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Presence, levels, and distribution of organic and elemental pollutants in Zooplankton from the Northwestern Mediterranean sea

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Persistent organic pollutants (POPs), such as the legacy contaminants polychlorinated biphenyls (PCBs) and dichlorodiphenyltrichloroethane (DDTs), as well as trace elements (TEs) pose a significant risk to marine ecosystems due to their toxicity, persistence, and bioaccumulative nature. Despite regulatory bans, PCBs and DDTs continue to be detected in the marine environment, while TEs levels remain conspicuous as a result of both natural and anthropogenic sources. In this study, we investigated the presence, concentrations, and spatial distribution of 32 PCB congeners, 6 DDT compounds, and 16 TEs in zooplankton collected from 40 sites across the Northwestern Mediterranean Sea. Results revealed widespread contamination, with PCBs detected in all samples (53.2 ± 63.0 ng g^{-1} dw) and DDTs present in over half the samples (5.1 ± 6.0 ng g^{-1} dw). Hotspots of POPs contamination were identified near Marseille, and in the wider Gulf of Lion, Barcelona, and the Ebro River mouth. All TEs were detected in zooplankton, with high concentrations of essential TEs, but also elevated levels of toxic elements such as Hg, Pb, and Cd in certain locations such as Barcelona, the Gulf of Lion, Balearic Islands, and southwestern Corsica. Spatial patterns of contamination were strongly linked to urban, industrial, riverine, and historical mining inputs. These results underline the important role of zooplankton as bioindicators for assessing pollutant transfer at the base of the marine food web. They also highlight the urgent need for integrated, long-term monitoring strategies to better understand contaminant dynamics and mitigate ecological risks in the Mediterranean Sea.

Keywords Metals, Plankton, Persistent organic pollutants, Bioaccumulation, Hg, PCBs, Western Mediterranean Sea

The Northwestern Mediterranean Sea (NWMS) is recognized as one of the most productive regions within the Mediterranean basin[1,2] characterized by high social and economic importance, but also by severe anthropogenic pressures(e.g., Cappelletto et al.[3]; Lleonart & Maynou[4]). Historically, the NWMS has experienced significant contaminant inputs, primarily from riverine sources. For instance, the Rhône River alone accounts for approximately 97% of trace elements (TEs) loads compared to other anthropogenic sources such as ports, urban runoff, and industrial discharges[5]. In Spain, long-term monitoring of the Ebro River has documented contamination not only by trace elements[6,7], but also persistent organic pollutants (POPs), including pesticides across sediments, water, and biota[8–11]. Similarly, NWMS features some of the most industrialized and densely populated coastal regions, which exhibit high levels of TEs and POPs largely driven by urban effluents and riverine discharges[12,13].

Among the most persistent and widespread marine contaminants are polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), and TEs, including mercury (Hg), lead (Pb), arsenic (As) and cadmium (Cd). PCBs and DDTs are classified as persistent organic pollutants, characterized by high chemical stability, lipophilicity, and potential for long-range transport and bioaccumulation[14,15]. Despite bans or severe restrictions implemented decades ago, these compounds persist in the aquatic ecosystems due to their historical inputs

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and limited degradation. On the contrary, TEs occur naturally, but are also introduced into the environment primarily through human activities such as industrial discharges, agricultural activities, mining, and waste disposal[16–18].

While comprehensive global data on POPs concentrations in marine zooplankton are limited and largely derived from localized studies[19–23], ranges of TEs in zooplankton are better documented, although most of the sources remain predominantly local studies[24–28]. Typical TEs concentrations in marine zooplankton range from 50 to 2000 mg kg^{-1} for Zn, from 10 to 1000 mg kg^{-1} for Cu, 1–100 mg kg^{-1} for Pb, 0.5–5 mg kg^{-1} for Cd, and from 0 to 1–2 mg kg^{-1} for Hg[29–31]. EU[32]/105/EC sets EQS for biota at Hg 1 mg kg^{-1}, Cd 1.25 mg kg^{-1}, Pb 2.5 mg kg^{-1}.

Organic and some inorganic contaminants entering the aquatic realm can be absorbed by organic matter, taken up and accumulated by plankton organisms[29,33]. Once accumulated in these organisms, both POPs and certain TEs can biomagnify through the food web, potentially threatening marine biodiversity and posing health risks to humans (e.g., Atwell et al.[34]; Boldrocchi et al.[35–37]; Borgå et al.[38]; Corsolini & Sarà[39]; Nfon et al.[40]). Indeed, prolonged or intermittent exposure to these pollutants has been associated with physiological, cellular, and behavioral alterations[41–43], as well as pathological damage to key organs including liver, kidneys, and gills[44,45]. Elevated concentrations in aquatic biota have been also associated with reproductive and growth impairments and potential immunosuppression[41,43,46,47].

While contamination in marine fish and mammals has been extensively investigated in the NWMS (e.g., Burgeot et al.[48]; Fossi et al.[49]; Grattarola et al.[50]; Pinzone et al.[51]; Rios-Fuster et al.[52]), information on the presence and concentrations of both TEs and organic contaminants at lower trophic levels remain limited[53,54]. This knowledge gap is particularly pronounced for zooplankton organisms, despite their critical function in the global cycling of contaminants, and their recognized role of bioindicators of aquatic pollution[16,20,55–59]. Currently, most existing and updated data come from either localized studies[60], such as those conducted in the Bay of Marseille (e.g., Castro-Jiménez et al.[61]; Tiano et al.[54]) or focus on a limited number of contaminants[62]. Dachs et al.[63], for instance, carried out extensive sampling monitoring on the levels and distribution of both PCBs and DDTs in zooplankton organisms, however, these findings date back approximately thirty years. In more recent years, only Chifflet et al.[29] conducted a large-scale investigation focusing on multiple TEs in zooplankton across the NWMS and adjacent areas. Nevertheless, comprehensive and updated studies covering a broader range of contaminants over larger spatial scales in the NWMS remain limited.

Monitoring POPs and TEs in zooplankton is therefore crucial to improve our understanding of the distribution and fate of these contaminants in a highly dynamic marine environment subject to anthropogenic pressure. The continuous need for data to inform marine conservation requires the implementation of diverse and innovative monitoring strategies to the development of cost-effective and non-invasive field survey techniques (es. Rezzolla et al.[64]). In this context, this study aims to provide updated data on the presence, levels and spatiotemporal variability of legacy contaminants (32 PCBs and 6 DDTs) and 16 TEs in zooplankton collected from 40 different sites across the NWMS region, with the goal of highlighting potential areas of concern.

Materials and methods
Study area
The NWMS encompasses the Algero-Provençal Basin and the Tyrrhenian Sea, stretching between the coasts of Spain, France, Corsica, Sardinia, and Northwestern Italy[65]. The Gulf of Lion plays a crucial role in this basin acting as a major site for deep water formation, affecting nutrient distribution, marine productivity[66] and receiving about 1,700 m^3 s^{-1} of freshwater (mainly from the Rhône River)[67]. In the NWMS area, a cyclonic circulation pattern dominates the water movement. Cold winds like the Mistral, combined with sea surface cooling, lead to strong heat loss. This drives the formation of Western Mediterranean Deep Water and intense convective events[68]. These processes help move contaminants both horizontally and vertically, affecting their distribution and fate in the marine environment[69].

