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Distribution and accumulation of metals and metalloids in planktonic food webs of the Mediterranean Sea (MERITE-HIPPOCAMPE campaign)

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Abstract :

Particle-size classes (7 fractions from 0.8 to 2000 μm) were collected in the deep chlorophyll maximum along a Mediterranean transect including the northern coastal zone (bays of Toulon and Marseilles, France), the offshore zone (near the North Balearic Thermal Front), and the southern coastal zone (Gulf of Gabès, Tunisia). Concentrations of biotic metals and metalloids (As, Cd, Cr, Cu, Fe, Mn, Ni, Sb, V, Zn) bound to living or dead organisms and faecal pellets were assessed by phosphorus normalisation. Biotic metals and metalloids concentrations (except Cr, Mn, and V) were higher in the offshore zone than in the coastal zones. In addition, biotic Sb and V concentrations appeared to be affected by atmospheric deposition, and biotic Cr concentrations appeared to be affected by local anthropogenic inputs. Essential elements (Cd, Cu, Fe, Mn, Ni, V, Zn) were very likely controlled both by the metabolic activity of certain organisms (nanoeukaryotes, copepods) and trophic structure. In the northern coastal zone, biomagnification of essential elements was controlled by copepods activities. In the offshore zone, metals and metalloids were not biomagnified probably due to homeostasis regulatory processes in organisms. In the southern coastal zone, biomagnification of As, Cu, Cr, Sb could probably induce specific effects within the planktonic network.

Highlights

► Bioaccumulation of metals and metalloids in the Mediterranean planktonic food webs ► Determination of biotic metal concentrations by P-normalisation ► Essential elements are controlled by nanoeukaryotes and copepods ► Anthropogenic inputs influence the biomagnification of non-essential elements

Keywords : Metals and metalloids, Planktonic food webs, Mediterranean Sea, Biomagnification, Contamination

Introduction

The fate of metals and metalloids bound to particles in marine ecosystems has been widely studied since the 1950s, and research shows that these particle-bound metals and metalloids play an essential role in regulatory processes (Goldberg, 1954; Redfield, 1958; Turekian, 1977). Some of these particles come from natural sources due to soil alteration or volcanic emissions, while others come from anthropogenic sources due to mining, industrial, and urban activities (Nriagu and Pacyna, 1988; Burton and Statham, 1990; Donat and Bruland, 1995; Rauch, 2010). Over the past 30 years, several studies have shown that the distribution of metals and metalloids bound to particles in marine ecosystems was determined by complex biogeochemical cycles including both biotic and geochemical processes (Collier and Edmond, 1984; Bruland and Lohan, 2003; Sunda, 2012). Basically, biotic metals and metalloids (bM) in particles bind to organisms (living or dead) and faecal pellets *via* chemical mechanisms, whereas geogenic metals and metalloids in particles are primarily due to *in-situ* geochemical transformations or external lithogenic inputs.

Metals and metalloids can be classified as essential or non-essential elements for the marine food webs according to their role in biogeochemical cycles. Essential elements are necessary for physiological functioning and are used in various metabolic processes through energy or ion transfers (Morel et al., 2003). Non-essential elements have no specific biological relevance and can be toxic even at low concentrations. Although metals and metalloids can be passively introduced into marine food webs through porous membranes (skin and gills), the dominant pathway remains planktonic grazing (Whitfield, 2001; Chouvelon et al., 2019; Gao et al., 2021; Madgett et al., 2021). Depending on their concentrations, essential and non-essential elements can trigger toxic effects in whole organisms by altering respiration or digestion processes (Wang, 2002; Pérez and Beiras, 2010).

To assess potential environmental and human health risks, it is important to understand how planktonic species transfer metals and metalloids through marine food webs (Maxwell et al., 2013; Hazem et al., 2019; Sanganyado et al., 2021). In the field, the separation of metals and metalloids in particles bound to biotic (*i.e.*, organic matter from living and dead organisms and their faecal pellets) and geogenic (*i.e.*, minerals from natural and anthropogenic sources) components remains an operational challenge and requires ultra-clean techniques and environments to avoid contaminations (Cullen and

Sherrell, 1999; Planquette and Sherrell, 2012). Furthermore, efforts to quantify the bM fraction using modelling remain underdeveloped (Ho et al., 2007, 2010; Liao et al., 2017). Using *in vitro* experiments, Ho et al. (2003) proposed an extended Redfield formula ($P_{1,000}\,Fe_{7.53}\,Mn_{3.84}\,Zn_{0.80}\,Cu_{0.38}\,Co_{0.19}\,Cd_{0.21}$) for eukaryotic phytoplankton species, but metals and metalloids contents relative to the biomass varied among species by a factor of about 20 (except for Cd, which varied by more than two orders of magnitude), this limiting attempt to generalise this model to ecological studies.

The transfer of metals and metalloids in marine food webs can be described using several metrics, such as the bioconcentration factor (BCF), bioaccumulation factor (BAF), biomagnification factor (BMF), or trophic magnification factor (TMF). However, these metrics are controlled by numerous parameters (species, size, metabolism, diet, community structure, environmental conditions, geographical location, *etc.*), which make ecotoxicological analysis an as-yet-unresolved challenge (Burkhard et al., 2011; Cossa et al., 2022).

The Mediterranean Sea is a semi-enclosed sea that represents ~ 0.7% of the total ocean surface (~ 0.25% in volume) and hosts 4%–18% of the world's marine biodiversity (Bianchi and Morri, 2000; UNEP/MAP-RAC-SPA, 2008). Due to low nutrient concentrations and a phosphate deficit, the Mediterranean Sea is considered as oligotrophic ocean with low primary production (Krom et al., 2010; Pujo-Pay et al., 2011; Tanhua et al., 2013). In open waters, the concentration of chlorophyll *a* rarely exceeds 2–3 µg/L (D'Ortenzio and d'Alcalà, 2009; The Mermex group, 2011; Marañón et al., 2021). Planktonic food webs are structured by phytoplanktonic communities and carbon fluxes are controlled by a large microbial loop (Uitz et al., 2006; Hunt et al., 2017; Mayot et al., 2017; Leblanc et al., 2018; Salhi et al., 2018; Ramírez-Romero et al., 2020). However, the Mediterranean Sea is under both natural and anthropogenic pressure, because its waters are enriched by the deposition of atmospheric particles from large plumes of Saharan dust (Guieu et al., 2002) and by the increasingly intensive anthropogenic activities of its 22 bordering countries (Grousset et al., 1995; Radakovich et al., 2008; Heimbürger et al., 2010; Chifflet et al., 2019; Migon et al., 2020). In this context, plankton could be a key agent in the transfer of metals and metalloids in marine food webs (Cossa and Coquery, 2005; Chouvelon et al., 2019). To gain insight into this issue, the MERITE-HIPPOCAMPE campaign aims to evaluate the accumulation and transfer of metals and metalloids (and other inorganic and organic contaminants) within planktonic food webs (bacterioplankton, phytoplankton, and zooplankton) in several geographical areas of the Mediterranean Sea. The objectives specifically addressed in this paper are: *i)* to determine the concentrations of metals and metalloids in different plankton size-fractions (from bacteria to zooplankton), *ii)* to assess the influence of plankton in the accumulation and transfer of metals and metalloids, and *iii)* to establish links between geographical areas and metals and metalloids concentrations in plankton.

1. Materials and methods

2.1 Study site

The MERITE-HIPPOCAMPE campaign was carried out in the spring of 2019 along a North-South transect running between the French coast (Toulon and Marseilles, northwestern Mediterranean) and the Tunisian coast (Gulf of Gabès, southeastern Mediterranean) in two legs (Leg 1: St2, St3, St4, S10 and St11; Leg 2: St1, St9, St15, St17, St19) (Tedetti et al., 2022) (Fig. 1a, b; Table S1). Ten stations were chosen according to different criteria based on physical, biogeochemical and biological conditions and anthropogenic influences. St1–2 and St3–4, located respectively in the bays of Toulon and Marseilles, are strongly impacted by anthropogenic activities, and are 'bloom' or 'intermittent bloom' areas according to D'Ortenzio and d'Alcalà (2009). St1 and St4 are the most 'coastal' stations whereas St2–3 are the most 'offshore' stations. Furthermore, St2–3 are located at the limit of the Ligurian ecoregion (Ayata et al., 2018). St9–10 are located near the northern zone of the North Balearic Front, and are 'bloom' and 'intermittent bloom' areas, respectively. The station St11, located in the Algerian ecoregion, is characterized by intense mesoscale eddies and is a 'no bloom' area according to the D'Ortenzio and d'Alcalà (2009) system. The station St15, located in the Gulf of Hammamet, is close to the Sicily Channel and exposed to influence from the Tunisian Atlantic current. It is a 'no bloom' area with a high density of small pelagic. St17 and St19 are located in the northern and southern parts of the Gulf of Gabès, respectively. The Gabès ecoregion (Ayata et al., 2018) is a hotspot of anthropogenic pressures and is characterized by shallow waters that are influenced by the Tunisian Atlantic current and by nutrient inputs from Saharan dust deposition or from sediment resuspension (Béjaoui et al., 2019).

2.2 Sampling and conditioning

Details of sampling procedures carried out as part of the MERITE-HIPPOCAMPE campaign can be found infra (Tedetti et al., 2022). The sampling strategy proposed a comprehensive end-to-end approach to study inorganic and organic contaminants in planktonic food webs (*i.e.* phyto-, zoo- and bacterio-plankton). Samples collected during this campaign had to be shared to carry out the numerous analyses planned. In order to collect enough plankton for all these analyses, we therefore focussed our strategy only on the deep chlorophyll maximum (DCM), during spring bloom (April to May), when maximum primary and secondary production occur (Lefevre et al., 1997; Marañón et al., 2021).

Briefly, at each station, various field operations were carried out at DCM to sample and sieve suspended particles (both biotic and geogenic) divided into 7 fractions (F1–7) ranging from 0.8 to 2000 µm. The smallest fractions (F1: 0.8–3 µm, and F2: 3–20 µm) were sampled using a McLane pump (WTS6-142LV, 4–8 L/min) with mixed cellulose ester filters (MCE, Millipore) according to GEOTRACES recommendations (Cutter et al., 2017). The McLane pump was equipped with a 3-stage filter-holder and pre-cleaned filters (0.8 µm MCE, 3 µm MCE, 20 µm nylon; Ø 142 mm) (Bishop et al., 2012; Planquette and Sherrell, 2012). Pumping in the DCM lasted ~ 50 min, thus filtering ~ 240 L of seawater. On board, the residual seawater in the 3-stage filter holder was gently cleared by a peristaltic pump to 'dry' filters before storing them at -20 °C. Three series of 'blank filters' were processed at the beginning, middle, and end of the campaign to assess possible contamination. These 'blank filters' were handled like all other filters without running McLane pumps.

Larger fractions (> 60 µm) were sampled using a plankton net (Multinet, Hydro-Bios). During horizontal deployment of the Multinet in the DCM, ship speed was reduced to 2 knots for 30–100 min to allow a 'gentle' collection of particles (both biotic and geogenic). Once on the ship's deck, the Multinet was rinsed with seawater and its contents (from five collectors) were transferred to pre-cleaned (HCl, 10%) 10-L perfluoroalkoxy (PFA) bottles. Then, working in a clean lab container, the particles (both biotic and geogenic) in the PFA bottle were fractionated using a nylon sieve column (60, 200, 500, 1000, and 2000-µm mesh sizes). The 5 fractions (F3: 60–200, F4: 200–500, F5: 500–1000, F6: 1000–2000, and F7 > 2000 µm) were sieved by 'gentle' filtration using a filtered seawater jet controlled by an

ASTI Teflon pump (Saint Gobain, model PFD2). Each fraction was transferred to pre-cleaned polycarbonate jars for storage (-20 °C) until analyses.

2.3 Metals and metalloids analyses

Sample processing was carried out according to GEOTRACES protocols (Bishop et al., 2012; Planquette and Sherrell, 2012; Cutter et al., 2017) in an ultra-clean trace metals laboratory (ISO 5), using high-purity acids (Fisher, Optima® grade or VWR, Normapur double-distilled acids) and MilliQ water. Before the MERITE-HIPPOCAMPE campaign, the MCE filters and their polyester sulfone storage boxes were pre-cleaned in 10% HCl (40 °C, overnight) and thoroughly rinsed with MilliQ water. Each MCE filter was slipped into a polyester sulfone box, dried under a laminar hood (ISO 1), labelled, pre-weighed, and stored in double-bagged polyethylene zip-lock bags. Likewise, polycarbonate jars equipped with screw caps (Nalgene) were pre-cleaned in 10% HCl (ultra-wave, 2 h) and thoroughly rinsed with MilliQ water, then the jars and caps were dried under a laminar hood (ISO 1), labelled, pre-weighed, and stored in double-bagged polyethylene zip-lock bags.

Back in the ultra-clean laboratory, the MCE filters (Ø142 mm) of the McLane pumps were freeze-dried, weighed, and sub-sampled using a stainless-steel cutter (Ø47 mm). Sub-samples were leached in PFA vials (Savillex) with 5 mL of a mixture of diluted acids (HF, 10%; HNO_3, 50%), heated on a hot-block (120 °C, 5 h), evaporated to near-dryness, then re-dissolved in 3 mL HNO_3 (10%). Likewise, in-jar samples were freeze-dried and sub-samples (~200 mg dw) were leached in PFA vials (Savillex) with 5 mL of a mixture of pure acids (HF, 0.5 mL; HNO_3, 4.5 mL), heated on a hot-block (120 °C, 24 h), evaporated to near-dryness, then re-dissolved in 3 mL HNO_3 (10%). Digested samples were then diluted using HNO_3 (2%) before running the metals and metalloids analyses. Metals and metalloids (As, Cd, Cr, Cu, Fe, Mn, Ni, Sb, Ti, V, Zn) were measured by inductively-coupled plasma mass spectrometry (Q-ICP-MS, Thermo-Scientific, iCAP-Q) using indium as an internal standard to correct for instrumental mass bias. The digestion procedure was assessed using a certified material for marine plankton (BCR 414, Commission of the European Communities). All elements were within the satisfactory recovery target of 100 ± 10% except for As (118%). Metals and metalloids concentrations in blank filters (0.8 and 3 µm MCE) were less than 1% of the mean metals and metalloids concentrations measured in samples. The analytical detection limits were well below the sample concentrations. Further details are reported as supplementary information in Tables S2 and S3.

2.4 Particulate organic phosphorus analyses

The particulate organic phosphorus (POP) samples were oxidised by wet oxidation according to the procedure of Raimbault et al. (1999). Briefly, the oxidation of POP was carried out by the action of an oxidising reagent at 120 °C under alkaline buffered conditions. All chemicals used were of analytical grade quality. The oxidising reagent consisted of 30 g of borax ($Na_2[B_4O_5(OH)_4]\cdot 8H_2O$) and 15 g of potassium peroxydisulfate ($K_2S_2O_8$) dissolved in 250 mL of MilliQ water. The digestion procedure was carried out in 50 mL pre-cleaned Pyrex bottles (Duran Schott). POP samples were placed in Pyrex bottles with 50 mL of MilliQ water and 5 mL of oxidising reagent and autoclaved at 120 °C for 30 min. Initial pH was 9.3 and pH remained alkaline (8.2) after digestion. After cooling at room temperature, the digestion mixture was directly pumped from the Pyrex bottle for colorimetric analysis using a Technicon AutoAnalyzer (Bran+Luebbe III) as described by Aminot et al. (2009).

2.5 Metals and metalloids in biotic component

According to our sampling strategy, metals and metalloids concentrations measured in samples can be composed of both biotic and geogenic components. Geochemical studies often use elemental ratios as proxies to assess the origin or type of particles sampled. Since Redfield's (1958) pioneering studies dealing with phytoplanktonic communities, normalised ratios of particulate organic phosphorus (P-normalisation) have been widely used to assess biotic metals and metalloids bound to particles. Likewise, Ti is known to be a lithogenic element (Ohnemus and Lam, 2015) that is unaffected by scavenging, biological uptake or particulate recycling (Dammshäuser et al., 2013) and can thus be used in normalisation ratios to assess geogenic metals and metalloids bound to particles (Lemaitre et al., 2020). Metals and metalloids concentrations in samples can therefore be expressed using the mass balance formula (Ho et al., 2007; Liao et al., 2017):

$$[M]_{sample} = a.[Ti]_a + b.[POP]_b \qquad (1)$$

where a is the Ti-normalised elemental ratio in the geogenic component, b is the P-normalised elemental ratio in the biotic component, $[M]_{sample}$ is the concentration of the element in the sample, $[Ti]_a$ is the concentration of Ti in the geogenic component, and $[POP]_b$ is the concentration of particulate organic phosphorus (POP) in the biotic component. Assuming that POP and Ti in samples are mainly due to the biotic and geogenic components, respectively ($[POP]_{sample} \equiv [POP]_b$; $[Ti]_{sample} \equiv [Ti]_a$), we can turn the mass balance formula into first-order equation 2:

$$\frac{[M]_{sample}}{[Ti]_{sample}} \equiv S.\frac{[POP]_{sample}}{[Ti]_{sample}} + C \qquad (2)$$

where S is the slope of the regression line between M/Ti and POP/Ti in the sample, and C is a constant value. Following this basic model, metals and metalloids concentrations in the biotic component (bM concentrations) were evaluated from the slopes of the regression lines between M/Ti and POP/Ti in the sample. The slope S was calculated for each station and for each element using the 7 particle-size classes from F1 to F7 (see Appendix 1 for supplementary information). Since the purpose of this study was to evaluate transfers and accumulations of metals and metalloids in planktonic food webs (bacterioplankton, phytoplankton and zooplankton), we focus here only on the bM component, as the geogenic component is not directly involved in these mechanisms.

2.6 Trophic magnification factor

The trophic magnification factor (TMF) represents the diet-weighted mean transfer of an element throughout food webs (Burkhard et al., 2011). In practice, TMF is most often derived from the slope of the regression of a log-transformed elemental against its corresponding trophic level (TL), and the N isotope ($\delta^{15}N$) is used as a proxy to assess the relative trophic position of an organism in food webs (Borgå et al., 2012; Kidd et al., 2018; Tesán-Onrubia et al., 2022).

$$Log_{10}(bM) = S.(TL) + C \qquad (3)$$

$$TMF = 10^S \qquad (4)$$

where bM is biotic elemental concentration, S is the slope of the linear equation 3, and TL is the trophic level corresponding to the sample. Specific TMFs (equation 4) were calculated for each geographical area from their respective data (see Appendix 2 for supplementary information). A TMF > 1 indicates accumulation of an elemental in food webs, while a TMF < 1 suggests dilution of an elemental in high trophic levels. TMF can be influenced by many factors, such as physiology, migration and lifetime of the species, spatio-temporal variability of the elements, metabolic functioning, *etc*.

