

The bioaccumulation of heavy metal (mercury) in the food chain

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Abstract

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The paper shows heavy metal (mercury) concentrations at selected points. The data was collected using the remote sensing method from the EMODnet network. The Mediterranean region was analyzed. The measured values were detected in sediments, water and biota. The paper presents the mechanism of mercury movement in the marine environment. Cases where the toxic effects of mercury were detected in the marine environment are discussed. The impact of mercury pollutants on the food chain in the sea is particularly emphasized. The highest measured mean values of mercury in sediments are in points 10 (71710.51), point 8 (6130.0; 4715.0) and point 5 (37794.0; 36805.0; 35061.0; 18279.0); in the biota at point 1 (311.0); in water at points 3 (0.05), point 6 (0.01), point 5 (0.01), point 4 (0.01) and point 2 (0.01).

Keywords: bioaccumulation; pollutants; environment; mercury; Mediterranean

Introduction

Heavy metals are in the strictest sense the ones that have a density higher than 5 g cm⁻³. This is certainly true for the five main species – mercury, lead, cadmium, chromium and arsenic. However, lighter elements such as zinc and aluminum tend to affect living organisms as well, and it becomes increasingly clear these days, that lighter metals are burdening the (marine) environment as strong as their heavier siblings. It is therefore not without reason that some scientists advise to speak only of “metal pollution”.

Metals are naturally present in the environment, albeit usually in their oxidized (cationic) form, for example in ores or in biological material. However, mankind has devised a great number of interesting applications for metals and alloys, enhancing the worldwide spread of metal pollution (even to those places that have never seen metal mining or

processing). On top of that, metals are chemical elements, and they cannot be degraded (like sugars into CO₂ and H₂O), only cycled and recycled from organism to organism. As such, they are an excellent illustration of the law of conservation of misery.

Some metals (Zn, Cu, Cr, Se, Ni, Al) are necessary for a biological organism, and a minimal uptake is needed for a healthy life. They are the essential metals. Other metals (Hg, Cd, Pb) are non-essential: they constitute just a burden for the organism and have a deleterious effect upon its metabolism. As soon as their levels in the cells or organs of an organism surpass a critical threshold, the organism will suffer a number of symptoms, ultimately leading, at higher doses, to death (Milunovic et al. 2021).

Mercury is a naturally occurring element that can be found all over the world, mostly as cinnabar (mercuric sulphide). In nature, it has been found in several forms: elemental or metal-

lic mercury, inorganic mercury compounds, and organic mercury compounds. Elemental or metallic mercury is a silver-white metal, and is liquid at room temperature. If heated, it is a colorless, odourless gas. Mercury is taken up into the food web in one of its organic forms: methylmercury (MeHg) or dimethylmercury (DMHg). This occurs by grazing zooplankton. Also, Hg has a high affinity for lipids, allowing the metal to cross cell membranes and to interfere with cell metabolism (Boening, 2000, Pinho et al., 2002). From these organisms onwards, mercury is biomagnified along the food chain up to marine mammals (Coelho et al., 2010).

Bioaccumulation is the gradual accumulation of substances, such as pesticides or other chemicals, in an organism. Bioaccumulation occurs, when an organism absorbs a substance faster than it is eliminated through catabolism and excretion. Thus, the longer the biological half-life of a toxicant, the greater the risk of chronic poisoning, even if the environmental levels of the toxin are not very high (Bryan, 1979). Bioaccumulation, for example in fish, can be predicted by models.(Stadnicka et al., 2012). The data do not support hypotheses for molecular size criteria for use as a potential indicator of bioaccumulation. Biotransformation can strongly modify the bioaccumulation of chemicals in an organism. Bioaccumulation refers to the uptake from all sources combined (e.g. water, food, air, etc.), while bioconcentration refers to the uptake and accumulation of a substance from water alone (Kotnik et al., 2014; Foucher et al., 2009).

Experiment

The experiment analyzed the Mediterranean area. In selected areas (10 points), mercury concentrations in water, sediments and biota were monitored. The goal of the experimental paperwork is to determine which selected point has the highest concentration values, that is, which has the highest risk for increased bioaccumulation in food. During the research, remote sensing was used. We collected data from EMODnet network .

