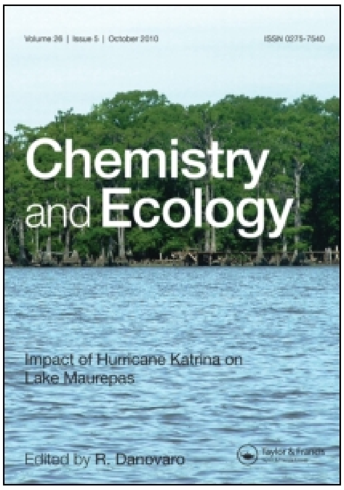

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Characterization of arsenic content in marine organisms from temperate, tropical, and polar environments

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Characterization of arsenic content in marine organisms from temperate, tropical, and polar environments

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Arsenic is a widely distributed element which occurs in several chemical forms in the marine environment. Inorganic arsenic mediates the most toxic effects and predominates in sea water and sediments, while organisms generally accumulate non-toxic organic forms to concentrations probably reflecting species-specific characteristics in arsenic metabolism. This work represents an additional contribution to our knowledge on natural levels and chemical speciation of arsenic in marine organisms; basal concentrations were characterized in several species (bivalves, crustaceans, and fishes) from different environments (polar, temperate, and tropical latitudes), and results revealed an elevated variability with values ranging from less than 5 to about 200 $\mu g\,g^{-1}$. No significant effects were observed as a function of the geographical area, with the only exception of crustaceans always showing more elevated arsenic concentrations in Mediterranean species (about 45–110 $\mu g\,g^{-1}$) compared with tropical species (lower than 30 $\mu g\,g^{-1}$). Chemical speciation of arsenic was investigated in representative species from the three studied taxa; the predominance of organic forms confirmed the general tendency of marine organisms to bioaccumulate non-toxic arsenic compounds, probably resulting from a detoxification pathway.

Keywords: Arsenic; Total content; Chemical speciation; Marine organisms; Bioaccumulation

1. Introduction

Arsenic is a widely distributed element in the marine environment with a complex biogeochemistry [1, 2] and several chemical forms characterized by a different biological reactivity [3–5]. Inorganic arsenic, like arsenite (As(III)) and arsenate (As(V)), are highly toxic, causing mitochondrial impairment and inhibition of glycolytic energy metabolism [6–10]; methylated compounds like methyl-arsonate (MMA), dimethyl-arsinate (DMA), trimethyl-arsine oxide (TMAO) and tetramethyl-arsonium (TETRA) are considered moderately toxic, despite a genotoxic potential has been shown [8, 9]. Non-toxic and more complex organoarsenic forms include arsenobetaine (AsB), arsenocholine (AsC), and specific As-containing ribosides (arsenosugars, AsS) [8, 9, 11–14].

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Inorganic arsenic, thermodynamically more stable, is the major form occurring in sea water and sediments [1, 2], while organisms normally accumulate arsenobetaine, arsenocholine and arsenosugars [15, 16]; although various mechanisms of bioaccumulation and biotransformation have been hypothesized for such As compounds, several aspects remain to be elucidated [11–18].

Variations in the levels and chemical forms of arsenic in tissues of different marine species can reflect the trophic position, the inherent capability of biotransformation, and other species-specific peculiarities in arsenic metabolism [1, 2, 15–17]. Interesting and unusual features have recently been reviewed for polychaetes [19]; some species can bioaccumulate extremely high levels of arsenic and/or possess the capability to operate biotransformation processes, like methylation, to produce relatively toxic molecules used as anti-predatory defences [19–21].

Anthropogenic inputs can modify the environmental bioavailability of arsenic to marine organisms, influencing both total levels and occurrence of specific chemical forms in target tissues [17]. Due to the ecological relevance of this element in the marine environment and the increasing use of organisms as bioindicators of chemical pollution, it is of utility to extend the dataset available on natural levels and fluctuations of arsenic between different species. In this respect, the aim of the present work was to characterize the basal concentrations in various organisms, including bivalve molluscs, crustaceans, and fish sampled from different geographical locations in the Mediterranean, Caribbean, and Antarctic regions. Selected species were also investigated for the chemical speciation, and the overall results were expected to represent an additional contribution to our knowledge on bioaccumulation and occurrence of arsenic compounds in marine organisms.