Sampling campaign
Sampling was carried out within the third monitoring campaign of *Marine Adventure for Research & Education Project* (M.A.R.E., https://www.progettomare.org/), a project lunched in 2022 by Centro Velico Caprera Foundation in collaboration with One Ocean Foundation. The M.A.R.E. initiative aims to assess the health of the Mediterranean Sea through a multidisciplinary and participatory approach. Ecotoxicology represents a core component of the initiative: during yearly sailing expeditions across the Mediterranean basin, zooplankton samples are collected to analyze the presence of chemical contaminants to characterize spatial patterns of pollution and support long-term environmental monitoring. A distinctive feature of M.A.R.E. is the strong integration of citizen-science. Volunteers, influencers, and students are directly involved in field activities after receiving targeted scientific training. This participatory model not only expands the spatial coverage of data collection but also enhances public awareness of marine ecotoxicology and the human impacts affecting Mediterranean ecosystems.

The monitoring took place between April 27 to July, 52,024 onboard a catamaran that sailed continuously for 10 weeks and for approximately 1,500 miles. The sailing route started in the northeastern Sardinia (Italy), where the catamaran initially proceeded northward into the Ligurian Sea. Subsequently, the vessel maintained a westerly trajectory, longitudinally following the coastal margins of France and Spain until approaching the geographical coordinates near Sagunto, Spain. At this juncture, the course shifted eastward, systematically transiting through the Balearic archipelago. Following this, the vessel traversed the open Mediterranean basin to reach the northern littoral zones of Sardinia. The navigation continued northward toward the geomorphologically distinct western canyons of Corsica, concluding the itinerary at the island of Caprera.

During the sailing route, a total of 40 samples of zooplankton organisms were collected. Sampling sites are shown in Fig. 1, and their coordinates are described in the Supplementary Information (Table S1). Samples of zooplankton were collected vertically at a depth of 20 m from surface using a 200 µm mesh zooplankton net. After collection, each zooplankton sample was stored frozen until laboratory analyses performed at the University of Insubria, Como (Italy).

Organic and elemental contaminants analysis

Zooplankton samples were collected, washed with Milli-Q water, and then lyophilized for 5 days to obtain a stable dry weight (dw). A total of 40 zooplankton samples were collected. TEs analysis, which require only 20 mg of lyophilized zooplankton, were performed on all 40 samples. In contrast, analyses for PCBs and DDTs were conducted on 27 samples. To obtain the necessary sample amount, 8 of these samples were combined based on their geographical closeness, resulting in a final dataset comprising 23 samples. From each sample, approximately 0.2 g of dried material was taken as an aliquot and extracted using a Soxhlet apparatus with a 1:1 acetone/hexane mixture for two hours[55]. The extract was then treated with sulfuric acid to remove interfering substances, followed by purification on a Florisil column. The purified extract was concentrated to 0.5 mL under a gentle stream of nitrogen. A total of 32 PCB congeners (18, 28, 31, 44, 52, 77, 81, 95, 99, 101, 105, 110, 114, 118, 123, 126, 128, 138, 146, 149, 151, 153, 156, 157, 167, 169, 170, 177, 180, 183, 187, 189) and 6 DDTs (p,p'-DDT, -DDE, -DDD and o.p'-DDT, -DDE, -DDD) were quantified using gas chromatography-mass spectrometry (GC–MS) (ThermoFisher GC Trace 1600 coupled with a Single Quadrupole ISQ 7610). The system was equipped with an autosampler for reproducible injections and a Programmable Temperature Vaporizing (PTV) injector. Separation was achieved using a 30 m capillary column (ThermoFisher TG-5MS, 0.25 mm I.D., 0.25 µm film thickness), and detection was performed in Selected Ion Monitoring (SIM) mode. Calibration was carried out using certified multistandard solutions of PCBs and DDTs, with eight isotopically labeled internal standards employed to ensure quantification accuracy. Quality assurance was maintained by analyzing certified reference material, with recoveries consistently ranging between 77 and 122%. RSD% were on average close to 8% (n = 3, range 1%—16%) and limits of detection were in the range 0.1—0.4 ng g^{-1} dw. All concentrations are reported as ng g^{-1} dw. Procedural blanks were also measured during each analysis batch.

With regards to TEs analyses, the concentrations of As, Al, Cd, Cu, Fe, Mn, Mo, Hg, Se, Sr, Zn, Cr, V, Co, Ni, and Pb were determined in the whole 40 zooplankton samples. The analytical methodology followed the protocol described in Boldrocchi et al.[70]. Approximately 20 mg of lyophilized zooplankton was subjected to microwave-assisted acid digestion (Milestone ETHOS One) using 0.5 mL of ultrapure HCl and 0.5 mL of ultrapure HNO_3, both obtained via sub-boiling distillation, as per Monticelli et al.[71]. The digestion was carried out in a multibatch setup optimized for small sample masses[72] using a temperature program consisting of a 10-min ramp from room temperature to 100 °C, a 5-min hold at 100 °C, a further 10-min increase to 150 °C, followed by a 15-min hold at 150 °C. Post-digestion, the solutions were transferred into low-density polyethylene containers and diluted with ultrapure water. The elemental concentrations were determined using an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Scientific ICAP Q) operating in kinetic energy discrimination (KED) mode to minimize spectral interferences. Concentrations are expressed in mg kg^{-1} dw. Quality control was ensured