Methods

The data collection method for this paperwork used EMODnet network. EMODnet –European MARINE Observation and Data network is a network of organization, supported by the EUs integrated maritime policy (Figure 1). EMODnet Chemistry provides easy access to marine chemical data, standardized harmonized validated data collections and reliable data products, which are highly relevant to assessing ecosystem status according to the Marine Strategy Framework Directive, for all European marine regions (Commission Decision EU 2017/848). Numerous substances are considered. Most of them are invisible to the naked eye, and can only be detected and tracked using special sensors or by laboratory analysis. This evidence-based information is essential for understanding seawater chemistry and its natural and/or human-induced variations. It is also essential for identifying and taking action against

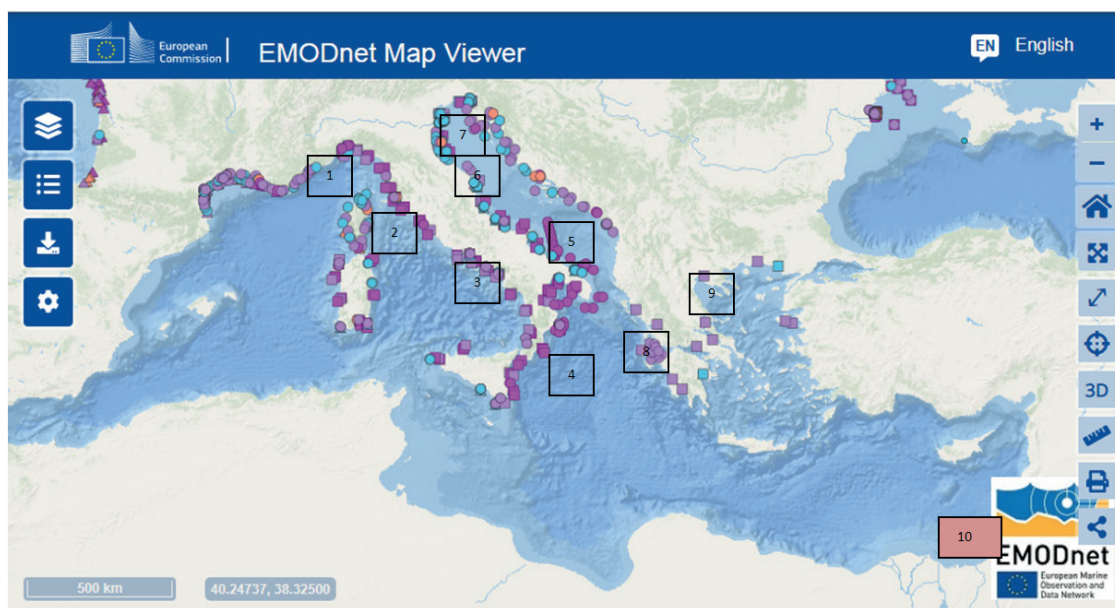


Fig. 1. EMODnet –European MARINE Observation and Data network (selected point)

Source: EMODnet

spatio-temporal environmental changes that pose risks to marine ecosystems and human health (EMODnetChemistry, 2024; National Oceanographic Data Center, 2024; Ocean Data View ODV, 2024).













Results and Discussion

Table 1 displays results for mercury median values of the last 6 available years that have been measured per matrix, and are present in EMODnet validated datasets. The median values ranges are derived from the following percentiles:

0–25%, 25–75%, 75–90%, >90%. Only “good data” are used, namely data with Quality Flag = 1, 2, 6, Q (SeaDataNet Quality Flag schema). For water, only surface values are used (0–15 m), for sediment and biota data at all depths are used.

The highest measured median values for mercury in sediments are at points 10 (71710.51), point 8 (6130.0, 4715.0) and point 5 (37794.0, 36805.0, 35061.0, 18279.0) unit ($\mu\text{g}/\text{kg}$); in biota in point 1 (311.0) unit ($\mu\text{g}/\text{kg}$); in water at points 3 (0.05), point 6(0.01), point 5(0.01), point 4(0.01) and point 2(0.01) unit ($\mu\text{g}/\text{l}$).

