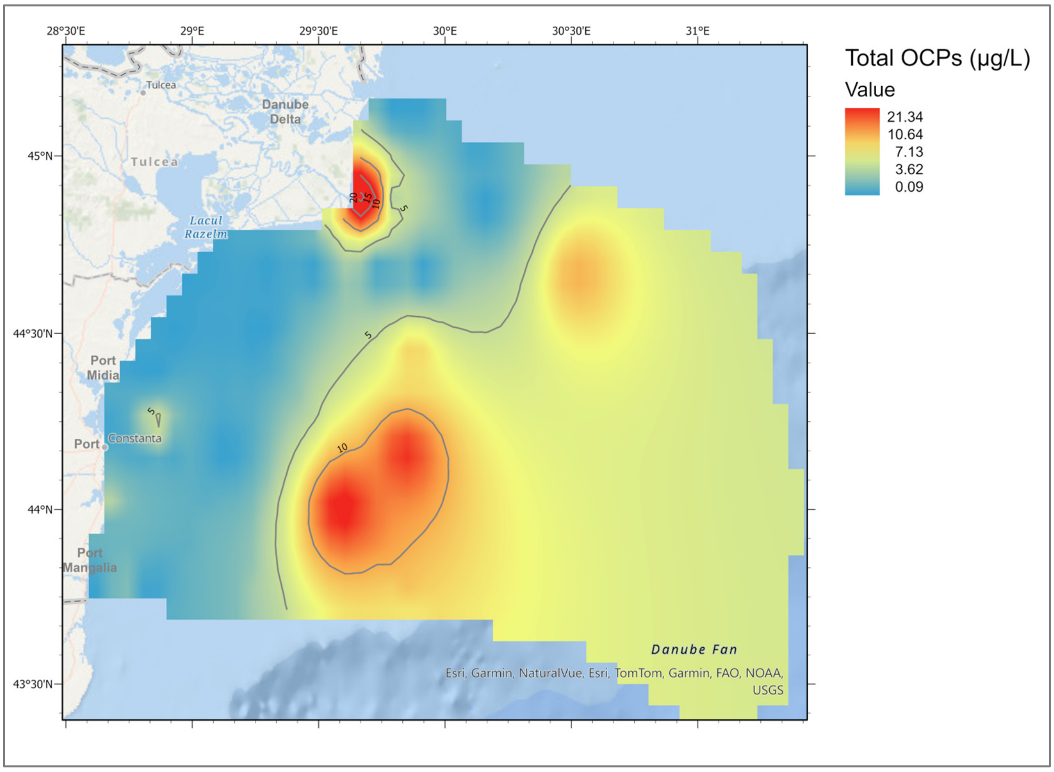

Figure 10. Total OCPs content in seawater—Romanian Black Sea.

The analysis of organochlorine pesticides (OCPs) in sediments suggested notable patterns of accumulation in specific areas. The highest levels of OCP accumulation were also observed in the northern shelf region (Figure 11). This area, influenced by various hydrodynamic and anthropogenic factors, appeared to be a significant sink for these persistent contaminants. The sediment here likely captures and retains OCPs transported by water currents, leading to high concentrations over time (Table S8). In addition to the northern shelf, other spots with elevated OCP levels were identified near the Sfântu Gheorghe arm and the southern shelf. Near the Sfântu Gheorghe arm, the accumulation of OCPs in sediments was consistent with the observed sources of contamination in the water column, primarily due to agricultural runoff. The sediments act as a repository for these pesticides, which settle out of the water and become part of the benthic environment. Overall, the sediment data indicated that the northern shelf is the primary area of OCP accumulation, with additional significant spots near Sfântu Gheorghe and the southern shelf.

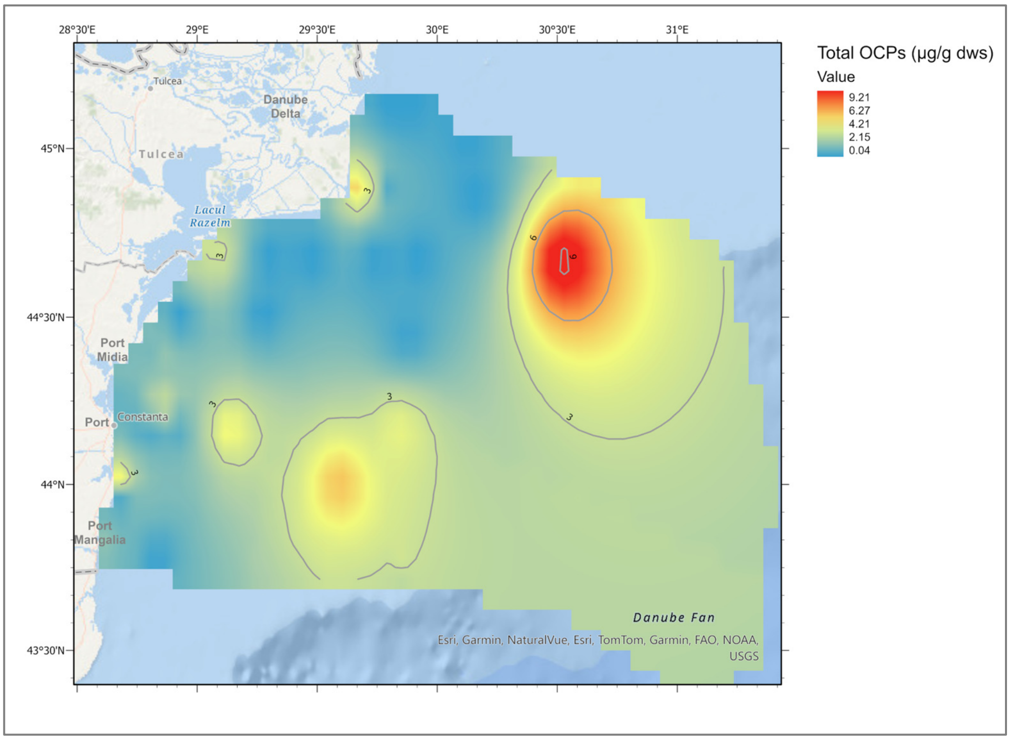

Figure 11. Total OCPs content in sediments—Romanian Black Sea.