2.7 Statistical analyses

All statistical analyses were performed using Xlstat software package version 2019.1.1 (Addinsoft 2020, Boston, USA, https://www.xlstat.com). First, Shapiro-Wilks tests were used to check the normality of variances. Next, parametric tests (ANOVA test) or non-parametric tests (Kruskal-Wallis test) were used to examine potential differences between data. Box plot were used to show variations of bM concentrations in size fractions per geographical areas. Parametric tests (Student t-test) or non-parametric tests (Mann-Whitney-Wilcoxon test) were used to examine the effect of geography on bM concentrations.

2. Results and discussion

3.1 Spatial variability and stoichiometry of metals and metalloids in the biotic compartment

Due to the high spatio-temporal variability between stations (Tedetti et al., 2022), bM concentrations were grouped by broad geographical areas, *i.e.* the northern coastal zone (4 stations, St1 to St4), the offshore zone (3 stations, St9 to St11) and the southern coastal zone (3 stations, St15, St17, and St19) based on the hydrological context (Boudriga et al., 2022). Table 1 summarises bM concentration ranges (mean ± standard deviation, min and max) in all fractions (F1–7) per element and geographical area, and Table S4 details the results per element, station, and fraction. Variations in bM concentrations were examined according to geographical areas and statistical tests (ANOVA or KW tests, $p < 0.05$) (Table S5). Most metals and metalloids were significantly found at higher mean bM concentrations in the offshore zone, except for Cr and V that had significantly higher mean bM concentrations in the northern coastal zone and Mn that displayed significantly higher mean bM concentration in the southern coastal zone. Large fluctuations were observed in bM concentrations, as indicated by the high coefficients of variation (CV), with no clear trends emerging, either by element or by geographical area (Table 1). For example, highest bM variations were found for V in the northern coastal zone (CV = 183%), for Sb in the offshore zone (CV = 166%) and for Mn in the southern coastal zone (CV = 159%). Conversely, lowest CV were found for Ni in the northern coastal zone (CV = 45%), for Cu in the offshore zone (CV = 40%) and for Cd in the southern coastal zone (CV = 48%). In the Mediterranean Sea, data of bM were sparse or incomplete and varied according to sampling strategy (sampling depth, spatio-temporal characteristics and, plankton size fractions), making comparisons a risky exercise. However, our results shared strong overlaps with metals and metalloids concentrations measured in zooplankton collected offshore of the Italian coasts in the cyclonic current of the Ligurian Sea (Battuello et al., 2016), and were less than or equal to the metals and metalloids concentrations of suspended particles collected at the DCM in the Gulf of Lions (Chouvelon et al., 2019).

Mean bM/POP ratios were calculated to present metals and metalloids stoichiometry per fractions (F1–7) and per geographical area (Table 2; Table S6 for bM/POP ratios detailed per station). Differences between geographical areas were tested using statistical analyses (ANOVA or KW tests, $p < 0.05$). Significant differences in bM/POP ratios were found for all metals and metalloids except Fe, V and Zn (Table S7). These results suggest that metals and metalloids (except Fe, V and Zn) influence the physiology and ecology of planktonic food webs (0.8–2000 µm) in the Mediterranean Sea. Indeed, metals and metalloids concentrations in marine food webs depend on the physiological accumulation strategies of pelagic species and may vary between different taxonomic groups in the same ecosystem (Ho et al., 2003; Quigg et al., 2003; Twining and Fisher, 2004; Morel, 2008). For example, in small planktonic food webs, metals and metalloids accumulation is particularly efficient when copepods feed on protozoa rather than phytoplankton (Twining and Fisher, 2004). By effectively controlling the efflux of metals and metalloids, copepods play a key role in metals and metalloids distribution within planktonic food webs (Wang et al., 2002; Battuello et al., 2017). Our results showed that mean bM/POP ratios varied in the same decreasing order Fe > Zn > As ~ Cr ~ Cu ~ Mn ~ V > Ni ~ Sb > Cd in the three geographical areas. These findings are in good agreement with Twining and Baines (2013) who generalised phytoplanktonic M/P ratios from geochemical data as follows: Fe ~ Zn > Mn ~ Ni ~ Cu >> Cd.

3.2 Biotic metals and metalloids distribution in planktonic food webs

Fig. 2 and 3 show boxplots representing the distribution of 7 major essential elements (Cd, Cu, Fe, Mn, Ni, V, Zn) and 3 non-essential elements (As, Cr, Sb) per fractions (F1–7) and geographical area (northern coastal zone, offshore zone, and southern coastal zone), respectively. Essential elements are known to control plankton physiology (Whitfield, 2001; Morel et al., 2003; Twining and Baines, 2013) but trophic relationships are extremely complex, and the distribution of bM in planktonic food webs can be influenced by many factors, such as community structure, environmental conditions, and spatio-temporal sampling plan (Battuello et al., 2016). Differences in bM concentrations between geographical areas were assessed using statistical tests (Student or Mann-Withney-Wilcoxon tests, $p < 0.05$) (Table S8).

The planktonic community related to the MERITE-HIPPOCAMPE campaign is extensively described in Boudriga et al. (2022) and Fierro-González et al. (2022) as companion papers. Briefly, the smallest phytoplanktonic fractions were mainly composed of picoeukaryotes for F1 and nanoeukaryotes for F2, while the largest zooplanktonic fractions were composed of nauplii and copepods for F3, copepods of increasing size for F4 and F5, large copepods and small crustaceans for F6, and crustaceans and gelatinous organisms for F7.

3.21 Essential elements

The concentration of essential elements followed three different patterns of distribution depending on the geographical area (Fig. 2). In the northern coastal zone, bM concentrations showed a bell-shaped distribution with a maximum in the F4–5 range (mainly composed of copepods). In the offshore zone, bM concentrations showed a flat-shaped distribution with a maximum in the F2–5 range (from nanoeukaryotes to copepods). In contrast, in the southern coastal zone, the bM concentrations showed increase from F1 to F5 (F6 and F7 were not available due to a lack of particles > 1000 µm).

Biotic Cd concentrations presented two-modal distributions in the three geographical areas, with two maxima (~ 1 µg/g) in the F1 and F4 fractions composed of picoeukaryotes and small copepods, respectively. No significant differences were found between the three geographical areas and bCd concentrations. Cd is considered an essential element as it influences both growth and structure of communities (Lee et al., 1995; Lane and Morel, 2000; Xu et al., 2008). The biochemical activity of Cd could be due to a strong reactivity with polyphosphate sites together with a rapid uptake into the cell *via* the Zn transport system (Whitfield, 2001). Cd speciation is planktonic species-dependent. For example, in small plankton sizes, Cd assimilation is particularly efficient when copepods feed on protozoa rather than phytoplankton (Twining and Fisher, 2004). In higher plankton sizes, cephalopods and crustaceans accumulate more Cd than other planktonic species (Liu et al., 2019). Therefore, the two-modal distribution of bCd in planktonic food webs might reveal prey-predator relationship between picoeukaryotes and small copepods in the three geographical areas. Unfortunately, due to the relatively small dataset, this suggestion needs further investigation.

Maximum bCu concentrations (~ 7 µg/g) were found in the F5 fractions in the three geographical areas. No significant differences in bCu concentrations were found between the northern and southern coastal zones, but significant differences in bCu concentrations were found between the northern coastal zone and offshore zone and between the offshore zone and the southern coastal zone. The Mediterranean Sea is under strong anthropogenic pressure, both on a large scale by atmospheric deposition and more locally near coastal zones by urban/industrial inputs (Guieu et al., 2010; Heimbürger et al., 2010; Chifflet et al., 2019; Gargouri et al., 2021). Surface waters can either be depleted or enriched in Cu according to the seasonal intensity of phytoplankton activity (Heimbürger et al., 2011. Migon et al., 2020). In the western Mediterranean Sea, the high Cu concentrations in atmospheric deposition, are known to decrease the phytoplanktonic biomass (Jordi et al., 2012). Cu is an essential element for organisms but can have a negative effect in eukaryote communities when free Cu exceeds 10 pM (Sunda and Huntsman, 1995). Above this threshold, primary producers (bacteria, prokaryotes and eukaryotes) exude organic ligands that strongly complex free Cu, rending it non-bioavailable (Moffett and Brand, 1996; Croot et al., 2000; Muller et al., 2005). The two-modal curve in the offshore and northern coastal zones could indicate an active homeostasis regulation of Cu within the smallest size fractions (F1–2). Furthermore, copepods (abundant in F5) have a high requirement for Cu because they used this metal in complexation reactions with amino acids or proteins such as glutathione or metallothionein, respectively (Roesijadi and Robinson, 1994; Rainbow, 2007; Barka et al., 2010; Tlili et al., 2016). Isotopes can also be used as proxies of biogeochemical processes (Takano et al., 2014; Moynier et al., 2017). In a companion study (Chifflet et al., 2022), statistical analyses (non-parametric

Spearman tests) were used to assess relationships between Cu isotopic compositions and copepods. In the northern coastal zone and offshore zone, Spearman's correlation coefficients were weak ($r = 0.14$ and -0.10, respectively) whereas in the southern coastal zone, the Spearman's correlation coefficient was significantly higher ($r = -0.94$, $p < 0.05$). This result suggests that Cu negatively impact copepods' activities in the southern coastal zone. Due to the large anthropogenic inputs in this area, effects of Cu on planktonic food webs should be further investigated.

Biotic Fe presented the same distribution patterns as bCu in the three geographic areas with the highest bFe concentrations for F5 (~ 250 µg/g) in the northern coastal zone, for F2 and F6 (~ 550 µg/g) in the offshore zone, and for F5 (~ 350 µg/g) in the southern coastal zone. No significant differences in bFe concentrations were found between the northern and southern coastal zones, but significant differences in bFe concentrations were found between the northern coastal zone and offshore zone and between the offshore zone and the southern coastal zone. This essential element is well-known to play a key role in biochemical electron transfer processes by increasing the amount of Fe in phytoplankton and heterotrophic bacteria (Whitfield, 2001). The Mediterranean Sea is subject to recurrent natural and anthropogenic dust deposition events leading to surface waters generally enriched in Fe so that the phytoplankton growth is not limited by Fe (Chester et al., 1996; Guieu et al., 1997; Heimbürger et al., 2011; Migon et al., 2020). Based on these considerations, our results suggest the absence of Fe limitation in Mediterranean Sea.

Biotic Mn was the only essential element that showed a bell-shaped distribution in the southern coastal zone, with a maximum bMn concentration in F2 (~ 30 µg/g). No significant differences were found between the three geographical areas and bMn concentrations. In a previous study, Mn was found to bioaccumulate significantly in the smallest marine species (Srichandan et al., 2016) and same Mn concentrations were found in plankton (0.7–20 µm) from the Gulf of Guinea (Chevrollier et al., 2022). Furthermore, feeding behaviour could influence the Mn concentrations in larger plankton (> 300 µm) (Battuello et al., 2017). High bMn concentrations in F2 (nanoeukaryotes) might be easily assimilated by larger plankton (F3–7) and partially excreted *via* dietary pathway. The decrease of bMn concentrations in larger plankton size might be also explained by a 'bio-dilution' effect due to variations in the size of organisms. Due to numerous mechanisms impacting Mn transfer, controlled laboratory experiments are needed to elucidate the role of plankton and environmental conditions in the bM distribution.

Biotic Ni concentrations showed higher variabilities in the offshore and the southern coastal zones (from ~ 1.5 to 3.5 µg/g and from ~ 1 to 3.5 µg/g, respectively) than in the northern coastal zone (from ~ 1 to 1.5 µg/g). No significant differences in bNi concentrations were found between the northern and southern coastal zones, but significant differences in bNi concentrations were found between the northern coastal zone and offshore zone and between the offshore zone and the southern coastal zone. Ni is an essential element for the assimilation of urea, which can be a significant source of nitrogen in biological processes (Whitfield, 2001; Morel et al., 2003). An increase in Ni uptake rates can be observed when phytoplankton (*Synechococcus*, *Prochlorococcus*) consume nitrate rather than ammonium (Dupont et al., 2008). Ni uptake by copepods depends on the exposure routes, and homeostasis regulation are species dependent (Kadiene et al., 2009). These authors showed that in copepods (*Pseudodiaptomus annandalei* and *Eurytemora affinis*), Ni uptake is substantially higher when this metal is absorbed directly from dissolved forms rather than from the diet. Furthermore, they showed that *P. annandalei* had a higher Ni excretion rate than *E. affinis* when copepods were exposed to dissolved forms and similar Ni excretion rates when copepods were exposed to the diet. According to these considerations, we might suggest that the low bNi concentrations in the northern coastal zone could be due to a better homeostasis regulation by planktonic species preferentially feeding on dissolved Ni. Further investigations are necessary to better understand how Ni impacts planktonic food webs in anthropized ecosystems.

Biotic V concentrations showed a two-modal distribution profiles in the three geographical areas with maxima values for F4 (~ 12 µg/g) in the northern coastal zone, for F2 and F6 (~ 2.5 µg/g) in the offshore zone, and for F2 (~ 7.5 µg/g) in the southern coastal zone. No significant differences in bV concentrations were found between the three geographical areas. V is an anthropogenic element that comes mainly from fossil fuel combustion, increasing globally by ~ 9% per year (Schlesinger et al., 2017). V enters the oceans through atmospheric deposition and is rapidly solubilised (Desboeufs et al., 2005). In oceans, V presents vertical profiles implying vertical transport by biological cycling (Jeandel et al., 1987, Sherrel and Boyle, 1988). Therefore, our results suggest that bV concentrations could be due to the atmospheric regional deposition of V in the Mediterranean Sea.

Biotic Zn concentrations followed the typical variations already observed for bCd, bCu, bFe and bNi (a bell-shaped distribution in the northern coastal zone, a flat-shaped in the offshore zone and an increasing gradient in the southern coastal zone) with the highest values for F5 at ~ 125 µg/g in the northern coastal zone, ~ 150 µg/g in the offshore zone, and ~ 110 µg/g in the southern coastal zone. No significant differences in bZn concentrations were found between the northern and southern coastal zones, but significant differences in bZn concentrations were found between the northern coastal zone and offshore zone and between the offshore zone and the southern coastal zone. Zn is an essential element, particularly for eukaryotes, but can readily be replaced by Cd or Co depending on the resident phytoplanktonic communities (Morel, 2008). The primary role of Zn (and Co, Cd) is to uptake inorganic carbon and fix it in the cells (Hudson et al., 1993). Since phytoplankton can adapt their Zn requirements to environmental conditions, even at low concentrations, the limitation of primary production by Zn is anecdotal (Fritzwater et al., 2000; Whitfield, 2001). No specific behaviour of Zn could be observed in the three geographical areas. Our results suggest the absence of Zn limitation in Mediterranean Sea.

3.22 Non-essential elements

Non-essential elements showed very different distribution patterns within the geographical areas (Fig. 3). Biotic As presented a bell-shaped distribution in the northern coastal zone and an increasing gradient in the southern coastal zone with a maximum in F5 (~ 10 µg/g). In the offshore zone, bAs concentrations showed the highest variability with two high values in F2 and F5 fractions (~ 20 µg/g). No significant differences were found between the northern coastal zone and the offshore zone, but significant differences were found between the northern and southern coastal zones and between the offshore zone and the southern coastal zone. Arsenic is a metalloid biochemically similar to P and accumulates in planktonic food webs during adenotriphosphate cycle (Wurl et al., 2013). The distribution and concentration of chemical forms of As vary according to the trophic position or the ability of marine organisms to biotransform As (Wrench et al., 1979; Fattorini et al., 2006). In marine ecosystems, As inputs are mainly from rivers affected by mine drainage and the phosphate fertiliser industry (Elbaz-Poulichet, 2005). Since 1972, several phosphate fertiliser plants have been set up in coastal industrial cities (Sfax, Skhira and Gabès) of the Gulf of Gabès (El Zrelli et al., 2018; Feki-Sahnoun et al., 2019; Gargouri et al., 2021). Moreover, As is also present in a many compound such as pesticides, fertilizers, piles, paints, *etc*. (Warnau et al., 2006). According to these considerations, in the northern and southern coastal zones, we can speculate that lower bAs concentrations could be due to a better homeostasis regulation of As by planktonic food webs. Conversely, offshore, the Mediterranean Sea are nutrient-limited, which is less common in the western basin but is generally due to a lack of phosphate rather than nitrate (Krom et al., 2010; Pujo-Pay et al., 2011; Lazzari et al., 2016). In response to phosphate limitation, Arsenic can be converted to organic forms and excreted *via* methionine metabolism (Maher and Butler, 1988; Uthus, 2003; Du et al., 2021). In this context, we can speculate that high bAs concentrations in the offshore zone could be due to P-substitution, the two-modal distribution showing competition between metabolic processes of nanoeukaryotes (F2) and copepods (F5).

Biotic Cr presented contrasted distribution in the three geographical areas. In the northern coastal zone, bCr concentrations showed two high values in F3 (~ 7.5 µg/g) and in F6 (~ 15 µg/g). In the offshore zone, bCr concentrations decreased with increasing size fractions (from ~ 5 to 0.3 µg/g). Conversely, in the southern coastal zone, bCr concentrations increased with increasing size fractions (from ~ 2.5 to 10 µg/g). No significant differences were found between the northern and southern coastal zones, but significant differences were found between the northern coastal zone and offshore zone and between the offshore zone and the southern coastal zone. In marine environments, Cr mainly exists in trivalent (Cr^{III}) and hexavalent (Cr^{VI}) forms. Cr^{III} can be adsorbed on plankton but hardly transferred to planktonic food webs (Pettine, 2000). In contrast, Cr^{VI} is highly soluble and readily incorporated into planktonic cells through strong oxidative pathways by reacting with nucleic acids and proteins (Levina and Lay, 2008). In the offshore zone, the decrease of bCr might be partly explained by Cr excretion *via* dietary pathway and a possible ‘bio-dilution’ effect due to the decrease surface/volume ratio in higher trophic level organisms. According to previous studies (Dumas et al., 2015; Chifflet et al., 2019), the increase of bCr in the northern and southern coastal zones could be linked to local Cr anthropogenic inputs. Differences between bCr distribution profiles in offshore and coastal zones would require additional study due to their impact on organisms.