Table 1. Result of Heavy metals – mercury (median values)

Heavy metals – mercury (median values)				Point 1 (Figure 2a)
Longitude	Latitude	Median Values	Matrix, unit	
5.054	43.324	252.5	Biota, $\mu\text{g}/\text{kg}$	
5.254	43.322	1163.0	 Sediment, $\mu\text{g}/\text{kg}$	
5.196	43.413	201.0	Sediment, $\mu\text{g}/\text{kg}$	
5.301	43.267	311.0	 Biota, $\mu\text{g}/\text{kg}$	
Heavy metals – mercury (median values)				Point 2 (Figure 2b)
Longitude	Latitude	Median Values	Matrix, unit	
10.655	42.904	0.01	Water, $\mu\text{g}/\text{l}$	
10.656	42.892	315.0	Sediment, $\mu\text{g}/\text{kg}$	
10.667	42.898	14.4	Biota, $\mu\text{g}/\text{kg}$	
10.689	42.892	260.0	Sediment, $\mu\text{g}/\text{kg}$	
10.673	42.892	255.0	Sediment, $\mu\text{g}/\text{kg}$	
10.619	42.862	0,01	 Water, $\mu\text{g}/\text{l}$	
Heavy metals – mercury (median values)				Pont 3(Figure 2c)
Longitude	Latitude	Median Values	Matrix, unit	
16.497	38.296	0.05	 Water, $\mu\text{g}/\text{l}$	
16.497	38.296	0.05	 Water, $\mu\text{g}/\text{l}$	
16.588	38.164	0.075	Water, $\mu\text{g}/\text{l}$	
15.897	38.451	50.0	Sediment, $\mu\text{g}/\text{kg}$	
15.893	38.445	50.0	Sediment, $\mu\text{g}/\text{kg}$	
Heavy metals – mercury (median values)				Point 4(Figure 2d)
Longitude	Latitude	Median Values	Matrix, unit	
17.155	40.487	0.1	Sediment, $\mu\text{g}/\text{kg}$	
17.19	40.468	0.09	Sediment, $\mu\text{g}/\text{kg}$	
17.156	40.432	0.01	 Water, $\mu\text{g}/\text{l}$	
17.096	40.289	0.01	 Water, $\mu\text{g}/\text{l}$	
17.848	40.215	0.01	 Water, $\mu\text{g}/\text{l}$	
Heavy metals – mercury (median values)				Point 5(Figure 2e)
Longitude	Latitude	Median Values	Matrix, unit	
16.906	41.135	0.055	Sediment, $\mu\text{g}/\text{kg}$	
16.885	41.145	0.06	Sediment, $\mu\text{g}/\text{kg}$	
16.964	41.152	0.01	 Water, $\mu\text{g}/\text{l}$	
17.059	41.284	0.01	 Water, $\mu\text{g}/\text{l}$	
16.937	41.474	35061.0	 Sediment, $\mu\text{g}/\text{kg}$	
16.907	41.571	36805.0	 Sediment, $\mu\text{g}/\text{kg}$	

16.876	41.669	18279.0	●	Sediment, µg/kg
16.815	41.863	37794.0	●	Sediment, µg/kg
Heavy metals – mercury (median values)				Point 6(Figure 2f)
Longitude	Latitude	Median Values	Matrix, unit	
12.613	44.042	7.5	Sediment, µg/kg	
12.636	44.113	0.01	■	Water, µg/l
12.812	44.209	0.01	■	Water, µg/l
12.685	44.223	20	Biota, µg/kg	
12.689	4.228	0.1	Sediment, µg/kg	
12.685	44.223	0.1	Sediment, µg/kg	
12.694	44.22	0.1	Sediment, µg/kg	
Heavy metals – mercury (median values)				Point 7(Figure 2g)
Longitude	Latitude	Median Values	Matrix, unit	
12.606	45.168	0.00125	Water, µg/l	
12.582	45.126	0.04	Sediment, µg/kg	
12.58	45.126	0.05	Sediment, µg/kg	
Heavy metals – mercury (median values)				Point 8(Figure 2h)
Longitude	Latitude	Median Values	Matrix, unit	
18.652	42.447	640	●	Sediment, µg/kg
18.687	42.436	6130.0	●	Sediment, µg/kg
18.691	42.433	4715.0	●	Sediment, µg/kg
Heavy metals – mercury (median values)				Point 9(Figure 2j)
Longitude	Latitude	Median Values	Matrix, unit	
22.951	40.536	0.0013	Water, µg/l	
25.1	40.983	0.00115	Water, µg/l	
25.934	40.833	6.0E-4	Water, µg/l	
Heavy metals – mercury (median values)				Point 10(Figure 2v)
Longitude	Latitude	Median Values	Matrix, unit	
35.082	32.909	71710.51	●	Sediment, µg/kg
35.074	32.918	279.5599976	Sediment, µg/kg	
35.077	32.918	283.4732513	Sediment, µg/kg	

