

Bioaccumulation of Metals in Tissues of Marine Animals, Part II: Metal Concentrations in Animal Tissues

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Abstract

The bioaccumulation of metals in an animal depends on a multitude of factors: biotic ones, like its body dimensions and mass, age, sex, diet, metabolism, and position in the trophic web; and abiotic ones, such as the distribution of metals in its environment, salinity, temperature, and pH of the water, habitat type, and interactions with other metals. But it is diet that has the greatest influence on the accumulation of metals in animal tissues. Bioaccumulation is a complex process, requiring the simultaneous examination of metal levels in the tissues of animals from at least two adjacent trophic levels. To illustrate the differences in metal concentrations in animals, data are presented on heavy metal levels in the tissues of different groups of animals (marine molluscs, crustaceans, echinoderms, fish, sea turtles, birds, and mammals) from various levels of the trophic pyramid. Most commonly, metal concentrations are higher in larger animals that are end members of a trophic chain than in the smaller organisms they feed on.

Since to a large extent an animal's habitat determines the level of metals in its body, these data are generally indicators of the extent of pollution of the water body in which it lives.

It has been found that carnivorous species bioaccumulate far greater quantities of metals than herbivores or omnivores, and that metal levels are lower in organisms capable of detoxifying or excreting metals.

Keywords: bioaccumulation, heavy metals, marine organisms, concentrations in tissues

Introduction

Various types of anthropogenic and natural contaminants get into the habitats of animals. Since the mid-20th century, the effects of pollutants discharged into the environment as a result of human activities have become serious. In consequence, the environment is loaded with substantial amounts of such xenobiotics as polycyclic aromatic hydrocarbons (PAHs) and heavy metals.

There is no unequivocal definition of the term heavy metals: in most cases it refers to metals and metalloids, together with their compounds, that are toxic or ecotoxic and are regarded as contaminating the environment [1].

The metals present in an animal may result in various interactions: some are essential for life, others can be harmful. Not without importance is their quantity. Some metals, present at certain levels, enable the organism to function properly, but if those levels are exceeded, they become pathogenic and can cause mortality. The biggest problem is the bioaccumulation of metals in the tissues of animals from the upper levels of the trophic pyramid [2].

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Heavy metal bioaccumulation by the tissues and organs of animals from the upper levels of the trophic pyramid is one of the most important processes currently taking place in the marine environment. It is governed mainly by the diet of consumers of food from lower trophic levels, as well as a number of other factors:

- abiotic: the distribution of metals in an animal's habitat or their sequence at the various stages of life or migration; salinity, temperature, and pH of the water; the type of habitat; interaction with other metals;
- biotic: body size and mass, age, phenotypic differences, sex, physiological conditions, developmental stage, metabolism, availability of food, and the growth factor [3-6].

The Effect of Diet on the Accumulation of Metals in the Tissues of Animals at Different Levels of the Food Pyramid

The most important factor affecting the level of metals in the tissues of a given animal appears to be the diet. Usually, the higher the level of metals in animals from a lower trophic level, the greater the concentration of metals in the tissues of higher-level animals.

Table 1 presents the types of food in the diet of animals from different trophic levels in the sea.

Metal concentrations in carnivores at the top of the trophic pyramid – fish, birds, mammals, and sea turtles – are higher than in herbivores (Tables 2, 3). In the case of omnivores such as copepods, average concentrations are found. It happens that the metal concentration in the body of animals from a higher trophic level is lower than that in its diet, which may be due to some specific aspect of its metabolism and/or its ability to excrete the metal.

The environmental availability of metals to animals depends on many factors. Mercury, for example, is more bioavailable after it is microbiologically methylated [57]: the transfer of MeHg from plankton to copepods is four times more efficient than in the case of inorganic mercury [58]. It has also been found that fish muscles contain almost 100% bioavailable methyl mercury, which is a serious threat to species above them in the trophic pyramid [59].

However, when investigating the accumulation of metals in living organisms from different trophic levels, other factors, not just the diet, have to be taken into consideration.

Food chains are often quite complex, and studies of bioaccumulation often require that two neighbouring levels be examined simultaneously [60]. It is often the case that metal levels in tissues are not dependent on their concentration in the prey item's body.

The Accumulation of Metals in the Tissues of Marine Animals

Xenobiotics in animal tissues are a threat not only to fish or predators, but also to the humans consuming them [14]. Some chemical compounds are suspected of being human carcinogens. High levels of metals can lead to serious health consequences, and even to death [61].

Table 1. Literature data on the dietary composition of organisms from different trophic levels in the sea.

Species	Type of food	References
Molluscs		
Eastern oyster (<i>Crassostrea virginica</i>)	Suspended matter	[7]
Sea snail (<i>Patella aspera</i>)	Herbivorous	[8]
Sea snail (<i>Patella caerulea</i>)	Herbivorous	[9-11]
Sea snail (<i>Patella lusitanica</i>)	Herbivorous	[10]
Sea snail (<i>Tympanotonus fuscatus</i>)	Herbivorous	[12]
Bellybutton nautilus (<i>Nautilus macromphalus</i>)	Small fish, crustaceans (including prawns)	[13]
Octopus (<i>Benthoctopus thielei</i>)	Crustaceans	[14]
Octopus (<i>Graneledone</i> sp.)	Crustaceans	
Mediterranean mussel (<i>Mytilus galloprovincialis</i>)	Suspended matter	[15, 16]
Crustaceans: copepods		
<i>Sergia</i> spp.	Usually omnivorous, feed on protozoa, rotifers, turbellarians, cladocerans, ostracods, oligochaeta, sometimes parasitic	[17]
<i>Acanthephyra</i> spp.		
<i>Rhincalanus gigas</i>		
<i>Calanus propinquus</i>		[18]
<i>Calanoides acutus</i>		
<i>Metridia curticauda</i>		
<i>Metridia gerlachei</i>		
<i>Calanus finmarchicus</i>		
<i>Calanus glacialis</i>		[19]
<i>Calanus hyperboreus</i>		
<i>Metridia longa</i>		
<i>Calanus finmarchicus</i>		
<i>Calanus hyperboreus</i>		
<i>Euchaeta barbata</i>		
<i>Euchaeta glacialis</i>		
<i>Euchaeta norvegica</i>		
<i>Metridia longa</i>		
<i>Acartia</i> sp.		[20]
<i>Calanus finmarchicus</i> / <i>C. helgolandicus</i>		
<i>Acartia</i> sp.		
<i>Anomalocera patersoni</i>		
<i>Calanus finmarchicus</i> / <i>C. helgolandicus</i>		
<i>Calanus finmarchicus</i> / <i>C. helgolandicus</i>		

Table 1. Continued.

Species	Type of food	References
Crustaceans: shrimps/prawns		
<i>Bentheogennema intermedia</i>	Algae, zooplankton	[17]
<i>Benthesicymus iridescentis</i>		
<i>Systellaspis debili</i>		
<i>Crangon crangon</i>		[21]
<i>Litopenaeus stylirostris</i>		[22]
<i>Pleoticus muelleri</i>		[23]
Crustaceans: lobsters, crabs		
<i>Jasus edwardsii</i>	Snails, bivalves, crabs, prawns, sea urchins, carrion	[24]
<i>Panulirus inflatus</i>		[25]
<i>Portunus pelagicus</i>	Bivalves, fish, macroalgae	[26]
Echinodermata: starfish		
<i>Asterias rubens</i>	Molluscs, bivalves, oysters, snails, echinoderms, fish, decaying plant and animal matter, coral polyps, sponges, suspended organic matter, plankton	[27-31]
Fish		
Swordfish (<i>Xiphias gladius</i>)	Cephalopods	[32]
Yellowfin Tuna (<i>Thunnus albacares</i>)	Fish, bivalves, squid	
Common Dolphinfish (<i>Coryphaena hippurus</i>)	Flying fish, crabs, squid, mackerel, small fish	
Skipjack Tuna (<i>Katsuwonus pelamis</i>)	Fish, crustaceans, cephalopods, molluscs	
Grass Goby (<i>Zosterisessor ophiocephalus</i>)	Mainly invertebrates, occasionally algae, other fish	[16]
Gilthead Seabream (<i>Sparus auratus</i>)	Crustaceans, molluscs: oysters	[4]
Mediterranean Sand Smelt (<i>Atherina hepsetus</i>)	Suspended matter	
Flathead Mullet (<i>Mugil cephalus</i>)	Zooplankton	
Red Gurnard (<i>Trigla cuculus</i>)	Zooplankton	
European Pilchard (<i>Sardina pilchardus</i>)	Molluscs	
Atlantic Saury (<i>Scomberesox saurus</i>)	Zooplankton, fish larvae	[6]
Swordfish (<i>Xiphias gladius</i>)	Cephalopods	
Bluefin Tuna (<i>Thunnus thynnus</i>)	Small fish (sardines, herring, mackerel), invertebrates (molluscs, squid)	

Table 1. Continued.