The analysis of PCBs indicated that the highest concentrations (Table S9) were found in the seawater from the Mangalia area. This suggests that Mangalia is a significant hotspot for PCB contamination. The presence of these high concentrations can be attributed to several factors, including historical industrial activities, ongoing maritime operations, and potential local sources of PCB discharge. Mangalia, being a key port and industrial zone, has a history of activities that could have introduced PCBs into the marine environment. These include shipbuilding, repairs, and various manufacturing processes that historically used PCBs for their chemical stability and insulating properties. Despite the ban on PCB production and use in many countries, these contaminants persist in the environment due to their resistance to degradation.

Although the sediments in Mangalia did not show high values of contaminants (Figure 12), Mangalia was a notable spot for high levels of contaminants in biota as well. This discrepancy suggests that PCBs and possibly other pollutants are more bioavailable and are being readily taken up by marine organisms, even if they are not as concentrated in the sediments (Table S10).

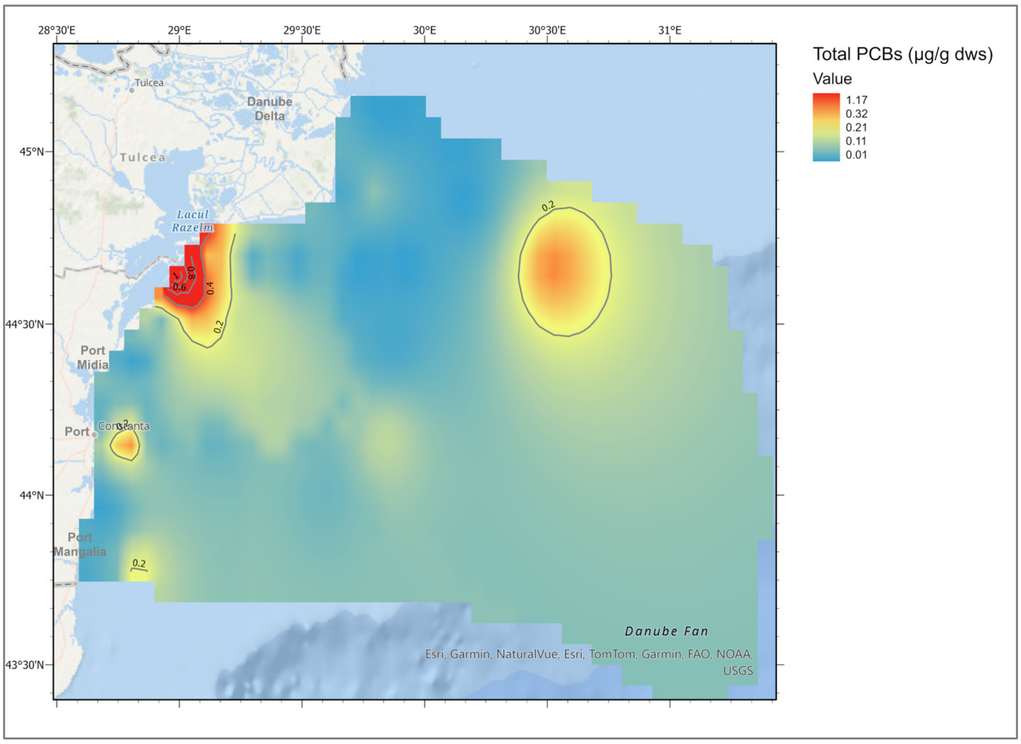

Figure 12. Total PCBs in sediments—Romanian Black Sea.

3.4. Organic Pollutants—PAHs—in Biota, Seawater, and Sediments

The statistical parameters provide insights into the variability of PAH concentrations in mussels (*M. galloprovincialis*) (Table 12), gastropods (*Rapana venosa*) (Table 13), and fish (Table 14) from the Romanian Black Sea.

Table 12. Variability of PAH concentrations in mussels (*M. galloprovincialis*)—Romanian Black Sea.