2. Materials and methods

2.1 *Samples and sites*

Basal levels and chemical speciation of arsenic were characterized in bivalves, crustaceans, and fish species sampled from unpolluted or relatively not impacted locations (table 1). Mediterranean sites included coastal and trawling areas in the Adriatic, Ionian, and Tyrrhenian Seas; organisms from the Caribbean were sampled in Cienfuegos Bay (Cuba), while Antarctic bivalves were collected at Terranova Bay (Ross Sea). Organisms were immediately dissected and stored at −20 °C until analysis. For bivalve molluscs, each individual sample was constituted by the whole soft tissues of at least three specimens; the entire edible soft parts of crustaceans were dissected and stored singularly after removing carapaces, legs, and chelipeds; fish samples were individually dissected to obtain muscle fillets and, for some species, also the liver.

2.2 *Arsenic total content and chemical speciation*

Determination of total arsenic was carried out as previously described [17, 19–21]. Samples were dried to constant weight at 60 °C overnight and digested with hydrogen peroxide (30%, Fluka) and nitric acid (purum p.a. ≥65%, Fluka) using a microwave digestion system (Mars CEM, CEM Corporation, Matthews NC) at 600 W as maximum powerful and at temperature of 160 °C for 25 min. Similarly, blank samples (reagents only) and standards reference material (Lyophilized Mussel Tissue, Standard Reference Material [SRM] NIST-2977, National Institute of Standards and Technology, Gaithersburg, MD, USA; lyophilized dogfish muscle, Standard Reference Material DORM-2, National Research Council, Ottawa, ON, Canada)

Table 1. Organism species and families (bivalve molluscs, crustaceans, and fishes) reported in this study, sample sizes (*n*) and sampling locations.

	Family	*n*	Location
Bivalves			
Adamussium colbecki	Pectinidae	15	Terra Nova Bay (Ross Sea, Antarctica)
Crassostrea virginica	Ostreidae	15	Cienfuegos Bay (Cuba, Caribbean Sea)
Isognomon alatus	Isognomonidae	15	Cienfuegos Bay (Cuba, Caribbean Sea)
Mytilus galloprovincialis	Mytilidae	60	Adriatic Sea (Mediterranean)
Yoldia eightsii	Yoldiidae	15	Terra Nova Bay (Ross Sea, Antarctica)
Crustaceans			
Callinectes sapidus	Portunidae	5	Cienfuegos Bay (Cuba, Caribbean Sea)
Carcinus mediterraneus	Portunidae	5	Adriatic Sea (Mediterranean)
Farfantepenaeus notialis	Penaeidae	8	Cienfuegos Bay (Cuba, Caribbean Sea)
Litopenaeus schmitii	Penaeidae	6	Cienfuegos Bay (Cuba, Caribbean Sea)
Melicertus kerathurus	Penaeidae	5	Adriatic Sea (Mediterranean)
Nephrops norvegicus	Nephropidae	5	Adriatic Sea (Mediterranean)
Squilla mantis	Squillidae	5	Adriatic Sea (Mediterranean)
Fishes			
Albula vulpes	Albulidae	5	Cienfuegos Bay (Cuba, Caribbean Sea)
Caranx hippos	Carangidae	5	Cienfuegos Bay (Cuba, Caribbean Sea)
Centropomus ensiferus	Centropomidae	5	Cienfuegos Bay (Cuba, Caribbean Sea)
Chelidonichthys lucernus	Triglidae	5	Ionian Sea (Mediterranean)
Chloroscombrus chrysurus	Carangidae	5	Cienfuegos Bay (Cuba, Caribbean Sea)
Diapterus auratus	Gerreidae	5	Cienfuegos Bay (Cuba, Caribbean Sea)
Eucinostomus havana	Gerreidae	5	Cienfuegos Bay (Cuba, Caribbean Sea)
Haemulon sp.	Haemulidae	5	Cienfuegos Bay (Cuba, Caribbean Sea)
Harengula clupeola	Clupeidae	5	Cienfuegos Bay (Cuba, Caribbean Sea)
Lutjanus synagris	Lutjanidae	5	Cienfuegos Bay (Cuba, Caribbean Sea)
Micropogonias furnieri	Sciaenidae	6	Cienfuegos Bay (Cuba, Caribbean Sea)
Mullus barbatus	Mullidae	5	Adriatic Sea (Mediterranean)
Pagellus erythrinus	Sparidae	5	Ionian Sea (Mediterranean)
Scyliorhinus canicula	Scyliorhinidae	5	Tyrrhenian Sea (Mediterranean)
Sphyraena guaguancho	Sphyraenidae	5	Cienfuegos Bay (Cuba, Caribbean Sea)
Sphyraena sphyraena	Sphyraenidae	5	Ionian Sea (Mediterranean)
Thunnus thynnus	Scombridae	5	Tyrrhenian Sea (Mediterranean)