Species	Type of food	References
Fish		
Herring (<i>Clupea harengus</i>)	Plankton	[33]
Sprat (<i>Sprattus sprattus</i>)	Plankton	
Cod (<i>Gadus morhua</i>)	Ammodytidae, whiting, haddock, small cod, squid, crabs, lobsters, bivalves, worms, mackerel, molluscs	
Red Mullet (<i>Mullus barbatus</i>)	Worms, crustaceans, molluscs	
Lanternfish, <i>Gymnoscopelus nicholasi</i>	Zooplankton	[35]
Lanternfish, <i>G. piabilis</i>	Zooplankton	
Marbled Rockcod (<i>Notothenia rossii</i>)	Krill (fragments)	
Magellanic Rockcod (<i>Paranotothenia magellanica</i>)	Small fish, crustaceans, cephalopods	
Unicorn Icefish (<i>Channichthys rhinoceratus</i>)	Krill	
Mackerel Icefish (<i>Champscephalus gunnari</i>)	Zooplankton, krill	
Grey Rockcod (<i>Lepidonotothen squamifrons</i>)	Krill	[36]
Leaping Mullet (<i>Liza saliens</i>)	Algae, eggs, and larvae of invertebrates	
Birds		
Razorbill (<i>Alca torda</i>)	Small fish, mainly Clupeidae, Ammodytidae, young Gadidae also worms, crustaceans	[37]
Barau's Petrel (<i>Pterodroma barau</i>)	Cephalopods, occasionally small fish	[38]
Audubon's Shearwater (<i>Puffinus lherminieri</i>)	Small fish, planktonic crustaceans, squid	
White-tailed Tropicbird (<i>Phaethon lepturus</i>)	Fish, squid	
Black-tailed Gull (<i>Larus crassirostris</i>)	Small fish, molluscs, crustaceans, carrion	[39]
Common Eider (<i>Somateria mollissima</i>)	Mussels, crabs	[40]
White-tailed Eagle (<i>Haliaeetus albicilla</i>)	Large fish, like common bream, carp, pike, aquatic birds (up to the size of herons/geese) – mainly grebes, ducks and coots	[41]

Table 1. Continued.

Species	Type of food	References
Birds		
American Avocet (<i>Recurvirostra americana</i>)	Crustaceans, molluscs, fish fry, insects	[42]
Black-necked Stilt (<i>Himantopus mexicanus</i>)	Small invertebrates	
Caspian Tern (<i>Hydroprogne caspia</i>)	Fish, invertebrates, occasionally the eggs of other birds	
Forster's Tern (<i>Sterna forsteri</i>)	Fish, insects, invertebrates	
Penguins (<i>Sphenisciformes</i>)	Fish, cephalopods, crustaceans	[43]
Laysan Albatross (<i>Diomedea immutabilis</i>)	Cephalopods	
Shearwaters (<i>Puffinus</i>)	Small fish, molluscs, cephalopods, detritus from the water surface	
Storm Petrels (<i>Hydrobatidae</i>)	Crustaceans, small fish, molluscs	
Gannets and Boobies (<i>Sula</i>)	Fish	
Cormorants (<i>Phalacrocoracidae</i>)	Fish, sometimes sea snakes	
Frigate Birds (<i>Fregatidae</i>)	Fish, small turtles	
Gulls (<i>Laridae</i>)	Starfish, crustaceans, coots	
Terns (<i>Sternidae</i>)	Fish, insects, invertebrates	
Skimmers (<i>Rynchopidae</i>)	Small marine animals	
Skuas (<i>Stercorariidae</i>)	Fish, invertebrates, starfish, crustaceans, coots, gulls, puffins	
Auks (<i>Alcidae</i>)	Small fish, mainly Clupeidae, Ammodytidae, young Gadidae; also worms, crustaceans	
Great Cormorant (<i>Phalacrocorax carbo</i>)	Fish (mainly ruffe, smelt)	[44]
Sea Turtles		
Olive Ridley Sea Turtle (<i>Lepidochelys olivacea</i>)	Lobsters, crabs, small prawns, algae	[45]
Hawksbill Sea Turtle (<i>Eretmochelys imbricata</i>)	Mainly sponges; also jellyfish, sea anemones, algae	[45,46]
Loggerhead Sea Turtle (<i>Caretta caretta</i>)	Fish, sponges, jellyfish, crabs, bivalves, squid, oysters	[45-48]
Green Sea Turtle (<i>Chelonia mydas</i>)	Sea grass, algae, rhodophyta	[45, 46, 48-51]

Table 1. Continued.

Species	Type of food	References
Mammals		
Northern Fur Seal (<i>Callorhinus ursinus</i>)	Fish, crustaceans, cephalopods	[52]
Risso Dolphin (<i>Grampus griseus</i>)	Cephalopods, crustaceans, small fish	
Minke Whale (<i>Balaenoptera acutorostrata</i>)	Small crustaceans, small fish	[53]
Grey Whale (<i>Eschrichtius robustus</i>)	Crustaceans, molluscs	[54]
Striped Dolphin (<i>Stenella coeruleoalba</i>)	Fish, cephalopods, crustaceans	[55]
Bowhead Whale (<i>Balaena mysticetus</i>)	Small crustaceans	[56]

For instance, a concentration of 5 ppm Hg in a muscle can lead to exhaustion, impair coordination, cause loss of appetite, and ultimately lead to death [62]. It would seem, therefore, that toxic effects are observed in some sensitive birds and mammals consuming fish containing fairly high levels of mercury [14].

Some contaminants can be deposited in tissues for longer periods of time, giving rise to toxic effects or mortality, unless the organism is capable of detoxifying itself or of excreting these substances. That is why it is important to examine the metal concentrations in animals from different levels of the trophic pyramid [63] (Table 3).

Accumulation of Metals in Invertebrate Tissues

Molluscs

Molluscs (and also fish) are specific indicators of different levels of xenobiotics bioaccumulation depending on habitat or food chain position [16, 66, 67]. Contaminants can be lethal at different levels of biological organization (cells, organs, individual animals, populations of animals). Bioindicators guarantee measurements at the cellular, biochemical, and physiological levels [16].

Snails are herbivores, so the level of metals in their soft tissues (Table 3) reflects these levels accumulated in the algae they feed on [10]. The relatively large concentrations of copper in the tissues of a snail from the Tyrrhenian Sea are due to the pollutants derived from the conurbations of Formia and Gaeta [9]. The highest copper levels were measured in the Bellybutton Nautilus, which may be a consequence of its longevity (10-15 years) [13]. *T. fuscatus* exhibits a substantial ability to accumulate lead and zinc in its tissues, but it is thought that it is not connected with any detoxification processes. Again, high levels of such metals as Zn, Fe, or Mn are due to the presence of enzymes and other substances important in the metabolism of molluscs [68].

Table 2. Heavy metal concentrations [$\mu\text{g/g d. wt.}$] in different animals with respect to the method of feeding.

Animal	Method of feeding	Metal concentration range [$\mu\text{g/g d. wt.}$]					References
		Cd	Zn	Cu	Pb	Hg	
Molluscs	Herbivorous	0.08-6.3	7.3-123	1.4-16	61	-	[8-12]
Molluscs	Carnivorous	0.2-16	113-260	3-73	-	-	[13, 14]
Copepods	Omnivorous	0.3-11	37-518	3.8-56	0.3-2	-	[17-20]
Crustaceans: Prawns	Herbivorous and carnivorous	0.17-16.3	5.65-79	2.75-55	0.4-0.66	-	[17, 21-23]
Crustaceans: Lobsters, Crabs	Herbivorous and carnivorous	0.02-0.3	19.8-206	8.1-124	0.05-1.9	-	[24-26]
Echinoderms: Starfish	Carnivorous	0.3-1.5	118-260	1.6-98	1-1.6	-	[27-31]
Fish ^a	Carnivorous	0.96-169	70-439	3.1-254	0.09-41	0.05-0.69	[4, 6, 16, 32-36]
Birds ^a	Carnivorous	0.15-67	70.9-316	13-712	0.048-1.1	1.72-24.3	[37-40, 42-44]
Sea Turtles ^a	Carnivorous	0.49-17.9	25.9-69	2.5-36.7	<1.23	1.6-2.4	[45-48]
Sea Turtles ^a	Herbivorous	0.9-17	62-212	9-77	<0.8	0.12-0.55	[45, 46, 48-51]

^a – concentration ranges given for liver tissue

Crustaceans

Zooplankton plays a crucial role in the biogeochemical cycle of metals in marine ecosystems, especially reactive metals [69]. Macro- and mesozooplankton can be utilized as bioindicators (like molluscs) to estimate the spatial and temporal bioavailability of metals [18, 19]. This is mainly because zooplankton is ubiquitous, being present in various regions of the world, and makes up a large proportion of the biomass, as a result of which it plays a significant part in the food chain [17].

In *C. propinquus*, *M. Curticauda*, and *M. gerlachei* (Table 3) Cu levels are twice as high as in *R. gigas* and *C. acutus*, which may be due to the fact that the latter two species enter diapause (a state of dormancy). Diet probably also has an effect, since *C. acutus* is a herbivore with a short reproductive period, tending to undertake seasonal migrations, whereas *M. curticauda* and *M. gerlachei* are, respectively, omnivores and carrion feeders with a longer reproductive period but a shorter diapause. *R. gigas* has intermediate features.

The highest Cu, Cd, and Pb levels were recorded in *Acanthephyra* sp. from the Iberian Deep Sea Plain. This region is somewhat isolated and the high Cd level is a consequence of a Cu deficit rather than of human activities [17, 68, 70, 71]. The large concentrations of Cu in North Sea animals are due to this participation of this metal in the actions of enzymes and haemocyanin [68].

The concentrations of lead in animals (not those from the North Sea) do not exceed 1 $\mu\text{g/g d. wt.}$, which is because Pb enters the sea mainly as a result of atmospheric deposition, raising levels in the plankton-rich, euphotic zone. Pb levels fall with increasing depth, which is not the case with other trace metals [17].