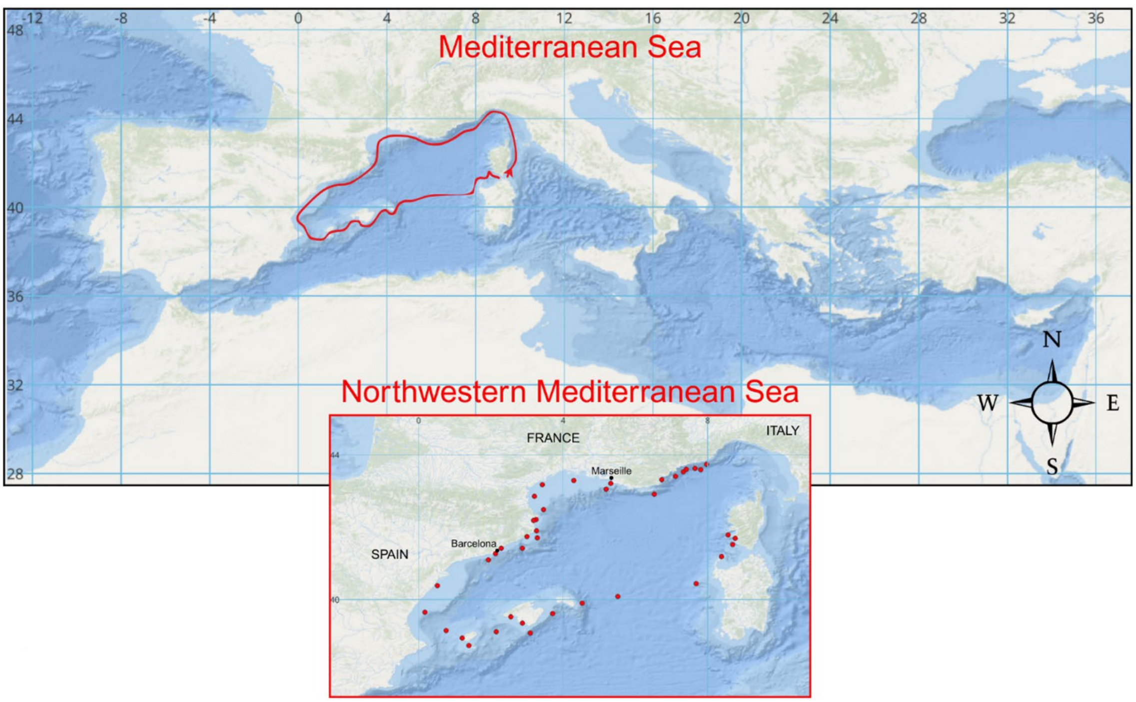

Fig. 1. Study area and zooplankton sampling points collected from the Northwestern Mediterranean Sea between April and July 2024. Map was generated by the authors using QGIS (version 3.1.8; QGIS Development Team, https://www.qgis.org).

by including one replicate of the certified reference material BCR-414 (plankton matrix) per analytical batch. Recoveries for certified elements (V, Cr, Mn, Ni, Cu, Zn, As, Se, Cd, Hg, and Pb) ranged between 87 and 120%, showing no significant deviation from certified values across four replicate runs. Relative standard deviations were around 20% for Hg, around 10% for Co, Sr, Se and Pb, and in the range 1–5% for all other elements (n = 4). Detection limits for solid samples were below 1 mg kg^{-1} for As, Cd, Co, Cu, Cr, Hg, Mo, Mn, Pb, Se, Sr, and V, while Fe, Ni, and Zn had detection limits between 1 and 10 mg kg^{-1}. Notably, the detection limit for Hg was 0.03 mg kg^{-1}. Procedural blanks were also measured during each analysis batch. The concentrations of Al, Fe, Zn, and Sr were less than 1% of those found in the samples, and below the detection limit for all other elements.

The Metal Pollution Index (MPI) was calculated as follows[73]:

$$\mathrm{MPI} = (\mathrm{Cf}_1 \times \mathrm{Cf}_1 ... \mathrm{Cf}_n \mathrm{a})^{1/n}$$

where Cf_i is the concentration of the metal(loid) in the sample.

Statistical analysis

The significance level was set to α = 0.05. The Shapiro–Wilk test was used to assess normality, and Levene's test was employed to evaluate homogeneity of variance. To test any statistical differences in the levels of TEs and POPs measured in zooplankton from the northwestern Mediterranean Sea (this study) with those from the Adriatic (N = 39)[59] and Tyrrhenian Sea (N = 53)[20], a One-Way Anova test was performed when assumptions of normality and homogeneity of variance were confirmed, otherwise the non-parametric Kruskal–Wallis test was used. In the case of PCBs, a One-Way Anova test was performed after a square root transformation to meet the assumptions of normality and homogeneity of variance. The Post Hoc Tukey's method (or the non-parametric Steel–Dwass test) was performed to examine the mean differences among element concentrations in each sub-basin.

Results and discussion

Globally, zooplankton is widely recognized as a sensitive early-warning indicator of aquatic pollution. In the Mediterranean Sea, research has mainly focused on zooplankton community structure and abundance, showing a spring–summer dominance of copepods (e.g., *Clausocalanus* spp., *Paracalanus parvus*, *Oithona* spp., *Acartia* spp.), cladocerans (e.g., *Penilia avirostris*, *Evadne spinifera*, *Pseudoevadne tergestina*), appendicularian tunicates, meroplanktonic decapod larvae, cnidarians, chaetognaths, and ostracods[24,74]. Building on this context, our study provides an updated, comprehensive assessment of baseline concentrations of both elemental and organic contaminants in zooplankton across multiple sites in the NWMS, offering a valuable reference for future ecotoxicological investigations.

PCBs

Among the 32 analyzed PCB congeners in this study, 19 were detected, with concentrations of sumPCB19 ranging from a minimum of 2.7 ng g^{-1} off the coast of San Remo (Italy) to a maximum of 287 ng g^{-1} offshore Marseille (France), with a mean concentration of 53.2 ± 63.0 ng g^{-1} (Table 1).

Tri-CBs were the most ubiquitous, being detected in 100% of the samples, with a mean of 10.3 ± 11.7 ng g^{-1} and PCB 18, 28 and 31 detected in all samples, indicating a pervasive contamination across the NWMS (Table 1). This consistent presence suggests ongoing or recent atmospheric deposition into the marine environment, likely driven by their low molecular weight and high volatility, which facilitates long-range atmospheric transport compared to higher-chlorinated congeners[75]. The widespread detection across the region points toward diffuse, regional contamination sources rather than localized point-source pollution. Hexa-CBs were the second most common frequently detected group, occurring in 87.0% samples, followed by Penta-CBs (78.3%), and Tetra-CBs (47.8%). Conversely, Hepta-CBs were rarely found, and Octa and Deca-CBs were never detected. Overall, the most ubiquitous congeners were PCB 18, PCB 28 + 31, PCB 169, PCB 101 and PCB 118 + 123. In terms of concentration, the highest levels were observed in Penta-CBs, with a mean of 18.3 ± 41.6 ng g^{-1}, followed by Hexa-CBs (15.7 ± 15.3 ng g^{-1}), and Tri-CBs (10.3 ± 11.7 ng g^{-1}) (Table 1). Specifically, among the most prevalent congeners, PCB 118 + 123 exhibited the highest mean concentration at 28.3 ± 50.6 ng g^{-1} (Table 1). These latter congeners, together with PCB 169 are among the 12 dioxin-like PCBs identified by the World Health Organization[76]. Dioxin-like PCBs have been associated with a range of adverse effects including carcinogenicity, immunotoxicity, endocrine disruption, and developmental impairments in both invertebrates and vertebrates[76,77]. Their detection in zooplankton is ecologically significant, as these organisms represent a key trophic level, serving as a vector for contaminant transfer through marine food webs. The differing detection frequencies observed among congener groups can be partly explained by the historical use and environmental behavior of technical PCBs mixtures in the NWMS. From the 1950s to the late 1970s, dielectric oils used across France, Italy and Spain included large quantities of PCBs-based formulations such as Aroclors, Phenoclor, and Pyralene/Askarel mixtures, widely employed in transformers, capacitors, ship electrical systems and industrial plants[78]. These technical products were particularly enriched in Tri-, Tetra-, Penta- and Hexa-CBs[78], homolog groups that dominate the congener profile observed in our samples, whereas Hepta- through Deca-CBs were only minor constituents. This composition helps to explain both the higher occurrence and higher concentrations of mid-chlorinated congeners as well as the near absence of Octa- and Deca-CBs in our dataset.

