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Organomercury compounds in environmental samples: emission sources, toxicity, environmental fate and determination

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Abstract

In view of the specific properties of mercury and its capability of forming compounds that can be bioaccumulated and biomagnified at successive levels of the trophic pyramid, it has become necessary to gather detailed information on the sources of emission of this element into the environment and its fate there. Moreover, the increasing awareness of the relationship between the toxicity of mercury and its chemical form has sharpened interest in the identification of its various forms in environmental samples. Investigating the speciation of mercury has therefore become of major importance with respect not only to determining its biogeochemical cycle but also to assessing the scale of this analytical challenge, given the need to design the appropriate analytical methodologies and reference materials that will constitute the tools for obtaining reliable analytical information.

Key words: methylmercury, ethylmercury, organomercury compounds, bioaccumulation, speciation analysis, speciation of mercury

1. *Introduction*

Experts from many different organizations, including the U.S. Environmental Protection Agency (EPA), regard mercury as one of the most toxic elements [1]. The toxicity, biochemical properties and environmental cycle of mercury depend on its concentration and the chemical form in which it is present [2-6].

Every form of mercury can undergo transformation in the environment [7]. The formation of organomercury compounds as a result of naturally occurring processes is

particularly dangerous, since the organic compounds of mercury are usually more toxic than its inorganic ones [8]. The most common organic form of mercury – methylmercury (MeHg) – is a strong neurotoxin that can be bioaccumulated, and its stability in organisms and the environment affects human health and growth as well as nature in general [1,9]. Table 1 lists information on the chemical forms of mercury that most frequently occur in different compartments of the environment.

Mercury can enter the environment naturally and as a result of human actions. Anthropogenic emissions include:

- the combustion of fossil fuels and the heating of other materials containing mercury,
- gold mining,
- the roasting of sulfide ores,
- the production of paper, drugs and the chloralkali process,
- agriculture [1,12-15].

The most important natural sources of mercury emissions are:

- volcanic eruptions,
- forest fires,
- weathering of rocks,
- tectonic movements and their associated degassing of the Earth's crust [16-19].

In the environment mercury is subject to numerous processes and transformations, such as:

- dry and wet deposition (in this way mercury gets into water bodies and ground waters),
- sorption/desorption,
- re-emission into the atmosphere of elemental mercury and/or its volatile forms,
- biomethylation/demethylation,
- bioaccumulation by fauna and flora,
- biomagnification [20].

Figure 1 illustrates the mercury cycle in diagrammatic form.

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The processes that are of the greatest significance as far as the toxicity of mercury and the effect of this element on human and animal health is concerned are its biomethylation and bioaccumulation.

2. *Methylation*

In view of the mercury cycle in nature and the transformations of the element in the environment, it is aquatic ecosystems (oceans, seas, lakes, rivers and bottom sediments) that are the most susceptible to MeHg contamination [21] since practically all forms of mercury can be converted into methylmercury as a result of natural processes [1, 10, 22, 23]. Certain groups of organisms are responsible for this process, e.g. fungi [24], macroalgae and bacteria participating in the ethylation of mercury (sulfate reduction), which mostly form MeHg under anaerobic conditions in the upper layers of bottom sediments (in the top 2 cm of the sediments, where microbiological activity is at its highest [25-34]. But because methylmercury is:

- readily assimilated,
- only slowly eliminated from the body [35],
- and has lipophilic properties,

it makes up from ca 60 to 90% of the total content of mercury in living organisms [36].

The rate and degree of methylation of mercury (II) ions in waters and bottom sediments depends on such factors as:

- the form of mercury,
- the methylation agent,
- the chemical composition of the sediment,
- the quantity of oxygen available in the sediment,
- the pH of the sediment [1].

The major factors capable of retarding the biological synthesis of methylmercury are:

- the difficulty of carrying out methylation reactions in water,
- the possible decomposition of organomercury compounds by solar UV light [1, 37].

Methylmercury can pass from sediment and water to the tissues of aquatic organisms [38], where they may be bioaccumulated and biomagnified [39]. It is for this reason that maximum permissible levels of mercury and methylmercury in food have been defined. Such levels have been established by, *inter alia*, the US Food and Drug Administration (FDA),

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which has stipulated a maximum level of methylmercury in fish tissue of 1 mg/kg wet weight [40].

3. Bioaccumulation

The bioaccumulation of methylmercury takes place up the aquatic food pyramid: sea water – phytoplankton – zooplankton – small herbivorous fish – large predatory fish – marine mammals [41]. Every organism from a given level in the trophic pyramid contains a higher concentration of methylmercury than organisms from lower levels, with the result that very much higher concentrations are reached in animals at the top of the pyramid in comparison with the initial concentration in water, bottom sediment or soil [42-46]**.**

The methylmercury content in soil samples is not normally very high. But there may be from 0.5 to 1.5% methylmercury in the total soil content of mercury [19]. Mercury accumulates mostly in the upper layers of the soil because of its very strong affinity for the organic substances and certain minerals in the soil [47], which means that the bioavailability of mercury in soil is low [48].

In aquatic ecosystems both inorganic and organic forms of mercury tend to accumulate in bottom sediments. Since some sediment organisms participate in the conversion of mercury compounds into methylmercury, levels of this toxic compound in sediments are usually higher than in the soil [49] or in the water itself.

Dangerously high levels of organic mercury have been found in the tissues of fish, and in fish-feeding aquatic and terrestrial birds and mammals. In fish tissue much of this organic mercury is the toxic methylmercury. The most significant factors affecting the degree of MeHg bioaccumulation in fish are the size of the fish and/or its fat content, the protein affinity mechanism [50], and the dissolved oxygen content in the waters that the fish inhabit. In favorable conditions fish can accumulate considerable amounts of methylmercury. Fish are a significant link in the biological circulation of organic mercury compounds in nature because they are not only a basic item in the diet of many aquatic organisms, they are also consumed by humans [51-55].

Figure 2 provides information on levels of total mercury and the percentage of methylmercury in samples of organisms making up a typical food pyramid in an aquatic ecosystem.

Marine mammals have the most diversified diet as they are at the top of the food pyramid. Mercury levels are high, particularly in the liver [56-59]. Studies to determine the

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toxic forms of mercury in tissues of marine mammals found that the liver contained far higher levels of mercury than the kidneys [27, 60-62]. This is connected with the storage and transformation of toxic forms of mercury in the liver [45]. The results of various studies indicate that organic forms of mercury, and methylmercury in particular, are converted to less toxic forms, e.g. HgSe, in the livers of marine mammals [45, 63]. The liver is the organ where metals accumulate, where they are detoxified and where metabolic processes involving metals take place.

Environmental contamination by organomercury compounds is not a problem solely of aquatic ecosystems: it can also affect terrestrial ecosystems, especially animals at the upper levels of the trophic pyramid [10, 64, 65].