The Cd, Cu, and Zn levels in crustaceans from the Fram Strait and Greenland Sea are rather low. This is probably due to the transport of these contaminants from afar as a

result of the exchange of oceanic waters, from local influxes of pollutants from rivers, the land, industry and atmospheric deposition [19].

Prawns are an important link in the trophic chain in marine ecosystems [21], as they constitute food for many species of fish, crabs, seals, and birds. The highest metal levels in such crustaceans were measured in *B. intermedia*, *B. Iridescens*, and *S. debilis* from the Iberian Deep Sea Plain. Many metals are stored in the form produced as a result of detoxification in different organs, and the toxic effects caused by metals will be less because of their reduced levels in the tissues of a given animal [17]. The large Cd concentrations, as mentioned in the case of copepods, are not due to human activities but are a sign of Cu deficiency [17, 70, 71]. The Cu concentrations measured in all prawns are far higher than those determined in most copepods, since Cu is an essential element in haemocyanin, present in prawns but not in most copepods [17, 68].

The high metal levels in crab organs in the Kuwait region are indicative of the considerable environmental pollution from industrial sources there, i.e. fertilizer production and crude oil refining [26]. The level of copper in lobsters and crabs is regulated depending on the animal in question and its size. The Cu concentration is far greater in larger lobsters, but is independent of the fishing grounds [24]. Large concentrations may also be due to the presence of haemocyanin, mainly in the gills [25, 68].

Echinodermata

The starfish *Asterias rubens* (Echinodermata, L.) is an important animal from the point of view of the bioaccumulation process being used in ecotoxicology tests [30, 31, 72-74]. Its status as a predator in the food chain (seston – bivalve – starfish), the fact that it is widespread, and that it occupies a key position in the North Sea all contribute to its high potential as an indicator organism [28, 30]. Various

Table 3. Mean metal concentrations [$\mu\text{g/g d. wt.}$] in the tissues of marine animals from different levels of the trophic pyramid*.

Subtype	Class	Species	Region of occurrence	Tissue examined	Average metal concentration [µg/g d. wt.]								Reference	
					Cu	Cd	Zn	Hg	Pb	Fe	Se	As		
Link in the food chain in the marine ecosystem	Molluscs	Mediterranean Mussel (<i>Mytilus galloprovincialis</i>)	Adriatic Sea	Whole animal	4.133	0.913	82.45	0.0315	0.8513	224.65	na	na	[15]	
		Mediterranean Mussel (<i>Mytilus galloprovincialis</i>)	Venice Lagoon	Whole animal	7.54	2.01	249.13	na	2.365	160.55	na	na	[16]	
		Sea snail (<i>Patella aspera</i>)	Portugal	Soft tissue	9.715	1.79	122.7	na	<LOD	1749.5	na	na	[8]	
		Sea snail (<i>Patella caerulea</i>) ^a	Favigana I., Sicily	Soft tissue	1.35	6.3	14.6	na	na	na	na	na	[11]	
		Sea snail (<i>Patella caerulea</i>)	Favigana I., Sicily	Soft tissue	1.485	6.25	14.7	na	na	na	na	na	[10]	
		Sea snail (<i>Patella caerulea</i>)	Tyrrhenian Sea	Soft tissue	15.85	3.55	101	na	na	na	na	na	[9]	
		Sea snail (<i>Patella lusitanica</i>)	Favigana I., Sicily	Soft tissue	3	4.35	17.85	na	na	na	na	na	[10]	
		Sea snail (<i>Tympanotonus fuscatus</i>)	Lagos Lagoon	Soft tissue	6.55	0.08	7.29	na	60.55	na	na	na	[12]	
		Eastern Oyster (<i>Crassostrea virginica</i>)	Apalachicola Bay, Florida	Soft tissue	na	2.975	584	na	na	na	na	na	[7]	
		Bellybutton Nautilus (<i>Nautilus macromphalus</i>)	New Caledonia	Soft tissue	73	16	260	na	na	258	na	na	[13]	
		Octopus (<i>Benthoctopus thielei</i>)	Kerguelen I.	Muscle	3	0.21	138	na	na	na	na	na	[14]	
		Octopus (<i>Graneledone</i> sp.)		Muscle	15	0.37	113	na	na	na	na	na		
	Invertebrates	Crustaceans – copepods	<i>Sergia</i> spec.	Iberian Deep Sea Plain	Whole animal	17	1.9	67	na	0.5	na	na	na	[17]
			<i>Acanthephyra</i> spec.			56	6.1	52	na	0.6	na	na	na	
			<i>Rhincalanus gigas</i>	Weddell Sea		11	3.7	432	na	0.17	na	na	na	[18]
			<i>Calanus propinquus</i>			26	5.6	191	na	0.51	na	na	na	
			<i>Calanoides acutus</i>			10	4.6	183	na	0.31	na	na	na	
			<i>Metridia curticauda</i>			21	9.6	278	na	0.48	na	na	na	
			<i>Metridia gerlachei</i>	Fram Strait		26	10.2	518	na	0.72	na	na	na	[19]
			<i>Calanus finmarchicus</i>			4.5	0.32	93	na	0.3	na	na	na	
			<i>Calanus glacialis</i>			12.4	0.63	79	na	0.3	na	na	na	
			<i>Calanus hyperboreus</i>			5.6	0.75	104	na	0.3	na	na	na	
			<i>Metridia longa</i>	4.5		0.71	351	na	0.6	na	na	na		
			<i>Calanus finmarchicus</i>	3.8		0.27	86	na	0.3	na	na	na		
			<i>Calanus hyperboreus</i>	4.4		0.69	88	na	0.3	na	na	na		
			<i>Euchaeta barbata</i>	4.5		0.16	225	na	0.3	na	na	na		
			<i>Euchaeta glacialis</i>	4.7		0.12	37	na	0.3	na	na	na		
			<i>Euchaeta norvegica</i>	4.5		0.13	172	na	0.3	na	na	na		
			<i>Metridia longa</i>	5.9		0.61	389	na	0.5	na	na	na		
			<i>Acartia</i> sp.	North Sea (central part)		15	1.7	491	na	2	na	na	na	[20]
			<i>Calanus finmarchicus</i> / <i>C. helgolandicus</i>			6.6	3.2	123	na	1	na	na	na	
			<i>Acartia</i> sp.	North Sea (central part)		9.7	2.5	225	na	0.7	na	na	na	
		<i>Anomalocera patersoni</i>	14		1.4	409	na	0.7	na	na	na			
		<i>Calanus finmarchicus</i> / <i>C. helgolandicus</i>	North Sea /Atlantic	7	10.9	70	na	1	na	na	na			
		<i>Calanus finmarchicus</i> / <i>C. helgolandicus</i>	North Sea (southern part)	7.1	1.8	129	na	1	na	na	na			
	Crustaceans - prawns	<i>Bentheogennema intermedia</i>	Iberian Deep Sea Plain	Whole animal	36	10.7	74	na	0.4	na	na	na	[17]	
		<i>Benthescymus iridescentis</i>		Whole animal	55	14.9	79	na	0.4	na	na	na		
		<i>Systellaspis debili</i>		Whole animal	49	16.3	62	na	0.6	na	na	na		
		<i>Crangon crangon</i>	Wadden Sea	Whole animal	na	0.17	na	na	0.66	na	na	na	[21]	
		<i>Litopenaeus stylirostris</i>	New Caledonia	Whole animal	40	<0.01	70	na	na	na	na	na	[22]	
		<i>Pleoticus muellerib</i>	Patagonia, Argentina	Muscle	2.75	na	5.65	na	na	na	na	na	[23]	



Table 3. Continued.