Variable	Descriptive Statistics (*M. galloprovincialis*)								
	N	Mean (µg/g ww)	Median (µg/g ww)	Minimum (µg/g ww)	Maximum (µg/g ww)	Lower Quartile (µg/g ww)	Upper Quartile (µg/g ww)	Std. Dev. (µg/g ww)	Coef. Var.
Naphthalene	31	0.032076	0.001742	0.000015 *	0.308768	0.000015	0.025195	0.078211	243.83
Acenaphtylene	31	0.000934	0.000015	0.000015	0.026547	0.000015	0.000015	0.004762	509.67
Acenaphtene	31	0.001006	0.000015	0.000015	0.028228	0.000015	0.000015	0.005063	503.50
Fluorene	31	0.088276	0.000030	0.000015	0.916860	0.000015	0.003438	0.267027	302.49
Phenanthrene	31	0.148162	0.000210	0.000015	1.110000	0.000015	0.164808	0.297260	200.63
Anthracene	31	0.046467	0.000015	0.000015	1.077823	0.000015	0.016141	0.192963	415.27
Fluoranthene	31	0.015393	0.000015	0.000015	0.121370	0.000015	0.001036	0.036919	239.84
Pyrene	31	0.044270	0.000015	0.000015	0.753889	0.000015	0.001592	0.144784	327.05
Benzo[a]anthracene	31	0.022441	0.000015	0.000015	0.686550	0.000015	0.000015	0.123260	549.26
Crysene	31	0.001378	0.000015	0.000015	0.030450	0.000015	0.000015	0.005518	400.30
Benzo[b]fluoranthene	31	0.010828	0.000015	0.000015	0.146306	0.000015	0.000015	0.029524	272.66
Benzo[k]fluoranthene	31	0.003217	0.000015	0.000015	0.058868	0.000015	0.000015	0.012589	391.34
Benzo[a]pyrene	31	0.007407	0.000015	0.000015	0.088664	0.000015	0.000420	0.022052	297.73
Benzo(g,h,i) perylene	31	0.001741	0.000015	0.000015	0.023093	0.000015	0.000015	0.005778	331.90
Dibenzo(a,h) anthracene	31	0.001463	0.000015	0.000015	0.022823	0.000015	0.000015	0.005540	378.65
Indeno (1,2,3-c,d)pyrene	31	0.001704	0.000015	0.000015	0.025751	0.000015	0.000015	0.006410	376.09

* LOD.

Table 13. Variability of PAH concentrations in gastropods (*Rapana venosa*)—Romanian Black Sea. Nd—not detected.

Variable	Descriptive Statistics (*Rapana venosa*)								
	N	Mean (µg/g ww)	Median (µg/g ww)	Minimum (µg/g ww)	Maximum (µg/g ww)	Lower Quartile (µg/g ww)	Upper Quartile (µg/g ww)	Std. Dev. (µg/g ww)	Coef. Var.
Naphthalene	9	0.002772	0.000015 *	0.000015	0.012087	0.000015	0.002928	0.004226	152.47
Acenaphtylene	9	Nd **	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Acenaphtene	9	0.000194	0.000015	0.000015	0.001622	0.000015	0.000015	0.000536	276.72
Fluorene	9	0.001602	0.000015	0.000015	0.009835	0.000015	0.000015	0.003422	213.64
Phenanthrene	9	0.034381	0.001800	0.000015	0.135450	0.000015	0.049054	0.049464	143.87
Anthracene	9	0.001062	0.000015	0.000015	0.008889	0.000015	0.000015	0.002941	276.86
Fluoranthene	9	0.001909	0.000015	0.000015	0.011486	0.000015	0.002597	0.003790	198.59
Pyrene	9	0.002751	0.000015	0.000015	0.017988	0.000015	0.002387	0.005912	214.89
Benzo[a]anthracene	9	0.000229	0.000015	0.000015	0.001937	0.000015	0.000015	0.000641	280.29
Crysene	9	0.000053	0.000015	0.000015	0.000354	0.000015	0.000015	0.000113	214.56
Benzo[b]fluoranthene	9	0.001499	0.000015	0.000015	0.011766	0.000015	0.000015	0.003887	259.35
Benzo[k]fluoranthene	9	0.000200	0.000015	0.000015	0.001681	0.000015	0.000015	0.000555	277.49
Benzo[a]pyrene	9	0.004659	0.000083	0.000015	0.037211	0.000015	0.002173	0.012242	262.75
Benzo(g,h,i) perylene	9	0.002821	0.000015	0.000015	0.023204	0.000015	0.000298	0.007666	271.73
Dibenzo(a,h) anthracene	9	0.001609	0.000015	0.000015	0.014360	0.000015	0.000015	0.004782	297.20
Indeno (1,2,3-c,d)	9	0.002246	0.000015	0.000015	0.020095	0.000015	0.000015	0.006693	297.99

* LOD ** Not detected.

Table 14. Variability of PAH concentrations in pelagic and demersal fish—Romanian Black Sea.

Variable	Descriptive Statistics (Fish)								
	N	Mean (µg/g ww)	Median (µg/g ww)	Minimum (µg/g ww)	Maximum (µg/g ww)	Lower Quartile (µg/g ww)	Upper Quartile (µg/g ww)	Std. Dev. (µg/g ww)	Coef. Var.
Naphthalene	8	0.012518	0.001779	0.000025 *	0.077349	0.000025	0.009582	0.026718	213.43
Acenaphtylene	8	0.002305	0.000129	0.000025	0.011294	0.000025	0.003406	0.004157	180.37
Acenaphtene	8	0.002648	0.000171	0.000025	0.012942	0.000025	0.003914	0.004763	179.85
Fluorene	8	0.002759	0.000262	0.000025	0.013670	0.000025	0.003901	0.004977	180.39
Phenanthrene	8	0.014600	0.003483	0.000025	0.071160	0.000132	0.019192	0.024433	167.36
Anthracene	8	0.011465	0.000147	0.000025	0.078800	0.000025	0.006276	0.027360	238.63
Fluoranthene	8	0.002575	0.000084	0.000025	0.013209	0.000025	0.003575	0.004911	190.70
Pyrene	8	0.002675	0.000191	0.000025	0.013076	0.000025	0.003933	0.004805	179.66
Benzo[a]anthracene	8	0.002717	0.000196	0.000025	0.013280	0.000025	0.003994	0.004871	179.29
Crysene	8	0.002695	0.000187	0.000025	0.013139	0.000025	0.003987	0.004829	179.17
Benzo[b]fluoranthene	8	0.001783	0.000113	0.000025	0.008647	0.000025	0.002657	0.003187	178.74
Benzo[k]fluoranthene	8	0.001872	0.000161	0.000025	0.009068	0.000025	0.002757	0.003329	177.82
Benzo[a]pyrene	8	0.001945	0.000136	0.000025	0.009466	0.000025	0.002873	0.003479	178.91
Benzo(g,h,i) perylene	8	0.000804	0.000089	0.000025	0.005192	0.000025	0.000494	0.001793	223.08
Dibenzo(a,h) anthracene	8	0.000855	0.000100	0.000025	0.005523	0.000025	0.000521	0.001907	223.12
Indeno (1,2,3-c,d)pyrene	8	0.002062	0.000098	0.000025	0.010115	0.000025	0.003053	0.003721	180.50