Spatial variability in PCBs concentrations revealed three main hotspots with concentrations of sumPCB19 ranging from 80 to 287 ng g^{-1}: offshore Marseille, Barcelona and at the Ebro River mouth (Fig. 2 and, Supplementary material S1). These findings are consistent with previous research identifying these zones as areas of concern. For instance, high PCBs levels have been reported in blue mussels collected around the cities of Barcelona and Marseille (with the highest values of up to 1,500 ng g^{-1}), as well as at the mouth of

Pollutants	Congeners	Mean ± SD	Min	Max
PCBs	PCB 18	2.9 ± 5.9	< LOD	26.8
	PCB 28 + 31	7.5 ± 7.1	0.4	28.8
	PCB 44	3.8 ± 3.5	1.6	910
	PCB 52	23.1 ± 33.2	1.2	92.1
	PCB 77	20	19.9	20
	PCB 99	4.5	4.5	4.5
	PCB 101	2.3 ± 1.6	0.6	5.9
	PCB 110	2.9 ± 2.6	1.3	5.9
	PCB 114	3.1	3.1	3.1
	PCB 118 + 123	28.4 ± 50.6	< LOD	181
	PCB 138	7.8 ± 3.3	3.1	11.8
	PCB 149	19.9 ± 23.5	4.9	47
	PCB 153	6.1 ± 3.9	1.5	11.6
	PCB 167 + 128	4.7 ± 1.9	1.9	6.5
	PCB 169	10.4 ± 6	2	27.9
	PCB 170	2.1 ± 1.6	1.0	3.2
	TOT	**53.2 ± 63**	**2.7**	**287**
Tri-CB	18–28-31	10.3 ± 11.7	0.58	55.6
Tetra-CB	44–52-77–81	8.7 ± 20.9	< LOD	94.3
Penta-CB	95–99-101–105-110–114-118 + 123–126	18.4 ± 41.6	< LOD	190
Hexa-CB	138–146-149–151-153–156-157–167 + 128–169	15.7 ± 15.3	< LOD	64
Hepta-CB	170–177-180–183-187–189	0.18 ± 0.7	< LOD	3.23
DDTs	o.p'-DDE			
	p.p'-DDE	5.9 ± 6.1	< LOD	10.2
	o.p'-DDD	< LOD	3.8	3.8
	p.p'-DDD	8.5 ± 5.3	0.1	15.6
	o.p'-DDT			
	p.p'-DDT			
	TOT	**5.1 ± 6**	**< LOD**	**15.6**

Table 1. Concentrations of PCBs and DDTs (ng g^{-1} dw) in zooplankton samples of the Northwestern Mediterranean Sea in 2024.

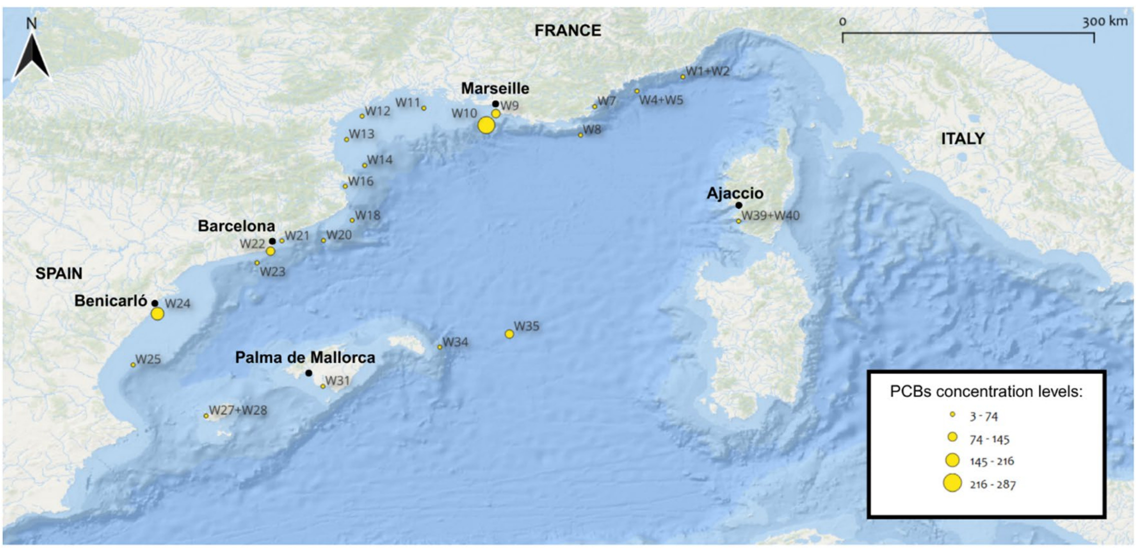

Fig. 2. Sum of PCBs concentrations (ng g^{-1} dw) determined in zooplankton samples from the northwestern Mediterranean Sea in 2024. Map was generated by the authors using QGIS (version 3.1.8; QGIS Development Team, https://www.qgis.org).

major rivers[79]. Similar contamination patterns were observed in suspended particulate matter[63], sediments[80] and various marine organisms, including flatfish[81], and plankton[54], particularly in the Gulf of Lion. Active monitoring using mussels as bioindicators[82] have previously confirmed elevated PCBs concentrations also in French Mediterranean coastal waters. The area from Marseille to the Rhône River is particularly affected (Fig. 2 and Supplementary material S1), likely due to combined contributions from river discharge, wastewater, port activities, and sediment resuspension[54,82–85]. Wind patterns, particularly the Mistral and southeasterly winds, can also enhance sediment resuspension, affecting contaminant distribution in the water column[86].

The Barcelona coast (126.9 ng g^{-1}) and Ebro River mouth (147.2 ng g^{-1}) are also critical areas of concern (Fig. 2; Supplementary material S1). This aligns with findings from the Mytilos project, which recorded PCBs concentrations between 30–60 ng g^{-1} in mussels near Barcelona and approximately 20 ng g^{-1} at the Ebro River delta[75]. The Ebro River has been recognized as a PCBs-contaminated system since the 1990s[87], primarily due to industrial and agricultural runoff and the application of pesticides in surrounding farmland[88].

In Barcelona's coastal zone, major PCBs inputs are primarily linked to the Llobregat and Besós rivers. The Llobregat basin is heavily influenced by urbanization and industrial sectors such as tanneries, textiles, pulp and paper manufacturing, and agriculture, which release diverse organic pollutants into the river system[75,89–91]. Among these activities, pulp and paper mills, as historical users of PCBs-containing carbonless copy paper, together with textile industries and tanneries, which employed PCBs in plasticizers, coatings and hydraulic fluids, represent the most plausible PCBs sources in the basin. Agriculture may also contribute indirectly through the application of sewage sludge from urban/industrial catchments. The elevated concentrations of PCBs observed in zooplankton from these hotspots therefore reflect a substantial environmental burden, which may have implications for higher trophic levels due to biomagnification.