Subtype	Class	Species	Region of occurrence	Tissue examined	Average metal concentration [µg/g d. wt.]								Reference		
					Cu	Cd	Zn	Hg	Pb	Fe	Se	As			
Link in the food chain in the marine ecosystem	Invertebrates	Crustaceans – lobsters, crabs	<i>Jasus edwardsii</i>	Victoria, Australia	Edible part	55	0.3	124.5	na	na	na	na	na	[24]	
			<i>Panulirus inflatus</i>	Pacific Coast of Mexico	Muscle	8.1	0.02	19.8	na	0.05	na	na	na	[25]	
			<i>Portunus pelagicus</i>	Kuwait	Muscle	124	na	206.2	na	1.9	na	na	na	[26]	
		Echinoderms - starfish	<i>Asterias rubens</i>	North Sea (Belgian coast)	Duodenum	21.7	1.22	118.12	na	1.43	na	na	na	[27]	
				North Sea (coasts of Holland and Germany)		1.647	0.337	149.09	na	1.105	na	na	na	[28]	
				Central North Sea		98.25	1.205	260	na	1.56	na	na	na	[29]	
				North Sea (between Holland, Germany, and England)		19.215	1.5315	na	na	1.023	na	na	na	[30]	
	Vertebrates	Fish	Swordfish (<i>Xiphias gladius</i>) ^c	Western Indian Ocean (Mozambique Channel)	Muscle	0.64	1.04	41.7	1.61	0.12	22.4	2.45	na	[32]	
					Liver	54.7	163	213	5.33	0.18	617	53.1	na		
					Kidney	4.7	31.8	173	2.93	0.29	340	49.4	na		
			Swordfish (<i>Xiphias gladius</i>) ^c	Western Indian Ocean (Réunion I.)	Muscle	0.65	0.6	73.5	3.97	0.01	18.9	4	na		
					Liver	65.4	169	239	9.44	0.09	558	77.6	na		
					Kidney	2.09	22.2	177	4.03	0.04	469	98.6	na		
			Yellowfin Tuna (<i>Thunnus albacares</i>) ^c	Western Indian Ocean (Mozambique Channel)	Muscle	0.97	0.25	64.1	0.56	0.09	39.6	5	na		
					Liver	121	138	439	0.65	0.13	743	90.8	na		
					Kidney	2.56	3.39	23554	1.57	0.13	2415	112	na		
			Yellowfin Tuna (<i>Thunnus albacares</i>) ^c	Western Indian Ocean (Réunion I.)	Muscle	1.99	0.23	160	1.15	0.02	50.6	6.26	na		
					Liver	240	126	516	3.27	0.05	211	83.5	na		
					Kidney	11.2	24.1	14.67	1.48	0.08	1068	125	na		
			Common Dolphinfish (<i>Coryphaena hippurus</i>) ^c	Western Indian Ocean (Mozambique Channel)	Muscle	0.78	0.12	44.7	0.98	0.14	12.6	1.85	na		
					Liver	40.2	32.3	146	0.61	0.21	341	13.8	na		
					Kidney	1.48	1.79	134	0.43	0.61	6394	125	na		
			Common Dolphinfish (<i>Coryphaena hippurus</i>) ^c	Western Indian Ocean (Réunion I.)	Muscle	0.88	0.13	65.8	0.21	0.06	23.4	3.17	na		
					Liver	60.7	18.7	135	0.2	0.01	211	13.5	na		
					Kidney	5.98	8.91	172	0.17	0.15	392	20	na		
			Skipjack Tuna (<i>Katsuwonus pelamis</i>) ^c	Western Indian Ocean (Réunion I.)	Muscle	1.02	0.61	125	0.67	0.07	70.2	15.8	na		
					Liver	93.6	153	208	0.51	0.12	1296	73.2	na		
					Kidney	6.97	55.7	114	0.57	0.15	1033	40	na		
			Grass Goby (<i>Zosterisessor ophiocephalus</i>) ^c	Venice Lagoon	Muscle	1.09	na	20.3	na	0.24	9.99	na	na		[16]
			Gilthead Seabream (<i>Sparus auratus</i>)	Mediterranean Sea	Muscle	2.84	0.37	26.66	na	5.54	19.6	na	na		[4]
					Liver	33.37	0.96	76.47	na	8.87	256.5	na	na		
			Mediterranean Sand Smelt (<i>Atherina hepsetus</i>)	Mediterranean Sea	Muscle	4	0.37	24.34	na	6.12	78.4	na	na		
					Liver	54.17	1.17	70.18	na	41.24	393.22	na	na		
			Flathead Mullet (<i>Mugil cephalus</i>)	Mediterranean Sea	Muscle	4.41	0.66	37.39	na	5.32	38.71	na	na		
Liver					202.8	1.64	110.03	na	12.59	370.43	na	na			
Red Gurnard (<i>Trigla cumulus</i>)	Mediterranean Sea	Muscle	2.19	0.79	24.89	na	4.27	30.68	na	na					
		Liver	26.09	4.5	108.64	na	23.01	582.37	na	na					
European Pilchard (<i>Sardina pilchardus</i>)	Mediterranean Sea	Muscle	4.17	0.55	34.58	na	5.57	39.6	na	na					
		Liver	29.26	2.99	73.22	na	39.43	225.37	na	na					
Atlantic Saury (<i>Scomberesox saurus</i>)	Mediterranean Sea	Muscle	2.34	0.45	16.48	na	2.98	29.82	na	na					
		Liver	18.18	1.72	68.99	na	17.54	407.08	na	na					



Table 3. Continued.

Subtype	Class	Species	Region of occurrence	Tissue examined	Average metal concentration [µg/g d. wt.]								Reference
					Cu	Cd	Zn	Hg	Pb	Fe	Se	As	
Link in the food chain in the marine ecosystem	Vertebrates	Fish	Mediterranean Sea	Muscle	na	na	na	0.19	0.05	na	na	na	[6]
				Liver	na	na	na	0.07	0.09	na	na	na	
			Mediterranean Sea	Muscle	na	na	na	0.39	0.02	na	na	na	
				Liver	na	na	na	0.2	0.31	na	na	na	
			Baltic Sea	Muscle	0.4616	0.0084	9.0529	0.025	0.0118 ^b	na	na	na	[33]
				Muscle	0.5686	0.01739	24.0614	0.018	0.0112 ^b	na	na	na	
				Muscle	0.17	0.00157	4.3843	0.036	0.0078 ^b	na	na	na	
			Aegean Sea	Muscle	na	0.00621	na	0.088	0.1262 ^b	na	na	na	[34]
			Kerguelen Is.	Muscle	2.5	0.01	9.2	0.205	na	na	na	na	[35]
				Liver	5.8	4.23	92.9		na	na	na	na	
				Muscle	1.2	0.016	9.9	0.31	na	na	na	na	
				Liver	10.2	28.5	142		na	na	na	na	
				Muscle	0.7	0.049	19.6	0.255	na	na	na	na	
				Liver	4.8	2.82	99	0.513	na	na	na	na	
				Muscle	0.9	0.035	22	0.14	na	na	na	na	
				Liver	16.8	4.15	143	0.37	na	na	na	na	
				Kidney	na	na	na	0.47	na	na	na	na	
				Muscle	0.5	0.051	33.2	1.19	na	na	na	na	
				Liver	4	4.37	70.4	0.686	na	na	na	na	
				Kidney	na	na	na	0.102	na	na	na	na	
				Muscle	0.6	0.086	29.1	0.044	na	na	na	na	
				Liver	3.1	5.52	62.7	0.047	na	na	na	na	
				Kidney	na	na	na	0.533	na	na	na	na	
				Muscle	1	0.053	19.9	0.126	na	na	na	na	
				Liver	3.8	10.8	110	0.078	na	na	na	na	
				Kidney	na	na	na	0.03	na	na	na	na	
			Esmoriz-Paramos Lagoon, Portugal	Muscle	2.64	na	503.4	na	na	na	na	na	[36]
		Birds	Portugal	Muscle	20.293	0.056	42.836	2.669	0.371	na	5.195	3.182	[37]
				Liver	23.306	0.655	95.191	6.094	<LOD	na	12.755	5.616	
				Kidney	18.487	6.141	86.425	3.939	0.254	na	19.072	3.34	
			Réunion I.	Muscle	27.7	9.28	101	2.84	na	404	37.9	na	[38]
				Liver	20.2	66.8	316	24.3	na	2620	81.7	na	
				Kidney	19.5	145	235	24.2	na	526	148	na	
				Muscle	21	4.55	73	0.38	na	365	25.7	na	
				Liver	16.5	53	288	1.72	na	1540	57.3	na	
				Kidney	15.4	147	224	1.16	na	499	145	na	
				Muscle	28.1	3.67	86.7	0.75	na	367	23.3	na	
				Liver	29.3	47	305	1.89	na	2120	68.5	na	
				Kidney	24.2	117	241	1.88	na	539	160	na	
			Rishiri I., Japan	Muscle	12.7	0.393	53.7	0.6	na	na	1.7	na	[39]
				Liver	14.3	4.8	70.9	2.1	0.048	na	4.5	na	
				Kidney	13.1	40.7	98.8	1.5	0.249	na	6.9	na	
			Finnish Archipelago	Liver	712	10.9	264	na	na	6296.5	22.5	na	[40]
			Baltic Sea	Kidney	87.6	63.8	274	na	na	549	<LOD	na	
			Finnish Archipelago	Liver	13	0.15	170	5.8	1.1	1200	na	na	[41]
				Kidney	14	1.5	140	52	0.92	1200	na	na	
			San Francisco Bay	Muscle	na	na	na	0.98	na	na	na	na	[42]
				Liver	na	na	na	2.59	na	na	na	na	
				Kidney	na	na	na	2.64	na	na	na	na	

Table 3. Continued.