* LOD.

The concentrations of PAHs in *Mytilus galloprovincialis* showed significant variability across samples. Naphthalene had a mean concentration of 0.032076 µg/g with a high coefficient of variation (243.83%), indicating substantial dispersion around the low median (0.001742 µg/g). Most PAHs, such as acenaphtylene and acenaphthene, exhibited extremely high coefficients of variation (over 500%) and had median values at or near the detection limit (0.000015 µg/g), reflecting many low or undetectable concentrations. Phenanthrene showed a relatively higher mean (0.148162 µg/g), but also a high variability (200.63%). Other PAHs, like fluoranthene, pyrene, and benzo[a]anthracene, followed similar patterns, with a high variability and median values at the detection limit, indicating sporadic contamination events with high peak values and numerous low-level detections.

Most PAHs exhibited a high variability in gastropods, indicated by large coefficients of variation (over 100% in all cases), with many median values at or near the detection limit (0.000015 μg/g). Naphthalene, phenanthrene, and benzo[a]pyrene showed notable means but also exhibited high standard deviations, reflecting significant dispersion in the data. Acenaphtylene was not detected in any samples. Overall, the data suggested a wide range of PAH contamination levels with substantial variability across samples (Table 13).

The concentrations of PAHs in fish (Table 14) highlighted a substantial variability across the samples. Naphthalene showed a mean concentration of 0.012518 μg/g and a high coefficient of variation (213.43%), indicating significant dispersion around a low median (0.001779 μg/g). Most PAHs, such as acenaphtylene and acenaphthene, also displayed a high variability (coefficients of variation around 180%) with median values near the detection limit, reflecting frequent low-level detections and occasional high values. Phenanthrene followed this pattern, with a mean of 0.014600 μg/g and a coefficient of variation of 167.36%. The high coefficients of variation across all PAHs suggested sporadic contamination events, with a few high concentrations skewing the data, as indicated by the significant differences between the median and maximum values.

The PAH values (Benzo[a]pyrene, sum of PAHs: benzo(a) pyrene, benzo(a) anthracene, benzo(b) fluoranthene, and chrysene) were compared to the values permitted by the European Commission Regulation (EU) 2023/915 [26] for consumed seafood. In mollusks, the maximum admissible concentrations (MACs) of 0.05 μg/g ww for benzo(a)pyrene were surpassed in 19% of mussels and in 1% of gastropods, respectively. The MAC for the sum of PAHs of 0.030 μg/g ww was surpassed in 0.09% of mussels. Considering that the legislation in force does not provide maximum permissible limits concerning the human consumption of fresh fish, the limits provided for fresh mollusks were used. In pelagic and demersal fish, the MAC for benzo(a)pyrene of 0.05 μg/g ww was surpassed in 33% of samples, and the MAC for the sum of PAHs: benzo(a) pyrene, benzo(a) anthracene, benzo(b) fluoranthene, and chrysene) of 0.030 μg/g ww was surpassed in 33% of samples. These findings highlight the importance of monitoring the organic pollutants levels in fish to ensure the safety of seafood consumption (Figure 13).

The PAH analysis in biota revealed high concentrations of PAHs in the northern shelf area (Figure 14), indicating a significant bioaccumulation risk, potentially impacting the food web and ecosystem health. The sources of these high PAH concentrations in biota appeared to be other rivers in the region that contribute to the PAH load, carrying contaminants from upstream industrial or urban areas. Additionally, maritime transport activities in the area could be a significant source, as ships often release various pollutants, including PAHs, through their exhaust, bilge water, and operational discharges.

The analysis revealed that the highest concentrations of PAHs in seawater were predominantly sourced from the Danube River (Figure 15). This suggests that the Danube is the primary pathway introducing these contaminants into the aquatic environment. In contrast, the PAHs found in sediments serve as markers for accumulation, indicating areas where these compounds settle and persist over time. Notably, the sediments from the Constanta and Mangalia ports' vicinity also showed significant concentrations of PAHs, pointing to these locations as notable areas of PAH accumulation (Figure 16).