When compared specifically with PCBs levels measured in zooplankton from other anthropogenically impacted Mediterranean regions, the concentrations observed in the NWMS fall within the same order of magnitude. For example, the mean PCBs concentration in NWMS zooplankton (34.8 ± 52.6 ng g^{-1}, considering only the congeners shared across studies) did not differ statistically from values reported for the Adriatic Sea, where Villa et al.[59] found ∑PCBs of 31.2 ± 29.6 ng g^{-1} in mesozooplankton. In contrast, the NWMS showed significantly lower PCBs levels compared to the Tyrrhenian Sea (46.9 ± 37.2 ng g^{-1}), as indicated by a one-way ANOVA followed by Tukey's post hoc test ($F(2,75) = 3.752$, $p = 0.0281$). These comparisons refer exclusively to zooplankton datasets, not to other sentinel species such as mussels. These differences among regions are consistent with basin-wide contamination patterns previously documented for the Mediterranean. In the Mediterranean Marine Pollution Assessment and Control Program inventory report, PCBs were shown to be unevenly distributed across the basin, with concentrations markedly higher in specific hotspot areas rather than uniformly spread. This spatial heterogeneity aligns with the elevated PCBs levels historically reported in marine biota from Tyrrhenian coastal zones, particularly near industrialized and densely populated areas[20,79].

Our findings are consistent also with previous research conducted in different Mediterranean sub-basins, which reported similar contamination patterns in planktonic organisms. For instance, Berrojalbiz and colleagues documented the accumulation of persistent organic pollutants in Mediterranean plankton, with ∑41 PCBs values in plankton samples ranging from 0.76 to 353 ng g^{-1} on dry weight basis[53]. Similarly, Castro-Jiménez and colleagues demonstrated trophic magnification of PCBs in pelagic food webs from the NWMS, confirming that these compounds persist and biomagnify despite regulatory bans[61]. These studies, together with our results, indicate that PCBs contamination is not restricted to localized hotspots but represents a basin-wide issue driven by historical inputs and ongoing anthropogenic pressures.

To contextualize the contamination status of the NWMS, PCBs concentrations measured in this study were compared with those reported from other regions worldwide in recent years. The mean concentration of PCBs detected in our zooplankton samples (sumPCB19 53.2 ± 63.0 ng g^{-1}) was substantially higher than values reported for polar zooplankton (Svalbard fjords, $sumPCB_7$ in copepods: 2.95 ± 8.79 ng g^{-1} dw; and $sumPCB_7$ all zooplankton taxa: 4.17 ± 6.42 ng g^{-1} dw)[92]. Conversely, it was lower than concentrations documented in Japanese coastal waters between 2013 and 2017 ($sumPCB_{13}$: 107 ± 299 ng g^{-1} dw)[93], and in Djibouti ($SumPCB_{13}$: 336 ± 254 ng g^{-1} dw)[56]. These findings indicate that, although the Mediterranean Sea is recognized as a significantly contaminated basin, PCB levels in its zooplankton do not reach the extreme values observed in regions affected by intense industrial activities or insufficient waste management. Instead, the NWMS appears to exhibit an intermediate contamination status.

DDTs

DDTs were detected in 56.5% of the zooplankton samples, with concentrations ranging from < LOD to 15.6 ng g^{-1}, with a mean of 5.3 ± 6 ng g^{-1} (Table 1; Figure S2). Among DDTs and its degradation products, the most frequently detected compound was p,p'-DDD identified in 52.2% samples, followed by p,p'-DDE (21.7%), and o,p'-DDD (4.3%). These findings align with previous observations of widespread DDE and DDD detection across the Gulf of Lion, including Marseille[81].

The absence of detectable p,p'-DDT, coupled with the prevalence of its degradation products like p,p'-DDE, strongly suggests that the observed contamination is due to historical use of DDT and its persistence in the environment, rather than recent discharges.

Regarding spatial variability, the highest DDTs concentrations (> 10 ng g^{-1}) were observed along the French coasts between Saint-Tropez and Marseille, as well as in the Gulf of Lion near Perpignan (Fig. 3; Supplementary material S2). The relatively high levels of DDTs accumulation in these regions can be likely attributed to historical pesticide use for mosquito control and agriculture[94]. Elevated levels were also recorded around Barcelona, including near the mouth of the Llobregat River (Fig. 3, Supplementary material S2). These results are consistent with findings from Campillo et al.[95], who reported that mussels collected along the Spanish Mediterranean coast exhibited their highest concentrations of p,p'-DDE in samples from Barcelona. Similarly, Scarpato et al.[75]

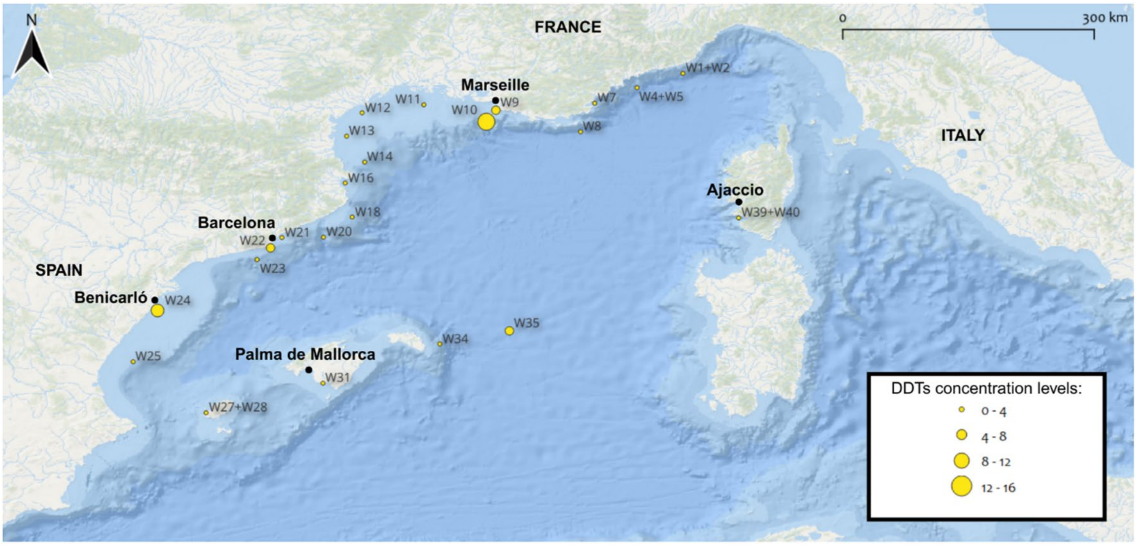

Fig. 3. Sum of DDTs concentrations (ng g^{-1} dw) determined in zooplankton samples from the northwestern Mediterranean Sea in 2024. Map was generated by the authors using QGIS (version 3.1.8; QGIS Development Team, https://www.qgis.org).

found that among 122 sampling sites, the most contaminated areas were Marseille, the Rhône River mouth, and the Barcelona metropolitan region, particularly near the Llobregat River, where DDTs exceeded 10 ng g^{-1} (Fig. 3,Figure S2).