Link in the food chain in the marine ecosystem													
Subtype	Class	Species	Region of occurrence	Tissue examined	Average metal concentration [μg/g d. wt.]								Reference
					Cu	Cd	Zn	Hg	Pb	Fe	Se	As	
Vertebrates	Birds	Black-necked Stilt (<i>Himantopus mexicanus</i>)	San Francisco Bay	Muscle	na	na	na	2.58	na	na	na	na	[42]
				Liver	na	na	na	7.56	na	na	na	na	
				Kidney	na	na	na	6.82	na	na	na	na	
		Caspian Tern (<i>Hydroprogne caspia</i>)		Muscle	na	na	na	2.97	na	na	na	na	
				Liver	na	na	na	8.22	na	na	na	na	
				Kidney	na	na	na	8.53	na	na	na	na	
		Forster's Tern (<i>Sterna forsteri</i>)		Muscle	na	na	na	3.13	na	na	na	na	
				Liver	na	na	na	9.5	na	na	na	na	
				Kidney	na	na	na	11.6	na	na	na	na	
		Great Cormorant (<i>Phalacrocorax carbo</i>) ^c	Vistula Lagoon	Muscle	na	na	na	2.15	na	na	na	na	[44]
	Liver			na	na	na	15.51	na	na	na	na		
	Kidney			na	na	na	30.21	na	na	na	na		
	Reptiles – Sea Turtles	Hawksbill Sea Turtle (<i>Eretmochelys imbricata</i>)	East China Sea	Muscle	na	na	na	na	na	na	na	253	[46]
				Liver	na	na	na	na	na	na	na	25.3	
				Kidney	na	na	na	na	na	na	na	28.3	
		Loggerhead Sea Turtle (<i>Caretta caretta</i>)	East China Sea	Muscle	na	na	na	na	na	na	na	20.6	
				Liver	na	na	na	na	na	na	na	6.32	
				Kidney	na	na	na	na	na	na	na	9.47	
		Green Sea Turtle (<i>Chelonia mydas</i>)	East China Sea	Muscle	na	na	na	na	na	na	na	24.1	
				Liver	na	na	na	na	na	na	na	1.76	
				Kidney	na	na	na	na	na	na	na	5.72	
		Loggerhead Sea Turtle (<i>Caretta caretta</i>)	Adriatic Sea	Muscle	na	0.55	na	0.69	0.54	na	na	68.94	
				Liver	na	7.6	na	1.68	1.23	na	na	21.67	
				Kidney	na	24.23	na	0.65	<LOD	na	na	29.91	
		Green Sea Turtle (<i>Chelonia mydas</i>)	South China Sea	Muscle	1.562	0.172	238.7	0.05252	0.264	na	na	14.61	
				Liver	9.168	1.455	211.6	0.1257	0.826	na	na	29.57	
				Kidney	na	na	na	na	na	na	na	na	
		Olive Ridley Sea Turtle (<i>Lepidochelys olivacea</i>)	Baja California peninsula	Muscle	1.28	0.48	85.78	na	<LOD	93.09	na	na	
				Liver	36.73	27.89	47.14	na	<LOD	731	na	na	
				Kidney	4.86	60.03	6.68	na	0.03	193	na	na	
		Hawksbill Sea Turtle (<i>Eretmochelys imbricata</i>)	Baja California peninsula	Muscle	3.68	1.02	82.45	na	<LOD	258	na	na	
				Liver	2.47	0.49	25.89	na	<LOD	71.88	na	na	
				Kidney	3.89	4.2	82.45	na	<LOD	362	na	na	
		Loggerhead Sea Turtle (<i>Caretta caretta</i>)	Baja California peninsula	Muscle	0.41	0.1	31.11	na	0.01	77.44	na	na	
				Liver	33.94	1.75	69.14	na	<LOD	301	na	na	
				Kidney	na	73.11	na	na	0.03	na	na	na	
		Green Sea Turtle (<i>Chelonia mydas</i>)	Baja California peninsula	Muscle	0.03	0.01	38.26	na	0.01	20.99	na	na	
				Liver	60.04	3.3	62.91	na	<LOD	14.35	na	na	
				Kidney	5.67	121	128	na	0.01	44.09	na	na	
		Loggerhead Sea Turtle (<i>Caretta caretta</i>)	Mediterranean Sea	Muscle	na	0.57	na	0.48	2.46	na	na	na	
				Liver	na	8.64	na	2.41	<LOD	na	na	na	
				Kidney	na	30.5	na	0.47	2.45	na	na	na	
	Green Sea Turtle (<i>Chelonia mydas</i>)	Mediterranean Sea	Muscle	na	0.37	na	0.09	<LOD	na	na	na		
			Liver	na	5.89	na	0.55	<LOD	na	na	na		
			Kidney	na	3.46	na	<LOD	1.81	na	na	na		
	Green Sea Turtle (<i>Chelonia mydas</i>)	Brazil, Atlantic coast	Muscle	na	na	na	na	na	na	na	na		
			Liver	39.9	0.957	na	na	na	na	na	na		
			Kidney	13.72	2.18	na	na	na	na	na	na		
	Green Sea Turtle (<i>Chelonia mydas</i>)	Bahia Magdalena, Mexico	Muscle	na	na	na	na	na	na	na	na		
			Liver	76.52	16.92	90.95	na	<LOD	350	na	na		
			Kidney	5.83	110	189	na	0.05	93.16	na	na		

Table 3. Continued.

Subtype	Class	Species	Region of occurrence	Tissue examined	Average metal concentration [µg/g d. wt.]								Reference
					Cu	Cd	Zn	Hg	Pb	Fe	Se	As	
Link in the food chain in the marine ecosystem	Vertebrates	Mammals	Northern Fur Seal (<i>Callorhinus ursinus</i>)	Liver	na	78.8	na	140	na	na	351	na	[52]
				Kidney	na	255	na	6.2	na	na	24	na	
				Liver	na	119	na	260	na	na	140	na	
				Kidney	na	109	na	28	na	na	21	na	
			Minke Whale (<i>Balaenoptera acutorostrata</i>) ^a	Liver	27.1	40.7	208.5	0.1745	na	na	13.25	na	[53]
			Grey Whale (<i>Eschrichtius robustus</i>)	Liver	57.3	1.77	141	na	na	na	na	na	[54]
				Kidney	27.7	15.4	120	na	na	na	na	na	
			Striped Dolphin (<i>Stenella coeruleoalba</i>)	Liver	22.1	4.43	111.06	592.97	na	na	265.95	na	[55]
				Kidney	14.2	27.51	100.21	43.75	na	na	26.11	na	
			Striped Dolphin (<i>Stenella coeruleoalba</i>)	Liver	39.24	3.95	161.53	1043.14	na	na	100.82	na	
				Kidney	12.27	8.38	82.09	62.84	na	na	51.32	na	
			Striped Dolphin (<i>Stenella coeruleoalba</i>)	Liver	11.6 ^e	3.39 ^e	111g	16.2	< 0.8 ^f	291 ^g	4.49 ^f	< 0.95 ^f	[64]
			Bowhead Whale (<i>Balaena mysticetus</i>)	Liver	20	31	137	0.264	na	na	4.14	na	[56]
			Harbour Porpoise (<i>Phocoena phocoena</i>)	Liver	19.8	0.24	91.9	21.9	< 0.8 ^f	928	6.09 ^f	< 0.95 ^f	[64]
			Harbour Porpoise (<i>Phocoena phocoena</i>) ^b	Liver	14.4	0.07	103	na	0.39	658	na	na	[65]
				Kidney	8.33	0.63	75.3	na	0.41	405	na	na	
			Harbour Porpoise (<i>Phocoena phocoena</i>) ^b	Liver	19.4	0.17	123	na	nd	964	na	na	
				Kidney	11.6	1.21	77.9	na	0.41	509	na	na	
			Harbour Porpoise (<i>Phocoena phocoena</i>) ^b	Liver	16.3	6.61	118	na	nd	502	na	na	
				Kidney	12.7	49.6	124	na	nd	233	na	na	
			Grey Seal (<i>Halichoerus grypus</i>)	Liver	20.0 ^g	0.16 ^g	74.7 ^g	113	< 0.8 ^f	1010 ^g	<1.7 ^f	< 0.95 ^f	[64]

a – values given for animals from the vicinity of the port

b – concentration given for males and females

c – mean values calculated from annual values

d – converted to wet weight

e – values given for adult specimens

f – maximum values

g – median

h – for 1-2 year old animals

na – not analyzed

nd – not detected

*all values given as reported in the cited papers

bioindicators have been used in *A. rubens*, e.g. the level of cytochrome P450 in the digestive and storage organs, the level of production of reactive oxygen species (ROS) by amoebocytes [28, 29], and the level of metallothionein [30].

The highest concentrations of copper (Table 3) were determined in starfish tissues from the central North Sea; this may be due to the fact that contaminants enter the sea from all countries with access to it.

The influence of various different factors, e.g. body part, season, sex, type of prey, has been studied in starfish [31]: it was shown that body part and area of occurrence were mainly responsible for the accumulation of metals (Table 4). It also turned out that gametogenesis also affects metal levels. Considerable interactions were observed

between body parts and area of occurrence in the case of elements like Zn, Cd, Fe, and Cu, although the availability of metals differs with respect to area of occurrence. The relationship between body part and sampling period was statistically not significant, which suggests that bioaccumulation took place simultaneously in many parts of the body. The above-mentioned factors have the greatest influence on Pb levels in starfish [31].

The accumulation of zinc was found to be at its most intense in the duodenum. Metabolic activity is highest in the duodenum and stores the largest amounts of metals with the aid of binding proteins like metallothionein. Zinc is a constituent of enzymes, which may also explain its high levels. Zn levels are also far higher in the female gonads

Table 4. Changes in metal concentrations [%] with respect to different factors and the interactions between them [31].

Factor	Change in metal concentration [%]				
	Zn	Pb	Cd	Fe	Cu
Part of the body	5.1	88.4	39.7	31.9	33.8
Site of occurrence	19.1	0.5	3.3	7.3	6.8
Sampling period	2.3	0.3	3.3	0.7	2.5
Part of the body × site of occurrence	24.6	1	8.1	29	18.8
Part of the body × sampling period	2.8	2.2	2.5	1.5	5.1

than in the male ones [31]. This is very likely because the high-molecular weight proteins in the starfish duodenum contain Zn, which in the form bound to metallothionein then gets into the gonads [68].

Accumulation of Metals in Vertebrate Tissues

Fish

Fish like swordfish (*Xiphias gladius*), yellowfin tuna (*Thunnus albacares*), skipjack tuna (*Katsuwonus pelamis*), and common dolphinfish (*Coryphaena hippurus*) are at the end of the food chain, so one can infer that these animals are particularly exposed to the high metal contents in their food. These are pelagic fish with high rates of metabolism, which means that their rate of xenobiotic uptake is also high. Because of their position in the trophic chain and their ability to bioaccumulate metals, these fish can be used as bioindicators for assessing pollution levels in the regions they inhabit [32]. Leaping Mullet (*Liza saliens*) is also suitable for this purpose [36].