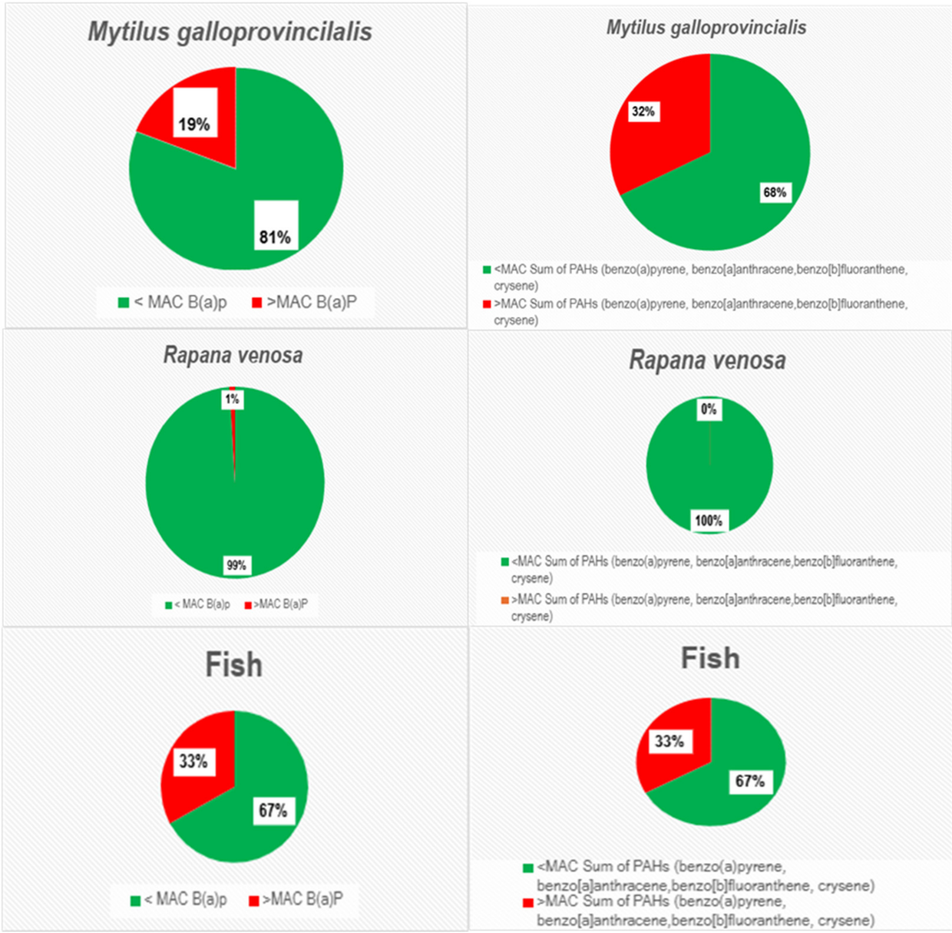

Figure 13. PAH (benzo(a)pyrene, sum of PAH: benzo(a)pyrene, benzo(a) anthracene, benzo(b) fluoranthene, and chrysene) values measured in mussels and fish, compared to the values permitted by European Commission Regulation (EU) 2023/915 for consumed seafood.

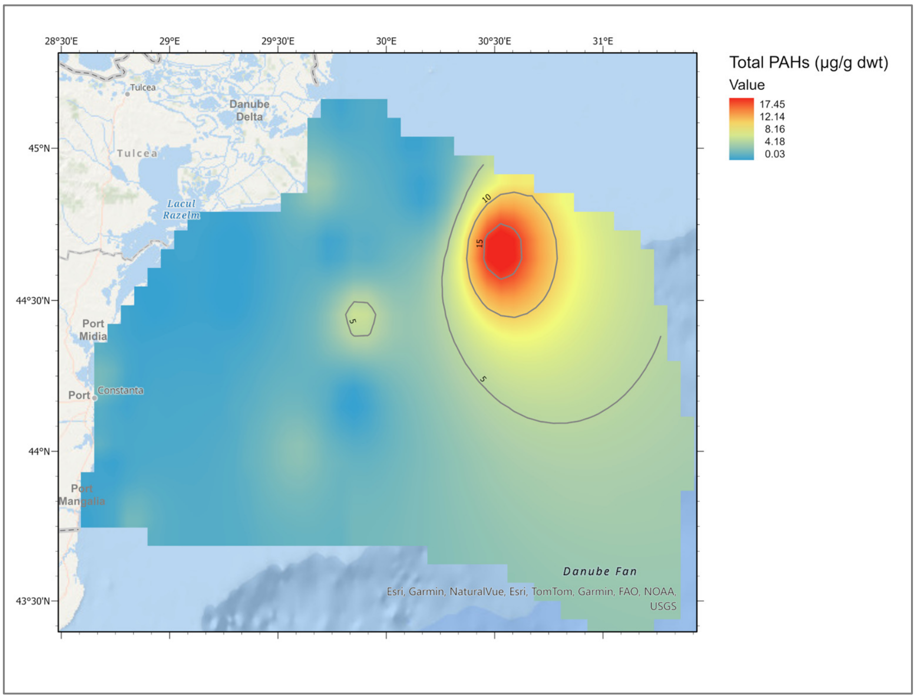

Figure 14. Distribution of total content of PAHs in biota—Romanian Black Sea.