Biotic Sb presented a bell-shaped distribution with high values in F5 (~ 10 µg/g) for the offshore zone and in F4 (~ 8 µg/g) for the southern coastal zone. Conversely, bSb concentrations were < 1 µg/g in the northern coastal zone. No significant differences were found between the offshore zone and southern coastal zones, but significant differences were found between the northern coastal zone and offshore zone and between the northern and southern coastal zones. Sb showed conservative profiles in the northernmost western Mediterranean Sea and, enriched surface profiles around the Strait of Sicily probably related to atmospheric deposition (Takayanagi et al., 1996). Sb is present in oxic seawaters as inorganic Sb^{III+V} and methylated species especially in surface waters (Andrea and Froelich, 1984; Cutter and Cutter, 2006). According to the same authors, it biogeochemical cycle is controlled by biogenic uptake, particle scavenging, and regeneration processes. Thus, we can be assumed that geographical differences in bSb arise from differences in Sb atmospheric deposition and/or Sb speciation.

3.3 Biomagnification of metals and metalloids

Various concepts have been mobilised to assess the transfer of metals and metalloids in trophic food webs. Bioconcentration is the absorption of an element into an organism directly from the water through cell membranes. Bioaccumulation refers to the increase of an element in an organism over its lifetime from both the environment and food consumption. To complete these metrics, biomagnification is the increase in the concentration of an element in organisms from prey to predators. While bioconcentration and bioaccumulation describe the increase in concentration of an element in an organism exposed to its environment, biomagnification can be viewed as the increase in the concentration of an element throughout food webs (US EPA 2007; OECD, 2012).

To focus on the objectives of the MERITE-HIPPOCAMPE campaign (contaminant transfer in planktonic food webs), we used the TMF (trophic magnification factor) model to explore the biomagnification of metals and metalloids in the Mediterranean Sea. TMF values were presented per geographical area and element, and statistical measures (r^2) indicated how the TMF model fit with values (Table 3).

3.31 Essential elements

TMF values for Cd were 3.9, 1.1 and 7.5 for the northern coastal, offshore and southern coastal zones, respectively. Due to multiple factors such as diet, excretion and biodilution, Cd does not biomagnify in high TL, but an opposite trend can be observed with lower TL under certain conditions (Liu et al., 2019; Annabi-Trabelsi et al., 2021). For example, *Cyanophyceae*, copepods, cephalopods, and crustaceans are the most Cd-sensitive species, and can accumulate Cd when nutrient inputs increase (Bai et al., 2022). The northern and southern coastal waters are influenced by both nutrients and Cd inputs from urban/industrial activities (Grousset et al., 1995; Teissier et al., 2011; Pasqueron de Fommervault et al., 2015; Heimbürger et al., 2013; El Zrelli et al., 2018; Feki-Sahnoun et al., 2019; Annabi-Trabelsi et al., 2022). According to these considerations, high TMF in the northern and southern coastal zones could possibly be sustained by local nutrients inputs.

TMF values for Cu were 2.2, 1.1 and 6.6 for the northern coastal, offshore and southern coastal zones, respectively. Cu is a micronutrient that plays a key role in primary production but it can also have a negative effect in planktonic species when dissolved Cu exceeds 10 pM (Brand et al., 1986; Peers et al., 2005). To prevent the negative effects, metallothionein and metallothionein-like proteins regulate the uptake, accumulation and excretion rates of certain elements in species (Nfon et al., 2009). Therefore, the low TMF (1.1) in the offshore zone could be explained by better homeostasis regulation of Cu in the species, thus indicating healthy planktonic webs. Conversely, high TMF values in northern and southern coastal zones can probably be due to high organic and mineral inputs to these waters due to the proximity to land.

TMF values for Fe were found at 1.4, 2.0 and 9.6 in the northern coastal, offshore and southern coastal zones, respectively. Due to its implication in nitrite reductase, Fe uptake is high when phytoplankton feed on nitrate rather than on ammonium (Milligan and Harrison, 2000). The high TMF in the southern coastal zone could possibly be influenced by the nitrogen forms originating from the Saharan dust (Khammeri et al., 2018) and local anthropogenic activities (El Zrelli et al., 2018; Chifflet et al., 2019; Feki-Sahnoun et al., 2019; Gargouri et al., 2021). Indeed, in the Gulf of Gabès, both diazotrophic cyanobacteria (*Anabaena sp.*, *Chlorococcus sp.*, *Trichodesmium erythraeum*, *Spirulina sp.*

and *Spirulina subsalsa*) and non-diazotrophic cyanobacteria (*Pseudoanabaena sp.* and *Microcystis sp.*) showed great flexibility in nitrogen assimilation, allowing algal blooms (Drira et al., 2017). The Gulf of Gabès is considered a highly productive area (D'Ortenzio and d'Alcalà, 2009; Ben Brahim et al., 2010). Conversely, the northern coastal zone does not have a high TMF value (1.4) despite atmospheric inputs (Guieu et al., 1997) and the influence of Rhône river inputs (Ollivier et al., 2011). As suggested in the previous section, Fe could appear as a co-factor of planktonic activity and its transfer in planktonic food webs might be species-dependent.

Mn presented few differences in TMF values with respect to geographical areas: 2.7 in the northern coastal zone, 2.0 in the offshore and, 1.2 in the southern coastal zones. Like Fe, Mn is an essential element involved in oxygen transport during photosynthesis (Bruland and Lohan, 2003). Mn biomagnification is poorly documented but is likely depend on both size and species composition (Battuello et al., 2016). In coastal ecosystems where concentrations of dissolved metals can be higher than in the offshore zone, there is a homeostasis regulation in cells with decreasing affinity for Mn and increasing affinity for Cu and Zn *via* metalloproteins (especially the metallothionein group) activity, thereby limiting Mn biomagnification (Whitfield, 2001). The few differences in Mn biomagnification could possibly be explained by the rate of Mn intake and the rate of Mn utilisation in the biochemical processes

TMF values for Ni were found at 1.6, 0.9 and 3.8 for the northern coastal, offshore and southern coastal zones, respectively. Same trends were also observed for Zn (2.5, 1.2 and 4.7 for the northern coastal, offshore and southern coastal zones, respectively). Metals transfers in planktonic food webs result from passive (adsorption and diffusion) and active uptake mechanisms controlled by the bioavailability of elements (Morel et al., 2003; Sunda, 2012). As previously observed, copepods (mainly in F5) play a key role in bM distribution. Indeed, the feeding of copepods can be based both on the absorption of dissolved substances and on the consumption of prey (Wang et al., 2002; Battuello et al., 2017). Coastal ecosystems are particularly sensitive to environmental variations (temperature, pH, salinity, nutrients, dissolved organic matter, light) that also influence the bioavailability of metals and metalloids (Sunda, 2012). Therefore, the biomagnification of Ni and Zn could depend on different environmental conditions between the three geographical areas, and the high TMF values in the southern coastal zone could indicate active biological uptake in this area. The findings agree with Madgett et al. (2021) who suggested a species-specific accumulation of Ni and Zn rather than biomagnification in trophic food webs (zooplankton, invertebrate, fish).

TMF values for V in the offshore and southern coastal zones (0.9 and 1.3, respectively) showed no biomagnification. However, in the northern coastal zone, we observed abnormally high bV concentrations at St4 (Table S3) possibly showing local contamination associated with fossil fuel combustion (Pacyna and Pacyna, 2001; Schlesinger et al., 2017). We therefore assessed the TMF of V using only data from St1–3 (2.2), which was more representative of this geographical area. Biomagnification of V is poorly documented in copepods but biomagnification of V was already observed in crustaceans (Asante et al., 2008). In the present study, decreasing bV concentrations were recorded in F6 and F7 fractions of the three geographical areas. This general pattern could be explained by a possible biodilution effect with increasing species size. However, high bV concentrations were found in the nearshore station of Marseilles bay (St4), where the impact of fossil fuel combustion on trophic food webs should be further investigated.

3.32 Non-essential elements

TMF values for As were 1.1, 1.3 and 3.9 for the northern coastal, offshore and southern coastal zones, respectively. In marine environment, trophic food webs show biodilution of As becoming significant at low phosphate concentrations (Cutter et al., 2001). Mean phosphate concentrations measured at the DCM depth in the MERITE-HIPPOCAMPE campaign were found at 0.09, 0.05 and 0.22 µM in the northern coastal, offshore and southern coastal zones, respectively (Tedetti et al., 2022). Under low phosphate concentrations, As can be converted to organic forms and excreted (Maher and Butler, 1988; Uthus, 2003; Du et al., 2021). This metabolism would limit As biomagnification in the offshore and northern coastal zones. Conversely, in the southern coastal zone, the Gulf of Gabès is surrounded by phosphate-industry plants that enrich the coastal waters through dust deposits or wastewater discharge (El Zrelli et al., 2018; Chifflet et al., 2019; Feki-Sahnoun et al., 2019; Gargouri et al., 2021), which could favour As biomagnification in this area.

Higher TMF values were observed for Cr in the northern (2.1) and southern (5.8) coastal zones compared to the offshore zone (0.8). While negative effects of Cr on cellular metabolism are well known (Levina and Lay, 2008), its transfer into the TL is poorly documented. Despite high bCr concentrations (~ 15 µg/g) at F6 (large copepods and small crustaceans), a moderate TMF (2.1) was found in the northern coastal zone. Previous studies have suggested that phytoplankton can assimilate Cr by extracellular adsorption and sequester it in their cells (Rentería-Cano et al., 2011; Semeniuk et al., 2016). Our study shows that despite Cr inputs from the anthropogenic activities of the cities of Marseilles and Toulon (Tessier et al., 2011; Dumas et al., 2015), excretion and biodilution might partly explain the lower concentrations in zooplankton, thus limiting Cr biomagnification in the northern coastal zone. However, in the southern coastal zone, we found a high TMF (5.8) with a moderate bCr (~ 5 µg/g). This geographical area is highly impacted by anthropogenic activities with recurrent metals and metalloids contamination (El Zrelli et al., 2018; Chifflet et al., 2019; Feki-Sahnoun et al., 2019; Gargouri et al., 2021). In Gdańsk Bay (Poland), Cr bioaccumulation is taxon-specific, with high concentrations for copepods (Pempkowiak et al., 2006). According to our results, under stressful conditions, Cr biomagnification may no longer be controlled by homeostasis regulation and be species-dependent, leading to increased Cr concentrations in planktonic food webs.

TMF values for Sb were found at 3.1, 1.3 and 5.7 for the northern coastal, offshore and southern coastal zones, respectively. Sb biomagnification in the planktonic food web is poorly documented, and to our knowledge the only existing work is in freshwater ecosystems. Sb biomagnification is species-dependent and governed by trophic ecology (Filella et al., 2002). Sb does not biomagnify in primary predators or with the upper TL, but there may be biomagnification processes in autotrophic and heterotrophic organisms under anthropogenic pressure (Obiakor et al., 2017). Our results show high TMF in the northern and southern coastal zones. Further investigation would greatly improve our understanding of the transfer and bioaccumulation processes of Sb on the marine planktonic community in anthropogenic ecosystems.

3. Conclusions

This study evaluated the transfer of metals and metalloids in planktonic food webs (from bacteria to zooplankton) along a North-South Mediterranean transect. Discrimination between biotic (living and dead organic matter and faecal pellets) and geogenic (authigenic and lithogenic matter) components was used to determine concentrations of metals and metalloids bound to the planktonic network. Biotic metals and metalloids concentrations (except Cr, Mn, and V) were higher in the offshore zone than in the coastal zones. In addition, biotic Sb and V concentrations appeared to be affected by atmospheric deposition, and biotic Cr concentrations appeared to be affected by local anthropogenic inputs. While essential elements (Cd, Cu, Fe, Mn, Ni, V, Zn) showed similar patterns of distribution controlled by nanoeukaryotes and copepods, non-essential elements (As, Cr, Sb) showed variable distributions depending on their biochemical characteristics, environmental conditions and the structure of plankton communities. Metals and metalloids were not biomagnified in the offshore zone, probably due to homeostasis regulatory processes in organisms. On the contrary, planktonic food webs presented high biomagnification factors in the northern and southern coastal waters possibly caused by anthropogenic inputs. An excess of non-essential elements can inhibit cell development and nutrient (C, N, P) inputs can improve productivity. Due to these synergistic and antagonistic interactions, more complete consideration should be given in the future to understand the interactive effects between metals and metalloids inputs and plankton growth. For example, in the southern coastal zone, anthropogenic inputs of As, Cd, Cu, Cr and Sb and nutrients could modify the interactions between species and promote metals and metalloids transfers into planktonic food webs. The impact of geogenic inputs on Cu and Zn biogeochemical cycles was studied in more detail using Cu and Zn isotopic compositions in a companion paper (Chifflet et al., 2022) in order to improve our understanding of the transfer of metals and metalloids in the planktonic network.

Supplementary information. The supplementary material related to this article is available online at XXX.

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References

Aminot, A., Kérouel, R., Coverly, S., 2009. Nutrients in seawater using segmented flow analysis. In O. Wurl, O., (Ed.), Practical guidelines for the analysis of seawater, 408p, CRC Press

Andreae, M.O., Froelich, P.N., 1984. Arsenic, antimony and germanium biochemistry in the Baltic Sea. Tellus, 36B, 101-117.

Annabi-Trabelsi, N., Guermazi, W., Karam, Q., Ali, M., Uddin, S., Leignel, V., Ayadi, H., 2021. Concentrations of trace metals in phytoplankton and zooplankton in the Gulf of Gabès, Tunisia. Mar. Pollut. Bull., 168, 112392.

Annabi-Trabelsi, N., Guermazi, W., Leignel, V., Al-Enezi, Y., Karam, Q., Ali, M., Ayadi, H., Belmonte, G., 2022. Effects of Eutrophication on Plankton Abundance and Composition in the Gulf of Gabès (Mediterranean Sea, Tunisia). Waters, 14, 2230.

Asante, K.A., Agusa, T., Mochizuki, H., Ramu, K., Inoue, S., Kubodera, T., Takahashi, S., Subramanian, A., Tanabe, S., 2008. Trace elements and stable isotope ($\delta^{13}C$ and $\delta^{15}N$) in shallow and deep-water organisms from the East China Sea. Environ. Pollut., 156, 862-873.

Ayata, S.D., Irisson, J.O., Aubert, A., Berline, L., Dutay, J.C., Mayot, N., Nieblas, A.E., D'Ortenzio, F., Palmieri, J., Reygondeau, G., Rossi, V., Guieu, C., 2018. Regionalisation of the Mediterranean basin, a MERMEX synthesis. Progr. Oceanogr., 163, 7-20.

Bai, X., Jiang, Y., Jiang, Z., Zhu, L., Feng, J., 2022. Nutrient potentiate the responses of plankton community structure and metabolites to cadmium: A microcosm study. J. Hazard. Mater., 430, 128506.

Barka, S., Pavillon, J.F., Amiard-Triquet, C., 2010. Metal distributions in *Tigriopus brevicornis* (Crustacea, Copepoda) exposed to copper, zinc, nickel, cadmium, silver, and mercury, and implication for subsequent transfer in the food web. Environ. Toxicol., 25, 350-360

Battuello, M., Brizio, P., Mussat, Sartor, R., Nurra, N., Pessani, D., Abete, M.C., Squadrone, S., 2016. Zooplankton from a North Western Mediterranean area as a model of metal transfer in a marine environment. Ecol. Indic., 66, 440-451.

Battuello, M., Sartor, R.M., Brizio, P., Nurra, N., Pessani, D., Abete, M.C., Squadrone, S., 2017. The influence of feeding strategies on trace element bioaccumulation in copepods (*Calanoida*). Ecol. Indic., 74, 311-320.

Béjaoui, B., Ben Ismail, S., Othmani, A., Ben Abdallah-Ben Hadj Hamida, O., Chevalier, C., Feki-Sahnoun, W., Harzallah, A., Ben Hadj Hamida, N., Bouaziz, R., Dahech, S., Diaz, F., Tounsi, K., Sammari, C., Pagano, M., Bel Hassen, M., 2019. Synthesis review of the Gulf of Gabes (eastern Mediterranean Sea, Tunisia): morphological, climatic, physical oceanographic, biogeochemical and fisheries features. Estuar. Coast. Shelf Sci., 219, 395-408.

Ben Brahim, M., Hamza, A., Hannachi, I., Rebai, A., Jarboui, O., Bouain, A., Aleya, L., 2010. Variability in the structure of epiphytic assemblages of *Posidonia oceanica* in relation to human interferences in the Gulf of Gabes, Tunisia. Mar. Environ. Res. 70, 411-421.

Bianchi, C.N., Morri, C., 2000. Marine biodiversity of the Mediterranean Sea: situation, problems and prospects for future research. Mar. Pollut. Bull., 40, 367-376.

Bishop, J.K.B., Lam, P.J., Wood, T.J., 2012. Getting good particles: Accurate sampling of particles by large volume in-situ filtration. Limnol. Oceanogr., 10, 681-710.

Borgå, K., Kidd, K.A., Muir, D.C.G., Berglund, O., Conder, J.M., Gobas, F.A.P.C., Kucklick, J., Malm, O., Powell, D.E., 2012. Trophic magnification factors: Considerations of ecology, ecosystems and study design. Integr. Environ. Assess. Manag., 8, 64-84.

Boudriga, I., Thyssen, M., Zouari, M., Garcia, N., Tedetti, M., Bel Hassen, M., 2022. Ultraphytoplankton community structure in subsurface waters along a North-South Mediterranean transect. Mar. Pollut. Bull., 182, 113977.

Brand, L.E., Sunda, W.G., Guillard, R.R.L., 1986. Reduction in marine phytoplankton reproduction rates by copper and cadmium. J. Exp. Mar. Biol. Ecol., 96, 225-250.

Bruland, K.W., Lohan, M.C., 2003. Control of trace metals in seawater. Treatise Geom., 6, 23-47.

Burkhard, L., Arnot, J.A., Embry, M.R., Farley, K.J., Hoke, R.A., Kitano, M., Leslie, H.A., Lotufo, G.R., Parkerton, T.F., Sappington, K.G., Tomy, G.T., Woodburn, K.B. 2011. Comparing laboratory and field measured bioaccumulation end points. IEAM, 8, 17-31.

Burton, J.D., Statham, P.J., 1990. Trace metals in seawater. In: Heavy Metals in the Marine Environment (Eds. P.S. Rainbow and R. W. Furness). CRC Press, Boca Raton, FL.

Campbell, L.M., Norstrom, R.J., Hobson, K.A., Muir, D.C.G., Backus, S., Fisk, A.T., 2005. Mercury and other trace elements in a pelagic Arctic marine food web (Northwater Polynya, Baffin Bay). Sci. Tot. Environ., 351-352, 247-263.