4. The harmful action of organomercury compounds

In the various compartments of the environment mercury is subject to transformation, and contact with any form of mercury has toxic effects. In the case of organomercury compounds, poisoning results mostly from the consumption of toxic methylmercury or other compounds together with food. Particularly dangerous are methylmercury and ethylmercury, which are almost entirely absorbed in the digestive tract [6, 8, 15, 50, 66], readily crossing biological barriers such as the blood-brain barrier, and also the placental barrier, accumulating in the fetus and maternal milk [67-70]. Even though ethylmercury is less toxic than methylmercury, both compounds elicit similar symptoms [71, 72]. Exposure to organic compounds of mercury, methylmercury in particular, in the prenatal period or directly after birth (these compounds are consumed with the mother's milk) affects early childhood development . Figure 3 illustrates the circulation of methylmercury in the mother's body and the fetus.

Following exposure to methylmercury, its metabolites (forming as a result of demethylation in the liver) are excreted in the urine and the stool, but only to a slight extent, because methylmercury is subject to hepato-intestinal recirculation [15].

Because of its strong affinity for sulfur, and hence for sulfhydryl groups, methylmercury reacts with proteins and enzymes causing dysfunction of organs, blockage of enzyme binding sites and protein synthesis, impedes thymidine incorporation into DNA [74] and has an extremely harmful influence on the entire central nervous system of humans and other organisms [23, 75]. That is why methylmercury accumulates to a far greater extent in

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tissues rich in the sulfhydryl groups of amino acids than, for example, in fatty tissue [23]. Moreover, short-chain compounds like methylmercury or ethylmercury readily penetrate red blood cells, where they bind to hemoglobin. This is the reason why methylmercury, unlike the inorganic forms of mercury, accumulates in erythrocytes [8].

A less often encountered but more toxic form of mercury – consumption of just 15-20 microliters is lethal – is dimethylmercury (DMM). The physical properties, along with its lipophilicity (stronger than that of MMM), which is due to the presence of the second alkyl group, mean that DMM is rapidly absorbed through the skin, lungs and digestive tract and is accumulated in the fatty tissue, blood serum proteins and the brain.

Once DMM gets into the body, it is first converted into the monomethyl form and is transported to the blood and tissues.

Therefore, the toxic effects of DMM are associated with its dealkylation, and all are exactly the same as those of MMM exposure. Methylmercury reacts with sulfur and the sulfur-containing thiol groups of enzymes, thereby inhibiting their action.

The other organic compounds of mercury are rarely encountered and are rarely investigated by analysts engaged in environmental studies. Table 2 provides information on the toxic effects of some organic forms of mercury.

The toxic effects of inorganic mercury have been known since antiquity [15]. But the first information on mortality that turned out to have been caused by mercury poisoning was published in the 19th century. Later reports on the poising of humans by organomercury compounds have come from many parts of the world. But most cases of disease or the adverse effects of organomercury compounds on humans have been recorded in Asia [1]. Table 3 lists information on the most important events associated with poisoning by organic compounds of mercury.

5. The content of organomercury compounds in environmental samples.

The most important factor governing the level of organomercury compounds in the tissues of an animal appears to be the diet [45, 85, 86]. Hence, the type and variety of food consumed is intimately connected with the level of mercury in the tissues and organs of organisms. Table 4 lists literature information on levels of organomercury compounds in samples of water, sediments and the tissues of animals at different levels of the trophic pyramid.

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6. *Speciation of mercury*

Human activities release into the environment large quantities of mercury, which can take on highly toxic forms. In view of the fact that the toxicity, mobility, bioavailability and bioaccumulation of mercury depends on its chemical form, it is necessary to determine the individual forms of mercury and not the total concentration of the metal in environmental samples. This type of determination is possible with the application of speciation analysis [1, 113].

Speciation as a field of research made its appearance in the 1970s at a time coinciding with the development of numerous analytical procedures and techniques, which enabled the quantitative determination of elements in amounts of the order of 10^{-6} % - 10^{-7} %.

Contemporary speciation analysis focuses primarily on biologically active elements. It is used to establish the metabolism and biological activity of different elements in living organisms. It is also applied in food chemistry, pharmacy, biology, toxicology and environmental studies, and even in studies of historical monuments.

Obtaining reliable measurements of the content of organomercury compounds in environmental samples requires the application of analytical procedures consisting of the following steps:

1. extraction of organic forms of mercury from samples (soil, sediment, living organisms) in such a way as to prevent degradation and chemical changes that could alter the original composition of the compounds in the sample; it should also fulfill the basic requirements of trace analysis with respect to analyte loss and possible sample contamination [1];
2. preconcentration of analytes, as a result of which the concentration ratio or the quantities of the microconstituents (trace constituents) and macroconstituents (matrix) increase in such a manner that it becomes possible to obtain values below the limit of detection of the chosen determination technique [1, 114];
3. isolation of the various forms of mercury in such a way as not to change the concentration of the individual compounds in the sample [1];
4. determination of each of the earlier isolated forms of mercury [1].

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7. Extraction

The extraction of the various forms of mercury is regarded as one of the most important stages in speciation analysis. Depending on the type and form of the sample, liquid-liquid and liquid-solid extraction are used for preparing samples for speciation.

Extraction should be efficient and effective and, above all, should not alter in any way the forms of mercury present in the sample and should not promote the formation of new compounds in the sample [5, 115]. It does happen, however, that the accuracy of the final results may deteriorate as a result of the formation of methylmercury from inorganic forms of mercury during extraction with a solution of an acid or base [5, 116, 117] or transformations of forms of mercury among themselves [3, 118, 119]. When choosing a suitable extraction technique or extractant, one should be guided by:

- ✓ the chemical properties of the analyte,
- ✓ the chemical form of the analyte,
- ✓ the matrix composition of the sample,
- ✓ the technique for determining the analyte.

To improve the efficacy of extraction some form of assistance is increasingly being applied, for example, with:

- ✓ ultrasound (UAE))[50, 115, 120],
- ✓ elevated pressure (PFE),
- ✓ microwave radiation (MAE) [121-125]

Figure 4 illustrates a scheme for the preliminary preparation of samples prior to the determination of the various forms of mercury [126].

8. The conversion of analytes into volatile derivatives

All types of environmental samples are highly complicated research materials because of their complex matrix composition, the diversity of compounds in the sample and the range of analyte concentrations. Despite the application of many different extraction techniques, the determination of some substances in unchanged form in environmental samples is impossible. In such cases, therefore, derivatization has to be resorted to, that is, the analyte is converted into derivatives that have properties enabling them to be determined with a particular analytical technique. Derivatization is very often used to isolate various forms of mercury from a sample or to pre-concentrate an analyte, in that mercury's ability to form vapors when

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reacting with a reducing agent is made use of. It is often the case that the conversion of mercury into volatile derivatives is preceded by isolation using gas chromatography.