High level of lead in muscle tissue was detected in *Zosterisessor ophiocephalus* (Table 3), which may well be due to the considerable pollution in Venice Lagoon resulting from the relatively long-standing human activities in this region [16]. Where the fish from the Mozambique Channel and the Island of Réunion are concerned, those from the former waters have a high level of lead in them, owing to the intensity of the pollution entering them from southeastern Africa and Madagascar.

These levels of Pb in fish muscles are similar to those determined in Halibut (*Reinhardtius hippoglossoides*) and shorthorn sculpin (*Myoxocephalus scorpius*) from Greenland [75, 76]. Much of the lead in their environment is due to volcanic activity, but in the case of the fish from Réunion, the low Pb level suggests that this particular source is only of minimal significance there. The relatively low degree of anthropogenic pollutants reaching the western Indian Ocean means that the fish there are less exposed to toxicants [32].

There are considerable differences in Pb levels in the tissues of fish from the Mediterranean Sea. This may be due to the various abilities of fish to induce metal-binding proteins (e.g. metallothionein) [68], whose activity rises substantially in the liver. This is confirmed by studies.

Moreover, the Mediterranean Sea is a semi-enclosed sea, surrounded by thickly polluted and highly industrialized countries, from which large quantities of pollutants enter this sea [6]. The highest amounts of Pb were detected in the Mediterranean sand smelt and European pilchard, which is probably a consequence of their dietary habits (Table 1). A relationship between bioaccumulation and diet has been observed in other organisms. Fish from the Baltic Sea have a lower level of lead than those from the Mediterranean Sea, mainly because they occupy a lower level in the trophic pyramid.

Pelagic fish are excellent bioaccumulators, differing in their rates of growth, maximum body sizes, life strategies, and food preferences. These are the main factors explaining the differences between the metal levels in their tissues. The swordfish, for example, is a large, long-lived fish, in consequence suffering long-term exposure to pollutants [32] and accumulating large quantities of metals in its tissues. swordfish feed on larger organisms (epipelagic and mesopelagic) than tuna or dolphinfish. Mesopelagic waters, being less well aerated than surface waters, favour the methylation of mercury and its transformation from inorganic to organic forms; this causes an increase in the absorption of metals and their compounds in animals [6].

Large quantities of cadmium are found in swordfish, which is a consequence of metal bioaccumulation from its prey items. This fish feeds mainly on cephalopods, whose tissues contain high levels of cadmium; this leads to high Cd levels in the tissues of marine predators at the end of the food chain [32]. On the other hand, the differences in Cd levels in swordfish and common dolphinfish tissues result from the different amounts of cephalopods they consume (50% for the swordfish and 38% for the common dolphinfish from the Mozambique Channel, and 31% and 2% respectively for the Island of Réunion [32]). It turns out, moreover, that metal concentrations (mainly Cd) in the tissues of these fish differ with respect to the season, because their diets change during the year [35].

Relatively high concentrations of copper and zinc were determined in leaping mullet from the Esmoriz-Paramos Lagoon in Portugal. As a result of industrial, agricultural, and other human activities, the ecosystem of this lagoon is gradually being destroyed. Heavy metal pollution is the deciding factor as regards the quality of the water and the health of the local fish [36].

In contrast to the yellowfin and skipjack tuna, the common dolphinfish contained lower concentrations of metals, which is probably due to its smaller size, short life (4 years) and high growth rate [32, 77].

Humans, too, are exposed to the heavy metals present in fish and crustaceans as a result of eating these animals. Fish and crustaceans are important components of the diet because of their content of essential elements and vitamins. But the consumption of marine animals containing large quantities of metals and other pollutants [61] may raise levels of these metals in human tissues [78]. A correlation has been demonstrated between blood levels of mercury and methyl mercury and the quantities of fish consumed [79]. It was also found that among the Faroe islanders, who consume considerable quantities of seafood, mercury levels in children's hair were found to increase with time of exposure [61, 79].

The highest Hg levels (Table 5) were determined in marlin and yellowfin tuna. This is because these fish are predators occupying quite a high position in the trophic chain [14, 61]. In the case of these fish, Hg concentrations are sufficiently high to cause serious health problems for the people eating them [61].

Manila Bay is not an area subjected to intensive human pressure [80], as a result of which the high levels of copper (Table 5) found in the tissues of the Indo-Pacific blue marlin (*Makaira mazara*) are due to the fish's demand for this element in order to ensure the correct functioning of the enzymes controlling metabolic processes. On the other hand, the highest quantities of arsenic were determined in flounder and angler, which may be due to the trophic status of these fish. Moreover, it seems that levels of Zn, Cd, and Pb are the highest in herbivorous fish; carnivorous fish only have high levels of Cu and Pb.

The interspecific differences in metal concentrations are probably due not only to the trophic level occupied by a particular fish species, but also to the region it inhabits, means of feeding and the ability of metals to be biomagnified in the food chain. That is why the concentrations of metals like mercury are high in fish from higher trophic levels [14]. The bioaccumulation of metals in tissues also depends on the size and age of fish [83, 84]; it was in the tuna, therefore, the largest and longest-lived of all fish, that determined levels of cadmium and mercury were high [14]. Like the Patagonian toothfish and the bluefish, cod are medium-sized predators, feeding on smaller fish, which is why higher metal levels were recorded in these species.

The analysis of the interspecific differences in the intensity of human pressure is a great challenge, since fish come from different regions, feed on different prey, are of different sizes, and live to different ages [14].

Birds

Seabirds spend most of their lives at sea or on coasts [43], and as predators they are exposed to a wide range of chemical compounds and, consequently, to the bioaccumulation and biomagnification of metals [85]. These birds are often regarded as bioindicators of marine pollution because

of their position in the food chain and the course taken by metal bioaccumulation [38, 86]. They are widespread, long-lived, easily observed and bioaccumulation of metals is dependent on time and region [43]. Marine pollution in overwintering areas and on migration pathways is a serious problem [37]. Relatively few data are available on the mechanisms governing the entry of metals into the eggs of seabirds [39].

It is those birds that feed on fish and invertebrates that are endangered by metals. Seabirds have an advantage over terrestrial birds in that they possess several mechanisms protecting them against the toxic action of metals [87]. Metals are not uniformly accumulated in all tissues. It is thought that Hg and Cd are deposited in the liver and kidneys of birds over a long period of time, an observation that is borne out by the increasing levels of these metals with a bird's age [38].

Seabirds are more resistant to the harmful effects of mercury because they are capable of detoxifying it [37, 68]. In the case of cadmium there is a correlation between the level of this metal in the kidneys and that in the liver [62]. The greater concentrations of Cd in the kidneys than in the liver of seabirds is indicative of their chronic exposure to this element.

Hg levels depend on the sex of the species exposed: they are lower in females because some 20% of MeHg is transferred from the soft tissues to the egg [88]. Moreover, the accumulation of Hg usually increases with a bird's age [37, 63, 68]. In the Black-tailed Gull, however, the reverse was found to be the case: kidney levels of Hg fell with age. A relationship was also found between the Hg and Cd levels in the liver and kidneys. The levels of these unwanted metals in this gull species is not controlled by homeostatic processes [39, 68].

The size of a bird and its longevity influence the levels of trace elements in its body in that dilution takes effect. A long life favours the accumulation of metals [38]. Some of the highest concentrations of metals have been found in the relatively large-sized and long-lived Barau's petrel (*Pterodroma barau*).

The highest levels of metals are recorded in the tissues of carnivorous seabirds (Tables 2, 3). But Barau's petrel rarely eats fish – its diet consists mostly of cephalopods. These inhabit poorly aerated waters, which increases the possibility of mercury methylation, facilitating the entry of this metal into animal organisms [89]. Seabirds also have higher Hg levels than land birds [38, 89]. Sometimes it turns out that metal levels are higher in young birds than in adults, for example, in the white-billed tropicbird, which may be due to the life cycles of this species [38].

Relationships have been found between the levels of Zn, Cu, and Hg in all tissues, which suggests that the relevant metabolic processes are similar; likewise there are relationships between Se and As, and between Se and Cr, indicating that Se plays a crucial part in the storage and detoxification of these elements [37, 68]. Cu, Zn, and Hg all tend to accumulate in the feathers [68, 90].

The registered metal concentrations may indeed reflect real pollution levels, or they may be the consequence of



Table 5. Concentrations of metals and arsenic [$\mu\text{g/g d. wt.}$] in the muscle tissue of fish eaten by humans.