were digested with the same procedures as controls for accuracy, precision, and recovery. Total arsenic concentration was determined by atomic absorption spectrometry with graphite furnace atomization and Zeeman effect (SpectrAA-300 Zeeman, Varian, Mulgrave, Victoria, Australia). The standard addition technique was applied for resolution of matrix effects, and palladium solution ($1\,\mathrm{g\,l^{-1}}$, 10% nitric acid, 5% citric acid) was added as chemical matrix modifier. The concentrations obtained for SRMs were always within the 95% confidence interval of certified values.

For chemical speciation of arsenic, samples were homogenized (1:10 w:v) in methanol (purum p.a. $\geq$99%, HPLC-grade Fluka) and arsenic species extracted using microwave (Mars CEM, CEM Corporation, Matthews NC) at 150 W as maximum power at 55 °C for 15 min [21]. After centrifugation at 2000 g for 5 min, supernatants were collected and the same extraction procedure was applied to SRM DORM-2. Arsenic compounds were separated by HPLC with a Supelcosil liquid chromatography-SAX1 column (25 cm × 4.6 mm ID × 5 µm, Supelco, Bellefonte, PA) and 15 mM KH_2PO_4 (pH = 6.1) as mobile phase at a flow rate of $1\,\mathrm{ml\,min^{-1}}$ for anionic forms; cationic exchange was performed with a Supelcosil liquid chromatography-SCX column (25 cm × 4.6 mm ID × 5 µm, Supelco) and 2.5 mM pyridine (pH = 2.65) as mobile phase at a flow rate of $1\,\mathrm{ml\,min^{-1}}$. Every 30 s from injection, 40 fractions were collected, added with 0.5 ml of nitric acid (purum p.a. $\geq$65%, Fluka), and analysed for total As content by atomic absorption spectrometry as previously described [21]. The SRM DORM-2 (containing certified levels of TETRA and AsB) and selected standards (As(V), DMA, TMAO, AsB) were processed and analysed with the same procedures as controls for accuracy, precision, and recovery.

2.3 *Statistical analyses*

Analysis of variance (ANOVA) was used to compare concentrations of total arsenic in different species of bivalves, crustaceans, and fishes. The homogeneity of variance was analysed by Levene's test, and post hoc tests (Newman–Keuls) were performed to distinguish between means of values.

3. Results

3.1 *Total arsenic content in bivalve molluscs*

Figure 1 shows concentrations of arsenic in the whole tissues of bivalve molluscs from unpolluted sites in Antarctica (*Adamussium colbecki* and *Yoldia eightsi*), the Caribbean (*Crassostrea virginica* and *Isognomon alatus*) and the Adriatic Sea (*Mytilus galloprovincialis*). Similar arsenic levels were measured in *A. colbecki* (10.9 ± 1.02 μg g^{-1}), *C. virginica* (10.6 ± 1.18 μg g^{-1}), *I. alatus* (13.2 ± 1.17 μg g^{-1}), and *M. galloprovincialis* (14.7 ± 4.10 μg g^{-1}), while *Y. eightsi*, from the same environment of *A. colbecki*, showed a much greater content