Mercury compounds are usually derivatized using one of three reactions:

1. Reaction with a reducing agent – sodium borohydride ($NaBH_4$). This type of reaction preserves the mercury-carbon bond in the target molecule. The reaction with $NaBH_4$ is easy to carry out (it takes place in an aqueous medium), but determining mercury compounds after such a reaction may be troublesome because of the instability of the derivatives formed and the possibility of disproportionation [140,141].
2. Alkylation. This requires less time and effort than derivatization with Grignard reagents because there is no need to change the solvents. Moreover, this method is neutral vis-à-vis most reagents, which caused problems during the formation of hydrides, i.e. the presence of metal ions, proteins, fats or humus substances; it can therefore be used for analyzing samples of diverse provenance, including biological ones [G32]. A particular advantage of alkylation is that extraction and derivatization can be performed simultaneously, which considerably shortens the sample preparation time. But there are also drawbacks to this method, the principal one being the small number of commercially available derivatizing reagents. The three main alkylating reagents are:

- ✓ Sodium tetraethyl borate,
- ✓ Sodium tetraphenyl borate,
- ✓ Tetrabutylammonium tetrabutyl borate.

   $NaBEt_4$ is universally used for the speciation of organometallic compounds, but it is of no use for derivatizing inorganic compounds of mercury or ethylmercury, since both forms produce the same compound, $HgEt_2$. These two forms of mercury can be distinguished if sodium phenyl borate is used – this reacts only with mercury derivatives [142-147].

3. Reaction with Grignard reagents [142,148,149] (alkylmagnesium halides, e.g. methyl, ethyl, propyl, butyl, pentyl, hexyl, or also phenylmagnesium chlorides or bromides). A serious problem limiting the use of such reactions for derivatization is the need to perform them in an anhydrous environment, which is time-consuming and labor-intensive. Prior to derivatization, extracts have to be dried and/or transferred to another solvent, and after derivatization the excess Grignard reagent has to be removed.

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Since the conversion of an analyte into volatile derivatives may be source of numerous errors, this step is avoided during speciation analysis if at all possible.

9. Techniques for isolating and detecting analytes

Since biological samples have a very complex composition and the organic forms of mercury are present in them at very low levels, selective isolation techniques with sensitive and targeted detection methods are needed. Known as conjugated, hybrid or linked systems, such combinations offer a substantial improvement in sensitivity, and the time of analysis is far shorter [113].

The choice of isolation technique is connected with the physicochemical properties of the target analyte. The most commonly used isolation techniques in speciation analysis are gas chromatography (GC), high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE). Table 5 lists basic information on the techniques used with environmental samples for detecting and determining various speciation forms of mercury in them. Just as the sample preparation technique depends on the type of matrix in which the target analytes are present, so the choice of isolation technique depends on the physicochemical properties of these analytes, i.e. volatility, charge, polarity. This is why GC is used to isolate volatile, thermally stable and neutral compounds (or those that can be converted into volatile and stable derivatives), whereas HPLC is suitable for isolating the remaining compounds.

In view of the wide variety of environmental and biological samples, not to mention the plethora of analytical techniques, procedures should be selected that enable the lowest possible levels of organomercury compounds to be determined. Table 6 lists basic information on the analytical procedures used in speciation studies of mercury in environmental samples.

10. Summary

The hazards arising out of the presence of mercury and its compounds in the environment, especially in aquatic ecosystems, make it necessary to understand the transformation pathways of these compounds and to monitor the contents of organomercury compounds in the tissues of organisms at all levels of the trophic pyramid. The possibility that organic forms of mercury can get into the human body with food is a serious threat because

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these compounds are highly toxic. Many cases – some fatal – have been reported of disease among both adults and children following their exposure to organomercury compounds. That is why it is so crucial to monitor levels of organomercury compounds in samples of water, sediments and tissues from all levels of the trophic pyramid using the tool of speciation analysis.

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Table 1: The main organic forms of mercury.

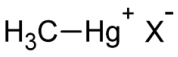
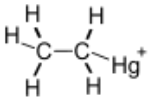
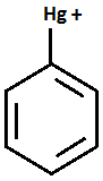
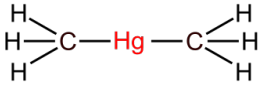
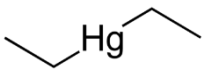
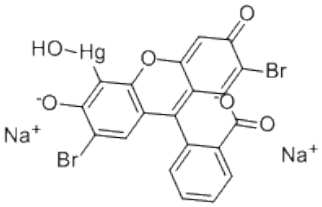
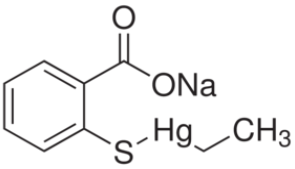
NAME	EMPIRICAL FORMULA	STRUCTURAL FORMULA	APPLICATION	REFERENCES
METHYL-MERCURY CATION	(CH_3Hg^+)		-	
ETHYLMERCURY CATION	($C_2H_5Hg^+$)		Used in industry, a metabolite of thimerosal.	
PHENYL-MERCURY CATION	($C_6H_5Hg^+$)		Used in industry. Phenylmercury acetate is used as a fungicide and in paints.	[7, 10, 11]
DIMETHYL-MERCURY	C_2H_6Hg		Used in toxicology as a reference toxin and to calibrate NMR instruments during Hg determination	
DIETHYL-MERCURY	$C_4H_{10}Hg$		-	
MERBROMIN, (MERCURO-CHROME)	$C_{20}H_8Br_2HgNa_2O_6$		Used as a disinfectant because of its antibacterial properties and as an analytical reagent.	[12]
THIMEROSAL	$C_9H_9HgNaO_2S$		Used as a preservative in vaccines, some ointments and other forms of drugs; sometimes as an antifungal drug and in dermatology.	[13, 14, 15]

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Table 2. The deleterious effects of exposure to organomercury compounds.

COMPOUND	SITE OF ACTION	TOXIC ACTION	REFERENCE(S)
Methylmercury	Central nervous system	Slurred speech, hypersalivation, shouting, dysphagia, scotoma, neurasthenia, loss of libido, depression, hallucinations, focal cramps, chorea, athetosis, myoclonus, paralysis, stupor, coma, and death.	[8]
Methylmercury	Fetus	Severe brain damage, profound mental retardation, spasticity, seizures, cerebral palsy, chorea, athetotic movements, ataxia, tremors, cataracts, hearing deficiency, small size, anemia, and renal dysfunction.	[8, 15, 76, 77]
Dimethylmercury	The whole body	Irritation of the eyes, respiratory tract and skin numbness and tingling of the mouth, hands and legs, joint pains, narrowing of the field of vision, emotional disturbances, lack of coordination, slurred speech, deafness, death. Also crosses biological barriers – toxic action like that of MeHg.	[78]

Table 3. Information on important events associated with poisoning by mercury and its compounds.