Species	Region	Metal concentration [$\mu\text{g/g d. wt.}$]						Reference
		Pb	Cu	Zn	Cd	Hg	As	
Indo-Pacific Blue Marlin (<i>Makaira mazara</i>) ^a	Taiwan	1.43	1.08	34.8	0.12	10.3	0.63	[61]
Yellowfin Tuna (<i>Thunnus albacares</i>) ^a		0.21	0.86	17.4	0.07	9.75	0.21	
Pacific Saury (<i>Cololabis saira</i>) ^a		0.055	4.66	63	0.03	1.58	4.39	
Largehead Hairtail (<i>Trichiurus lepturus</i>) ^a		0.13	0.985	20.6	0.13	1.28	0.935	
Japanese Seabass (<i>Lateolabrax japonicus</i>) ^a		0.145	1.3	38	0.035	1.045	0.56	
Milkfish (<i>Chanos chanos</i>) ^a		0.3	3.06	60.5	0.035	1.96	0.375	
Mozambique Tilapia (<i>Tilapia mossambica</i>) ^a		0.125	1.56	64	0.105	2.54	0.355	
Common Carp (<i>Cyprinus carpio</i>) ^a		0.045	4.85	121	0.01	2.41	4.64	
(<i>Leiognathus brevivirostris</i>) ^b Leiognathidae	Manila Bay, Philippines	0.0598	2.14	46.7	0.0075	0.0554	na	[80]
(<i>Leiognathus bonus</i>) ^b Leiognathidae		0.17	3.46	124	0.0215	0.19	na	
(<i>Upeneus moluccensis</i>) ^b Mullidae		0.0951	2.12	66.1	0.015	0.125	na	
(<i>Therapon jarbua</i>) ^b Perciformes		0.0375	1.11	80.4	0.0229	0.0868	na	
(<i>Apolectus miger</i>) ^b Bramidae		0.178	2.26	75.1	0.0491	0.128	na	
(<i>Valamugil siheli</i>) ^b Mugilidae		0.301	2.84	62.9	0.01	0.0488	na	
(<i>Sillago sihama</i>) ^b Gadidae		0.106	1.68	108	0.0689	0.101	na	
(<i>Lutjanus russeli</i>) ^b Lutjanidae		0.1	1.19	43.9	0.0609	0.107	na	
<i>Siganidae</i> ^b		0.134	2.48	42.3	0.071	0.204	na	
(<i>Decapterus macrosoma</i>) ^b Carangidae		0.0589	5.45	72.3	0.0674	0.35	na	
(<i>Sardinella leiogaster</i>) ^b Clupeidae		0.271	3.74	94.2	0.013	0.138	na	
(<i>Selaroides leptolepis</i>) ^b Carangidae		0.296	3.4	68.9	0.0269	0.235	na	
(<i>Sardinella punctatus</i>) ^b Clupeidae		0.24	4.7	113	0.012	1.39	na	
Largehead Hairtail (<i>Trichiurus lepturus</i>) ^b		0.0574	2.34	39	0.0149	0.123	na	
Climbing Perch (<i>Anabas testudineus</i>) ^b		0.0813	1.99	59.7	0.0164	0.179	na	
Narrow-Barred Spanish Mackerel (<i>Scomberomorus commerson</i>) ^b		0.13	2.75	69.7	0.0095	0.73	na	
(<i>Scomberoides</i> sp.) ^b Carangidae		0.0752	1.88	55.1	0.00245	0.204	na	
Bluefish (<i>Pomatomus saltatrix</i>) ^c	New Jersey	0.06	na	na	0.006	0.26	0.26	[14]
Patagonian Toothfish (<i>Dissostichus eleginoides</i>) ^c		0.11	na	na	0.004	0.38	1.7	
<i>Sciaenidae</i> ^c		0.09	na	na	0.001	0.14	1.9	
Flounder (<i>Pleuronectes</i>) ^c		0.06	na	na	0.01	0.05	3.3	
<i>Sparidae</i> ^c		0.14	na	na	0.004	0.1	1.8	
Red Snapper (<i>Lutjanus campechanus</i>) ^c		0.12	na	na	0.002	0.24	0.23	
Whiting (<i>Merlangius merlangus</i>) ^c		0.09	na	na	0.009	0.04	1.9	
Atlantic Cod (<i>Gadus morhua</i>) ^c		0.12	na	na	0.0005	0.11	2.2	
Yellowfin Tuna (<i>Thunnus albacares</i>) ^c		0.04	na	na	0.03	0.65	1	
Angler (<i>Lophius piscatorius</i>) ^c	Rockall Trough	<0.002	0.15	na	<0.002	na	8.63	[81]
Black Scabbardfish (<i>Aphanopus carbo</i>) ^c		0.009	0.12	2.85	0.004	na	1.25	
Blue Ling (<i>Molva dypterygia</i>) ^c		0.003	0.15	na	0.002	na	8.03	
Blue Whiting (<i>Micromesistius poutassou</i>) ^c		0.008	0.29	na	0.022	na	2.24	
European Hake (<i>Merluccius merluccius</i>) ^c		0.008	0.27	na	0.034	na	1.37	
White Seabream (<i>Sargus sargus</i>) ^c	El-Mex Bay, Egypt	0.53	1.05	4.86	0.19	na	na	[82]
Marbled Spinefoot (<i>Siganus rivulatus</i>) ^c		0.82	1.78	8.26	0.49	na	na	
Flathead Mullet (<i>Mugil cephalus</i>) ^c		0.73	1.22	6.75	0.47	na	na	
Blue Runner (<i>Caranx crysos</i>) ^c		0.89	2.76	3.82	0.21	na	na	

a – geometric means given

b – data given for the whole body

c – data converted to wet weight



contaminants reaching a given level as a result of the activity of sea currents or of the migration of predatory species [38]. Birds can be used as organisms providing early warning of metals to which humans and other compartments of the environment may be exposed [43].

Sea Turtles

Sea turtles are classified into two families: *Cheloniidae* and *Dermochelyidae*, which occur mainly in tropical, subtropical, and temperate waters. They undertake migrations of hundreds of kilometres between foraging and breeding areas. Being in danger of extinction, they are afforded protection; this applies in particular to the loggerhead sea turtle [45, 47].

Young turtles are absolute carnivores; it is only when they reach adulthood that they begin to vary their diet. For example, the green sea turtle (*Chelonia mydas*) prefers algae, occasionally taking crustaceans, molluscs, and jellyfish. The loggerhead sea turtle (*Caretta caretta*) consumes mostly fish, bivalves, cephalopods, and sponges. These last are the main component in the diet of the hawksbill sea turtle (*Eretmochelys imbricata*).

These reptiles are exposed to a particularly broad spectrum of marine pollutants [46, 48]. They are capable of swallowing plastic waste; they are affected by oil spills, heavy metals, and stable organochlorine compounds. Pieces of plastic, glass, and paper have often been found in the intestines of turtles caught off the Azores and the north-west coasts of Europe [47]. They are known to mistake plastic bags for jellyfish, one of their natural sources of food.

Sea turtles are long-lived animals, exposed to the action of xenobiotics in sediments, water and food. Moreover, they have a varied diet, depending on their position in the trophic web and their areas of occurrence. They reflect well the state of pollution in their environments [91, 92, 50], which means they give a better indication of potential threats to humans than physical measurements. High tissue levels of metals tend to be found in turtles inhabiting coastal waters [50].

Because of the nature of the diet of green and loggerhead sea turtles, large quantities of e.g. arsenic are to be expected [68]. The accumulation of this element in sea turtle tissues depends to a large extent on the dietary preferences of a given species (Table 1) [46]. For example, green sea turtles inhabiting the Bahia Magdalena, foraging mainly on red algae, are exposed to far higher levels of arsenic, since rhodophyta accumulate greater concentrations of arsenic pollutants in their thalli than other algae [51].

Chromatographic analysis of solvent extracts of sea turtle tissues indicates that the prevalent compound of arsenic is arsenobetaine. Moreover, considerable amounts of dimethylarsinic acid were found in liver and kidney samples from hawksbill and green sea turtles, but this compound was not found in the muscle tissue of any of the sea turtle species examined, or in any tissues of the loggerhead [46].

In the case of the leatherback sea turtle, practically all the arsenobetaine was determined in the pectoral muscle, whereas arsenocholine and arsenates were also found in the cardiac muscle [93]. Moreover, the tetramethylarsenium ion, arsenocholine, and large quantities of arsenobetaine were determined in jellyfish, the principal constituent of the leatherback's diet [94]. On the other hand, arsenobetaine was the main arsenic compound determined in the marine algae and tissues of the molluscs eaten by these turtles [68].

The interspecific differences in the intensity of Cd accumulation are probably due to the different metabolisms and capacities to accumulate Cd in the two sea turtle species (Table 1) [48]. Cd levels are decidedly higher in the kidneys than in their livers. More Cd was determined in the liver following short-term exposure, but more in the kidneys after long-term exposure, which provides confirmation of the relationship between Cd levels in tissues and the duration of exposure to this element [68]. Even though Cd levels in sea turtle kidneys may be a good reflection of the state of health of these reptiles, its levels in the liver better reflect the contamination of the animal's food, and hence the environmental exposure to this element can be defined more precisely [51]. Unlike arsenic, greater concentrations of cadmium were found in the tissues of older turtles [45, 50, 91].

Table 6 lists data from the literature on metal concentrations in plants consumed by sea turtles and in plants found in their stomachs. Comparison of the levels of these metals in plants with those in sea turtle livers and kidneys indicates that it is that dietary constituent present in the highest concentration in plants that has the greatest effect on metal levels in tissues.

The levels of metals in marine plants is governed by the bioavailability of the metals and the capacity of particular plant species to bioaccumulate them. Marine algae are superior to other plants in this respect [51, 95]. Red algae, like *Gracilaria* sp., are capable of bioaccumulating larger amounts of Cd, Cu, and Zn than macroalgae [95], which may be the cause of high levels of these metals in the tissues of green sea turtles [51].

A significant relationship has been found between Cd and Hg levels in the tissues of young sea turtles [47]. These metals accumulate in these young individuals, possibly as a consequence of their sexual immaturity. Species from the genus *Caretta* achieve sexual maturity on reaching a weight of around 80 kg. During this time their hormonal activity increases, which may affect the metabolic processes responsible for the uptake and distribution of metals in the various tissues of these animals [47].

The high concentrations of Cu may be due to the particular way in which it is bioaccumulated in these reptiles, and do not therefore reflect the pollution of the environment and turtle habitats. Metal levels in the tissues of sea turtles from the same region can differ considerably, which indicates that diet and metabolism govern the bioaccumulation of metals in particular individuals.