Similarly to PCBs, DDTs concentrations measured in NWMS zooplankton in this study were compared to other Mediterranean sub-basins. A non-parametric Kruskal–Wallis test detected no significant differences among the three areas (NWMS: 5.1 ± 6 ng g^{-1}; Adriatic: 3.1 ± 2.7 ng g^{-1}; Tyrrhenian Sea: 8.9 ± 10.7 ng g^{-1}). Taken together, these comparisons highlight the utility of zooplankton as a sensitive indicator of spatial differences in legacy pollutant distribution across the Mediterranean. They also underscore that, despite regulatory bans, persistent organic pollutants such as PCBs and DDTs continue to pose environmental risks, particularly in regions with concentrated urban, industrial, and agricultural activities.

With regard to DDT levels, the mean concentration measured in zooplankton from the NWMS (5.3 ± 6.0 ng g^{-1} dw) are higher than values reported for tropical coral reef ecosystems of the northern South China Sea (0.77 ± 0.20 ng g^{-1} dw)[96]. Nevertheless, DDT concentrations in the NWMS remain substantially lower than those observed in well-known polluted environments such as Sagar Island, India (6.3–87.6 ng g^{-1} dw)[97], and Djibouti in the Gulf of Aden (44.7 ± 27.4 ng g^{-1} dw)[56].

Regarding polar regions, data on DDTs in Arctic zooplankton remain limited due to their typically low concentrations[98]. However, the levels detected in the NWMS are comparable to those reported for both the Alaskan and Canadian Arctic (5.33 ± 0.94 and 5.57 ± 0.58 ng g^{-1} dw, respectively)[99], as well as the North Water Polynya (4.74 ± 0.74 ng g^{-1} dw)[98], suggesting that DDT contamination in the NWMS aligns more closely with low-to-moderate pollution scenarios characteristic of high-latitude marine systems.

Elemental contaminants

All 16 TEs were detected in every zooplankton sample from the NWMS, albeit at varying concentrations. While TEs occur naturally in aquatic ecosystems[100], inputs from industrial, urban, mining, and agricultural sources can elevate their levels significantly[100,101]. In this study, TEs found at highest concentrations were Sr, Al, Zn, Cu, and Fe, while intermediate concentrations were reported for Mn, As, Pb Ni, Cr, V, and Se (Table 2). Cd, Co, Hg and Bi were detected at lower concentrations (Table 2). Among the TEs detected at the highest concentrations, Fe, Cu, and Zn are essential for the physiology of planktonic organisms, consistently, the level of these elements is expected to be high. For instance, Zn is of major importance in metabolic processes, ensuring the proper functioning of many enzymes and other compounds of crucial significance in metabolism, while Cu is a constituent of haemocyanin in crustaceans[30]. Conversely, Pb, Hg, and Cd are non-essential TEs, lacking any known physiological role in marine invertebrates, and can exert high toxicity even at low concentrations by mimicking essential metals and disrupting biological functions[30,100,102].

Spatial patterns in TEs show specific hotspots with relatively high levels of multiple elements (Fig. 4; Supplementary material S3, S4, S5, S6, S7). For instance, the highest values of Metal Pollution Index (MPI) were recorded in the area of Barcelona (MPI = 32), followed by southwestern Corsica Island (MPI = 11.5 to 18), the Ebro River mouth (MPI = 16.9), the Orb River mouth (MPI = 14.3), offshore Valencia area (MPI = 14.4 and 15), Minorca (MPI = 15.5 and 16.3) and Formentera Island (MPI = 13.9) (Fig. 4). These hotspots reflect the combined influence of urbanization, industrial operations, port activities, riverine inputs, and other regional pressures.

The continental shelf off Barcelona is a well-documented example of a coastal environment heavily impacted by urban and industrial activities[103]. Although TEs pollution has declined over time, concentrations remain

TEs	Mean ± Std	Min	Max
Sr	7341 ± 6977	308	27,109
Al	1381 ± 1387	77	5991
Zn	527 ± 600	72	2724
Cu	405 ± 1110	6.0	4981
Fe	231 ± 1267	1.3	7998
Mn	37.2 ± 30.5	2.8	137
As	10.8 ± 7.6	3.0	51.7
Pb	9.4 ± 25.4	0.23	129.83
Ni	8.1 ± 6.3	1.7	31.3
Cr	6.6 ± 6.4	0.20	23.4
V	6.0 ± 12.4	0.06	78.7
Se	3.2 ± 1.2	0.88	5.6
Cd	2.0 ± 0.1	0.33	4.3
Co	1.0 ± 0.7	0.19	3.0
Hg	0.2 ± 0.2	0.03	1.01
Bi	0.1 ± 0.4	0.004	2.7

Table 2. Concentrations of TEs (mg kg^{-1} dw) in zooplankton samples of the Northwestern Mediterranean Sea in 2024.

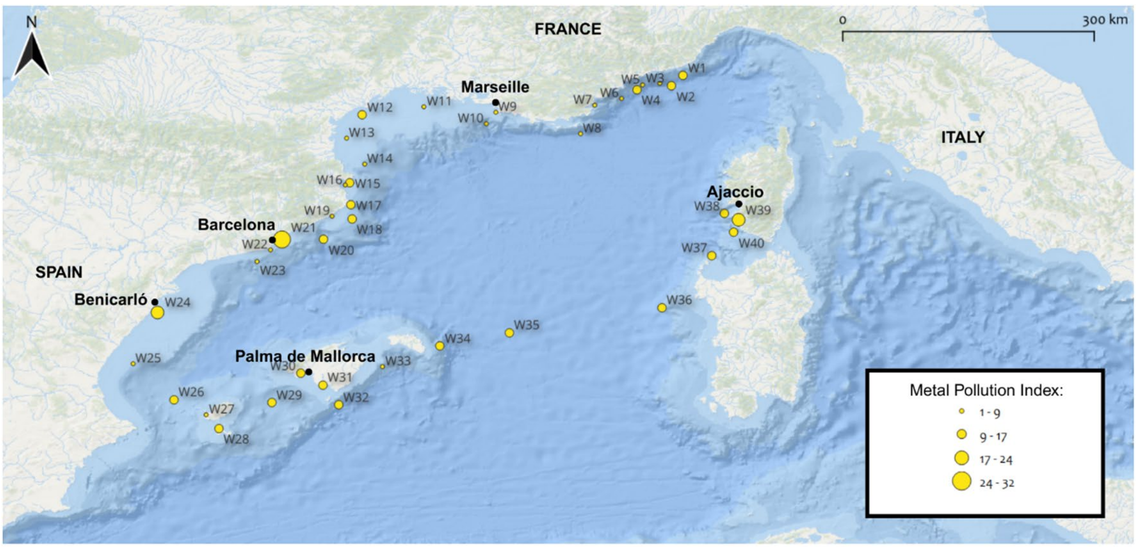

Fig. 4. Metal pollution index determined for 16 TEs measured in zooplankton from the northwestern Mediterranean Sea in 2024. Map was generated by the authors using QGIS (version 3.1.8; QGIS Development Team, https://www.qgis.org).

high due to challenges in managing water and sediment pollution in this densely populated and industrialized region[103]. Barcelona is in fact the second most populous urban area on the Mediterranean coast, with an estimated 5 million inhabitants. During heavy rain events, untreated water is often discharged directly into the sea, contributing significantly to contamination[103]. Consistently, among all locations, zooplankton sampled offshore Barcelona exhibited the highest levels of multiple TEs, including Hg (0.7 mg kg^{-1}) (Figure S3), Co (2.0 mg kg^{-1}), Cr (13.6 mg kg^{-1}), Mn (87.6 mg kg^{-1}), Zn (693 mg kg^{-1}), Cu (362 mg kg^{-1}) and Pb (13.7 mg kg^{-1}) (Figure S5). The elevated concentrations of certain elements that are known to biomagnify, such as Hg, may pose a particular risk for their transfer and increase along the marine food web.