Source: Authors' own elaboration

Legend		
Heavy metals – mercury (median values) Biota, µg/kg	Heavy metals – mercury (median values) Sediment, µg/kg	Heavy metals – mercury (median values) Water, µg/l
0 – 17.0 ▲	0 – 25 ○	0 – 0.00076 □
17.0 – 130.0 ▲	25 – 198.6 ●	0.00076 – 0.0040 ■
130.0 – 216.3 ▲	198.6 – 385.2 ●	0.0040 – 0.0096 ■
> 216.3 ▲	>385.2 ●	> 0.0096 ■

Source: EMODnet MAP Viewer

Impact heavy metal mercury

The bioaccumulation of mercury has proven to be fatal on a large scale in at least one instant: the disaster at Minamata (Japan) in 1956. Hg entered the local food chain as a result of the release of methyl-mercury in the industrial wastewater from the Chisso Corporation's chemical factory. The metal then accumulated in shellfish and fish in the local bay, serving as food for the local population (Table 2).

The severe pollution that ensued brought about a number of neurological problems, such as hearing and speech damage, a perturbed vision, muscle weakness and ataxia, leading, in extreme cases to insanity, paralysis, coma and death.

The discovery of these toxic effects has caused a steady replacement of Hg in a number of production processes and applications. Most of the medical applications have been phased out, such as the antiseptic mercurochrome, or the use of thiomersal in the preservation of vaccines. Mercury-based

Table 2. Mercury in tissue samples from Minamata, ppm

Fish & shellfish		Cats		Humans	
Oyster	5.6	Control	0.9 – 3.66	Control	less than 3.0 gray
Mullet	10.6	Kidney	12.2 – 36.1	Kidney	3.1 – 144.0
Short-necked clam	20.0	Liver	37 – 145.5	Liver	0.3 – 70.5
China fish	24.1	Brain	8 – 18	Brain	0.1 – 24.8
Crab	35.7	Hair	21 – 70	Hair	96 – 705

Source: Allchin, 2008

fever thermometers are banned in the US. The metal is still in use for the production of reference calomel electrodes, mirror telescopes and fluorescent lamps. Due to this decreasing use of the metal, its input into the sea has declined over the past decades, as well. Currently around 75% of the Hg (3600 – 4500 tons) in the marine environment, comes from natural sources like eroding ores.

In seawater, dissolved mercury ions occur as HgCl_3^- . They are easily adsorbed to the sediment and suspended particulate matter, thereby being removed from the solution. They also form complexes with organic molecules in the sea, such as cysteine residues on proteins or humic acids. In anaerobic conditions, Hg may be present in its metallic form, or as sulphide.

Hg^{2+} is further methylated to MeHg and DMHg by bacteria and algae in the photic zone of the ocean. A similar reaction goes on in the (dark) sediments. Other microbes are present to demethylate DMHg to MeHg. The methylated forms of mercury are more easily taken up by the organisms on the lowest trophic levels. From there on, the mercury com-

pounds bioaccumulate, as represented for the Arctic ecosystem (Kirk et al., 2012).

This diagram represents the different processes affecting MeHg concentrations in the water column of the Arctic Ocean: the various Hg methylation and (photo) demethylation pathways (thin arrows), each governed by their respective rate constants (k , expressed in d^{-1} ; values displayed above the arrows), as well as the associated biogeochemical fluxes (thick arrows). The pie charts depict the proportions of MeHg in photic zone and in the deeper waters, which are estimated to originate from Hg (II) methylation in the water column (Kirk et al., 2012).

Invertebrates collected include: calanus copepods, collected from the coastal shelf (Cal SH), calanus copepods (Cal Pel) and hyperiid amphipods (*Themisto libellula*) from off-shore pelagic zone, mixed zooplankton from near the coastline (Est Zoo), and mysids, gammarid amphipods (*Anonyx* spp.) and shrimp from benthic zones. Fish collected include: pacific herring, Arctic cisco, least cisco, rainbow