Chester, R., Nimmo, M., Keyse, S., 1996. The influence of Saharan and Middle Eastern desert-derived dust on the trace metal composition of Mediterranean aerosols and rainwater: An Overview. In: Guerzoni, S., Chester, R. (eds). Environmental Science and Technology Library, 11. 253-273, Springer, New York.

Chevrollier, L.A., Koski, M., Søndergaard, J., Trapp, S., Aheto, D.W., Darpaah, G., Nielsen, T.G., 2022. Bioaccumulation of metals in the planktonic food web in the Gulf of Guinea. Mar. Pollut. Bull., 179, 113662.

Chifflet, S., Tedetti, M., Zouch, H., Fourati, R., Zaghden, H., Elleuch, B., Quéméneur, M., Karray, F., Sayadi, S., 2019. Dynamics of trace metals in a shallow coastal ecosystem: insights from the Gulf of Gabès (southern Mediterranean Sea). AIMS Environ. Sci., 6, 277-297.

Chifflet, S., Briant, N., Freydier, R., Araújo, D.F., Quéméneur, M., Zouch, H., Bellaaj-Zouari, A., Carlotti, F., Tedetti, M. 2022. Isotopic compositions of Copper and Zinc in plankton from the Mediterranean Sea (MERITE-HIPPOCAMPE campaign): tracing trophic transfer and geogenic inputs. Mar. Pollut. Bul., in revision, this special issue.

Chouvelon, T., Strady, E., Harmelin-Vivien, M., Radakovitch, O., Brach-Papa, C., Crochet, S., Knoery, J., Rozuel, E., Thomas, B., Tronczynski, J., Chiffoleau, J.F., 2019. Patterns of trace metal bioaccumulation and trophic transfer in a phytoplankton-zooplankton-small pelagic fish marine food web. Mar. Pollut. Bull., 146, 1013-1030.

Collier, R., Edmond, J., 1984. The trace element geochemistry in marine biogenic particulate matter. Progr. Oceanogr., 13, 113-199.

Cossa, D., Coquery, M., 2005. The Mediterranean mercury anomaly, a geochemical or a biological issue. In: Saliot, A. (Ed.), The Mediterranean Sea. Handbook of Environmental Chemistry, pp. 177-208.

Cossa, D., Knoery, J., Banaru, D., Harmelin-Vivien, M., Sonke, J.E., Hedgecock, I.M., Bravo, A.G., Rosati, G., Canu, D., Horvat, M., Sprovieri, F., Pirrone, N., Heimbürger-Boavida, L.E., 2022. Mediterranean Mercury Assessment 2022: An Updated Budget, Health Consequences, and Research Perspectives. Environ. Sci. Technol., 56, 3840-3862.

Croot, P.L., Moffett, J.W., Brand, L.E., 2000. Production of extracellular Cu complexing ligands by eukaryotic phytoplankton in response to Cu stress. Limnol. Oceanogr., 45, 619-627.

Cullen, J., Sherrell, R.M., 1999. Techniques for determination of trace metals in small samples of size-fractionated particulate matter: Phytoplankton metals off central California. Mar. Chem., 67, 233-247.

Cutter, G.A., Cutter, L.S., Featherstone, A.M., Lohrenz, S.E., 2001. Antimony and arsenic biogeochemistry in the western Atlantic Ocean. Deep-Sea Res. II, 48, 2895–2915.

Cutter, G.A., Cutter, L.S., 2006. Biogeochemistry of arsenic and antimony in the North Pacific Ocean. Geochem, Geophys, 7, 1-12.

Cutter, G., Casciotti, K., Croot, P., Geibert, W., Heimbürger, L.E., Lohan, M., Planquette H., Van de Flierdt, T., 2017. Sampling and sample-handling protocols for GEOTRACES cruises. GEOTRACES Community Practices, Version 3, 139 pp. & Appendices.

D'Ortenzio, F., d'Alcalà, M.R., 2009. On the trophic regimes of the Mediterranean Sea: a satellite analysis. Biogeosciences, 6, 139-148.

Dammshäuser, A., Wagener, T., Garbe-Schönberg, D., Croot, P., 2013. Particulate and dissolved aluminum and titanium in the upper water column of the Atlantic Ocean. Deep-Sea Res. I, 73, 127-139.

Desboeufs, K.V., Sofikitis, A., Losno, R., Colin, J.L., Ausset, P., 2005. Dissolution and solubility of trace metals from natural and anthropogenic aerosol particulate matter. Chemosphere, 58, 195-203.

Donat, J. R., Bruland, K.W., 1995. Trace elements in the oceans. In: Trace Elements in Natural Waters (Eds. E. Steinnes and B. Salbu). CRC Press, Boca Raton, FL.

Drira, Z., Chaari, D., Hamza, A., Bel Hassen, M., Pagano, M., 2017. Diazotrophic cyanobacteria signatures and their relationship to hydrographic conditions in the Gulf of Gabes, Tunisia. J. Mar. Biolog. Assoc. U.K., 97, 69-80.

Du, S., Zhou, Y., Zhang, L., 2021. The potential of arsenic biomagnification in marine ecosystems: A systematic investigation in Daya Bay in China. Sci. Tot. Environ., 773, 145068.

Dumas, C., Ludwig, W., Aubert, D., Eyrolle, F., Raimbault, P., Gueneugues, A., Sotin, C., 2015. Riverine transfer of anthropogenic and natural trace metals to the Gulf of Lions (NW Mediterranean Sea). Appl. Geochemistry, 58, 14-25.

Dupont, C.L., Barbeau, K., Palenik, B., 2008. Ni uptake and limitation in marine *Synechococcus* strains. Appl. Environ. Microbiol., 74, 23-31.

El Zreli, R., Rabaoui, L., Alaya, M.B., Daghbouj, N., Castet, S., Besso, P., Michel, S., Bejaoui, N., Courjault-Radé, P., 2018. Seawater quality assessment and identification of pollution sources along the central coastal area of Gabes Gulf (SE Tunisia): Evidence of industrial impact and implications for marine environment protection. Mar. Pollut. Bull., 127, 445-452.

Elbaz-Poulichet, F., 2005. River Inputs of Metals and Arsenic. In: Saliot, A. (Ed). The Mediterranean Sea, Handbook of Environ. Chem., Springer, Berlin, 5, 211-235.

Fattorini, D., Notti, A., Regoli, F., 2006. Characterization of arsenic content in marine organisms from temperate, tropical, and polar environments. 22, 405-414.

Feki-Sahnoun, W., Njah, H., Barraj, N., Mahfoudi, M., Akrout, F., Rebai, A., Bel Hassen, M., Hamza, A. 2019. Influence of phosphorus-contaminated sediments in the abundance of potentially toxic phytoplankton along the Sfax Coasts (Gulf of Gabes, Tunisia). Journal of Sedimentary Environments, 4, 458-470.

Fierro-González, P., Pagano, M., Guilloux, L., Makhlouf, N., Carlotti F. 2022. Comparative zooplankton structure and functioning in epipelagic layers of different Mediterranean regions during the HIPPOCAMPE cruise. Mar. Pollut. Bul., in preparation, this special issue.

Filella, M., Belzile, N., Chen, Y.W., 2002. Antimony in the environment: A review focused on natural waters. I. Occurence. Earth-Sci. Rev., 57, 125-176.

Fritzwater, S.E., Johnson, K.S., Gordon, R.M., Coale, K.H., Smith, W.O., 2000. Trace metal concentration in the Ross Sea and their relationship with nutrients and phytoplankton growth. Deep Sea Res., 47, 3159-3179.

Gao, Y., Wang, R., Li, Y., Ding, X., Jiang, Y., Feng, J., Zhu, L., 2021. Trophic transfer of heavy metals in the marine food web based on tissue residuals. Sci. Tot. Environ., 772, 145064.

Gargouri, D., Annabi-Trabelsi, N., Karam, Q., Ali, M., Ayadi, H., 2021. Assessment of metallic pollution in the waters, suspended particulate matter, and surface sediments of the central coastal area of the Gulf of Gabès, Mediterranean Sea. J. Mater. Environ. Sci., 12, 584-594.

Goldberg, E.D., 1954. Marine Geochemistry 1. Chemical Scavengers of the Sea. J. Geol., 62, 249-265.

Grousset, F. E., Quetel, C. R., Thomas, B., Donard, O. F. X., Lambert, C. E., Guillard, F., Monaco, A., 1995. Anthropogenic vs. lithogenic origins of trace elements (As, Cd, Pb, Rb, Sb, Sc, Sn, Zn) in water column particles: northwestern Mediterranean Sea. Mar. Chem., 48, 291-310.

Guieu, C., Chester, R., Nimmo, M., Martin, J. M., Guerzoni, S., Nicolas, E., Mateu, J., Keyse, S., 1997. Atmospheric input of dissolved and particulate metals to the northwestern Mediterranean. Deep Sea Res., Part II, 44, 655 – 674

Guieu, C., Loÿe-Pilot, M.D., Ridame, C., Thomas, C., 2002. Chemical characterization of the Saharan dust end-member: Some biogeochemical implications for the western Mediterranean Sea. J. Geophys. Res., 107 (D15), 4258.

Guieu, C., Loÿe-Pilot, M.D., Benyaya, L., Dufour, A., 2010. Spatial variability of atmospheric fluxes of metals (Al, Fe, Cd, Zn and Pb) and phosphorus over the whole Mediterranean from a one-year monitoring experiment; biogeochemical implications. Mar. Chem., 120, 164-178.

Hazen, E.L., Abrahms, B., Brodie, S., Carroll, G., Jacox, M.G., Savoca, M.S., Scales, K.L., Sydeman, W.J., Bograd, S.J., 2019. Marine top predators as climate and ecosystem sentinels. Front. Ecol. Environ. 17, 565-574

Heimbürger, L.E, Migon, C., Dufour, A., Chiffoleau, F., Cossa, D., 2010. Trace metal concentrations in the North-western Mediterranean atmospheric aerosol between 1986 and 2008: Seasonal patterns and decadal trends. Sci. Tot. Environ., 408, 2629-2638.

Heimbürger, L.E., Mignon, C., Cossa, D., 2011. Impact of atmospheric deposition of anthropogenic and natural trace metals on Northern Mediterranean surface waters: A box model assessment. Environ. Pollut., 159, 1629-1634.

Heimbürger, L.E, Lavigne, H., Migon, C., D'Ortenzio, F., Estournel, C., Coppola, L., Miquel, J.C., 2013. Temporal variability of vertical export flux at the DYFAMED time-series station (Northwestern Mediterranean Sea). Progr. Oceanogr., 119, 59-67.

Ho, T.Y., Quigg, A., Finkel, Z.V., Milligan, A.J., Wyman, K., Falkowski, P.G., Morel, F.M.M, 2003. The elemental composition of some marine phytoplankton. J. Phycol., 39, 1145-1159.

Ho, T.Y., Wen, L.S., You, C.F., Lee, D.C., 2007. The trace metal composition of size-fractionated plankton in the South China Sea: Biotic versus abiotic sources. Limnol. Oceanogr., 52, 1776-1788.

Ho, T.Y., Chou, W.C., Wei, C.L., Lin, F.J, Wong, G.T.F., Lin, H.L., 2010. Trace metal cycling in the surface water of the South China Sea: Vertical fluxes, composition, and sources. Limnol. Oceanogr., 55, 1807-1820.

Hudson, R.J.M., Morel, F.M.M., 1993. Trace metal transport by marine microorganisms. Implications of metal coordination kinetics. Deep Sea Res. Part I, 40, 129-150.

Hunt, B.P.V., Carlotti, F., Donoso, K., Pagano, M., D'Ortenzio, F., Taillandier, V., Conan, P., 2017. Trophic pathways of phytoplankton size classes through the zooplankton food web over the spring transition period in the north-west Mediterranean Sea. J. Geophys. Res., 122, 6309–6324.

Jeandel, C., Caisso, M., Minster, J.F., 1987. Vanadium behavior in the global ocean and in the Mediterranean Sea. Mar. Chem., 21, 51-74.

Jordi, A., Basterretxea, G., Tovar-Sánchez, A., Alastuey, A., Querol, X., 2012. Copper aerosols inhibit phytoplankton growth in the Mediterranean Sea. PNAS, 109, 21246-21249.

Kadiene, E.U., Ouddane, B., Hwang, J.S., Souissi, S., 2019. Bioaccumulation of metals in calanoid copepods by oral intake. Sci. Rep., 9, 9492.

Khammeri, Y., Hamza, I.S., Bellaaj-Zouari, A., Hamza, A., Sahli, E., Akrout, F., Ben Kacem, M.Y., Messaoudi, S., Bel Hassen, M., 2018. Atmospheric bulk deposition of dissolved nitrogen, phosphorus and silicate in the Gulf of Gabès (South Ionian Basin); implications for marine heterotrophic prokaryotes and ultraphytoplankton. Cont. Shelf Res., 159, 1-11.

Kidd, K.A., Burkhard, L.P., Babut, M., Borgå, K., Muir, D., Perceval, O., Ruedel, H., Woodburn, K., Embry, M.R., 2018. Practical advice for selecting or determining trophic magnification factors for application under the European Union Water Framework Directive. Integr. Environ. Assess. Manag., 15, 266-277.

Krom, M. D., Emeis, K.-C., and Cappellen, P. V., 2010. Why is the Eastern Mediterranean phosphorus limited? Prog. Oceanogr., 85, 236-244.

Lane, T.W., Morel, F.M.M., 2000. A biological function for cadmium in marine diatoms. PNAS, 97, 46627-4631.

Lazzari, P., Solidoro, C., Salon, S., Bolzon, G., 2016. Spatial variability of phosphate and nitrate in the Mediterranean Sea: A modeling approach. Deep-Sea Res., 108, 39-52.

Leblanc, K., Quéguiner, B., Diaz, F., Cornet, V., Michel-Rodriguez, M., Durrieu de Madron, X., Bowler, C., Malviya, S., Thyssen, M., Gregori, G., Rembauville, M., Grosso, O., Poulain, J., de Vargas, C., Pujo-Pay, M., Conan, P., 2018. Nanoplanktonic diatoms are globally overlooked but play a role in spring blooms and carbon export. Nature Communication, 9, 953.

Lee, J.G., Roberts, S.B., Morel, F.M.M., 1995. Cadmium: A nutrient for the marine diatom *Thalassiosira weissflogli*. Limnol. Oceanogr., 40, 1056-1063.

Lefevre, D., Mins, H.J., Robinson, C., Williams, P.J. Le B., Woodward, E.M.S., 1997. Review of gross community production, primary production, net community production and dark community respiration in the Gulf of Lions. Deep Sea Res. II, 44, 801-832.

Lemaitre, N., Planquette, H., Dehairs, F., Planchon, F., Sarthou, G., Gallinari, M., Roig, S., Jeandel, C., Castrillejo, M., 2020. Particulate Trace Element Export in the North Atlantic (GEOTRACES GA01 Transect, GEOVIDE Cruise). ACS Earth Space Chem., 4, 2185-2204.

Levina, A., Lay, P., 2008. Chemical properties and toxicity of chromium (III) nutritional supplements. Chem. Res. Toxicol., 21, 563-571.

Liao, W.H., Yang, S.C., Ho, T.Y., 2017. Trace metal composition of size-fractionated plankton in the Western Philippine Sea: The impact of anthropogenic aerosol deposition. Limnol. Oceanogr., 62, 2243-2259.

Liu, J., Cao, L., Dou, S., 2019. Trophic transfer, biomagnification and risk assessments of four common heavy metals in the food web of Laizhou Bay, the Bohai Sea. Sci. Tot. Environ., 670, 508-522.

Madgett, A.S., Yates, K., Webster, L., McKenzie, C., Moffat, C.F., 2021. The concentration and biomagnification of trace metals and metalloids across four trophic levels in a marine food web. Mar. Pollut. Bull., 173, 112929.

Maher, W., Butler, E., 1988. Arsenic in the marine environment. Appl. Oceanogr. Chem., 2, 191-214.

Martin, J.M., Whitfield, M., 1983. The significance of the river input of chemical elements to the ocean. In: Wong, C.S., Boyle, E., Bruland, K.W., Burton, J.D., Goldberg, E.D., (Ed). Trace Metals in Seawater. Plenum, New York, 265-296.

Marañón, E., Wambeke, F., Uitz, J., Boss, E., Dimier, C., Dinasquet, J., Engel, A., Haëntjens, N., Pérez-Lorenzo, M., Taillandier, V., Zäncker, B., 2021. Deep maxima of phytoplankton biomass, primary production and bacterial production in the Mediterranean Sea. Biogeosciences, 18, 1749-1767.

Maxwell, S.M., Hazen, E.L., Bograd, S.J., Halpern, B.S., Breed, G.A., Nickel, B., Teutschel, N.M., Crowder, L.B., Benson, S., Dutton, P.H., Bailey, H., Kappes, M.A., Kuhn, C.E., Weise, M.J., Mate, B., Shaffer, S.A., Hassrick, J.L., Henry, R.W., Irvine, L., McDonald, B.I., Robinson, P.W., Block, B.A., Costa, D.P., 2013. Cumulative human impacts on marine predators. Nat. Commun. 4, 1–9

Mayot, N., D'Ortenzio, F., Uitz, J., Gentili, B., Ras, J., Vellucci, V., Golbol, M., Antoine, D., Claustre, H., 2017. Influence of the Phytoplankton Community Structure on the Spring and Annual Primary Production in the Northwestern Mediterranean Sea, J. Geophys. Res., 122, 9918–9936. doi:10.1002/2016JC012668

The MerMex Group, 2011. Marine ecosystems' responses to climatic and anthropogenic forcings in the Mediterranean. Progr. Oceanogr., 91, 97-166.

Migon, C., Heimbürger-Boavida, L.E., Dufour, A., Chiffoleau, J.F., Cossa, D., 2020. Temporal variability of dissolved trace metals at the DYFAMED time-series station, Northwestern Mediterranean. Mar. Chem., 225, 103846.

Mille, T., Cresson, P., Chouvelon, T., Bustamante, P., Brach-Papa, C., Bruzac, S., Rozuel, E., Bouchacha, M., 2018. Trace metal concentrations in the muscle of seven marine species: Comparison between the Gulf of Lions (North-West Mediterranean Sea) and the Bay of Biscay (North-East Atlantic Ocean). Mar. Pollut. Bull., 135, 9-16.

Milligan, A.J., Harrison, P.J., 2000. Effects of non-steady-state iron limitation on nitrogen assimilatory enzymes in the marine diatom *Thalassiosira weissflogii* (Bacillariophyceae). J. Phycol., 36, 78-86.

Moffett, J. W., Brand, L. E., 1996. Production of strong, extracellular Cu chelators by marine cyanobacteria in response to Cu stress. Limnology and oceanography, 41, 388-395.