PERIOD	DESCRIPTION OF EVENT	REFERENCE(S)
1865	The deaths of two chemists, who used dimethylmercury during investigations to define the valences of a number of metals.	[15]
1940	The inhalation of methylmercury by four workers at a factory producing fungicides for protecting grain crops. In one of the poisoned men cerebral atrophy with cortical loss was found; since then, this has been known as the Hunter-Russell syndrome.	[15, 79, 80]
1920 - 1960	In a Japanese chemical works mercury was used as a catalyst in the production of acetaldehyde and vinyl chloride. The effluents of this process, containing methylmercury chloride, were discharged into Minamata Bay, on the south-western coast of Kyushu - nearly 150 tons of methylmercury during forty years. Through the consumption of fish and other frutti di mare, harmful methylmercury was ingested by humans, causing damage to the central nervous system, and the	[8, 15, 33, 79-81]

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	children of women who had consumed the poisoned fish were afflicted by mental retardation, developmental disruption, hepatic diseases, hypertension, retarded metabolism and even death (chorea, ataxia, tremors and seizures). These symptoms were given the name "Minamata disease" by doctors at the Kumamoto University Hospital.	
1965	At Niigata in Japan industrial effluents containing mercury were discharged into the River Agano. As in Minamata Bay, the water was polluted, and as a consequence, the organisms at successive levels in the aquatic trophic pyramid, and ultimately humans.	[8, 79]
1959 - 1972	More than 6000 persons in Iraq were hospitalized as a result of methylmercury poisoning. MeHg got into their diet via bread produced from grain that had been sprayed with fungicides containing MeHg. A study of a group of Iraqi children exposed to MeHg before birth, like those at Minamata, exhibited developmental anomalies. Prenatal exposure to MeHg also inhibited neuronal migration.	[15, 50, 82, 83]
1997	The death of Karen Wetterhahn, a world-famous scientist specializing in toxic metal exposure. Death ensued just a few months after a one-off exposure to less than 1 ml of dimethylmercury, which had spilt onto her hand, covered with a latex glove.	[78]
At present	In Brazilian Amazonia, the inhabitants of fishing villages (consuming fish poisoned by MeHg) situated near gold mines suffered mild neurological symptoms characteristic of MeHg poisoning, i.e. sensory disorders, tremors and balance disorders.	[84]

Table 4. Literature data on the content of organic mercury and methylmercury in environmental samples from different parts of the world**.**

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Type of sample	Geographical region	Analytical procedure	Kingdom	Phylum	Class	Family	Species	Mean concentration of compound [mg/kg d.w.] *		MeHg/THg [%] **	Reference
								OHg	MeHg		
Bottom sediment	Beni River, Bolivia - Amazonia	GC - CV- AFS						-	0.4-1.2	-	[87]
River sediment	Loučka River, Czech Republic	HPLC - CV-AFS	------	------	------	------	------	-	0.022	18.5	[20]
	Bečva River, Czech Republic							-	0.031	22.3	
	Jihlava River, Czech Republic							-	0.046	32	
	Haihe River, Tianjin, China	HPLC – CV - AFS						-	1	-	[88]
	Dagu Drainage Canal, Tianjin, China							-	21.7	-	
Water	Tapaj´os River, Brazil	GC-CV - AFS						-	0.02	1.8	[89]
	Piedras River, SW Spain	HPLC–CV/HG–mAFS–AFS						-	49.5	-	[90]
	San Pedro River, SW Spain							-	50.4	-	
	Guadalete River, SW Spain							-	51.2	-	
	Carreras River, SW Spain							-	52	-	

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Type of sample	Geographical region	Analytical procedure	Kingdom	Phylum	Class	Family	Species	Mean concentration of compound [mg/kg d.w.]		MeHg/THg [%]	Reference
								OHg	MeHg		
Whole organisms	Lake Gaobeidian, Beijing, China	HPLC-UV-AFS	Plants	-	Chlorophytes	Zygnematacae	*Spirogyra*	-	<0.05	-	[10]
Whole organisms	Tapaj´os River, Brazil	CV-AFS			-	-	Phytoplankton	-	0.01	14.8	[89]
Whole organisms	Guanabara Bay, Brazil	GC - ECD	Plants / Animals	-	-	-	Microplankton	-	0.0089	33.8	[91]
							Mesoplankton	-	0.0359	75.4	
Whole organisms	Lake Superior, USA	GC – CV - AAS	Animals	-	-	-	Zooplankton *(Mysis relicta)*	-	0.033-0.054	-	[92]
Whole organisms	Lake Superior, USA	GC-CV - AAS					Zooplankton	-	0.035 - 0.050	-	
Whole organisms	Lake Gaobeidian, Beijing, China	HPLC-UV-AFS					Zooplankton *(Monia rectirostris, Monia micrura, Monia macrocopa)*		<0.05	-	[10]
Whole organisms	Tapaj´os River, Brazil	CV-AFS					Zooplankton		0.073	48.25	[92]
Whole organisms	Bečva River, Czech Republic	HPLC - CV-AFS					Zoobenthos	-	0.082	33.7	[20]
	Loučka River, Czech Republic							-	0.158	43.6	
	Jihlava River, Czech Republic							-	0.168	66	
Whole organisms	Lake Superior, USA	GC – CV - AAS	Animals	Arthropods	Insects	Chironomidae	Chironomid larvae	-	0.008	-	[92]

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Muscles	Kagoshima Bay, Japan	CV - AAS		Annelids	Polychaetes	Siboglinidae	*Lamellibrachia satsuma*	0.014	-	-	[41]
Whole organism	Coast of Novaya Zemlya, Arctic Ocean	-	Animals	Echinoderms	Starfish	-	*(Asteroidea)*	-	0.008	2.4	[93]
							Maldanes sarsi	-	0.16	48.6	
Muscles	Malaysia	INAA		Mollusks	Cephalopods	Loliginidae	*Loligo* sp.	0.22	-	64.4	[92]
Muscles	USA	-					Calamar Lanceolado (*Loligo bleekeri*)	-	0.01	33	[94]
Soft tissues	Dunkirk and Calais, north coast of France	GC – CV - AFS			Mussels	Mytilidae /Ostreidae	Pacific oyster *(Crassostrea gigas)*, Edible mussel *(Mytilus edulis)*	-	0.056	66	[95]
	Toulon, southeast coast of France							-	0.073	37	
	Basque Region, southwest coast of France							-	0.094	52	
	Lorient, west coast of France							-	0.113	74	
Body integument	Coast of Portugal	GC - AFS			Cephalopods	Octopoidiae	Common octopus *(Octopus vulgaris)*	-	0.11-0.75	-	[96]
Digestive tract								-	0.18-5.0	-	
ft tissues	Terra Nova Bay, Antarctica	AAS			Mussels	Pectinidae	Mussels *(Adamussium colbecki)*	-	0.295	49.55	[97]
ft tissues	Malaysia	INAA				Arcidae	Blood cockle *(Anadara granosa)*	0.32	-	75.5	[98]

