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

Sandrine Chifflet^{a*}, Nicolas Briant^b, Javier Angel Tesán-Onrubia^a, Noureddine Zaaboub^c, Sirine Armi^c, Olivier Radakovitch^{d,e}, Daniel Bănaru^a, Marc Tedetti^a

^a Aix Marseille Univ., Université de Toulon, CNRS, IRD, MIO UM 110, 13288, Marseille, France

^b Ifremer, CCEM Contamination Chimique des Écosystèmes Marins, F-44000 Nantes, France

^c Institut National des Sciences et Technologies de la Mer (INSTM), 28, rue 2 mars 1934, Salammbô 2025, Tunisia

^d Aix Marseille Univ., CNRS, IRD, Collège de France, INRAE, CEREGE, 13545 Aix-en-Provence Cedex 4, France

^e IRSN (Institut de Radioprotection et de Sûreté Nucléaire), PSE-ENV/SRTE/LRTA, Saint-Paul-Les-Durance, France

* Corresponding author: sandrine.chifflet@mio.osupytheas.fr; Phone: + 33 4 86 09 05 32; Fax: + 33 4 91 82 96 41

For submission to Marine Pollution Bulletin Special issue "Plankton and Contaminants in the Mediterranean Sea: Biological pump and interactions from regional to global approaches" as full-length research paper

Revised version 04 November 2022

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):

$$[M]_{sample} = a. [Ti]_a + b. [POP]_b$$
(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:

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

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:

$$[bM] \equiv b. [POP]_{sample} \tag{3}$$

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):

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

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 ¹⁵N 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 (δ^{15} N) is used as proxy to assess the relative trophic position of an organism in marine food webs.

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

$$TMF = 10^{S} \tag{3}$$

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).

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 sizefractionated 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 $\mu g/g$. The limit of detection (LOD) are expressed in $\mu g/L$.

	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											
<i>Mean</i> $0.8\mu m$ ($n = 6$)	0.03	0.05	2.21	0.41	10.57	0.33	0.31	0.01	2.65	0.06	8.16
$\sigma 0.8 \mu m \ (n=6)$	0.01	0.01	0.64	0.3	3.94	0.09	0.05	0.00	0.29	0.01	5.14
Mean $3\mu m (n = 3)$	0.03	0.05	1.48	0.48	10.02	0.49	0.34	0.02	2.43	0.06	3.44
σ 3 μ m (n = 3)	0.01	0.01	0.07	0.16	2.16	0.01	0.03	0.00	0.01	0.01	0.08
$LOD (\mu g/L)$	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 ($\mu g/g$) 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	<i>F1</i>	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	<i>F6</i>	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	<i>F7</i>	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	<i>F1</i>	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	<i>F6</i>	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	<i>F7</i>	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	<i>F1</i>	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	<i>F7</i>	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	<i>F1</i>	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	<i>F6</i>	-	243.14	7.26	0.13	23.03	16.99	1724.68	29.33	18.73	37.75	43.28	149.42
St04	<i>F7</i>	-	-	-	-	-	-	-	-	-	-	-	-
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	<i>F6</i>	-	37.78	24.25	0.65	0.62	7.50	151.64	2.80	2.17	1.65	1.39	132.38
St09	<i>F7</i>	-	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	<i>F</i> 7	-	-	-	-	-	-	-	-	-	-	-	-
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	<i>F7</i>	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	<i>F1</i>	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	<i>F</i> 7	-	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	<i>F6</i>	-	-	-	-	-	-	-	-	-	-	-	-
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	<i>F</i> 7	-	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 ($\mu g/g$) according to the 7 size fractions (F1: 0.8-3 μ m; F2: 3-20 μ m; F3: 60-200 μ m; F4: 200-500 μ m; F5: 500-1000 μ m; F6: 1000-2000 μ m; F7 > 2000 μ m) 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	<i>F1</i>	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
	<i>F7</i>	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
	<i>F</i> 7	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	-	-	-	-	-	-	-	-	-	-	-
	<i>F</i> 7	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	-	-	-	-	-	-	-	-	-	-	-
	<i>F</i> 7	-	-	-	-	-	-	-	-	-	-	-
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	-	-	-	-	-	-	-	-	-	-	-
	<i>F</i> 7	-	-	-	-	-	-	-	-	-	-	-
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	<i>F1</i>	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
	<i>F7</i>	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	-	-	-	-	-	-	-	-	-	-	-
	<i>F7</i>	-	-	-	-	-	-	-	-	-	-	-
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	-	-	-	-	-	-	-	-	-	-	-
	<i>F7</i>	-	-	-	-	-	-	-	-	-	-	-
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
	<i>F6</i>	-	-	-	-	-	-	-	-	-	-	-
	F7	-	-	-	-	-	-	-	-	-	-	-

Table S5: Results of ANOVA (A) or Kruskal-Wallis (KW) tests per element to examine the potentialvariations 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	А	KW	А	А	А	KW	А	А	KW	А
p-Value	0.003	0.008	0.015	0.026	0.005	0.038	< 0.0001	0.012	0.086	0.009

	As	Cd	Cr	Cu	Fe	Mn	Ni	Sb	V	Zn
North co	astal 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 co	astal 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 S6. Detail of bM/POP ratios in planktonic food webs per elements and stations.

Table S7: Results of ANOVA (A) or Kruskal-Wallis (KW) tests per element to examine the potentialvariations 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	А	KW	А	KW	А	А	А	А	А	А
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 th	e northe	rn coastal :	zone and i	the offshor	re 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 th	e northe	rn coastal :	zone and	the southe	rn 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 th	ne offshor	e zone and	l the south	iern coaste	al 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 z	one									
St0.	1 0.62	0.04	0.64	0.79	31.98	0.74	0.24	0.03	0.16	9.54
St02	2 0.96	0.06	1.41	2.96	50.34	1.77	0.21	0.03	0.25	19.64
St0.	3 0.47	0.04	0.78	1.09	24.58	1.39	0.20	0.03	0.26	13.96
St04	4 2.41	0.01	0.74	0.63	45.11	0.82	0.32	0.02	12.74	9.17
Offshore zone										
StO	9 1.60	0.13	1.34	0.72	23.83	0.54	0.37	0.08	0.16	17.88
Stl	0 0.19	0.05	0.73	0.11	73.03	0.64	0.39	0.02	0.46	13.53
St1	1 1.37	0.02	0.48	0.18	39.08	0.68	0.27	0.40	0.19	10.56
Southern coastal z	one									
St1.	5 0.35	0.08	0.61	1.01	45.90	0.65	0.49	0.29	0.10	15.02
St1	7 0.54	0.05	0.52	0.73	40.51	9.37	0.42	0.78	3.84	11.87
St1	9 0.29	0.05	0.81	0.99	34.70	0.06	0.22	0.07	0.23	10.53