Morel, F.M.M., Milligan, A.J., Saito, M.A. 2003. Marine bioinorganic chemistry: The role of trace metals in the oceanic cycles of major nutrients. Treatise Geochem., 6, 113-143.

Morel, F.M.M., 2008. The co-evolution of phytoplankton and trace element cycles in the oceans. Geobiology, 6, 318-324.

Moynier, F., Vance, D., Fujii, T., Savage, P., 2017. The Isotope Geochemistry of Zinc and Copper. Rev. Mineral. Geochem., 82, 543-600.

Muller, F.L.L., Larsen, A., Stedmon, C.A., Sondergaard, M., 2005. Interactions between algal–bacterial populations and trace metals in fjord surface waters during a nutrient-stimulated summer bloom. Limnol. Oceanogr., 50, 1855-1871.

Nfon, E., Cousins, I.T., Jarvinen, O., Mukherjee, A.B., Verta, M., Broman, D., 2009. Trophodynamics of mercury and other trace elements in a pelagic food chain from the Baltic Sea. Sci. Total Environ., 407, 6267-6274.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature, 333, 134-139.

Obiakor, M.O., Tighe, M., Pereg, L., Wilson, S.C., 2017. Bioaccumulation, trophodynamics and ecotoxicity of antimony in environmental freshwater food webs. Crit. Rev. Environ. Sci., 47, 2208-2258.

OECD, 2012. Test Guideline 305. Bioaccumulation in Fish: Aqueous and Dietary Exposure. Adopted 2 October 2012.

Ohnemus, D., Lam, P.J., 2015. Cycling of lithogenic marine particles in the US GEOTRACES North Atlantic transect. Deep-Sea Res. II, 116, 283-302.

Ollivier, P., Radakovitch, O., Hamelin, B., 2011. Major and trace element partition and fluxes in the Rhône River. Chem. Geol., 285, 15-31.

Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environ. Rev., 9, 269-298.

Pasqueron de Fommervault, O., Migon, C., D'Ortenzio, F., Ribera d'Alcalà, Coppola, L., 2015. Temporal variability of nutrient concentrations in the northwestern Mediterranean Sea (DYFAMED time-series station). Deep Sea Res. I, 100, 1-12.

Peers, G., Quesnel, S.A., Price, N.M., 2005. Copper requirements for iron acquisition and growth of coastal and oceanic diatoms. Limnol. Oceanogr., 50, 1149-1158.

Pempkowiak, J., Walkusz-Miotk, J., Beldowski, J., Walkusz, W., 2006. Heavy metals in zooplankton from the Southern Baltic. Chemosphere, 62, 1697-1708.

Pérez, S., Beiras, R., 2010. The mysid *Siriella armata* as a model organism in marine ecotoxicology: comparative acute toxicity sensitivity with *Daphnia magna*. Ecotoxicol., 19, 196-206.

Pettine, M., 2000. Redox Processes of Chromium in Sea Water. In: Gianguzza, A., Pelizetti, E., Sammartano, S. (Ed). Chemical Processes in Marine Environments. Environmental Science. Springer, Berlin.

Planquette, H., Sherrell, R.M., 2012. Sampling for particulate trace element determination using water sampling bottles: methodology and comparison to in situ pumps. Limnol. Oceanogr. Methods, 10, 367-388.

Pujo-Pay, M., Conan, P., Oriol, L., Cornet-Barthaux, V., Falco, C., Ghiglione, J.-F., Goyet, C., Moutin, T., Prieur, L., 2011. Integrated survey of elemental stoichiometry (C, N, P) from the western to eastern Mediterranean Sea, Biogeosciences, 8, 883–899.

Quigg, A., Finkel, Z.V., Irwin, A.J., Rosenthal, Y., Ho, T.Y., Reinfelder, J.R., Schofield, O., Morel, F.M.M., Falkowski, P.G., 2003. The evolutionary inheritance of elemental stoichiometry in marine phytoplankton. Nature, 425, 291-294.

Radakovich, O., Roussiez, V., Ollivier, P., Ludwig, W., Grenz, C., Probst, J.L., 2008. Particulate heavy metals input from rivers and associated sedimentary deposits on the Gulf of Lions continental shelf. Estuar. Coast. Shelf Sci., 77, 285-295.

Raimbault, P., Diaz, F., Pouvesle W., Boudjellal, B., 1999. Simultaneous determination of particulate organic carbon, nitrogen and phosphorus collected on filters, using a semiautomatic wet-oxidation method. Mar. Ecol. Prog. Ser., 180, 289-295.

Rainbow, P.S., 2007. Trace metal bioaccumulation: models, metabolic availability and toxicity. Environ. Int., 33, 576-582.

Ramírez-Romero, E., Molinero, J.C., Sommer, U., Salhi, N., Kefi- Daly Yahia, O., Daly Yahia, M.N., 2020. Phytoplankton size changes and diversity loss in the southwestern Mediterranean Sea in relation to long-term hydrographic variability. Estuarine, Coastal and Shelf Science, 235, 106574.

Rauch, J.N., 2010. Global spatial indexing of the human impact on Al, Cu, Fe and Zn mobilization. Environ. Sci. Technol., 44, 5728-5734.

Redfield, A.C., 1958. The biological control of chemical factors in the environment. Am. Sci., 46, 205-221.

Rentería-Cano, M.E., Sánchez-Velasco, L., Shumilin, E., Lavín, M.F., Gómez-Gutiérrez, J., 2011. Major and trace elements in zooplankton from the northern gulf of California during summer. Biol. Trace Elem. Res., 142, 848–864

Roesijadi, G., Robinson, W.E., 1994. Metal regulation in aquatic animals: mechanisms of uptake, accumulation and release. Aquat. Toxicol. 102, 125-133.

Salhi, N., Zmerli Triki, H., Molinero, J.C., Laabir, M., Sehli, E., Bellaaj-Zouari, A., Daly Yahia, N., Kefi-Daly Yahia, O., 2018. Seasonal variability of picophytoplankton under contrasting environments in northern Tunisian coasts, southwestern Mediterranean Sea. Marine Pollution Bulletin, 129, 866–874.

Sanganyado, E., Bi, R., Teta, C., Buruaem Moreira, L., Yu, X., Yajing, S., Dalu, T., Rajput, I.R., Liu, W., 2021. Toward an integrated framework for assessing micropollutants in marine mammals: challenges, progress, and opportunities. Crit. Rev. Environ. Sci. Technol. 51, 2824–2871

Schlesinger, W.H., Klein, E.M., Vengosh, A., 2017. Global biogeochemical cycle of vanadium. Proc. Nat. Acad. Sci. U. S. A., 114, E11092-E11100.

Semeniuk, D.M., Maldonado, M.T., Jaccard., S.L., 2016. Chromium uptake and adsorption in marine phytoplankton – Implications for the marine chromium cycle. Geochim. Cosmochim. Acta, 184, 41-54

Sherrell, R.M., Boyle, E.A., 1988. Zinc, chromium, vanadium and iron in the Mediterranean Sea. Deep Sea Res., 35, 1319-1334.

Srichandan, S., Panigraphy, R.C., Baliarsingh, S.K., Srinivasa, R.B., Premalata, P., Sahu, B.K., Sahu, K.C., 2016. Distribution of trace metals in surface seawater and zooplankton of the Bay of Bengal, off Rushikulya estuary, East Coast of India. Mar. Pollut. Bul., 111, 468-475.

Sunda, W., 2012. Feedback interactions between trace metal nutrients and phytoplankton in the ocean. Front. Microbiol., 3, 204.

Sunda, W., Huntsman, S.A., 1995. Regulation of copper concentration in the oceanic nitracline by phytoplankton uptake and regeneration cycles. Limnol. Oceanogr., 40, 132-137.

Takano, S., Tanimizu, M., Hirata, T., Sohrin, Y., 2014. Isotopic constraints on biogeochemical cycling of copper in the ocean. Nat. Com., 5, 5663.

Tanhua, T., Hainbucher, D., Schroeder, K., Cardin, V., Alvarez, M., Civitarese, G., 2013. The Mediterranean Sea system: a review and an introduction to the special issue. Ocean Sci., 9, 789-803.

Takayanagi, K., Cossa, D., Martin, J.M., 1996. Antimony cycling in the western Mediterranean. Mar. Chem., 54, 303-312.

Tedetti, M., Tronczynski, J., Carlotti, F., Pagano, M., Sammari, C., Bel Hassen, M., Ben Ismail, S., Desboeufs, K., Poindron, C., Chifflet, S., Abdennadher, M., Amri, S., Bănarua, D., Ben Abdallah, L., Bhairy, N., Boudriga, I., Bourin, A., Brach-Papa, C., Briant, N., Cabrol, L., Chevalier, C., Chouba, L., Coudray, S., Daly Yahia, M.N., de Garidel-Thoroni T., Dufour, A., Dutay, J.-C., Espinasse, B., Fierro, P., Fornier, M., Garcia, N., Giner, F., Guigue, C., Guilloux, L., Hamza, A., Heimbürger-Boavida, L.-E., Jacquet, S., Knoery, J., Lajnef, R., Makhlouf Belkahia, N., Malengros, D., Martinot, P.L., Bosse, A., Mazur, J.-C., Meddeb, M., Misson, B., Pringault, O., Quéméneur, M., Radakovitch, O., Raimbault, P., Ravel, C., Rossi, V., Rwawi, C., Sakka Hlaili, A., Tesán-Onrubia, J.A., Thomas, B., Thyssen, M., Zaaboub, N., Bellaaj-Zouari, A., Garnier, C., 2022. Contamination of planktonic food webs in the Mediterranean Sea: Setting the frame for the MERITE-

HIPPOCAMPE oceanographic cruise (spring 2019). Mar. Pollut. Bull., submitted to this special issue.

Tesán-Onrubia, J.A., Tedetti, M., Carlotti, F., Tenaille, M., Guilloux, L., Pagano, M., Lebreton, B., Guillou, G., Fierro-Gonzalez, P., Guigue, C., Chifflet, S., Garcia, T., Boudriga, I., Belhassen, M., Bellaaj-Zouari, A., Bănaru, D. Spatial variations of stable isotope ratios and biochemical content of size-fractionated plankton in the Mediterranean Sea (MERITE-HIPPOCAMPE campaign). Mar. Pollut. Bull., submitted to this special issue.

Tessier, E., Garnier, C., Mullot, J.U., Lenoble, V., Arnaud, M., Raynaud, M., Mounier, S., 2011. Study of the spatial and historical distribution of sediment inorganic contamination in the Toulon bay (France). Mar. Pollut. Bull., 62, 2075-2086.

Tlili, S., Ovaert, J., Souissi, A., Ouddane, B., Souissi, S., 2016. Acute toxicity, uptake and accumulation kinetics of nickel in an invasive copepod species: *Pseudodiaptomus marinus*. Chemosphere, 144, 1729-1737.

Twining, B.S., Baines, S.B., 2013. The trace metal composition of marine phytoplankton. Annu. Rev. Mar. Sci., 5, 191-215.

Twining, B.S., Fisher, N.S., 2004. Trophic transfer of trace metals from protozoa to mesozooplankton. Limnol. Oceanogr., 49, 28-39.

Turekian, K.K., 1977. The fate of metals in the ocean. Geochim. Cosmochim. Acta, 41, 1139-1144.

UNEP/MAP-RAC-SPA, 2008. Impact of climate change on biodiversity in the Mediterranean Sea. In: Perez T., RAC/SPA (Eds.), Tunis, 1-61.

US EPA. 2007. Framework for Metals Risk Assessment. EPA-120-R-07-001. United States Environmental Protection Agency, Washington DC.

Uitz, J., Claustre, H., Morel, A., Hooker, S.B., 2006. Vertical distribution of phytoplankton communities in open ocean: An assessment based on surface chlorophyll. J. Geophys. Res., 111, C08005.

Uthus, E.O., 2003. Arsenic essentiality: a role affecting methionine metabolism. J. Trace Elem. Exp. Med., 16, 345-355.

Wang, W.X., 2002. Interactions of trace metals and different marine food chains. Mar. Ecol. Prog. Ser., 243, 295-309.

Warnau, M., Gómez-Batista, M., Alonso-Hernández, Carlos, Regoli, F., 2006. Arsenic: is it worth monitoring in the Mediterranean Sea? In: CIESM Workshop Monographs n°31, 83-86.

Whitfield, M., 2001. Interactions between phytoplankton and trace metals in the ocean. Adv. Mar. Biol., 41, 1-128.

Wrench, J., Fowler, S.W., Ünlü, M.Y., 1979. Arsenic metabolism in a marine food chain. Mar. Pollut. Bull., 10, 18-20.

Wurl, O., Zimmer, L., Cutter, G.A., 2013. Arsenic and phosphorus biogeochemistry in the ocean: Arsenic species as proxies for P-limitation. Limnol. Oceanogr., 58, 729-740.

Xu, Y., Feng, L., Jeffrey, P.D., Shi, Y.D., Morel, F.M.M., 2008. Structure and metal exchange in the cadmium carbonic anhydrase of marine diatoms. Nature, 452, 56-61.

Table 1. Variations of biotic metal (bM) concentrations in all fractions reported per element and per geographical areas. Statistical values (mean ± standard deviation, min and max concentrations) were expressed in µg/g. The coefficient of variation (CV) was expressed in %. Data were compared with other values from suspended particulate matter and zooplankton collected in Mediterranean Sea.

Biotic trace metals	**As**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Sb**	**V**	**Zn**
North coastal zone (Marseilles-Toulon bays, 4 stations: St1, St2, St3, St4; n = 25)										
Mean (µg/g)	6.7±3.6	0.52±0.44	7.9±8.1	5.9±3.9	212±119	6.7±4.6	1.4±0.6	0.41±0.27	8.4±15	93±63
Min (µg/g)	1.8	0.04	0.08	1.6	35	0.84	0.55	0.10	0.27	25
Max (µg/g)	14	1.7	26	17	527	20	2.7	1.0	49	261
CV (%)	54	84	102	66	56	69	45	66	183	68
Offshore zone (Western Mediterranean Sea, 3 stations: St9, St10, St11; n = 18)										
Mean (µg/g)	12.7±13.1	0.83±0.60	2.1±3.0	6.9±2.8	389±258	5.3±3.2	2.9±1.3	4.9±8.0	2.0±1.3	139±58
Min (µg/g)	0.60	0.10	0.27	1.6	50	1.5	0.78	0.01	0.48	41
Max (µg/g)	50	2.4	13	13	838	14	5.9	25	3.9	260
CV (%)	103	72	146	40	66	60	44	166	63	42
South coastal zone (Gulf of Gabès, 3 stations: St15, St17, St19; n = 12)										
Mean (µg/g)	2.4±1.3	0.52±0.25	4.0±2.8	3.5±2.3	209±146	11±17	1.9±1.4	4.7±4.4	4.0±6.1	75±44
Min (µg/g)	0.14	0.03	0.39	0.4	13	0.02	0.08	0.07	0.08	5.0
Max (µg/g)	4.6	0.84	9.3	7.0	523	55	5.0	13	19	133
CV (%)	52	48	71	64	70	159	70	94	154	59
Suspended particulate matter at the deep chlorophyll maximum (spring and summer 2010), Gulf of Lions[1]										
Mean (µg/g)	-	0.35±0.19	-	14±15	-	-	16±25	-	-	152±
Min (µg/g)	-	0.14	-	3.3	-	-	1.8	-	-	41
Max (µg/g)	-	0.58	-	20	-	-	66	-	-	439
Zooplankton (Spring 2014), Offshore Italian coasts[2]										
5-50 m depth (µg/g)	0.46	0.08	7.25	4.64	539	5.55	5.48	0.48	0.89	132
50-100 m depth (µg/g)	0.65	0.16	0.87	3.72	1742	8.82	2.04	0.59	1.18	80

[1]Choulevon et al., 2019 ; [2]Battuello et al., 2016

Table 2: Mean bM/POP ratio ± standard deviation (mmol/mol) in planktonic food webs per element and geographical areas. Mean bM/POP ratios were calculated including all fractions (n = 25 in the northern coastal zone; n = 18 in the offshore zone; n = 12 in the southern coastal zone).

	Northern coastal zone	**Offshore zone**	**Southern coastal zone**
As	1.11 ± 0.74	1.06 ± 0.76	0.39 ± 0.11
Cd	0.04 ± 0.02	0.06 ± 0.05	0.06 ± 0.03
Cr	1.37 ± 1.36	0.33 ± 0.39	0.91 ± 0.26
Cu	0.89 ± 0.34	0.85 ± 0.37	0.65 ± 0.15
Fe	38.0 ± 11.0	45.3 ± 23.0	40.4 ± 10.1
Mn	1.18 ± 0.51	0.62 ± 0.13	3.36 ± 5.1
Ni	0.24 ± 0.04	0.35 ± 0.07	0.37 ± 0.12
Sb	0.03 ± 0.01	0.17 ± 0.31	0.38 ± 0.54
V	3.35 ± 6.28	0.27 ± 0.14	1.39 ± 2.04
Zn	13.08 ± 5.00	13.98 ± 5.22	12.47 ± 3.95

Table 3: Trophic magnification factor (TMF) of essential (Cd, Cu, Fe, Mn, Ni, V, Zn) and non-essential (As, Cr, Sb) elements along the North-South Mediterranean transect. TMF values were calculated from the regression line between log-transformed bM and trophic level (see Appendix 2 for supplementary information), per geographic area and element. Statistical measures (r^2) indicated how the model fit with values.