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Edible part	Mouth of the Krka River, Croatia	CV - AAS				Mytilidae /Ostreidae	Mediterranean mussel *(Mytilus galloprovincialis)*	-	5.925	32.5	[99]
Muscles	USA	-	Animals	Arthropods	Malacostraca	Lithodidae	King crab *(Paralithodes camtschaticus)*	-	0.01	50	[94]
Whole organism	Lake Superior, USA	GC-CV - AAS				-	*Amphipoda*	-	0.032	-	[92]
Muscles	Malaysia	INAA				Penaeidae	Shrimps *(Penaeus sp.)*	0.23	-	62.6	[98]
Whole organism	Ligurian Sea	GF - AAS				Euphausiidae	Northern krill *(Meganyctiphanes norvegica)*	0.24	-	71.3	[100]
						Benthesicymidae	*(Gennadas elegans)*	0.252	-	70.9	
						Pasiphaeidae	Shrimp *(Pasiphaea sivado)*	0.81	-	84.6	
							Pink shrimps *(Pasiphaea multidentata)*	2.68	-	88.22	
Muscles							Red shrimps *(Aristeus antennatus)*	2.933	-	85.28	

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Muscles	Mediterranean Sea	GC- ECD	Animals	Vertebrates	Chondrichthyes	Torpedinidae	Atlantic torpedo*(Torpedo nobiliana)*	-	1.90	81	[101]
						Chimaeridae	Rabbit fish *(Chimaera monstrosa)*	-	2.67	83.6	
Muscles	Nyumba' ya Mungu Nature Reserve, Tanzania	GC - ECD	Animals	Vertebrates	Actinopterygii	Cichlidae	Tilapia *(Tilapia urolepis)*	-	0.0051	83.6	[102]
						Clariidae	*(Clarias mossambicus)*	-	0.007	77.8	
						Mochokidae	*(Synodontis maculipinna)*	-	0.0078	72.9	
Muscles	Kidatu Nature Reserve, Tanzania					Cichlidae	Tilapia *(Tilapia urolepis)*	-	0.0086	57	

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Muscles	Hyogo Prefecture, Japan	GC	Animals	Vertebrates	Actinopterygii	Carangidae	Japanese horse mackerel *(Trachurus japonicus)*	-	0.01	62	[94]
Muscles	Oita Prefecture, Japan							-	0.02	51	
Muscles	Kagoshima Prefecture, Japan							-	0.02	74	
Muscles	Mie Prefecture, Japan							-	0.02	50	
Muscles	USA	GC				Salmonidae	Sockeye salmon *(Oncorhynchus nerka)*	-	0.02	67	[94]
Muscles	Kidatu Nature Reserve, Tanzania	GC - ECD				Mochokidae	*(Synodontis maculipinna)*	-	0.0258	63.7	[102]
Muscles	Philippines	GLC	Animals	Vertebrates	Actinopterygii	Scombridae	Skipjack tuna *(Katsuwonus pelamis)*	-	0.03	60	[94]
Muscles	Kiribati, Pacific Ocean							-	0.03	75	
Muscles	Marshall Islands						Yellowfin tuna *(Thunnus albacares)*	-	0.03	75	
Muscles	Hale and Pangani Nature Reserve, Tanzania	GC - ECD				Clariidae	*(Clarias mossambicus)*	-	0.0335	100	[102]
Muscles	Mtera Nature Reserve, Tanzania					Cichlidae	Tilapia *(Tilapia urolepis)*	-	0.0347	87.45	

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Muscles	Kidatu Nature Reserve, Tanzania					Claroteidae	*(Bagrus orientalis)*	-	0.040	92.8	
Muscles	Guanabara Bay, Brazil					Mugilidae	*(Mugil liza)*	-	0.0415	59.9	[91]
Muscles						Clupeidae	*(Sardinella brasiliensis)*	-	0.0491	59.6	
Muscles	Lake Ya-Er, China	HPLC-AFS				Cyprinidae	Crucian carp *(Carassius carassius)*	-	0.05233	-	[103]
Muscles	Hale and Pangani Nature Reserve, Tanzania	GC – ECD	Animals	Vertebrates	Actinopterygii	Mochokidae	*(Synodontis maculipinna)*	-	0.0526	83.4	[102]
Muscles	Mtera Nature Reserve, Tanzania					Claroteidae	*(Bagrus orientalis)*	-	0.053	90.4	
Muscles						Alestidae	*(Brycinus affinis)*	-	0.056	95.6	

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Muscles	Mtera Nature Reserve, Tanzania					Characidae	Tiger Fish *(Hydrocynus vittatus)*	-	0.08555	68.85	[102]
Muscles	Kidatu Nature Reserve, Tanzania							-	0.116	97.5	
	Lake Ya-Er, China	HPLC-AFS				Channidae	*(Ophiocephalus argus cantor)*	-	0.16438	-	[103]
	Perlis, Kedah, Malaysia	GC	Animals	Vertebrates	Actinopterygii	Scombridae	Short mackerel *(Rastrelliger brachysoma)*	-	0.179	76	[27]
							Longtail tuna*(Thunnus tonggol)*	-	0.187	81	
	Indian Ocean	GLC					Southern bluefin tuna *(Thunnus maccoyii)*	-	0.19	71	[94]
	Atlantic Ocean						Bigeye tuna *(Thunnus obesus)*	-	0.19	71	
	Australia						Southern bluefin tuna(farmed) *(Thunnus maccoyii)*	-	0.19	64	
	Lake Ya-Er, China	HPLC-AFS				Cyprinidae	Silver carp *(Hypophthalmichthys molitrix)*	-	0.19515	-	[103]

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	Kuantan, Pahang Malaysia	GC	Animals	Vertebrates	Actinopterygii	Scombridae	Short mackerel*(Rastrelliger brachysoma)*	-	0.219	70	[33]
Liver	Perlis, Kedah, Malaysia						Longtail tuna*(Thunnus tonggol)*	-	0.236	45	[27]
Muscles	Atlantic Ocean					Istiophoridae	Blue marlin (*Makaira nigricans*)	-	0.24	43	[94]
Liver	Perlis, Kedah, Malaysia					Scombridae	Short mackerel *(Rastrelliger brachysoma)*	-	0.242	41	[27]
Muscles	Terra Nova Bay, Antarctica	AAS				Bathydraconidae	Ploughfish (*Gymnodraco acuticeps*)	-	0.2543	65.45	[97]
	Atlantic Ocean	GLC				Scombridae	Atlantic bluefin tuna *(Thunnus thynnus)*	-	0.29	70	[94]
	Guanabara Bay, Brazil	GC – ECD				Ariidae	*(Bagre bagre)*	-	0.2973	97.9	[91]