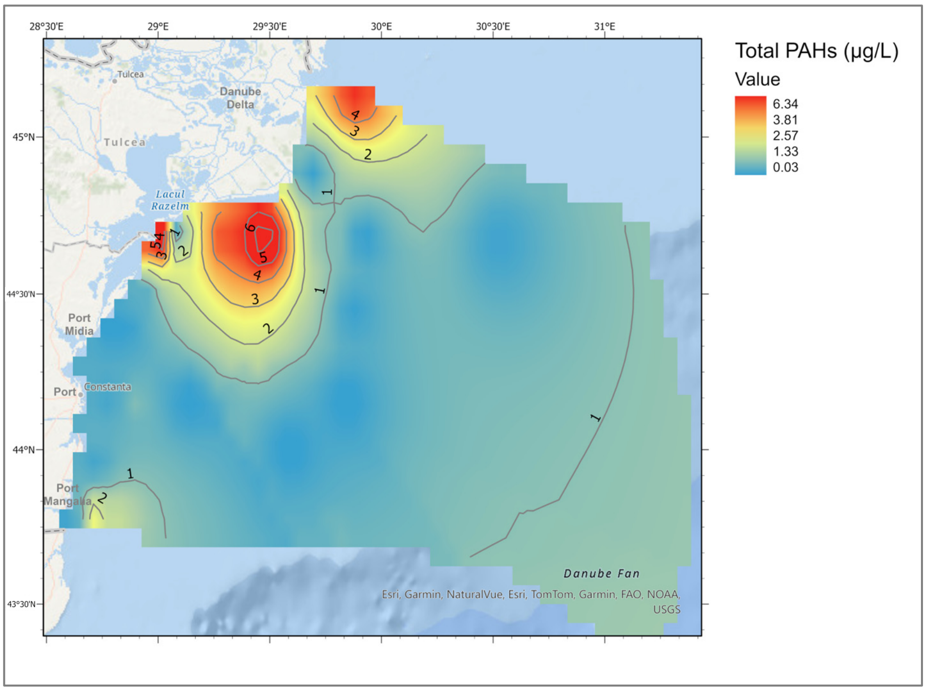

Figure 15. Distribution of total content PAHs in seawater—Romanian Black Sea.

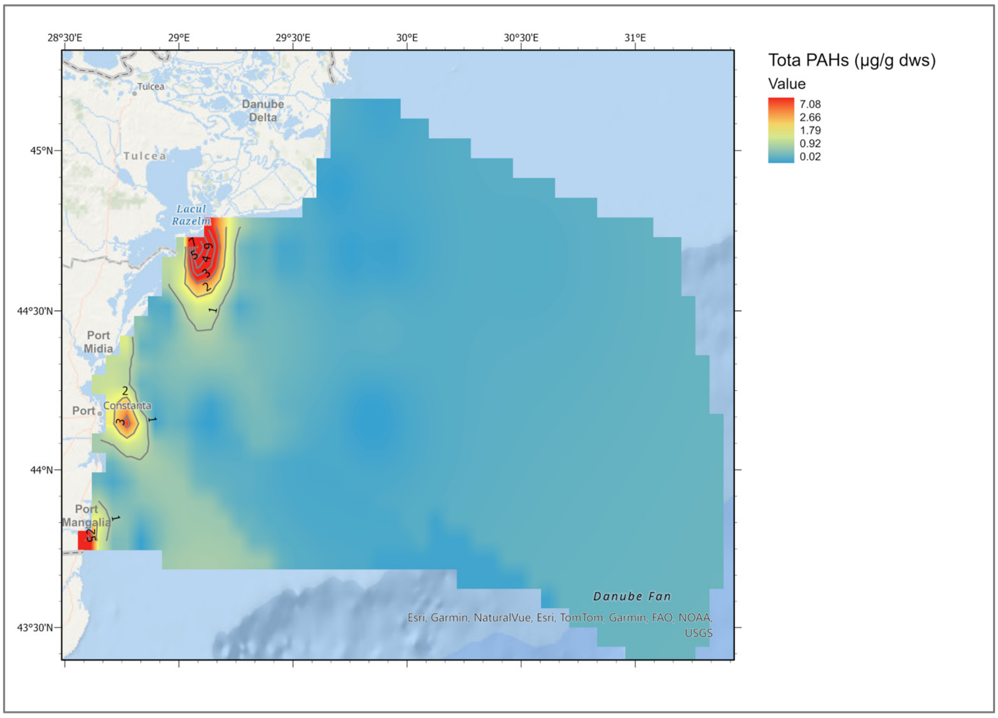

Figure 16. Distribution of total content of PAHs in sediments—Romanian Black Sea.

4. Discussion

Our findings indicated that the levels of copper (Cu), cadmium (Cd), chromium (Cr), nickel (Ni), and lead (Pb) in mussels (*M. galloprovincialis*) remained within safe limits, as evidenced by the calculated hazard quotients (THQs, TTHQ, and CRI). The results align with previous studies involving mussels from the Turkish coast of the Black Sea that highlighted that the concentrations of heavy metals in mussels are safe for consumers in terms of their toxicity, according to the estimated daily intake (EDI) and the target hazard quotients [27,47,48].

However, our conclusions regarding the risks posed by chemicals to human health are limited by the scope of our analysis, which focused solely on heavy metals in mollusks. It is important to note that fish consumption, which, in many cases, showed exceedances of the MACs values, was not accounted for. This study represents the first assessment of the combined impacts of metals in mussels and provides preliminary results that highlight the need for further research on other contaminants and species.

Compared to the limits set by the European Commission Regulation (EU) 2023/915 for consumed seafood, we found that cadmium (Cd) contamination was present in 6% of mussel samples and 30% of gastropod samples, whereas lead (Pb) levels remained well below the established limits. In pelagic and demersal fish, where stricter limits apply, the MACs for cadmium and lead were exceeded in 35% and 48% of samples, respectively.