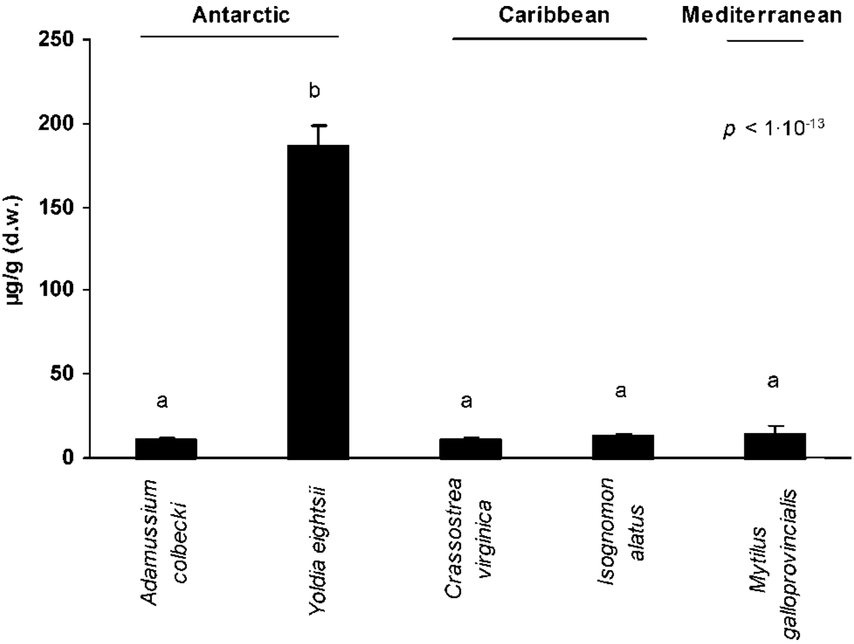

Figure 1. Concentrations of total arsenic (μg g^{-1} dry weight) in the entire soft parts of bivalve molluscs, from unpolluted sites in Antarctica, Caribbean and Mediterranean. Data are expressed as mean values ± standard deviations (*n* values are given in table 1). Different letters indicate statistical variations between the group of means according to the post hoc test.

up to $186 \pm 11.5\ \mu g\, g^{-1}$. Results for the Mediterranean mussel *M. galloprovincialis* represent the mean value for organisms seasonally collected, reflecting physiological fluctuations ranging from about 7 to $30\ \mu g\, g^{-1}$.

3.2 *Total arsenic in crustaceans*

Significant differences were obtained between Caribbean and Mediterranean crustaceans ($p < 0.000001$, figure 2): arsenic levels were $10.5 \pm 2.86\ \mu g\, g^{-1}$ in *Litopenaeus schmitii*, $16.3 \pm 5.39\ \mu g\, g^{-1}$ in *Farfantepenaeus notialis* and $28.2 \pm 6.84\ \mu g\, g^{-1}$ in *Callinectes sapidus*, while consistently higher contents were measured in Mediterranean species, respectively, $46.5 \pm 11.1\ \mu g\, g^{-1}$ in *Melicertus kerathurus*, $57.3 \pm 13.2\ \mu g\, g^{-1}$ in *Nephrops norvegicus*, $79.5 \pm 28.9\ \mu g\, g^{-1}$ in *Squilla mantis* and $112 \pm 46.8\ \mu g\, g^{-1}$ in *Carcinus mediterraneus*. Comparing the content of arsenic in organisms from the same location, *C. sapidus* exhibited significantly higher values among Caribbean crustaceans ($p < 0.001$), while levels measured in Mediterranean species were not statistically different ($p = 0.102$).

3.3 *Total arsenic content in fishes*

Levels of total arsenic in muscle tissues of Caribbean and Mediterranean fish species (figure 3a) revealed that species-specific characteristics, more than geographical location, influence arsenic bioaccumulation in these organisms; significant differences were observed comparing arsenic levels in organisms from the Caribbean ($p < 1 \times 10^{-16}$) or from the Mediterranean ($p < 0.0001$), but the range measured in fishes from these two areas was very similar ($p = 0.160$). Arsenic concentrations in Caribbean species varied from $2.18 \pm 0.55\ \mu g\, g^{-1}$ in *Caranx hippos* to $26.5 \pm 0.77\ \mu g\, g^{-1}$ in *Haemulon sp.*, while for Mediterranean