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Muscles	Terra Nova Bay, Antarctica	AAS				Channichthyidae	*(Chionodraco hamatus)*	-	0.307	81.9	[97]
	Indonesia	GLC				Scombridae	Bigeye tuna *(Thunnus obesus)*	-	0.31	66	[94]
	Chile	GC				Nothoteniidae	Patagonian toothfish *(Dissostichus eleginoides)*	-	0.31	54	
	Guanabara Bay, Brazil	GC – ECD				Haemulidae	*(Orthopristis ruber)*	-	0.3388	95.3	[91]
	Atlantic Ocean	GC	Animals	Vertebrates	Actinopterygii	Xiphiidae	Swordfish (*Xiphias gladius*)	-	0.34	72	[94]
Liver	Kuantan, Pahang Malaysia					Scombridae	Short mackerel*(Rastrelliger brachysoma)*	-	0.388	40	[27]
Muscles	Atlantic Ocean					Istiophoridae	Striped marlin (*Tetrapturus audax*)	-	0.39	76	[94]

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Muscles	Kuantan, Pahang Malaysia	GC				Scombridae	Longtail tuna*(Thunnus tonggol)*	-	0.405	78	[27]
	Pacific Ocean	GLC					Atlantic bluefin tuna *(Thunnus thynnus)*	-	0.49	77	[94]
	Guanabara Bay, Brazil	GC – ECD				Sciaenidae	*(Micropogonias furnieri)*	-	0.5051	98.2	[91]
						Centropomidae	*(Centropomus undecimalis)*	-	0.5184	96	
	Shizuoka and Chiba Prefectures, Japan	GC	Animals	Vertebrates	Actinopterygii	Berycidae	Splendid alfonsino*(Beryx splendens)*	-	0.52	67	[94]
	Italy	GLC				Scombridae	Atlantic bluefin tuna *(Thunnus thynnus)*	-	0.56	58	
Liver	Chendring, Terengganu, Malaysia	GC					Short mackerel*(Rastrelliger brachysoma)*	-	0.616	46	[27]
	Kuantan, Pahang Malaysia						Longtail tuna*(Thunnus tonggol)*	-	0.619	43	
	Chendring, Terengganu, Malaysia							-	0.651	47	
Muscles							Short mackerel*(Rastrelliger brachysoma)*	-	0.665	82	

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Muscles	Guanabara Bay, Brazil	GC - ECD				Trichiuridae	Largehead hairtail (*Trichiurus lepturus*)	-	0.678	99.2	[91]
	Pacific Ocean	GLC				Scombridae	Bigeye tuna *(Thunnus obesus)*	-	0.69	71	[94]
	Chendring, Terengganu, Malaysia	GC					Longtail tuna*(Thunnus tonggol)*	-	0.708	76	[27]
	Italy	GLC					Atlantic bluefin tuna (farmed) *(Thunnus thynnus)*	-	1.02	70	[94]
Liver	Shizuoka and Chiba Prefectures, Japan	GC	Animals	Vertebrates	Actinopterygii	Berycidae	Splendid alfonsino*(Beryx splendens)*	-	1.12	32	
Muscles	Terra Nova Bay, Antarctica	AAS				Nototheniidae	*(Trematomus pennelli)*	-	1.356	45.3	[97]
						Bathydraconidae	Mawson's dragonfish *(Cygnodraco mawsoni)*	-	6.702	73.9	
	Malaysia	INAA				Scombridae	Indian mackerel *(Rastrelliger kanagurta)*	0.21	-	75.8	[98]
							Narrow-barred Spanish mackerel*(Scomberomorus*	0.31	-	77	

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							commersoni)				
Fatty tissue	Bay of California	CV - AFS			Sauropsida	Cheloniidae	Green sea turtle (*Chelonia mydas*)	-	0.001	17	[104]
Muscles								-	0.006	22	
Kidneys								-	0.019	23	
Liver								-	0.027	19	
Muscles								-	0.17	100	
Kidneys								-	0.208	56	
Liver								-	0.338	41	
Muscles	Southeastern Bay of California, USA	CV - AAS	Animals	Vertebrates	Birds	Anatidae	Northern Shoveler (*Anas clypeata*)	-	0.47	100	[105]
Intestines	Czech Republic	HPLC/CV-AFS				Accipitridae	Common buzzard (*Buteo buteo)*	-	0.57	71.3	[7]
Muscles	Chaun River, Siberia, Russia					Laridae	Herring Gull(*Larus argentatus*)	-	0.6	-	[106]
	Southeastern Bay of California, USA	CV - AAS				Anatidae	Blue-winged Teal (*Anas discors*)	-	0.77	26.1	[105]
Feathers	Chaun River, Siberia, Russia	GC					Long-tailed Duck (*Clangula hyemalis*)	-	0.9	-	[106]
Muscles	Southern Indian Ocean					Procellariidae	White-chinned Petrel (*Procellaria aequinoctialis*)	-	0.9	-	

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Muscles	Northern Pacific Ocean	GC	Animals	Vertebrates	Birds	Procellariidae	Northern Fulmar (*Fulmarus glacialis*)	-	0.9	-	[106]
Intestines	Czech Republic	HPLC/CV-AFS				Phalacrocoradcidae	Great Cormorant *(Phalacrocorax carbo)*	-	0.99	82.1	[7]
Muscles						Accipitridae	Common buzzard (*Buteo buteo)*	-	1.02	84.8	
	Southeastern Bay of California, USA	CV - AAS				Anatidae	Lesser Scaup(*Aythya affinis*)	-	1.06	60.8	[105]
	Southern Indian Ocean	GC				Diomedeidae	Southern Royal Albatross (*Diomedea epomophora*)	-	1.1	-	[106]
	Chaun River, Siberia, Russia					Laridae	Arctic Tern (*Sterna paradisaea*)	-	1.1	-	
Feathers								-	1.1	-	

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Intestines	Czech Republic	HPLC/CV-AFS				Podicipedidae	Great-crested Grebe *(Podiceps cristatus)*	-	1.13	75.0	[7]
Liver	Chaun River, Siberia, Russia	GC				Laridae	Herring Gull(*Larus argentatus*)	-	1.2	-	[106]
	Czech Republic	HPLC/CV-AFS				Accipitridae	Common buzzard (*Buteo buteo)*	-	1.24	47.8	[7]
Kidneys	Chaun River, Siberia, Russia	GC				Laridae	Herring Gull(*Larus argentatus*)	-	1.3	-	[106]
Intestines	Czech Republic	HPLC/CV-AFS				Phalacrocoradcidae	Great Cormorant *(Phalacrocorax carbo)*	-	1.41	78.4	[7]
Kidney						Accipitridae	Common buzzard (*Buteo buteo)*	-	1.44	71.9	