In southern France, major rivers like the Rhône, Orb, Aude, and Herault, with former metal(-loid) mining sites in their watersheds, still pose a potential environmental threat[104]. Samples collected in the Rhône and Valras plage, where the Orb River discharges, are characterized by very high levels of multiple TEs, including V (78.7 mg kg^{-1}), Co (1.5 mg kg^{-1}), Mn (137 mg kg^{-1}), As (51.7 mg kg^{-1}) (Figure S6) and Pb (11.7 mg kg^{-1}) (Figure S5). Rivers are known to transport mining contaminants far from their sources into marine ecosystems. Similarly, the sample southern Ebro River mouth, where the plume is usually deviated[105] exhibited a general enrichment of TEs.

In the Balearic Islands, with minimal industrial and riverine inputs, pollution is primarily attributed to harbors, marinas, agriculture, construction materials, and tourism[106,107]. Zooplanktonic organisms from this area showed high peaks of Hg (1 mg kg^{-1}) (Figure S3), Co (2.5 mg kg^{-1}), Cr (23.4 mg kg^{-1}), Mn (100 mg kg^{-1}), Zn (7777 mg kg^{-1}) and As (18.7 mg kg^{-1}) (Figure S6) in Formentera, while Hg (0.2 mg kg^{-1}) (Figure S3), Cr (15.2 mg kg^{-1}), Zn (10,002 mg kg^{-1}), Cd (4 mg kg^{-1}) (Figure S7) and Ni (28.9 mg kg^{-1}) (Figure S4) in Minorca. Similar values have been recorded also for Maiorca Island, with high concentrations of Co, Cr, Mn, Ni, Zn and Cu. In general, harbors represent a major source of Cu and Zn, due to the leaching of antifouling paints and port runoff Maiorca[108], which is in line with the high concentrations recorded especially off the port of Minorca, near Formentera and Minorca. Agricultural practices contribute As, Hg, and Cd through fertilizers and pesticides, while construction materials (cement, steel, coatings) are known sources of Hg, Cu, As, Cd, aligning with the high values of these elements detected in the area[79]. Finally, tourism pressures, including wastewater inputs and intense maritime traffic, can enhance pollutants remobilization in coastal sediments[106].

Zooplankton collected from the southwestern of Corsica exhibited elevated concentrations of Zn, Cu, Cr, and Cd (Figure S7), which may be linked to surrounding urban and industrial influence, including wastewater discharge and port operations[109]. Results align with previous monitoring indicating that the area of Ajaccio contains notable levels of both TEs and organic contaminants in marine sediments and biota (e.g.Galgani et al.[110]; Ternengo et al.[111]).

With regards to samples collected offshore Valencia, zooplankton accumulated elevated concentration of Co (2.9 mg kg^{-1}), Cr (16.4 mg kg^{-1}), Mn (77.8 mg kg^{-1}), Ni (31.3 mg kg^{-1}) (Figure S4), Zn (1083 mg kg^{-1}) and Cd (4.3 mg kg^{-1}) (Figure S7). The combination of urban, industrial, aquaculture, and agricultural activities likely drives these contamination patterns[112].

The levels of contamination by TEs measured in this study were compared to those determined in the Adriatic Sea[59] and in the Tyrrhenian Sea[20]. These works are the most recent and comprehensive of both areas, using comparable methodologies.

Among all TEs, significant differences in the mean concentrations of Hg, Zn, Cd, Ni, and Pb were observed among the three Mediterranean sub-basins. Specifically, the mean concentration of Cd in the NWMS (2.0 ± 1.0 mg kg^{-1}) was significantly higher than the other two areas (Adriatic: 1.5 ± 0.8 mg kg^{-1}; Tyrrhenian Sea: 1.6 ± 0.9 mg kg^{-1}) ($F(2,129) = 3.415$, $p = 0.0359$). This is consistent with previously reported high Cd levels in sediments along the coasts of France (Marseille-Fos) and Spain[79], driven by intense industrial and urban activity, including chemical and metallurgical industries that represent potential sources of Cd discharge into marine environments[113]. In addition, the Rhône River is one of the main terrestrial inputs in this region and has been shown to transport TEs, including Cd, to the continental shelf[114]. High levels of Cd have been detected also in biota from several sites along the southern and southeastern coasts of Spain, which represents an intensely mined region, as well as in some areas along French coastlines[79].

In contrast, mean levels of Pb and Ni were higher in the Tyrrhenian Sea compared to the other sub-basins ($F(2,128) = 2.128$, $p < 0.0001$ and $F(2,129) = 2.129$, $p < 0.0001$, respectively). Moreover, mean Pb concentration in the Adriatic was statistically lower than the NWMS ($p = 0.0362$). This is consistent with previous studies reporting elevated Pb levels in blue mussels, zooplankton as well as in sediments at multiple locations along the Tyrrhenian Sea, from the Gulf of Genoa to Naples, in the Italian west coast, northern Sicily and southern Sardinia[20,79]. High Pb levels in biota are correlated with the distribution of discharges and nonpoint sources of pollution from mining, industry and sewage[79]. Similarly, mean levels of Hg and Zn in the Adriatic were statistically lower than both the NWMS and the Tyrrhenian Sea ($\chi^2 = 15.62$, $df = 2$, $p = 0.0004$ and $\chi^2 = 40.48$, $df = 2$, $p = 0.0001$, respectively). The presence of metallurgical industries on the NWMS coasts and also in the Tyrrhenian Seas might explain the higher levels of both Zn and Hg in these sub-basins compared to the Adriatic Sea. In addition to direct coastal emissions, atmospheric deposition and the remobilization of historically contaminated sediments may further elevate Hg concentrations in these western Mediterranean regions.

In a broader geographical context, the trace element (TE) concentrations measured in the NWMS fall within the range reported for other semi-enclosed basins subject to substantial anthropogenic pressure. For example, the Baltic and Black Seas—both characterized by restricted water circulation and intense riverine inputs—exhibit comparable or even higher levels of several TEs, including Pb and Cd[115,116]. These similarities reinforce the notion that semi-enclosed systems are particularly vulnerable to the accumulation of land-based contaminants.