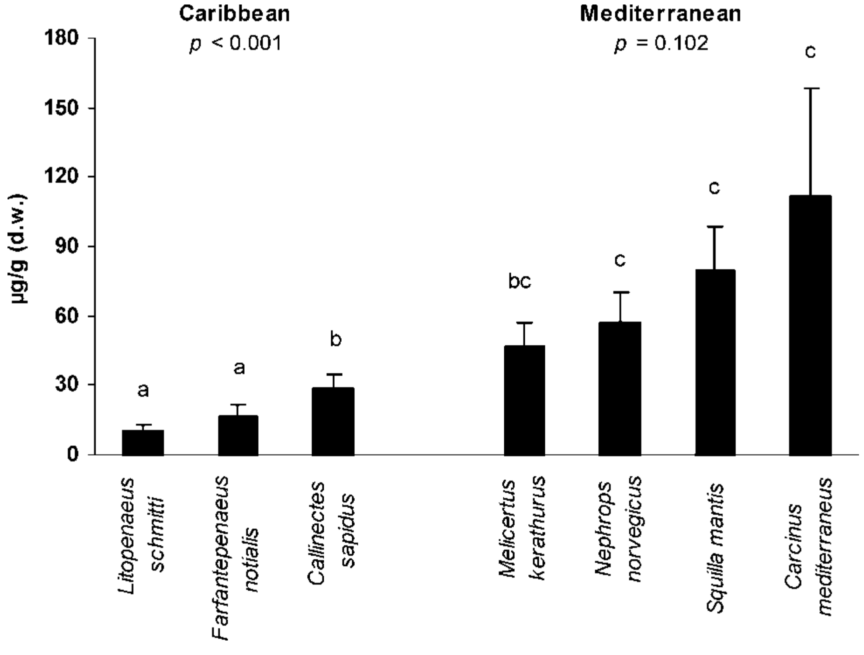

Figure 2. Concentrations of total arsenic ($\mu g\, g^{-1}$ dry weight) in crustaceans from unpolluted sites in the Caribbean and Mediterranean. Data are expressed as mean values ± standard deviations (*n* values are given in table 1). Different letters indicate statistical variations between the group of means according to the post hoc test.