High levels of Ni and Cu have been found in the tissues of some sea turtles. This is particularly dangerous, because the toxicity of nickel increases in the presence of copper [68].



Table 6. Metal concentrations [$\mu\text{g/g d. wt.}$] in plants consumed by the Green Sea Turtle (*Chelonia mydas*) [51].

Species	Metal concentrations [μg/g d. wt.]							Content in the stomach [%]*
	Pb	Cd	Ni	Mn	Fe	Zn	Cu	
In the bay								
<i>Codium amplivesiculatum</i>	0.8	0.01	7.29	20.4	350	8.75	0.98	
<i>Gracilaria textorii</i>	0.83	3.65	4.94	46.92	401	12.31	1.34	
<i>Gracilaria vermiculophylla</i>	0.84	1.4	4.26	19.33	236	9.59	0.99	
<i>Ruppia maritima</i>	2.12	4.52	2.29	30.6	1230	16.93	0.45	
<i>Zostera marina</i>	1.23	1.09	2.94	56.25	341	15.04	0.98	
In the stomach								
<i>Codium amplivesiculatum</i>	0.01	2.49	0.9	12.73	173	8.82	0.79	
<i>Gracilaria textorii</i>	<LOQ	6.31	2.66	11.89	49.43	11.19	0.69	16.5
<i>Gracilaria vermiculophylla</i>	<LOQ	5.79	2.77	6.25	40.54	13.8	1.11	36.4
<i>Ruppia maritima</i>	0.12	11.11	9.67	10.55	209	60.96	5.7	8.7
<i>Zostera marina</i>	0.07	4.69	3.03	7.92	97.8	38.67	0.49	6.9
<i>Kidney of Chelonia mydas</i>	0.05	110	3.19	1.15	93.16	189	5.83	
<i>Liver of Chelonia mydas</i>	<LOQ	16.92	<LOQ	0.24	350	90.95	76.52	
LOD	0.006	0.0009	0.004	0.002	0.005	0.0008	0.0025	
LOQ = 3 LOD	0.018	0.0027	0.012	0.006	0.015	0.0024	0.0075	

*the remaining 17.7 % consisted of other plants

Table 7. Concentrations of metals [$\mu\text{g/g d. wt.}$] in the fatty tissue of different species of Sea Turtle [45].

Species	Region	Concentration of metals [$\mu\text{g/g d. wt.}$]						
		Cd	Cu	Zn	Pb	Fe	Ni	Mn
Olive Ridley Sea Turtle (<i>Lepidochelys olivacea</i>)	Baja California	0.69	0.83	3.7	<LOD	27.91	0.03	2.1
Hawksbill Sea Turtle (<i>Eretmochelys imbricata</i>)		0.43	0.72	42.39	<LOD	11.14	<LOD	2.53
Loggerhead Sea Turtle (<i>Caretta caretta</i>)		0.5	0.69	12.66	<LOD	1.33	0.17	1.82
Green Sea Turtle (<i>Chelonia mydas</i>)		0.002	0.01	49.82	0.03	2.63	0.02	0.003
LOD		0.0009	0.0025	0.0008	0.006	0.005	0.004	0.002

The most serious toxic effects can therefore be expected in those turtles in which high levels of both these elements have been found.

The high concentrations of anthropogenic lead in the northern Atlantic in comparison with the relatively clean waters of the southern Atlantic [50] are put forward as an explanation for the high and age-related rise in Pb accumulation in the kidneys and muscles of the Mediterranean loggerhead sea turtle, although no Pb was detected in its liver [50].

Metal levels have been determined not only in the liver, kidneys, and muscles, but also in the fatty tissue of sea turtles (Table 7): they depend on the species of sea turtle, which is no doubt a reflection of the different diets and metabolisms in these animals.

It has been found that in sea turtles metals are transferred from the maternal organism to the eggs (Fig. 1), the most mobile metals being Fe, Mn, Zn, and Cu, and to a lesser extent the toxic Cd and Hg [96].

Mammals

Levels of accumulated toxic metals like Hg and Cd in the tissues of marine mammals are high in consequence of the position they occupy in the food chain [52]. Most of these animals are capable of accumulating large quantities of Hg in the liver and Cd in the kidneys without showing any signs of having been poisoned [52].

Particularly high levels of Hg (Table 3) have been determined in the liver of striped and Risso dolphins, which may

be due to the deposits of cinnabar (HgS) at the bottom of the Mediterranean Sea. Human activities and the distribution of metals can also affect Hg levels in marine organisms [55]. Mercury accumulated in the liver is usually in inorganic form. In the kidneys and skin the largest concentrations of Hg were determined in the striped dolphin, which has a very poor capacity to excrete mercury. In dolphins the accumulation of mercury increases with age: Hg levels in older animals are several orders of magnitude higher than in younger animals [55, 68].

A correlation has also been found between levels of Hg and Se in the liver, which is confirmation of selenium's protective role against the toxic effects of mercury. That is why it is thought that elevated levels of Hg in the tissues of mammals inhabiting the waters of the Baltic Sea, among others, are not a threat to their health. Mercury is bound by selenium to form the non-toxic compound HgSe in mammalian livers [64, 68].

The largest concentrations of Cd were found in Risso and striped dolphins – this is a consequence of their diet (Table 1), which differs, depending on foraging conditions and food availability [55].

The highest levels of Cu and Zn were determined in liver and kidney samples from Minke and grey whales. The levels of these metals in the tissues of marine mammals are regulated by homeostatic mechanisms [55], existing independently of species [54, 68].

In the case of metals not eliciting toxic effects, like Cu or Zn, their levels in mammalian tissues do not usually reflect their levels in seawater. This is because these elements are often components of the many enzymes participating in homeostatically regulated biochemical and physiological processes [64, 68]. Only an excess or a deficiency of Zn is noticeable, because then undesirable effects begin to appear in mammals [64].

Conclusions

The bioaccumulation of metals in animals from different levels of the trophic pyramid is a serious problem for their health. This process depends on both biotic and abiotic factors. The most important one is considered to be the diet of these animals.

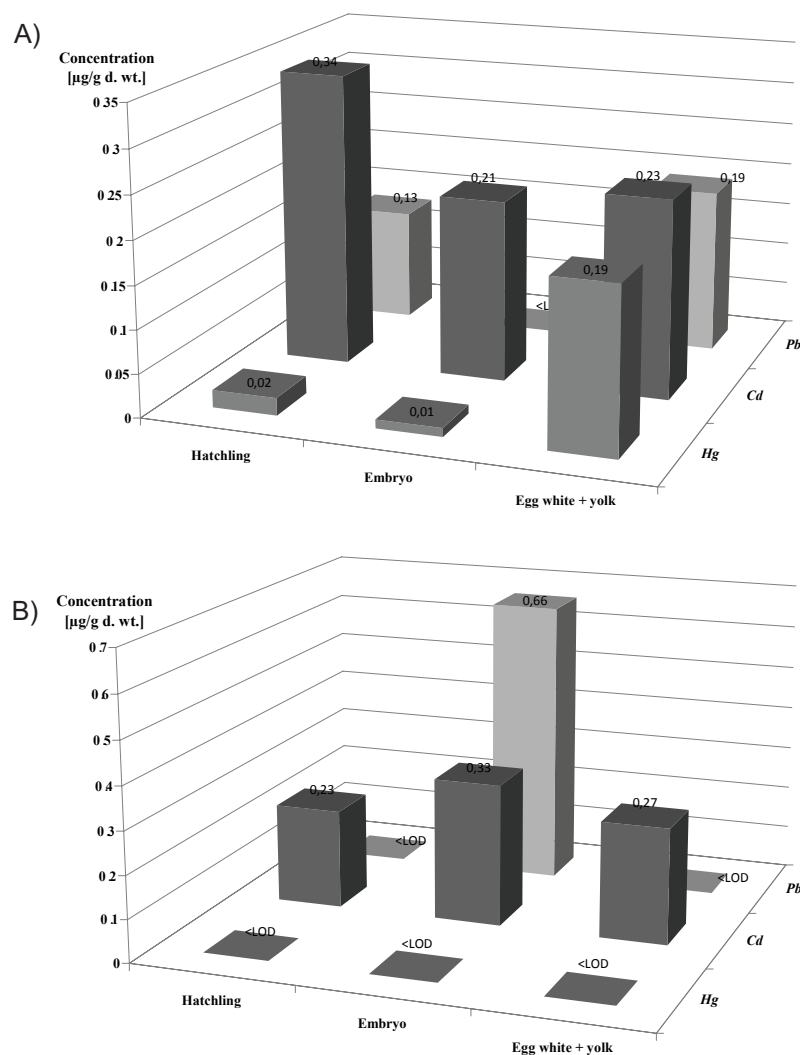


Fig. 1. Concentrations of cadmium [$\mu\text{g/g d. wt.}$] in Sea Turtle eggs. A – loggerhead sea turtle (*Caretta caretta*), B – green sea turtle (*Chelonia mydas*) [48].

Many molluscs, crustaceans or echinoderms act as indicators for assessing the bioavailability of metals. Their levels in the tissues of animals from different parts of the trophic web and levels of the trophic pyramid in the marine ecosystem show that they are accumulated to various degrees, depending on both the properties of the species in question and the environmental conditions in which it lives.

The animals most exposed are those at the top of the trophic pyramid – metal levels in their tissues are the highest. The type of food ingested is also important, so when analyzing the accumulation of metals one should not focus solely on the species from one trophic level. The investigation should be expanded to include adjacent trophic levels, located above or below the one under scrutiny, including the level occupied by human beings.

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