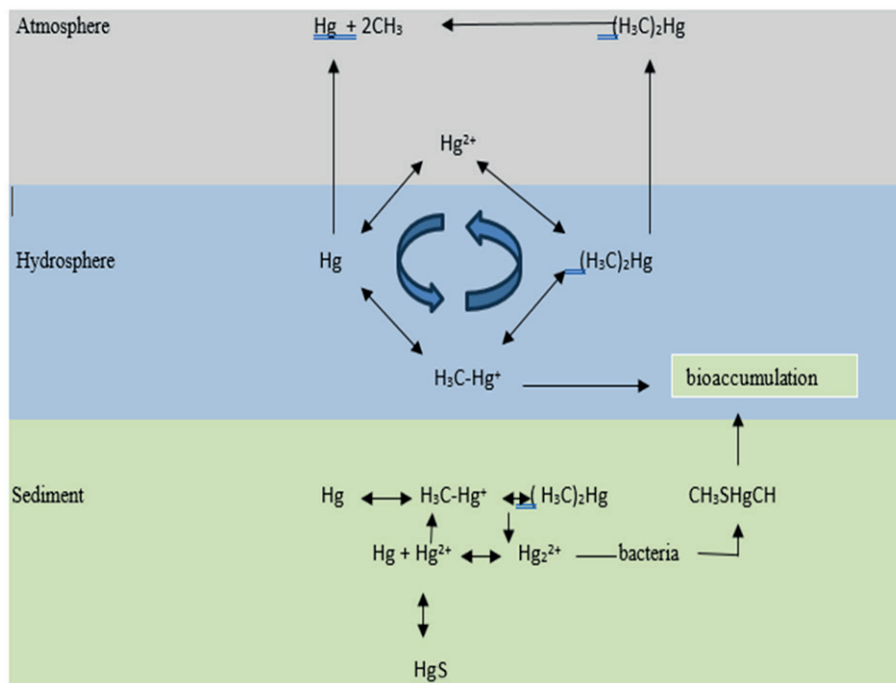


Fig. 2. Environmental chemistry of mercury

Source: Authors' own elaboration

smelt, and saffron cod from the coastal shelf, Arctic cod from the off-shore pelagic zone, and flounder and sculpin from the benthic regions. Three groups of beluga whales, which utilize different habitats and foraging areas, are also shown: Beluga 1: shallow coastal areas; Beluga 2: along ice edges; and Beluga 3: deep off-shore waters. The food chain progression is given as the $\delta^{15}\text{N}$ signature. (Loseto et al., 2008a, b; Kirk et al., 2012).

Figure 2 shows the impact of mercury on the environment, and the transformation of mercury compounds in air, water and sediments. Figure 2 also shows the bioaccumulation that takes place in the hydrosphere. To evaluate mercury from an environmental-toxicological standpoint, one must consider the various bond types (metal species): metallic Hg (differentiating between liquid and vapour); inorganic Hg salts, with extremely differing water solubilities between HgS and the nitrates or chlorides; and organic, lipophilic compounds such as dimethyl mercury. Borrowing from Wood, the most important chemical and biochemical reaction are shown in Hg cycle, whereby the process of methylation stands at the fore because of the high bioaccumulation of the organic Hg species. In the atmosphere, methylation can occur photochemically if CH_3 radicals and Hg vapor are present. It is assumed that microbial methylation takes place under both anaerobic (via methylcobalamine) and aerobic conditions (in cell that produce methionine). As a result of microbial processes, Hg (II) ions are reduced to form elemental Hg or are biomethylated. An additional methylation, or else the process of disproportionation, leads to dimethylmercury, which can accumulate in food chains, and which can also end up in the atmosphere due to the high vapor pressure. In sediments, Hg can temporarily be removed from the cycle as slightly soluble sulphide, but it can be remobilized by bacteria- even as $\text{CH}_3\text{S-Hg-CH}_3$, which is also bio accumulated (Yin et al., 2015).

Conclusion

The paper presented natural and anthropological sources of water pollution with metals. Metals are known as pollutants that can significantly affect the environment (water, air, soil). Metals are, after a certain limit, behaving like toxins in the natural environment, man or other living beings that are in water, air or soil of particular importance is the circular cycle, in which it is seen how a metal can pass from one form to another living form. Toxin transfer in the aquatic ecosystem is important for health and the environment. (Ketin et al., 2020). The paper presents mercury concentrations at selected points, in sediments, water and biota. The mechanism of mercury movement in the environment indicates the pos-

sibility of bioaccumulation and a large impact on the food chain. The highest measured median values for mercury in sediments are at points 10 (71710.51), point 8 (6130.0, 4715.0) and point 5 (37794.0, 36805.0, 35061.0, 18279.0); in biota in point 1 (311.0); in water at points 3 (0.05), point 6(0.01), point 5(0.01), point 4(0.01) and point 2(0.01). The mechanism of mercury movement in the environment indicates the possibility of bioaccumulation and a large impact on the food chain. It is recommended to control heavy metals (mercury) in the Mediterranean and monitor bioaccumulation.

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