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Muscles	Southeastern Bay of California, USA	CV - AAS				Phalacrocoradcidae	Neotropic Cormorant *(Phalacrocorax brasilianus)*	-	1.49	46.9	[105]
Intestines	Czech Republic	HPLC/CV-AFS				Podicipedidae	Great-crested Grebe *(Podiceps cristatus)*	-	1.57	80.0	[7]
Muscles	Chaun River, Siberia, Russia	GC				Anatidae	Long-tailed Duck (*Clangula hyemalis*)	-	1.6	-	[106]
	Czech Republic	HPLC/CV-AFS				Podicipedidae	Great-crested Grebe *(Podiceps cristatus)*	-	1.68	83.8	[7]
Kidneys	Northern Pacific Ocean	GC	Animals	Vertebrates	Birds	Procellariidae	Northern Fulmar (*Fulmarus glacialis*)	-	1.7	-	[106]
	Chaun River, Siberia, Russia					Laridae	Arctic Tern (*Sterna paradisaea*)	-	1.9	-	
Muscles	Czech Republic	HPLC/CV-AFS				Podicipedidae	Great-crested Grebe *(Podiceps cristatus)*	-	1.98	85.9	[7]

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Muscles	Northern Pacific Ocean	GC				Diomedeidae	Black-footed Albatross (*Phoebastria nigripes*)	-	2.0	-	[106]
	Czech Republic	HPLC/CV-AFS				Phalacrocoradcidae	Great Cormorant *(Phalacrocorax carbo)*	-	2.11	84.3	[7]
Liver	Chaun River, Siberia, Russia	GC				Anatidae	Long-tailed Duck (*Clangula hyemalis*)	-	2.2	-	[106]
						Laridae	Arctic Tern (*Sterna paradisaea*)	-	2.3	-	
Muscles	Czech Republic	HPLC/CV-AFS				Podicipedidae	Great-crested Grebe (*Podiceps cristatus*)	-	2.44	90.3	[7]
	Southeastern Bay of California, USA	CV - AAS				Pelecanidae	Brown Pelican (*Pelecanus occidentalis*)	-	2.85	93.9	[105]

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Kidney	Czech Republic	HPLC/CV-AFS				Phalacrocoradcidae	Great Cormorant *(Phalacrocorax carbo)*	-	2.87	70.0	[7]
Muscles	Southeastern Ryukyu Islands, Japan	GC				Sulidae	Brown Booby (*Sula leucogaster*)	-	2.9	-	[106]
	Czech Republic	HPLC/CV-AFS				Phalacrocoradcidae	Great Cormorant *(Phalacrocorax carbo)*	-	3.04	89.3	[7]
Liver	Northern Pacific Ocean	GC	Animals	Vertebrates	Birds	Procellariidae	Northern Fulmar (*Fulmarus glacialis*)	-	3.1	-	[106]
Kidney	Czech Republic	HPLC/CV-AFS				Podicipedidae	Great-crested Grebe *(Podiceps cristatus)*	-	3.50	74.4	[7]
Kidneys	Southern Indian Ocean	GC				Diomedeidae	Southern Royal Albatross (*Diomedea epomophora*)	-	3.6	-	[106]

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Kidneys	Southeastern Ryukyu Islands, Japan	GC				Sulidae	Brown Booby (*Sula leucogaster*)	-	3.6	-	[106]
Liver								-	3.7	-	
Kidneys	Czech Republic	HPLC/CV-AFS				Podicipedidae	Great-crested Grebe *(Podiceps cristatus)*	-	3.71	72.7	[7]
	Chaun River, Siberia, Russia	GC				Anatidae	Long-tailed Duck (*Clangula hyemalis*)	-	3.8	-	[106]
Muscles	Baffin Bay, Canada	GC - AED				Laridae	Glaucous Gull *(Larus hyperboreus)*	-	4.0	77.5	[107]
Liver	Czech Republic	HPLC/CV-AFS				Podicipedidae	Great-crested Grebe *(Podiceps cristatus)*	-	4.1	62.1	[7]
Kidneys	Southern Indian Ocean	GC				Procellariidae	White-chinned Petrel (*Procellaria aequinoctialis*)	-	4.3	-	[106]

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Liver	Czech Republic	HPLC/CV-AFS				Podicipedidae	Great-crested Grebe *(Podiceps cristatus)*	-	4.34	60.3	[7]
Liver						Phalacrocoradcidae	Great Cormorant *(Phalacrocorax carbo)*	-	4.49	59.9	
Kidney			Animals	Vertebrates	Birds		Great Cormorant *(Phalacrocorax carbo)*	-	4.56	63.3	
Liver						Podicipedidae	Great-crested Grebe (*Podiceps cristatus*)	-	4.72	55.5	
Muscles	Georgia, USA	-				Rallidae	Clapper Rail *(Rallus longirostris)*	-	5.0	99	[108]
Kidneys	Northern Pacific Ocean	GC				Diomedeidae	Black-footed Albatross (*Phoebastria nigripes*)	-	6.2	-	[106]
Muscles	Georgia, USA	-				Ardeidae	Snowy Egret *(Leucophoyx thula)*	-	6.3	79	[108]

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Feathers	Chaun River, Siberia, Russia	GC				Laridae	Herring Gull(*Larus argentatus*)	-	6.5	-	[106]
Liver	Czech Republic	HPLC/CV-AFS				Phalacrocoradcidae	Great Cormorant *(Phalacrocorax carbo)*	-	6.46	15.3	[7]
	Southern Indian Ocean	GC				Procellariidae	White-chinned Petrel (*Procellaria aequinoctialis*)	-	8.0	-	[106]
						Diomedeidae	Southern Royal Albatross (*Diomedea epomophora*)	-	9.8	-	
	Northern Pacific Ocean						Laysan Albatross (*Phoebastria immutabilis*)	-	11.2	-	
							Black-footed Albatross (*Phoebastria nigripes*)	-	20.4	-	
Fat	Black Sea	GLC - ECD	Animals	Vertebrates	Mammals	Phocoenidae	Harbor porpoise *(Phocoena phocoena)*	-	0.0049	-	[109]
Muscles								-	0.216	-	

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Kidney	Japan	AFS				Delphinidae	Killer whale *(Orcinus orca)*	-	0.24	3.2	[110]
Brain	Ontario, Canada					Mustelidae	North American river otter *(Lontra canadensis)*	-	0.25	-	[66]
							American mink *(Mustela vison)*	-	0.26	-	
Lungs	Japan					Delphinidae	Killer whale *(Orcinus orca)*	-	0.31	-	[110]
Liver	Black Sea	GLC - ECD				Phocoenidae	Harbor porpoise *(Phocoena phocoena)*	-	0.322	-	[109]
	Ontario, Canada	AFS				Mustelidae	North American river otter *(Lontra canadensis)*	-	0.87	-	[66]
Muscles	Japan					Delphinidae	Killer whale *(Orcinus orca)*	-	0.90	74	[110]
Kidney	Ontario, Canada					Mustelidae	American mink *(Mustela vison)*	-	0.94	-	[66]