	Essential elements							**Non-essential elements**		
	Cd	**Cu**	**Fe**	**Mn**	**Ni**	**V**	**Zn**	**As**	**Cr**	**Sb**
Northern coastal zone (n = 25)										
TMF	3.9	2.2	1.4	2.7	1.6	2.2*	2.6	1.1	2.1	3.1
r^2	0.26	0.34	0.22	0.45	0.20	0.49	0.40	0.30	0.38	0.37
Offshore zone (n = 18)										
TMF	1.1	1.1	2.0	2.0	0.9	0.9	1.2	1.3	0.8	1.3
r^2	0.12	0.3	0.59	0.86	0.20	0.30	0.74	0.23	0.23	0.17
Southern coastal zone (n = 12)										
TMF	7.5	6.6	9.6	1.2	3.8	1.3	4.7	3.9	5.8	5.7
r^2	0.71	0.47	0.45	0.24	0.36	0.10	0.63	0.50	0.39	0.11

* TMF (n = 20)

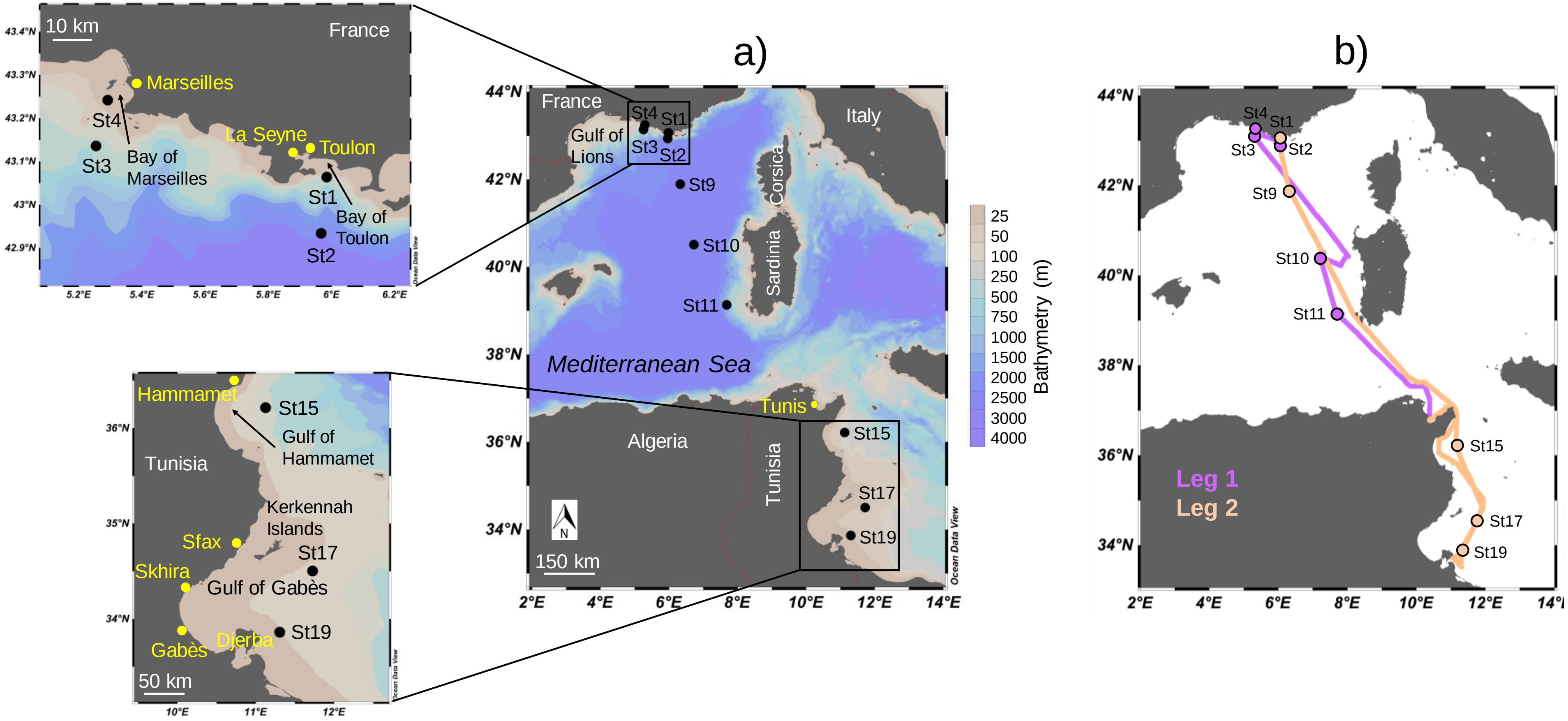


Figure 1. a) Location of the sampling stations in the Mediterranean Sea. b) Details of the MERITE-HIPPOCAMPE campaign tracks: Leg 1 (from La Seyne-sur-Mer to Tunis) with 5 sampling stations (St2, St4, St3, S10 and St11 in chronological order); Leg 2 (from Tunis to the Gulf of Gabès to La Seyne-sur-Mer) with 5 sampling stations (St15, St17, St19, St9 and St1 in chronological order).

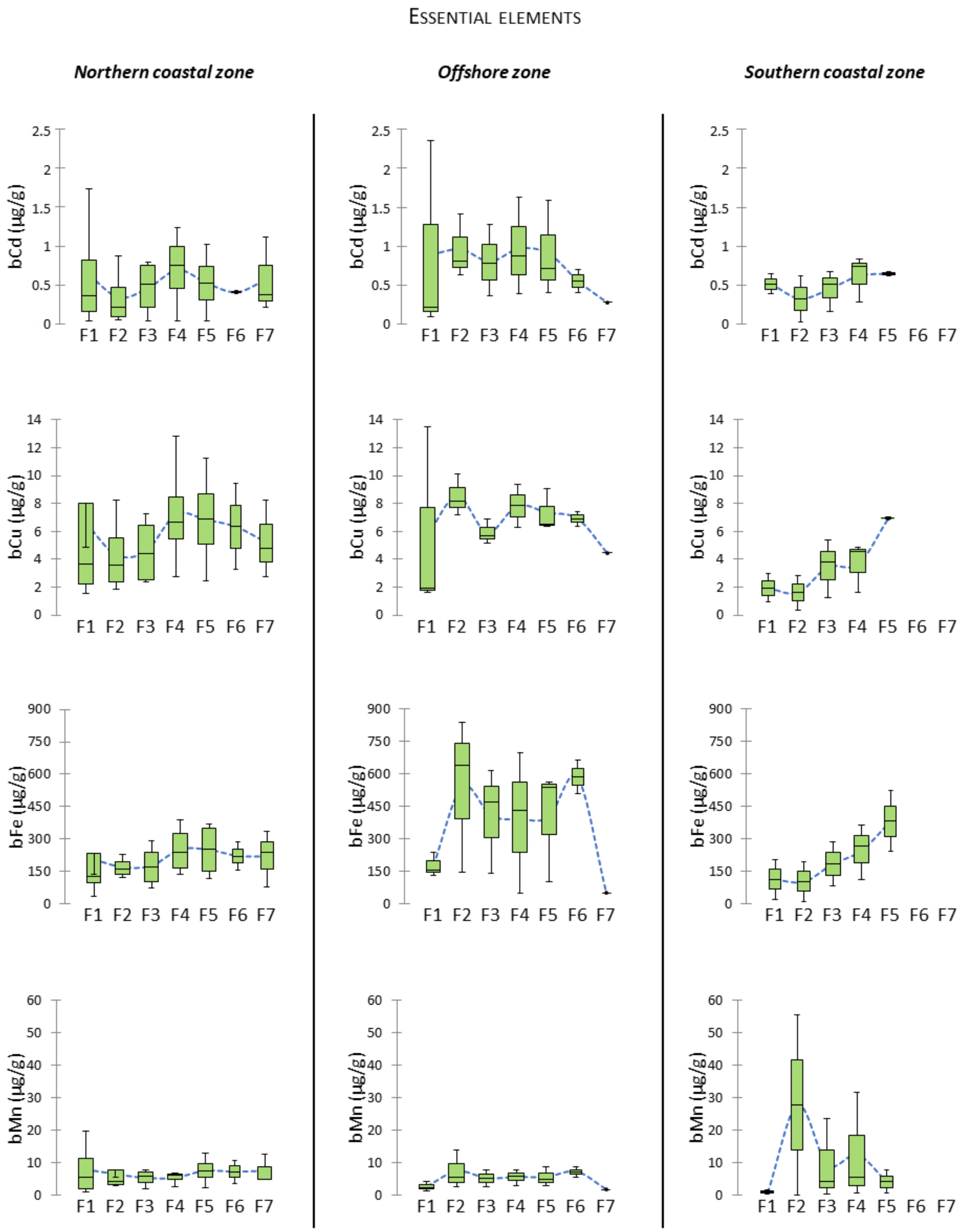


Figure 2. Trophic distribution of 7 essential elements (Cd, Cu, Fe, Mn, Ni, V, Zn) in 3 geographical areas along the North-South Mediterranean transect. The boxplots represent the variations in bCd, bCu, bFe, bMn, bNi, bV and bZn concentrations (µg/g) in the northern coastal zone (4 stations, St1-4), offshore zone (3 stations, St9-11) and southern zone (3 stations, St15, St17, St19) and include the 7 particle size-fraction classes (F1: 0.8–3 µm; F2: 3–20 µm; F3: 60–200 µm; F4: 200–500 µm; F5: 500–

1000 µm; F6: 1000–2000 µm; F7 > 2000 µm). Boxplots show the first quartile (25%), median, and third quartile (75%). The dashed blue line plots the median bM concentrations. Box plots were created using Xlstat software package version 2019.1.1 (Addinsoft 2020, Boston, USA, https://www.xlstat.com).

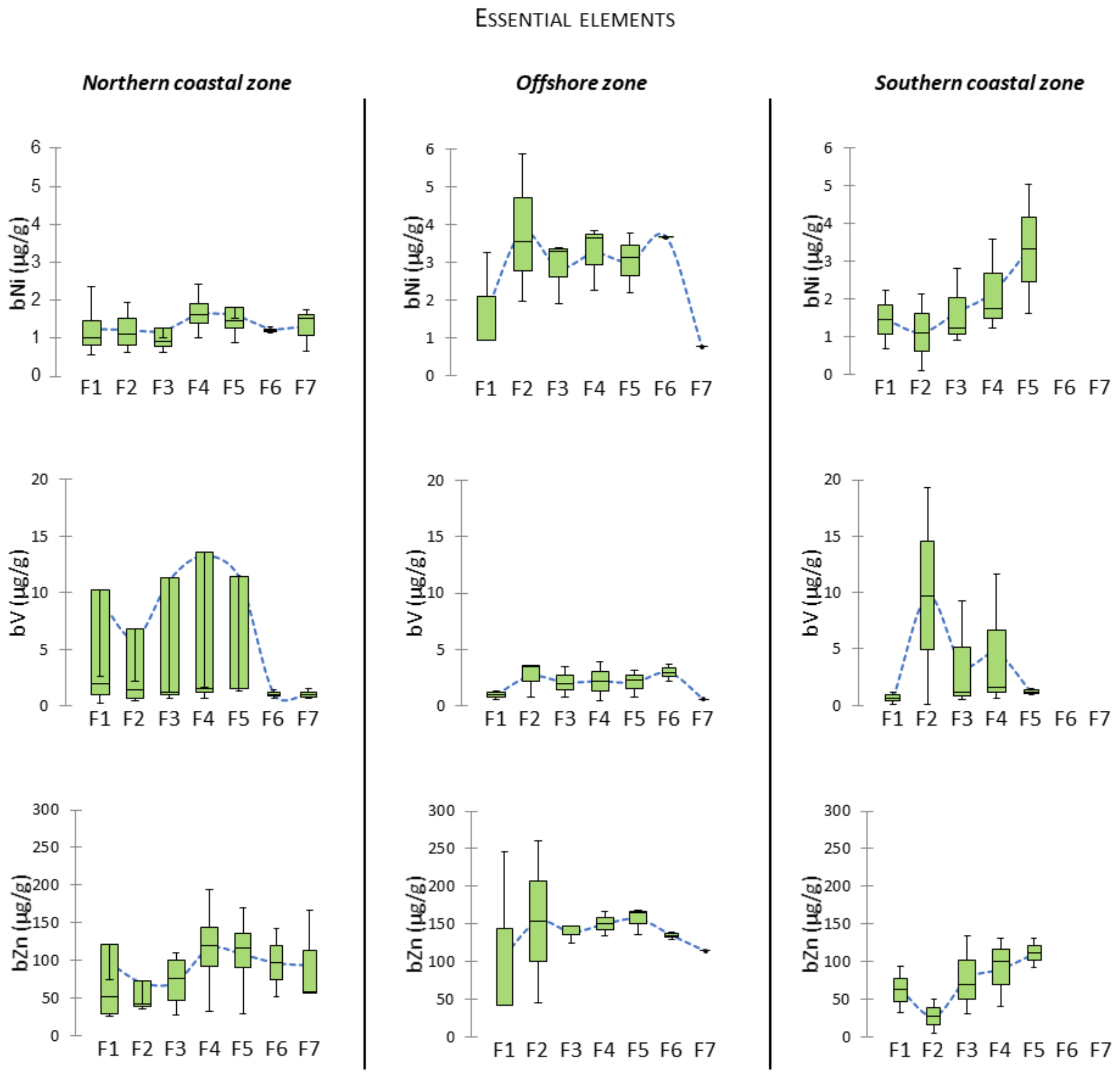


Figure 2 (continue)

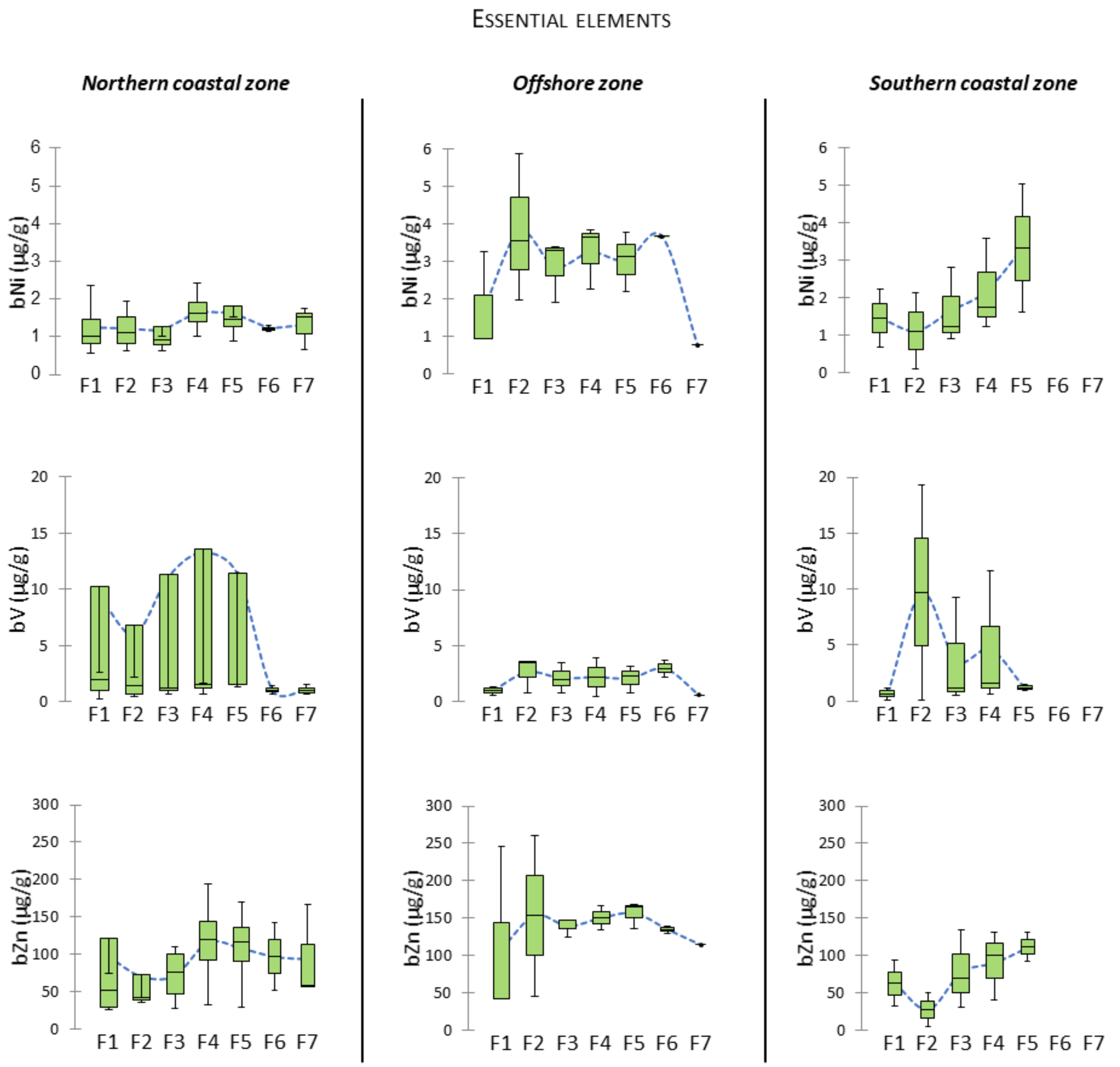


Figure 3. Trophic distribution of 3 non-essential elements (As, Cr, Sb) in 3 geographical areas along the North-South Mediterranean transect. The boxplots represent the variations in bAs, bCr and bSb concentrations (µg/g) in the northern coastal zone (4 stations, St1-4), offshore zone (3 stations, St9-11) and southern zone (3 stations, St15, St17, St19) and include the 7 particle size-fraction classes (F1: 0.8–3 µm; F2: 3–20 µm; F3: 60–200 µm; F4: 200–500 µm; F5: 500–1000 µm; F6: 1000–2000 µm; F7 > 2000 µm). Boxplots show the first quartile (25%), median, and third quartile (75%). The dashed blue line plots the median bM concentrations. Box plots were created using Xlstat software package version 2019.1.1 (Addinsoft 2020, Boston, USA, https://www.xlstat.com).

APPENDIX 1

Data processing: determination of biotic metal concentrations

Metals and metalloids concentrations in samples can be expressed using the mass balance formula (equation 1):

$$[M]_{sample} = a.[Ti]_a + b.[POP]_b \qquad (1)$$

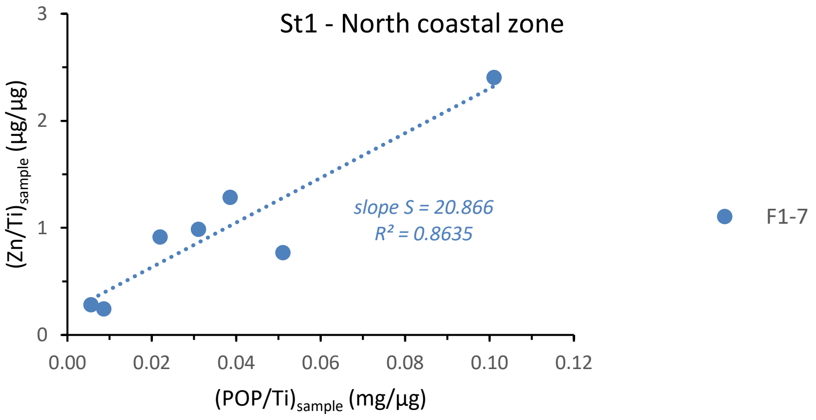
where a is the Ti-normalized elemental ratio in geogenic component; b is the P-normalized elemental ratio in biotic component; $[M]_{sample}$ is the elemental concentration in the sample; $[Ti]_a$ is the Ti concentration in geogenic component and $[POP]_b$ is the particulate organic phosphorus concentration in the biotic component. Assuming that P and Ti concentrations in samples are mainly due to the biotic and geogenic components, respectively ($[POP]_{sample} \equiv [POP]_b$; $[Ti]_{sample} \equiv [Ti]_a$), we can turn the mass balance formula into the first-order equation 2:

$$\frac{[M]_{sample}}{[Ti]_{sample}} \equiv S.\frac{[POP]_{sample}}{[Ti]_{sample}} + C \qquad (2)$$

where S is the slope of the regression line between M/Ti and POP/Ti in the sample; C is a constant value. Following this basic model, metals and metalloids concentrations in biotic component were evaluated from equation 3:

$$[bM] \equiv b.[POP]_{sample} \qquad (3)$$

The slope S was calculated for each station and for each element using the samples in the 7 particle size classes F1-7 (Fig. S1). Detailed of $[M]_{sample}$ and $[POP]_{sample}$ were presented in Table S3.