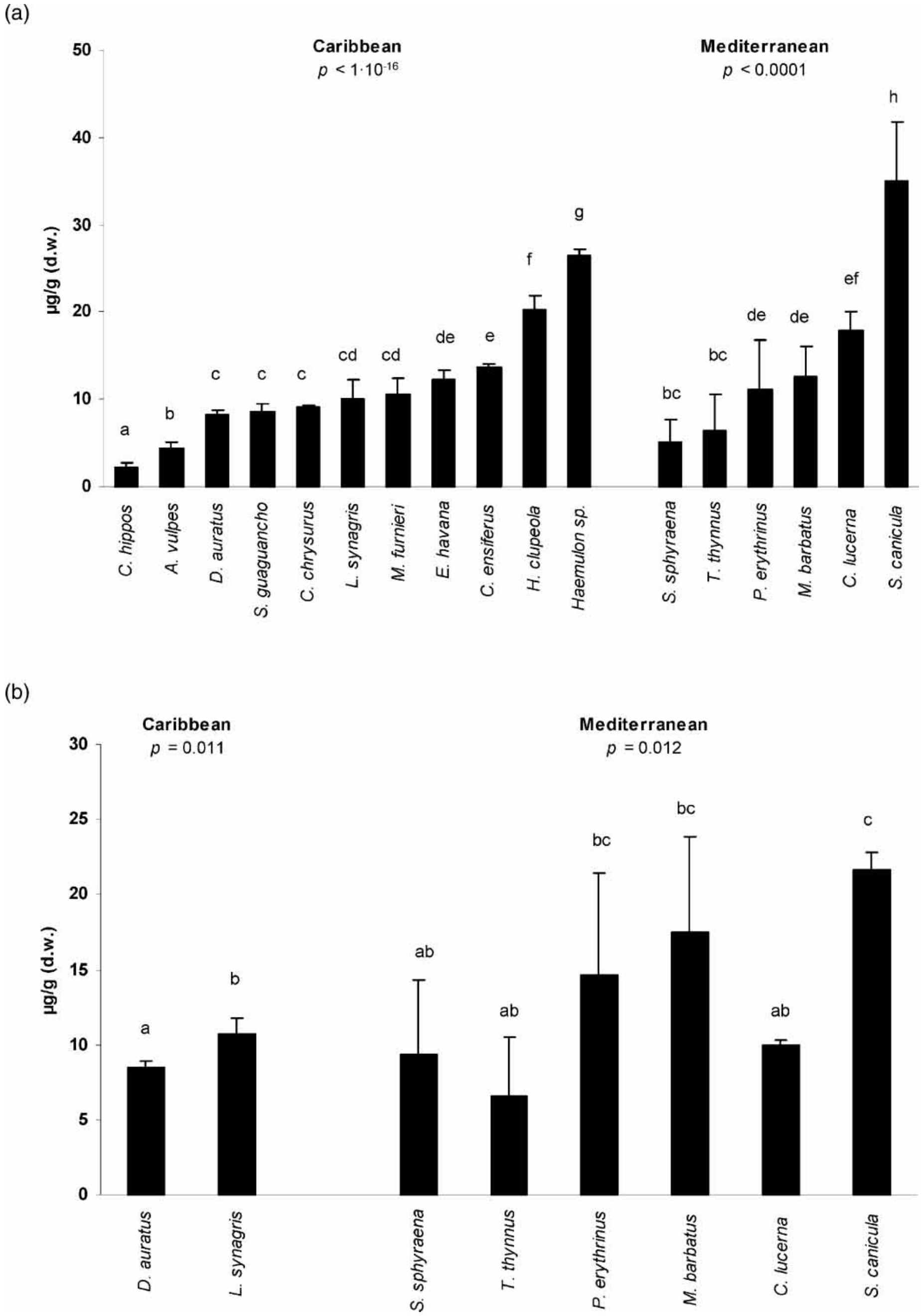

Figure 3. Concentrations of total arsenic ($\mu g\,g^{-1}$ dry weight) in the muscle (a) and in the liver (b) of various fish species from unpolluted sites in the Caribbean and Mediterranean. Data are expressed as mean values ± standard deviations (*n* values are given in table 1). Different letters indicate statistical variations between the group of means according to the post hoc test.

organisms, the concentrations ranged from $5.19 \pm 2.47\,\mu g\,g^{-1}$ in *Sphyraena sphyraena* to $34.9 \pm 6.84\,\mu g\,g^{-1}$ in *Scyliorhinus canicula*.

Arsenic concentrations measured in the liver of *Diapterus auratus* and *Lutjanus synagris* for Caribbean fish and in all Mediterranean species are given in figure 3b. Also, for this

Table 2. Percentage distribution of different arsenic compounds in marine species (mussels, crustaceans, and fishes) from unpolluted sites.

Species		(i)As (%)	DMA (%)	TMAO (%)	TETRA (%)	AsB (%)	AsC (%)	Unk (%)
Mytilus galloprovincialis	Mussel				12.7	67.4	19.9	
Callinectes sapidus	Crab	1.2				95.2	1.7	1.9
Farfantepenaeus notialis	Shrimp					7.1	92.9	
Haemulon sp.	Fish	0.5		0.6	1.8	0.4	96.7	
Lutjanus synagris	Fish	3.77	2.06		2.97	2.06	89.14	

Note: Arsenic species were: inorganic arsenic, (i)As; trimethyl-arsine oxide, TMAO; tetramethyl-arsonium, TETRA; arsenobetaine, AsB; arsenocholine, AsC; unknown arsenic compounds, Unk.

tissue, arsenic concentrations were not statistically different as a function of sampling area ($p = 0.158$), and limited differences were obtained between species from both the Caribbean ($p = 0.011$) and the Mediterranean ($p = 0.012$) sites. Arsenic concentrations in fishes liver were generally similar to those measured in muscle tissues with the only exceptions of the Mediterranean *Chelidonichthys lucernus* and *S. canicula* showing significantly lower hepatic concentrations ($p = 0.004$ and $p = 0.008$, respectively).

3.4 *Arsenic speciation in marine organisms*

The distributions of arsenic compounds in tissues of *M. galloprovincialis*, *C. sapidus*, *F. notialis*, *Haemulon* sp. and *Lutjanus synagris* are reported in table 2. In the Mediterranean mussel, about 87% of total arsenic was represented by organic species, 67.4% AsB, 19.9% AsC, and the remainder as TETRA. Arsenocholine (AsC) was the predominant form in the muscle of *Haemulon* sp. (~97%) and *L. synagris* (~90%), and in the edible tissues of the Caribbean shrimp *F. notialis* (>90%); arsenobetaine (AsB) was mostly accumulated in tissues of the blue crab *C. sapidus*, contributing for about 95% of the total content of arsenic.