Mean Zn levels in NWMS zooplankton (527 ± 600 mg kg^{-1}) were comparable to those reported for the Arabian Sea (374 mg kg^{-1}) and the Red Sea (416 ± 375 mg kg^{-1})[117], yet remained well below the extreme concentrations historically measured in the Bay of Bengal (≈2000 mg kg^{-1})[118]. Copper displayed a similar pattern: mean concentrations (405 ± 1110 mg kg^{-1}) were within the range reported for several contaminated regions worldwide, including the Gulf of Aden and the Bay of Bengal[119,120], supporting the hypothesis that diffuse anthropogenic inputs—largely from industrial and urban activities—continue to influence metal levels in the NWMS.

Ni concentrations (8.1 ± 6.3 mg kg^{-1}) were lower than those reported for heavily impacted coastal areas in Djibouti (25.1 ± 18.6 mg kg^{-1})[120] and Taiwan (20.7 ± 7.7 mg kg^{-1})[121], but considerably higher than values from polar systems (1.8–7.4 mg kg^{-1}[122,123]. This intermediate positioning suggests that Ni levels in the NWMS reflect moderate anthropogenic pressure superimposed on natural background contributions.

Pb concentrations (9.4 ± 25.4 mg kg^{-1}) were lower than those observed in highly industrialized regions such as southern Taiwan (24.9 ± 23.1 mg kg^{-1})[121] or the Bay of Bengal (38.6 mg kg^{-1})[119], yet still indicative of anthropogenic influence, consistent with known atmospheric and coastal inputs affecting the western Mediterranean basin.

More toxic elements, including Cd, Hg, and Cr, were present at levels that generally fall between those measured in industrial hotspots and those characteristic of high-latitude, low-impact systems. Cd concentrations (2.0 ± 1.0 mg kg^{-1}) were markedly lower than those documented in Djibouti, Taiwan, and the Bay of Bengal[119–121], and closer to the range reported for Arctic regions[123]. Hg, historically considered one of the most concerning contaminants in the Mediterranean[129], exhibited moderate concentrations (0.2 ± 0.2 mg kg^{-1}), higher than those typical of Arctic pelagic food webs (0.002–0.1 mg kg^{-1})[124,125], yet substantially lower than values recorded in severely impacted coastal areas of the Gulf of Aden[120]. Cr levels (6.6 ± 6.4 mg kg^{-1}) were lower than those measured in Asian industrial regions but comparable to concentrations reported for Arctic environments[122].

Overall, when positioned in a global framework, TE concentrations in the NWMS reflect an intermediate contamination status: several essential metals (e.g., Zn, Cu) occur at levels comparable to those of other impacted marine regions, while more toxic elements (e.g., Cd, Hg, Cr) remain within moderate concentration ranges. This pattern is consistent with the NWMS being a semi-enclosed basin influenced by both direct coastal inputs and long-range atmospheric deposition and underscores the need for continued monitoring to assess temporal trends and potential ecosystem implications.

Finally, it is important to note that our study did not include species-level or trophic-level data for the zooplankton samples, which limits the assessment of how community composition and feeding strategies may influence contaminant accumulation and bioaccumulation patterns. Lower trophic levels are highly diverse in species, functional groups, and life cycles (e.g., meroplankton), which affects trophic interactions and contaminant transfer[61,126,127]. Previous studies have shown that trophic position, body size, and feeding mode can strongly affect the uptake and transfer of persistent organic pollutants and TEs within marine food webs[63,128]. Consequently, future investigations integrating contaminant measurements with taxonomic characterization and trophic markers (e.g., stable isotope analysis, $\delta^{15}N/\delta^{13}C$) would provide a more comprehensive understanding of the role of zooplankton biology in modulating contaminant bioaccumulation and the potential transfer to higher trophic levels in the Mediterranean Sea.

Conclusions

This study provides a comprehensive, spatially resolved dataset on both persistent organic pollutants (PCBs and DDTs) and trace elements in zooplankton across the Northwestern Mediterranean Sea. Our results demonstrate the continued presence of POPs in zooplankton, confirming the presence of these contaminants in biota, despite regulatory bans in act since decades, with few areas of concerns (e.g. Barcelona, Marseille – and the wider Gulf of Lion – and the Ebro, Rhône and Llobregat River mouths). This study also confirmed the presence of elevated toxic TEs (e.g. Hg, Cd and Pb) in zooplankton from multiple locations such as the Gulf of Lion, the Ebro River mouth and the coastal zone near Barcelona, which can be considered hotspots of TEs contamination.

Spatial contamination patterns for both groups of contaminants are clearly linked to anthropogenic pressures. Both groups of contaminants were found at higher levels in areas of intense industrialization and at the mouths of major rivers and densely populated coastal regions. These hotspots, like Barcelona's industrial zone, French and Spanish river mouths (Rhône, Orb), reflect the ongoing influence of urban discharge, agriculture, tourism, and historical mining activities, and represent key drivers of POPs and TEs contamination in the NWMS.

The ecotoxicological implications of these findings are significant. Zooplankton, as a fundamental component of marine food webs, can act as a vector for bioaccumulation and biomagnification of both organic and inorganic contaminants to higher trophic levels. Even sub-lethal concentrations of PCBs and toxic TEs can impair physiological functions, enzymatic activity, and reproductive success in planktonic and benthic invertebrates. Specifically, dioxin-like PCBs can induce immunotoxicity, endocrine disruption, and developmental impairments, while Cd, Hg, and Pb can cause oxidative stress and interfere with essential metal homeostasis.

The detection of these contaminants in hotspots such as Marseille, Barcelona, and major river mouths suggests an elevated ecological risk, potentially affecting local community structure, trophic interactions, and overall ecosystem functioning. Given the persistence and potential for long-term biomagnification of these pollutants, continuous monitoring using zooplankton as sentinel organisms is recommended, integrating chemical analyses with biomarkers of physiological stress to better assess ecological consequences and inform management strategies.

Furthermore, all sampling in this study was conducted during the spring season (April–June), minimizing the influence of seasonality on contaminant concentrations. Future studies spanning multiple seasons would help elucidate temporal variability in zooplankton contaminant bioaccumulation across the basin. Analyses of relative distributions among individual PCB congeners and correlations among trace elements were limited by the available data. Future research could focus on these aspects to provide deeper insights into contaminant sources, interactions, and spatial patterns, enhancing the ecological relevance of baseline contaminant assessments.

Overall, our results highlight the urgent need for a regionally coordinated, integrated pollution assessment framework in the Mediterranean Sea to guide policy, management actions, and long-term ecosystem protection strategies, particularly in areas of sustained anthropogenic pressure.

Data availability

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

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Author contributions
Gi.B. conceived the study, supervised the work, contributed to methodology, investigation, validation, formal analysis, and wrote the original draft. B.V. contributed to methodology, formal analysis, visualization, and co-wrote the original draft. She also created Fig. 1 to 4. D.B. worked on methodology, investigation, formal analysis, and manuscript review and editing. D.M. contributed to methodology, validation, formal analysis, and manuscript review and editing. J.P. was responsible for resources, project administration, and funding acquisition. L.B., C.S., G.L. and Ga.B. contributed to investigation and manuscript review and editing. M.M. and C.C. contributed to investigation, validation, and manuscript review and editing. R.P. contributed to validation and manuscript review and editing. R.B. supervised the work, provided resources, and contributed to manuscript review and editing. All authors reviewed the manuscript.

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