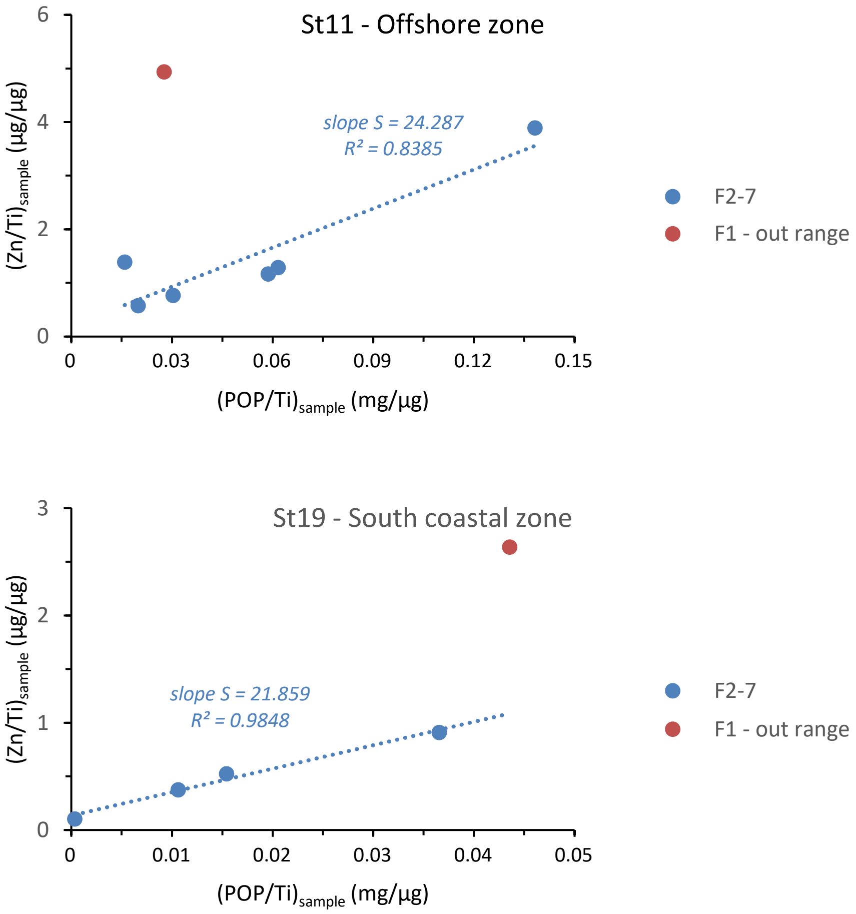


Figure S1. Linear regressions between $(Zn/Ti)_{sample}$ and $(POP/Ti)_{sample}$ in St1 (northern coastal zone), St11 (offshore zone) and St19 (southern coastal zone). Data were from particulate size classes (F1: 0.8-3; F2: 3-20; F3: 60-200; F4: 200-500; F5: 500-1000; F6: 1000-2000 and F7 > 2000 µm) collected at the deep chlorophyll maximum. Concentrations were expressed in µg/g for Zn and Ti, and in mg/g for POP. At St19, data for F6 and F7 were not available. Zn_{sample} concentrations in F1 at St11 and St19 (red point) were higher than expected and were not included in the linear regression.

APPENDIX 2

Data processing: determination of trophic magnification factors

Due to the complexity and variability of taxonomic groups, planktonic marine food webs were structured in trophic level (TL) according to the following equation (Kidd et al, 2018):

$$TL_{Fn} = 1.0 + \frac{(\delta^{15}N_{Fn} - \delta^{15}N_{baseline})}{\Delta^{15}N} \qquad (1)$$

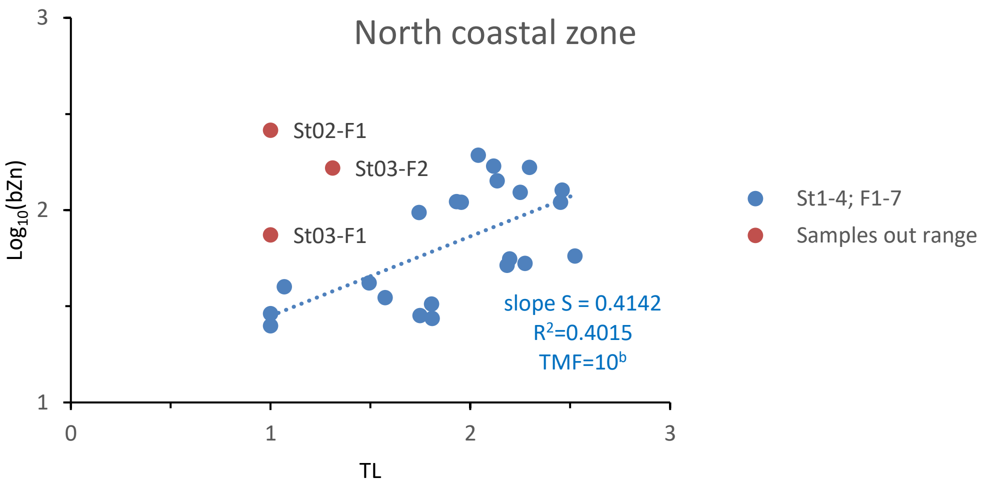
where TL_{Fn} is the TL of the sample corresponding to the fraction Fn, $\delta^{15}N_{Fn}$ and $\delta^{15}N_{baseline}$ are the $\delta^{15}N$ values of fractions Fn and a baseline, respectively. The fraction F1 (0.8-3 µm) is assumed to be the baseline fraction with a TL_{F1} defined to 1.0 as TL corresponding to the phytoplankton communities. $\Delta^{15}N$ (= $\delta^{15}N_{prey} - \delta^{15}N_{predator}$) is the isotopic ^{15}N fractionation between prey and predator. For marine food webs, $\Delta^{15}N$ vary from +3.3 to +3.8‰ (Liu et al., 2019) and a value of +3.4‰ is recommend without precise knowledge on the composition of the trophic structure (Post, 2002). TL determination were detailed in a companion study (Tésan-Onrubia et al., 2022) and results shown in Table S4.

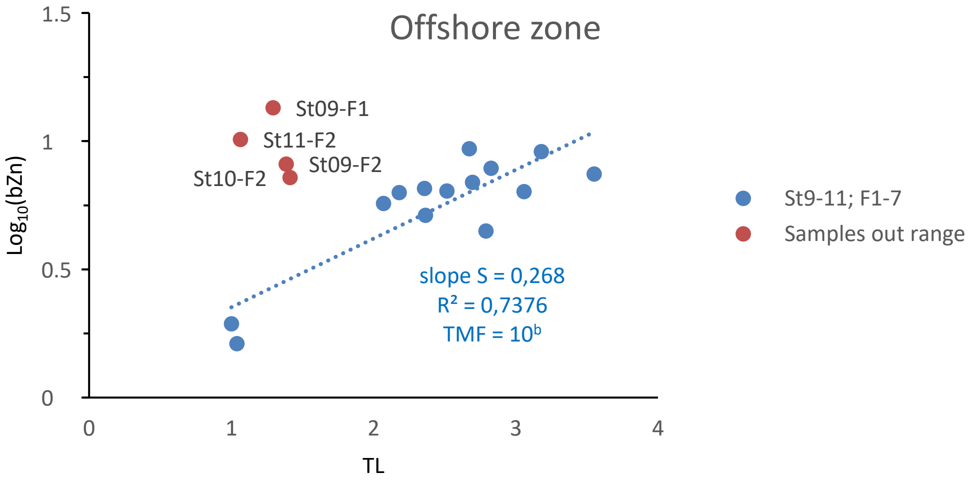
Trophic magnification factor (TMF) is most often derived from the slope of the regression of log-transformed element against their corresponding trophic level (TL) and, N isotope ($\delta^{15}N$) is used as proxy to assess the relative trophic position of an organism in marine food webs.

$$Log_{10}(bM) = S.(TL) + C \qquad (2)$$

$$TMF = 10^{S} \qquad (3)$$

where bM is the biotic metal concentration, S is the slope of the linear equation 2 and, TL is the trophic level corresponding to the sample (Fig. S2). Specific TMF (equation 3) were calculated for each geographical area (the northern coastal zone, the offshore zone and the southern coastal zone) from their respective data (stations and fractions).


North coastal zone
Log$_{10}$(bZn)
TL
3
2
1
0
1
2
3
St02-F1
St03-F2
St03-F1
slope S = 0.4142
R^2=0.4015
TMF=10^b
St1-4; F1-7
Samples out range


Offshore zone
Log$_{10}$(bZn)
TL
1.5
1
0.5
0
0
1
2
3
4
St09-F1
St11-F2
St09-F2
St10-F2
slope S = 0,268
R² = 0,7376
TMF = 10^b
St9-11; F1-7
Samples out range

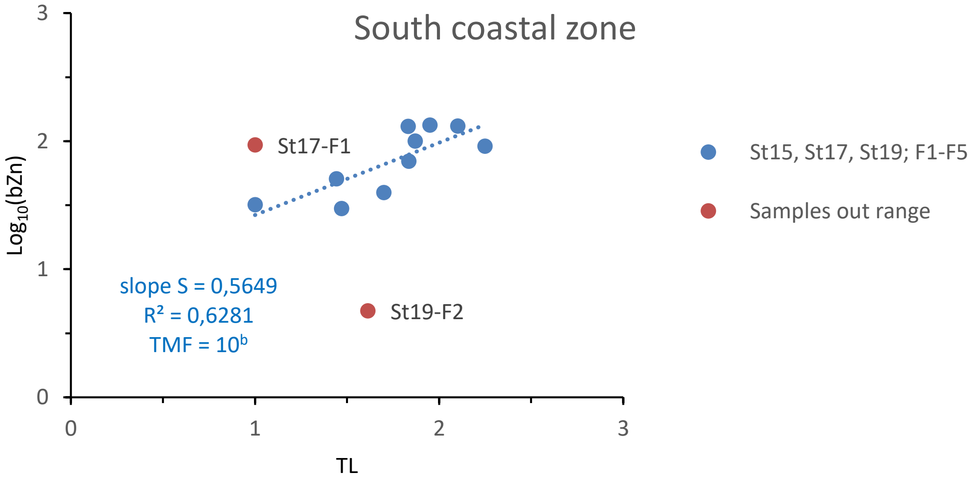

South coastal zone
Log$_{10}$(bZn)
TL
3
2
1
0
0
1
2
3
St17-F1
St19-F2
slope S = 0,5649
R² = 0,6281
TMF = 10^b
St15, St17, St19; F1-F5
Samples out range

Figure S2. Determination of the linear regressions between the log-transformed of bZn concentrations in relation to the trophic level (TL) in the 3 geographical areas (the northern coastal zone, the offshore zone and the southern coastal zone). The northern coastal, offshore and southern coastal zones included 25, 18 and 12 data from available stations and fractions. Detailed values were presented in Table S4.

References:

Kidd K.A., Burkhard L.P., Babut M., Borga K., Muir D., Perceval O., Ruedel H., Woodburn K., Embry M.R., 2018. Practical advice for selecting or determining trophic magnification factors for application under the European Union Water Framework Directive. Integr. Environ. Assess. Manag., 15, 266-277.

Liu J., Cao L., Dou S., 2019. Trophic transfer, biomagnification and risk assessments of four common heavy metals in the food web of Laizhou Bay, the Bohai Sea. Sci. Tot. Environ., 670, 508-522.

Post DM., 2002. Using stable isotopes to estimate trophic position: Models, methods, and assumptions. Ecol., 83,703-718.

Tesán-Onrubia, J.A., Tedetti, M., Carlotti, F., Tenaille, M., Guilloux, L., Pagano, M., Lebreton, B., Guillou, G., Fierro-Gonzalez, P., Guigue, C., Chifflet, S., Garcia, T., Boudriga, I., Belhassen, M., Zouari, A., Bănaru, D. Spatial variations of stable isotope ratios and biochemical content of size-fractionated plankton in the Mediterranean Sea (MERITE-HIPPOCAMPE campaign). Mar. Pollut. Bull., submitted to this special issue.

Table S1. GPS position of sampling stations

Station	**Latitude (North)**	**Longitude (East)**
St01	43°3.819'	5°59.080'
St02	42°56.020'	5°58.041'
St03	43°8.150'	5°15.280'
St04	43°14.500'	5°17.500'
St09	41°53.508’	6°19.998'
St10	40°18.632'	7°14.753'
St11	39°7.998'	7°41.010'
St15	36°12.883'	11°7.641'
St17	34°30.113’	11°43.573'
St19	33°51.659'	11°18.509'

Table S2. Detail of the quality control of metals metalloids analyses (certified material for marine plankton, BCR 414; blank filters, MCE; limit of detection, LOD). Mean metals and metalloids concentrations and standard deviation (σ) associated are expressed in µg/g. The limit of detection (LOD) are expressed in µg/L.

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Sb**	**Ti**	**V**	**Zn**
CMR BCR 414											
Mean (n = 3)	8.03	0.36	21.97	29.08	1702.68	-	19.27	-	-	8.71	121.70
σ (n = 3)	0.07	0.04	2.62	0.96	160.79	-	0.10	-	-	0.34	19.31
Recovery (%)	117.7	93.9	92.3	98.6	92.0	-	102.5	-	-	107.6	109.1
BLANK MCE filter, 47mm											
Mean 0.8µm (n = 6)	0.03	0.05	2.21	0.41	10.57	0.33	0.31	0.01	2.65	0.06	8.16
σ 0.8µm (n = 6)	0.01	0.01	0.64	0.3	3.94	0.09	0.05	0.00	0.29	0.01	5.14
Mean 3µm (n = 3)	0.03	0.05	1.48	0.48	10.02	0.49	0.34	0.02	2.43	0.06	3.44
σ 3µm (n = 3)	0.01	0.01	0.07	0.16	2.16	0.01	0.03	0.00	0.01	0.01	0.08
LOD (µg/L)	0.01	0.005	0.008	0.01	0.2	0.008	0.2	0.005	0.02	0.008	0.1

Table S3. Detail of total metals and metalloids (M_{sample}) concentrations (µg/g) and particulate organic phosphorus (POP_{sample}) concentrations (mg/g) in samples from the MERITE-HIPPOCAMPE campaign. Particles were collected in the deep chlorophyll maximum, at 10 stations (St1-4, St9-11, St15, St1, St19) and sieved into 7 size fractions (F1: 0.8-3 µm; F2: 3-20 µm; F3: 60-200 µm; F4: 200-500 µm; F5: 500-1000 µm; F6: 1000-2000 µm; F7 > 2000 µm).

Station	***Fraction***	**POP**	**Ti**	**As**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Sb**	**V**	**Zn**
St01	*F1*	1.20	54.75	1.85	0.65	0.08	6.80	35.39	0.84	1.22	-	0.27	50.01
St01	*F2*	1.92	222.40	12.59	1.04	2.98	21.10	2046.29	155.80	13.54	0.28	9.62	54.16
St01	*F3*	4.67	150.25	14.88	1.40	4.93	8.63	964.05	23.85	6.85	1.24	4.35	148.10
St01	*F4*	5.32	52.66	10.48	1.15	2.39	8.95	303.00	6.85	4.41	0.99	1.38	126.70
St01	*F5*	5.94	153.94	20.28	1.10	7.82	10.85	940.75	20.17	8.73	4.28	4.05	197.97
St01	*F6*	2.48	445.09	23.40	0.53	8.91	11.60	2243.06	66.28	11.13	14.61	12.12	125.54
St01	*F7*	3.84	75.24	5.19	0.38	0.78	4.76	261.46	4.96	2.73	0.29	0.96	57.85
St02	*F1*	5.81	178.12	14.04	3.45	14.69	72.41	1151.66	96.98	22.61	0.32	5.67	702.33
St02	*F2*	1.56	164.06	2.31	0.10	-	10.63	311.84	20.39	5.44	0.33	1.02	35.16
St02	*F3*	2.45	59.07	10.22	1.18	18.63	20.57	630.02	7.72	9.09	0.94	1.42	216.00
St02	*F4*	4.31	36.71	13.02	1.24	8.12	13.49	498.32	6.47	6.43	0.70	0.74	193.30
St02	*F5*	3.78	93.59	10.67	0.64	39.55	13.58	1404.05	13.11	18.07	1.94	1.36	214.78
St02	*F6*	3.16	132.60	6.38	0.39	78.14	12.81	5336.71	32.82	25.22	1.96	1.54	160.32
St02	*F7*	3.72	204.53	6.31	1.44	41.74	8.21	1207.48	13.19	13.47	3.43	1.51	242.53
St03	*F1*	3.05	281.64	7.63	1.51	2.80	39.57	671.96	16.39	10.00	0.13	1.81	74.43
St03	*F2*	5.15	217.47	13.35	2.66	9.47	53.76	1201.47	74.83	26.41	0.62	3.81	278.15
St03	*F3*	1.64	79.50	6.68	0.58	12.99	9.69	537.55	7.74	8.89	5.10	2.40	165.67
St03	*F4*	3.97	54.81	5.90	0.60	5.85	10.42	277.98	5.52	7.41	5.99	1.81	530.69
St03	*F5*	3.71	61.61	5.92	0.40	7.92	6.82	311.61	6.45	8.03	8.61	2.01	110.16
St03	*F6*	3.17	-	-	-	-	-	-	-	-	-	-	-
St03	*F7*	1.74	47.76	11.46	0.21	3.00	5.78	202.60	6.31	5.72	10.24	1.32	60.04
St04	*F1*	1.48	113.04	16.22	1.38	6.88	28.60	975.87	29.86	7.49	0.10	33.25	221.92
St04	*F2*	2.26	100.38	13.58	0.05	-	1.86	225.40	9.30	5.29	0.16	20.64	41.83
St04	*F3*	1.40	32.29	17.27	0.08	3.10	4.07	345.98	5.09	2.25	1.16	44.83	33.63
St04	*F4*	1.67	91.86	55.40	0.27	5.33	8.37	816.25	11.94	4.57	3.78	181.14	70.51
St04	*F5*	1.45	197.55	8.78	0.21	18.17	12.55	1483.43	20.42	9.78	12.28	40.97	111.47
St04	*F6*	-	243.14	7.26	0.13	23.03	16.99	1724.68	29.33	18.73	37.75	43.28	149.42
St04	*F7*	-	-	-	-	-	-	-	-	-	-	-	-
St09	*F1*	4.61	272.74	32.77	9.13	12.67	22.59	837.73	20.41	12.21	0.13	4.30	1406.61
St09	*F2*	2.79	75.47	24.08	1.61	-	9.38	311.79	16.13	5.29	0.11	2.25	45.59
St09	*F3*	2.70	59.35	9.61	1.27	2.14	5.14	268.96	4.48	3.66	1.23	1.42	124.11
St09	*F4*	3.19	16.46	13.63	1.76	0.48	9.65	50.21	3.07	6.47	1.90	0.48	149.54
St09	*F5*	3.11	37.56	12.98	1.88	1.81	9.36	103.79	3.05	6.92	2.01	0.78	197.92
St09	*F6*	-	37.78	24.25	0.65	0.62	7.50	151.64	2.80	2.17	1.65	1.39	132.38
St09	*F7*	-	125.60	1.92	0.75	2.18	11.59	76.35	9.63	3.85	0.03	0.69	63.88
St10	*F1*	1.30	82.28	11.71	1.16	9.97	11.05	159.17	5.06	3.90	0.01	2.89	419.09
St10	*F2*	4.82	266.50	59.10	5.26	-	54.68	855.84	73.65	21.62	0.49	9.76	190.45