4. Discussion

Due to the large use of bivalves in monitoring programs, concentrations of arsenic in these species have been reported by several authors. Levels indicatively ranging from 10 to 20 $\mu g\, g^{-1}$ have been measured in *Cerastoderma edule* and *Mytilus edulis* from estuarine and coastal sites in the UK [22, 23], from 10 to 15 $\mu g\, g^{-1}$ in Artic populations of *Machoma balthica* and *Mytilus edulis* [24], from 25 to 45 $\mu g\, g^{-1}$ in *Chlamys islandica* and *Placopecten magellanicus* [14], from 25 to 50 $\mu g\, g^{-1}$ in tissues of Japanese oyster *Pinctada fucata* [25], from 13 to 32 $\mu g\, g^{-1}$ in *Perna viridis* from Singapore [26], and from 5 to 40 $\mu g\, g^{-1}$ in various species of clams, mussels, and scallops from clean and polluted sites in Alaska and California [27]. Valette-Silver *et al.* [28] have recently observed a geographical and seasonal variability in the arsenic levels measured in tissues of oysters and mussels (*Crassostrea* sp., *Chama sinuosa*, and *Mytilus* sp.) along the US coast, with concentrations ranging from less than 10 to 100 $\mu g\, g^{-1}$, generally more elevated in bivalves from the south-eastern sites [28–30]; such a geographical anomaly was explained as a naturally enhanced arsenic bioavailability due to phosphate-enriched sediments [28].

Our results on bivalve molluscs, showed that Antarctic organisms collected in the same location and period (*A. colbecki* and *Y. eightsi*) exhibit markedly different levels of arsenic in their tissues (10 vs. 190 $\mu g\, g^{-1}$); the scallop *A. colbecki* is a filter- and deposit-feeder, resuspending sediments by valve clapping, while the clam *Y. eightsi* lives within sediments and is a classical deposit feeder. The relatively similar trophic strategy suggests that species-specific characteristics related to arsenic metabolism, more than environmental features, are responsible for the elevated basal concentrations of arsenic in *Y. eighitsi* [1, 2, 15–17]. Caribbean bivalves (*C. virginica* and *I. alatus*) and Mediterranean mussels had baseline levels of arsenic similar to those measured in *A. colbecki* (between 10 and 20 μg g^{-1}), indicating the absence of a large-scale geographical difference in arsenic bioavailability for these organisms.

Geographical differences were suggested in this study by arsenic concentrations in crustacean tissues with values ranging from about 10 to 30 μg g^{-1} in crabs and shrimps collected in the tropical environment (Caribbean) and from about 50 to 110 μg g^{-1} in those from temperate latitudes (Mediterranean). Although climatic characteristics have never been related to arsenic bioaccumulation in crustaceans, several authors reported relatively low concentrations of this element in organisms from tropical areas. Arsenic contents lower than 0.6 μg g^{-1} were measured in tissues of the shrimp *Penaeus semisulcatus* [31] and in the blue crab *Portunus pelagicus* [32] from the Arabian Gulf; several crustacean species from Costa Rica, Hong Kong, and Taiwan showed mean levels ranging, respectively, from 11 to 28 μg g^{-1}, from 0.9 to 44 μg g^{-1} and from 0.03 to 14.5 μg g^{-1} [33–35]. Meador *et al.* [27] compared arsenic concentrations in tissues of crustaceans from various sites along California and Alaska; with the exception of *Pandalus platycerus*, showing approximate arsenic levels of 300 μg g^{-1}, concentrations in five species from Californian sites were always lower than 15 μg g^{-1}, while values up to 100 μg g^{-1} were measured in shrimps from Alaska. Other studies on arsenic bioaccumulation in crustaceans from temperate or cold environments reported means values indicatively ranging from 14 to 42 μg g^{-1} in species from Atlantic Ocean and from 19 to 65 μg g^{-1} in shrimp from Chile [36–38]. Values similar to those reported in the present work were measured in *Nephrops norvegicus* (45 μg g^{-1}) and in other Mediterranean crustaceans [39].