The current study on the Black Sea confirms findings from similar research highlighting the bioaccumulation of heavy metals in marine organisms and varying contamination levels across different regions. An ecological risk assessment conducted along the mid-Black Sea coast of Turkey found higher levels of heavy metals in sediments and mussels compared to water, with the highest concentrations occurring in mussel samples from Samsun city harbor, also suggesting urban influence and ongoing pollution from domestic and industrial sources [49] Similarly, investigations along the Romanian Black Sea coast indicated that sediments near harbors and wastewater treatment plants contained higher levels of lead, copper, and cadmium. Algae were found to accumulate copper most effectively, while mollusks and demersal fish concentrated various metals to different degrees. Although the safety limits for cadmium and lead were not widely exceeded, bioaccumulation in bottom-feeders raises potential concerns [50]. Additional studies from the Black Sea coast of Turkey on three benthic seafood species (mussels, whelks, and crabs) detected aluminum, arsenic, copper, zinc, iron, and cadmium in all three organisms, with most metals being below the safety limits for human consumption. However, cadmium in veined Rapa whelk approached the limit [51]. In Varna Bay, Bulgaria, cadmium was the most prevalent metal in mussels and whelks, followed by lead and mercury. Similar to our findings, the estimated daily intake and hazard quotients for adults consuming these seafood items were below the established safety limits [52].

Several studies have assessed heavy metal bioaccumulation in fish from various regions. For instance, fish from the Mediterranean Sea near a petrochemical area in Siracusa had high levels of cadmium, lead, and chromium, with some exceeding European safety limits, but the overall risk to human health was deemed low. In the Red Sea, significant variations in heavy metal concentrations were found in fish muscle tissues, with some exceeding safety standards, indicating contamination concerns despite the nutritional value of these fish [53,54] Research on grey mullet from the Black Sea and Ionian Sea revealed significant differences in the heavy metal levels between regions, highlighting varying degrees of pollution. A comprehensive study in the Black Sea region of Turkey concluded that the heavy metal concentrations in common fish species posed no threat to human health, with the levels of various metals being below the recommended daily intake limits [55,56].

Investigations on cadmium, lead, OCPs, and PCBs in anchovy muscle tissue from Romania's Black Sea coast revealed occasional exceedances of the safety limits for cadmium and lead. However, these OCP and PCB levels were not considered to be a threat. Similarly, a study on fish species from Bulgaria's Black Sea found acceptable metal concentrations within safety limits, despite some species showing higher levels of specific metals [57,58]. Another study on Black Sea turbot highlighted the influence of fish gender, environment, and diet on the bioconcentrations of toxic metal levels in muscle tissue [59].

Overall, these studies, including the current one, consistently demonstrate significant anthropogenic impacts on the heavy metal levels in the Black Sea region, particularly near urban and industrial areas. Although some studies have suggested that the metal concentrations in marine organisms are generally within safe limits for human consumption, localized hotspots and certain species present potential health concerns that necessitate continuous monitoring and management.

Our investigation into persistent organic pollutants (POPs) revealed significant differences in the concentrations of organochlorine pesticides between fish and mollusks. Fish exhibited lower levels of these pesticides compared to mollusks, which showed a wide range of concentrations. Notably, gastropods had particularly high levels of Dieldrin, Endrin, Lindane, and total DDT. Mussels (M. galloprovincialis) also showed significant concentrations of Heptachlor and total DDT. This pattern can be attributed to the feeding behaviors of these organisms; mussels filter large quantities of water, while gastropods, being the next trophic level, feed on mussels [60].

Except for DDT, Heptachlor, and Dieldrin, the levels of most OCPs remained within the safe limits, as the surpassing of the values permitted by national legislation (Order 147/2004) was lower than 25% in all studied species. PCBs were accumulated mainly in fish, where the maximum admissible levels stipulated by the European Commission Regulation (EU) 2023/915 for consumed seafood were exceeded in 43% of samples.

When comparing the PAH concentration ranges in mussels from various locations, significant geographical differences in contamination levels were highlighted [61–66]. The present study, focusing on the Black Sea coast (Romania), reported a notably broader range and included higher maximum concentrations than other locations. For instance, the Prince Islands (Marmara, Turkey) reported [62] a narrower interval with a lower upper limit. Similarly, there were the findings from Saronikos Gulf (Greece) [66] and the Bizerte lagoon (north Tunisia) [61]. In contrast, the eastern Aegean Coast (Turkey) [63] and the Iberian Mediterranean Coastal area (Spain) showed much lower concentrations, [64]. The Ionian Sea (Italy) [65] data were also much narrower and lower in terms of maximum values compared to the present study.

These comparisons underscore the relatively high and variable PAH contamination levels along the Romanian Black Sea coast. The broad range of values in the present study suggests a significant impact of local environmental and anthropogenic factors, highlighting the critical need for targeted pollution monitoring and mitigation strategies in this region (Table 15).

In comparison to the values (MACs) permitted by European Commission Regulation (EU) 2023/915 for consumed seafood, we noticed that, while benzo(a)pyrene contamination was observed in both mussels (19% of samples) and gastropods (1% of samples) investigated, the sum of PAH (benzo(a)pyrene, benzo(a) anthracene, benzo(b) fluoranthene, and chrysene) levels remained well below the established limits. In the pelagic and demersal fish investigated, the MAC for benzo(a)pyrene of 0.005 µg/g ww was surpassed in 33% of samples, whereas the MAC for the sum of PAHs (benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, and chrysene) of 0.030 µg/g ww was surpassed in 33% of samples.