St10	*F3*	4.61	267.03	12.90	1.64	13.35	9.81	1633.36	31.99	12.47	7.39	7.47	189.76
St10	*F4*	5.24	133.86	7.40	1.13	4.53	9.14	890.99	15.60	8.66	11.62	4.30	177.28
St10	*F5*	4.24	186.16	8.87	0.82	5.26	8.76	1151.63	24.55	10.05	22.25	5.91	141.08
St10	*F6*	4.98	274.68	11.53	0.71	8.39	9.59	1466.68	37.43	14.16	34.95	7.61	139.39
St10	*F7*	-	-	-	-	-	-	-	-	-	-	-	-
St11	*F1*	1.65	59.70	3.35	0.55	2.01	9.20	185.21	2.98	2.45	0.03	0.78	294.65
St11	*F2*	10.31	516.78	50.05	4.53	-	71.22	1827.99	154.07	36.26	0.78	13.73	297.99
St11	*F3*	5.80	191.10	16.74	1.47	5.05	9.32	892.33	16.07	7.50	17.60	6.47	147.16
St11	*F4*	6.39	103.69	11.07	1.23	1.57	8.17	430.96	7.64	6.12	16.49	9.20	133.56
St11	*F5*	6.64	417.43	57.16	5.91	11.86	40.09	2013.35	37.76	30.71	82.17	36.96	580.68
St11	*F6*	6.48	110.36	12.34	1.07	1.88	9.21	508.19	10.11	4.77	16.57	3.94	129.32
St11	*F7*	4.52	32.72	24.89	1.72	0.27	5.11	51.11	1.72	0.78	1.96	0.55	127.42
St15	*F1*	0.72	25.49	1.98	1.05	1.24	8.09	22.95	0.14	2.33	-	0.67	176.64
St15	*F2*	10.52	617.62	42.59	8.37	-	65.05	4624.77	161.33	28.58	0.93	66.75	438.98
St15	*F3*	3.03	316.03	17.87	0.68	5.98	9.28	1322.87	28.57	8.79	12.65	14.96	148.03
St15	*F4*	3.83	234.89	9.93	0.84	4.22	7.33	1153.40	15.07	5.80	14.70	10.62	130.82
St15	*F5*	5.47	146.14	11.45	0.62	2.15	9.14	692.88	13.66	5.03	7.70	7.52	130.38
St15	*F6*	-	264.53	11.46	0.59	6.16	8.18	1740.47	18.71	5.17	9.72	10.80	108.30
St15	*F7*	-	59.99	8.77	0.40	1.14	3.26	393.85	5.47	1.47	4.46	3.41	42.61
St17	*F1*	2.81	240.31	6.42	0.65	2.96	19.25	246.77	1.56	6.30	-	1.18	308.61
St17	*F2*	2.68	675.56	10.63	0.69	11.71	20.25	4803.63	63.26	11.69	0.32	19.30	50.58
St17	*F3*	1.14	178.13	31.09	0.16	3.26	5.81	920.72	26.82	6.03	7.76	9.30	29.63
St17	*F4*	1.52	290.34	34.57	0.28	4.90	5.85	1475.74	34.71	6.74	12.62	11.62	39.70
St17	*F5*	-	590.41	3.11	0.71	150.45	21.92	2238.08	37.59	158.97	1.90	6.90	192.53
St17	*F6*	-	-	-	-	-	-	-	-	-	-	-	-
St17	*F7*	-	-	-	-	-	-	-	-	-	-	-	-
St19	*F1*	12.83	294.63	13.09	20.33	-	40.99	1002.86	18.47	17.30	0.33	3.39	777.14
St19	*F2*	0.20	596.53	9.36	3.41	9.60	14.09	4740.58	119.91	13.42	0.28	16.18	61.76
St19	*F3*	2.96	278.59	5.83	1.13	8.12	10.08	857.71	20.56	12.57	3.14	3.49	104.96
St19	*F4*	4.26	116.46	4.30	1.10	2.10	4.52	411.88	8.44	2.12	3.88	1.76	105.83
St19	*F5*	3.88	251.62	4.79	1.10	13.68	7.02	850.06	17.62	11.90	11.14	3.60	132.35
St19	*F6*	-	842.93	5.55	0.52	18.68	5.62	3858.54	67.05	8.29	82.28	13.57	67.74
St19	*F7*	-	542.25	2.35	0.56	118.58	8.92	2170.58	27.20	79.21	1.90	5.48	87.51

Table S4. Detail of biotic metal (bM) concentrations (µg/g) according to the 7 size fractions (F1: 0.8-3 µm; F2: 3-20 µm; F3: 60-200 µm; F4: 200-500 µm; F5: 500-1000 µm; F6: 1000-2000 µm; F7 > 2000 µm) and the 10 stations (St1-4. St9-11. St15. St1. St19) of the MERITE-HIPPOCAMPE campaign. TL determination were discussed in a companion study (Tésan-Onrubia et al., 2022).

Station	***Fraction***	***TL***	**As**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Sb**	**V**	**Zn**
St01	*F1*	*1.0*	1.82	0.21	0.08	1.58	35	0.84	0.55	0.00	0.27	25
	F2	*1.1*	2.92	0.33	2.98	2.53	120	2.75	0.88	0.28	0.52	40
	F3	*1.7*	7.09	0.80	4.93	6.15	292	6.68	2.13	0.82	1.26	97
	F4	*1.9*	8.08	0.91	2.39	7.01	303	6.85	2.43	0.93	1.38	111
	F5	*2.2*	9.02	1.01	7.82	7.82	371	8.49	2.71	1.04	1.60	124
	F6	*2.2*	3.77	0.42	7.39	3.27	155	3.55	1.13	0.43	0.67	52
	F7	*2.5*	5.19	0.38	0.78	4.76	240	4.96	1.75	0.29	0.96	58
St02	*F1*	*1.0*	14.04	1.74	14.69	17.32	527	19.81	2.36	0.32	2.64	261
	F2	*1.6*	2.31	0.10	-	4.65	142	5.31	0.63	0.20	0.71	35
	F3	*2.0*	7.83	0.73	17.34	7.30	222	7.72	0.99	0.31	1.11	110
	F4	*2.0*	13.02	1.24	8.12	12.84	391	6.47	1.75	0.54	0.74	193
	F5	*2.1*	10.67	0.64	26.76	11.26	343	12.88	1.53	0.48	1.36	170
	F6	*2.1*	6.38	0.39	22.40	9.43	287	10.78	1.28	0.40	1.44	142
	F7	*2.3*	6.31	1.11	26.36	8.21	338	12.69	1.51	0.47	1.51	167
St03	*F1*	*1.0*	3.43	0.51	2.80	4.87	135	8.60	1.16	0.13	1.27	74
	F2	*1.3*	5.80	0.87	9.47	8.23	228	14.52	1.95	0.62	2.15	166
	F3	*2.3*	1.85	0.28	3.88	2.63	73	4.64	0.62	0.30	0.69	53
	F4	*2.5*	4.47	0.60	5.85	6.34	176	5.52	1.51	0.71	1.65	128
	F5	*2.5*	4.17	0.40	7.92	5.92	164	6.45	1.41	0.67	1.54	110
	F6	-	-	-	-	-	-	-	-	-	-	-
	F7	*2.2*	1.96	0.21	3.00	2.78	77	4.91	0.66	0.31	0.73	56
St04	*F1*	*1.0*	8.65	0.04	1.88	2.47	121	2.15	0.89	0.10	33.25	29
	F2	*1.5*	13.18	0.05	-	1.86	184	3.28	1.36	0.16	20.64	42
	F3	*1.8*	8.18	0.04	1.78	2.34	114	2.03	0.84	0.11	41.72	27
	F4	*1.8*	9.71	0.04	2.11	2.78	135	2.41	1.00	0.13	49.51	33
	F5	*1.7*	8.44	0.04	1.83	2.41	118	2.10	0.87	0.11	40.97	28
	F6	-	-	-	-	-	-	-	-	-	-	-
	F7	-	-	-	-	-	-	-	-	-	-	-
St09	*F1*	*1.3*	18.18	2.35	12.67	13.49	241	4.39	3.28	0.13	1.36	245
	F2	*1.4*	10.98	1.42	-	8.15	145	2.65	1.98	0.11	0.82	46
	F3	*2.4*	9.61	1.27	2.14	5.14	141	2.57	1.92	1.23	0.79	124
	F4	*2.7*	12.57	1.63	0.48	9.33	50	3.04	2.27	1.90	0.48	150
	F5	*3.2*	12.26	1.59	1.81	9.10	104	2.96	2.21	2.01	0.78	165
	F6	-	-	-	-	-	-	-	-	-	-	-
	F7	-	-	-	-	-	-	-	-	-	-	-
St10	*F1*	*1.0*	0.60	0.22	0.27	1.94	159	1.46	0.96	0.01	0.97	41
	F2	*1.4*	2.25	0.81	N/A	7.21	643	5.45	3.56	0.49	3.60	153
	F3	*2.7*	2.15	0.78	0.95	6.90	615	5.21	3.41	0.62	3.44	147

	F4	*2.8*	2.44	0.88	1.08	7.83	697	5.91	3.86	0.70	3.91	166
	F5	*3.1*	1.98	0.72	0.88	6.35	565	4.79	3.13	0.57	3.17	135
	F6	*3.6*	2.32	0.71	1.03	7.44	663	5.62	3.67	0.67	3.71	139
	F7	-	-	-	-	-	-	-	-	-	-	-
St11	*F1*	*1.0*	3.35	0.10	0.73	1.62	134	2.21	0.94	0.03	0.56	42
	F2	*1.1*	50.05	0.64	-	10.15	838	13.83	5.87	0.78	3.48	260
	F3	*2.1*	16.74	0.36	2.57	5.72	472	7.79	3.31	17.60	1.96	147
	F4	*2.2*	11.07	0.40	1.57	6.30	431	7.64	3.64	16.49	2.16	134
	F5	*2.4*	35.55	0.41	2.93	6.54	540	8.90	3.78	25.51	2.24	167
	F6	*2.5*	12.34	0.40	1.88	6.38	508	8.70	3.69	16.57	2.19	129
	F7	*2.8*	24.24	0.28	0.27	4.46	51	1.72	0.78	1.96	0.55	114
St15	*F1*	*1.0*	0.60	0.39	1.23	0.91	23	0.14	0.67	-	0.12	32
	F2	-	-	-	-	-	-	-	-	-	-	-
	F3	*2.0*	2.53	0.68	5.15	3.82	289	4.19	2.81	6.53	0.50	133
	F4	*2.1*	3.20	0.84	6.52	4.83	366	5.30	3.56	8.26	0.63	131
	F5	*1.8*	4.58	0.62	9.32	6.90	523	7.58	5.03	7.70	0.90	130
	F6	-	-	-	-	-	-	-	-	-	-	-
	F7	-	-	-	-	-	-	-	-	-	-	-
St17	*F1*	*1.0*	3.66	0.65	3.42	2.99	205	1.56	2.22	-	1.18	93
	F2	*1.4*	3.49	0.62	3.26	2.86	196	55.31	2.12	0.32	19.30	51
	F3	*1.5*	1.49	0.16	1.39	1.22	84	23.63	0.91	7.76	9.22	30
	F4	*1.7*	1.99	0.28	1.86	1.62	111	31.45	1.21	12.62	11.62	40
	F5	-	-	-	-	-	-	-	-	-	-	-
	F6	-	-	-	-	-	-	-	-	-	-	-
	F7	-	-	-	-	-	-	-	-	-	-	-
St19	*F1*	-	-	-	-	-	-	-	-	-	-	-
	F2	*1.6*	0.14	0.03	0.39	0.36	13	0.02	0.08	0.07	0.08	5
	F3	*1.8*	2.07	0.51	5.79	5.36	185	0.34	1.22	0.96	1.12	70
	F4	*1.9*	2.97	0.74	2.10	4.52	266	0.48	1.75	1.38	1.61	100
	F5	*2.2*	2.71	0.67	7.58	7.02	243	0.44	1.59	1.26	1.47	91
	F6	-	-	-	-	-	-	-	-	-	-	-
	F7	-	-	-	-	-	-	-	-	-	-	-

Table S5: Results of ANOVA (A) or Kruskal-Wallis (KW) tests per element to examine the potential variations of bM concentrations across all stations and fractions (n = 55). Significant differences ($p < 0.05$) are in bold.

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Sb**	**V**	**Zn**
Test	A	KW	A	A	A	KW	A	A	KW	A
p-Value	**0.003**	**0.008**	**0.015**	**0.026**	**0.005**	**0.038**	**< 0.0001**	**0.012**	0.086	**0.009**

Table S6. Detail of bM/POP ratios in planktonic food webs per elements and stations.

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Sb**	**V**	**Zn**
North coastal zone										
St01	0.62	0.04	0.79	0.64	31.98	0.74	0.24	0.03	0.16	9.54
St02	0.96	0.06	2.96	1.41	50.34	1.77	0.21	0.03	0.25	19.64
St03	0.47	0.04	1.09	0.78	24.58	1.39	0.20	0.03	0.26	13.96
St04	2.41	0.01	0.63	0.74	45.11	0.82	0.32	0.02	12.74	9.17
Offshore zone										
St09	1.60	0.13	0.72	1.34	23.83	0.54	0.37	0.08	0.16	17.88
St10	0.19	0.05	0.11	0.73	73.03	0.64	0.39	0.02	0.46	13.53
St11	1.37	0.02	0.18	0.48	39.08	0.68	0.27	0.40	0.19	10.56
South coastal zone										
St15	0.35	0.08	1.01	0.61	45.90	0.65	0.49	0.29	0.10	15.02
St17	0.54	0.05	0.73	0.52	40.51	9.37	0.42	0.78	3.84	11.87
St19	0.29	0.05	0.99	0.81	34.70	0.06	0.22	0.07	0.23	10.53

Table S7: Results of ANOVA (A) or Kruskal-Wallis (KW) tests per element to examine the potential variations of bM/POP ratios across all stations and fractions (n = 55). Significant differences ($p < 0.05$) are in bold.

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Sb**	**V**	**Zn**
Test	A	KW	A	KW	A	A	A	A	A	A
p-Value	**0.014**	**0.038**	**0.035**	**0.022**	0.298	**0.018**	**< 0.0001**	**< 0.0001**	0.112	0.579

Table S8: Results of Student (t) or Mann-Whitney-Wilcoxon (MW) tests per element to examine the potential differences in bM concentrations between geographical areas (n = 25 in the northern coastal zone; n = 18 in the offshore zone; n = 12 in the southern coastal zone). Significant differences ($p < 0.05$) are in bold.

	As	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Sb**	**V**	**Zn**
Differences between the northern coastal zone and the offshore zone										
Test	MW	MW	MW	MW	t	MW	t	MW	MW	MW
p-Value	0.207	0.066	**< 0.001**	0.190	**0.040**	0.428	**< 0.001**	**0.015**	0.724	**0.014**
Differences between the northern coastal zone and the southern coastal zone										
Test	t	MW	MW	MW	t	MW	t	MW	MW	MW
p-Value	**< 0.001**	0.713	0.221	**0.049**	0.956	0.227	0.082	**0.010**	0.327	0.554
Differences between the offshore zone and the southern coastal zone										
Test	MW	MW	MW	t	t	MW	t	MW	MW	MW
p-Value	**0.015**	0.158	**0.021**	**0.002**	**0.037**	0.346	**0.005**	0.408	0.573	**0.001**

Table S6: Elemental stoichiometry (bM/POP ratio. mmol/mol) in planktonic food webs including the 7 size fractions (F1-7) from the MERITE-HIPPOCAMPE campaign (Mediterranean Sea) detailed for the 10 stations (St1-4. St9-11. St15. St1. St19).

	As	**Cd**	**Cu**	**Cr**	**Fe**	**Mn**	**Ni**	**Sb**	**V**	**Zn**
Northern coastal zone										
St01	0.62	0.04	0.64	0.79	31.98	0.74	0.24	0.03	0.16	9.54
St02	0.96	0.06	1.41	2.96	50.34	1.77	0.21	0.03	0.25	19.64
St03	0.47	0.04	0.78	1.09	24.58	1.39	0.20	0.03	0.26	13.96
St04	2.41	0.01	0.74	0.63	45.11	0.82	0.32	0.02	12.74	9.17
Offshore zone										
St09	1.60	0.13	1.34	0.72	23.83	0.54	0.37	0.08	0.16	17.88
St10	0.19	0.05	0.73	0.11	73.03	0.64	0.39	0.02	0.46	13.53
St11	1.37	0.02	0.48	0.18	39.08	0.68	0.27	0.40	0.19	10.56
Southern coastal zone										
St15	0.35	0.08	0.61	1.01	45.90	0.65	0.49	0.29	0.10	15.02
St17	0.54	0.05	0.52	0.73	40.51	9.37	0.42	0.78	3.84	11.87
St19	0.29	0.05	0.81	0.99	34.70	0.06	0.22	0.07	0.23	10.53