Fishes collected from the same geographical area of crustaceans exhibited a much greater inter-specific variability of arsenic concentrations, with similar ranges for both tropical and temperate species and comparable with those already reported for other marine fish [18, 27, 31, 34, 40]. The elevated variability of arsenic concentrations in fish could not be explained by phylogenetic similarities between species, also because of the high number of families represented by the analysed species (14 families for 17 species; table 1). Considering a potential relationship between arsenic content in fish and diet habit [41], the greater variations were observed in fish preferentially feeding on benthic crustaceans (eight species: *A. vulpes*, *C. ensiferus*, *C. hippos*, *C. lucernus, D. auratus*, *E. havana*, *Haemulon* sp., *S. canicula*) with muscle concentrations ranging from about 2 to 35 μg g^{-1}. On the contrary, more similar arsenic values were measured in species feeding on detritus (*C. chrysurus*, *M. furnieri*), finfish (*L. synagris*, *T. thynnus*), molluscs (*S. guaguancho*, *S. sphyraena*) and polychaetes (*M. barbatus*, *P.erythrinus*), with levels from about 5 to 12 μg g^{-1}; concentrations of 20 μg g^{-1} were obtained in *H. clupeola*, the only species feeding on planktonic crustaceans. Although the number of fish species for each category was too limited, trophic levels, feeding strategy, or diet preferences do not appear to explain differences observed in arsenic total levels.

In Mediterranean fish, arsenic concentrations were characterized also in the liver, and the results obtained revealed that only *S. canicula* and *C. lucernus* had hepatic levels of arsenic lower than those measured in muscle tissues. The distribution of arsenic in tissues of *Mugil cephalus* confirmed higher values in the liver (19.2 μg g^{-1}) than in the muscle (4.7 μg g^{-1}) [18], while similar concentrations in these tissues were measured in other fish species; levels ranged from 7 to 60 μg g^{-1} in *Pleuronectes ferruginea* collected in various sites of Canada [40], from 3.5 to 19.4 μg g^{-1} in *Genyonemus lineatus*, and from 40.5 to 45.6 μg g^{-1} in *Pleuronectes vetulus* from California [27]. Levels of arsenic were also comparable in muscle and liver of *Hippoglossoides elassodon* collected from clean areas, while concentrations increased in the liver, but not in muscle tissues of organisms sampled from Alaskan polluted sites [27].

Marine organisms, including algae, bivalves, crustaceans, gastropods, and fishes, generally bioaccumulate arsenic as complex organic compounds, *i.e.* arsenobetaine (AsB), arsenocholine (AsC), and arsenoribosides (AsS) [11–14, 18, 42]. Our results on chemical speciation confirmed the prevalence of such non-toxic forms in tissues of *M. galloprovincialis*, *C. sapidus*, *F. notialis*, *Haemulon* sp., and *L. synagris*. Although the mechanisms of arsenic transformation have not been fully clarified, some hypotheses consider organoarsenic compounds as the final products of detoxification processes [11–16], and the occurrence of these As molecules is a typical feature of marine organisms with no ecotoxicological implication. However, chemical speciation of arsenic can drastically change in polluted areas as previously demonstrated in fish, *L. synagris*, collected after an acute arsenic contamination in Cuba [17]: concentrations of inorganic arsenic greatly increased in tissues of impacted organisms, while levels of methylated and organic arsenic compounds remained almost constant [17]. Although only a few studies have considered the chemical speciation of arsenic in polluted organisms [17, 27, 43], this approach appears to be of great importance to distinguish anthropogenic inputs from natural variability and for the toxicological implications of inorganic arsenic in tissues of marine organisms.

In conclusion, an elevated variability of natural arsenic concentrations can be expected in different marine species among bivalve molluscs, crustaceans, and fishes which, however, confirmed the predominance of organicated non-toxic compounds. Species-specific characteristics more than environmental factors appear to modulate basal arsenic bioaccumulation; for crustaceans, these data and literature would support a greater As bioavailability in temperate or cold regions compared with tropical latitudes, but additional investigations on these organisms will be necessary to confirm a similar relationship.

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