Table 15. PAH levels measured in mussels (*M. galloprovincialis*) from different seas (ng/g dw).

Location	Concentration Range (ng/g dw)	References
Bizerte lagoon (north Tunisia)	107.4–430.7	Barhoumi et al. [61]
Prince Islands (Marmara, Turkey)	664–9083	Balcıoğlu [62]
Eastern Aegean Coast (Turkey)	29.4–64.2	Küçüksezgin et al. [63]
Iberian Mediterranean Coastal area (Spain)	75–390	Leon et al. [64]
Ionian Sea (Italy)	14.8–645.3	Storelli et al. [65]
Saronikos Gulf (Greece)	1480–2400	Valavanidis et al. [66]
Black Sea coast (Romania)	3.80–17,758.8	Present study

Similar studies on the chemical contamination (HMs, PAHs, OCPs, and PCBs) of marine organisms (mussels, veined rapa whelk, pelagic, and demersal fish) from various Black Sea regions (Ukraine, Romania, Bulgaria, and Turkey) have been conducted [67]. An integrated hazardous substances assessment [68] evinced sub-regional differences in the contamination status, with a worse status predominating in the northwestern part of the Black Sea (rivers influenced coastal areas and hotspots) and a better status in the open sea area and the southern part of the Black Sea [69].

Considering the results, the cumulative effect of heavy metals, POPs, and PAHs found in mollusks and fish should be considered in further studies. Excessive consumption, especially over long periods, may lead to health risks for humans. Individual factors such as age, weight, and existing health conditions should be considered. Transparent communication between scientists, policymakers, and the public is vital to provide clear guidelines on safe consumption levels based on scientific evidence and emphasize that the occasional consumption of seafood within recommended limits is safe.

The continuous monitoring of heavy metal, POP, and PAH concentrations in mussels and fish is crucial. Regular sampling and analysis allow us to track any fluctuations or trends over time. Environmental agencies, research institutions, and seafood industry stakeholders should collaborate to establish monitoring programs that can help to identify potential contamination sources and assess the overall health of marine ecosystems.

Another concern regards environmental safety. Due to its specific characteristics, morphological climatic, and hydrological properties, the Black Sea is highly susceptible to environmental damage caused by human activities, which disrupts the balance of the marine ecosystem, putting the health of fish and shellfish at risk

These findings constitute additional arguments for the continuous monitoring of marine environment abiotic and biotic components, especially near the Danube discharge area or various hot spots where elevated hazardous substances levels were measured, activity that is essential to ensure the safety of consumed seafood. Areas near river discharge, industrial zones, wastewater discharge points, and shipping routes are more likely to have elevated contaminant levels. Coastal regions with historical pollution or heavy human activity should also receive special attention.

5. Conclusions

This study revealed significant spatial variations in the levels of hazardous substances (HMs, PAHs, OCPs, and PCBs) in the seawater, sediments, and biota across the Romanian Black Sea coast. Areas with high levels of pollutants were identified as the Danube-influenced area, harbors, or areas affected by wastewaters discharges, intensified maritime traffic, and offshore oil and gas platforms, s.a. The bioaccumulation of contaminants in various marine organisms (mollusks and fish) raises concerns about food safety and potential risks to human health. Specific pollutants exceeding safe limits were identified during our investigations (cadmium, lead, heptachlor, dieldrin, total DDT, sum of six PCBs, benzo (a) pyrene, sum of PAHs: benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, and chrysene).

Given our findings on the bioaccumulation levels of hazardous substances, there is a need for further research on this topic to consider the cumulative effect of HMs, POPs, and PAHs in mollusks and fish for accurate risk assessments and to better understand the long-term impacts. The complex interactions and potential synergistic effects of these pollutants can lead to a greater combined toxicity, posing significant risks to human health.

Our findings constitute additional arguments for the continuous monitoring of marine environment abiotic and biotic components, especially near the Danube discharge area or various hot spots where elevated hazardous substances levels were measured, to ensure the safety of consumed seafood. Areas near river discharge, industrial zones, wastewater discharge points, and shipping routes are more likely to have elevated contaminant levels. Coastal regions with historical pollution or heavy human activity should also receive special attention.

This study offers a comprehensive analysis that can be used for informed decision making regarding environmental management and pollution mitigation in the Black Sea and it emphasizes the urgency for action to protect the marine environment and human health.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/fishes9070274/s1, Figure S1: Distribution of cadmium in biota; Table S1: Biota sampling data; Table S2: Retention time, monitored ion, linearity, and limits of detection (LOD) of OCPs for biota (mollusks and fish); Table S3: Retention time, monitored ion, linearity, and limits of detection (LOD) of PCBs for biota (mollusks and fish); Table S4: Retention time, monitored ion, linearity, and limits of detection (LOD) of PAHs for biota (mollusks and fish); Table S5: Variability of heavy metal concentrations in seawater from the Romanian Black Sea; Table S6: Variability of heavy metal concentrations in sediments from the Romanian Black Sea; Table S7: Variability of OCPs concentrations in seawater from the Romanian Black Sea; Table S8: Variability of PCBs concentrations in seawater from the Romanian Black Sea; Table S9: Variability of OCPs concentrations in sediments from the Romanian Black Sea; Table S10: Variability of PCBs concentrations in sediments from the Romanian Black Sea.

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