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Kidney	Ontario, Canada	AFS				Mustelidae	North American river otter *(Lontra canadensis)*	-	0.94	-	[66]
Muscles	Japan	GC-ECD				Phocoenidae	Dall's porpoise *(Phocoenoides dalli)*	-	1.02	84	[111]
Liver		AFS	Animals	Vertebrates	Mammals	Delphinidae	Killer whale *(Orcinus orca)*	-	1.11	1.9	[68]
Liver	Ontario, Canada	AFS				Mustelidae	American mink *(Mustela vison)*	-	1.21	-	[66]
Muscles	Japan	GC-ECD				Delphinidae	Short-finned pilot whale (N) *(Globicephala macrorhynchus)*	-	1.25	81	[111]
						Ziphiidae	Baird's beaked whale *(Berardius bairdii)*	-	1.25	78	
						Delphinidae	Pantropical spotted dolphin *(Stenella attenuata)*	-	2.62	54	
							Risso's dolphin *(Grampus griseus)*	-	3.15	74	
							Rough-toothed dolphin *(Steno bredanensis)*	-	3.51	74	

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Muscles	Japan	GC-ECD				Delphinidae	Striped dolphin *(Stenella coeruleoalba)*	-	3.74	63	[111]
	North Sea, Denmark					Phocoenidae	Harbor porpoise *(Phocoena phocoena)*	-	4.0	-	[112]
	Japan					Delphinidae	Short-finned pilot whale (S) *(Globicephala macrorhynchus)*	-	6.45	64	[111]
							Common bottlenose dolphin *(Tursiops truncatus)*	-	6.83	54	
Liver	North Sea, Denmark		Animals	Vertebrates	Mammals	Phocoenidae	Harbor porpoise *(Phocoena phocoena)*	-	6.9	-	[112]
Muscles	North Sea - Belgium							-	7.3	-	
Fur	Ontario, Canada	AFS				Mustelidae	North American river otter *(Lontra canadensis)*	-	8.24	-	[66]
Liver	North Sea - Belgium	GC -ECD				Phocoenidae	Harbor porpoise *(Phocoena phocoena)*	-	8.6	-	[112]
Muscles	Japan					Delphinidae	False killer whale *(Pseudorca crassidens*)	-	11.2	36	[111]

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Fur	Ontario, Canada	AFS				Mustelidae	American mink *(Mustela vison)*	-	11.25	-	[66]
Liver	South coast of Brazil	CV - AAS				Pontoporiidae	La Plata dolphin (*Pontoporia blainvillei)*	0.05-4.21	-	-	[45]
	Southeast coast of Brazil							0.12-2.36	-	-	
Kidney								0.16-1.13	-	-	
Kidney	South coast of Brazil							0.26-1.82	-	-	

*,** - the numerical values are given as originally stated in the cited literature

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Table 5. Basic information on the techniques used in the speciation analysis of mercury.

ISOLATION TECHNIQUE	ADVANTAGES	DRAWBACKS	DETECTION TECHNIQUE	LIMIT OF DETECTION			REFERENCES
				MeHg(I)	EtHg(I)	PhHg(I)	
High-performance liquid chromatography (HPLC)	✓ High selectivity ✓ A universal, integrated, fully automated method of mercury speciation ✓ Quick and simple ✓ Does not require conversion of target analytes into volatile derivatives ✓ Isolation of mercury compounds possible at room temperature	✓ Such low LODs as with GC are not obtainable ✓ Poorer selectivity in the analysis of complex matrices ✓ Poorer sensitivity then with GC ✓ Large quantities of organic solvents consumed	CV - AFS	27 pg 0.015 - 0.1 µg	26 pg	-	[150] [151-153]
			CV - AAS	0.1-16 µg/dm^3	-	-	[1,154]
			ICP - MS	16- 400 ng/ dm^3	-		[1]
			ICP - AES	0.1ng/ cm^3	-	-	[1]
			(CV) MIP - AES	0.35 ng/ cm^3	-	-	[1]
			UV - PCO - CVAFS	0.015 µg/kg	-	-	[153]
			HF – LLLME	3.8 ng/ cm^3	-	0.3 ng/ cm^3	[155]
			UV - Vis	7.0–95.1 µg/dm^3			[156]
Gas chromatography (GC)	✓ High precision ✓ Far lower LODs obtainable than with HPLC ✓ Both organic and inorganic mercury compounds can be determined ✓ Usually used to determine MeHg in environmental samples ✓ High degree of target analyte isolation ✓ Can be hyphenated with many different detection systems	✓ Target analytes in the sample have to be converted into volatile derivatives ✓ Specific analytical conditions are required ✓ For determining MeHg cleanup is required, to eliminate the interference of organic halides ✓ Sample preparation has a significant effect on efficacy and accuracy	MIP-AES	0.01-0.06 µg/g 0.04-10 ng/ dm^3	-	-	[1,157-160]
			AFS and GC-(CV) - AFS	5 pg and 0.01-6 ng/ dm^3; 0.6-1.3 pg	5pg	-	[1,161-163]
			(CV) - AAS	5-167 pg	-	-	[1,143,164]
			ICP - MS	0.9 pg 0.5 pg 0.12-1 pg	- 1.0 pg	-	[1,163,165]
			ICP - AES	3 pg. 0.6 ng/ dm^3	-	-	[1]
Capillary electrophoresis (CE)	✓ Highly effective isolation of analytes ✓ Only a small volume of sample is needed ✓ Short separation time	✓ Poor sensitivity ✓ Poor stability	UV	47.5 ng/ cm^3 680 ng/ cm^3	-	4.1 ng/ cm^3 -	[166,167]
			DF – ICP - MS	54 ng/ cm^3	-	-	[167,168]
			ICP - MS	2.3 pg 128 ng/ cm^3 80 ng/ cm^3 13.6 ng/ cm^3 149 ng/ cm^3	-		[167-170]
			VSG - AFS	2.5 pg 16.5 ng/ cm^3	2.4 pg	13.3 ng/ cm^3	[168,171]
			AAS	2.9 pg	-	-	[172]

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Table 6. Analytical procedures used in the speciation analysis of mercury

TYPE OF SAMPLE	EXTRACTION	ANALYTE CLEANUP	EXTRACTION EFFICIENCY AS RECOVERY [%]				ANALYTICAL TECHNIQUE	METROLOGIAL PARAMETERS	REFERNCES
				MeHg	OHg	THg			
Water	Approximately 30 cm^3 of water was weighed in a Teflon tube, 0.2 ml of 1% ammonium pyrrolidinedithiocarbamat, 0.5 ml 4 mol/dm^3 KBr and 0.5 cm^3 2 mol/dm^3 H_2SO_4.	Solution distilled at 110° C in the presence of N2 for 4-5 h. Derivatization of MeHg with $NaBEt_4$ in a buffer solution at pH 4.5. MeEtHg was trapped on a Tenax column.	-	-	-	-	GC – CV - AFS	20 pg/dm^3 (for MeHg)	[89]
Water		Collection of samples *in situ* by pumping them through a minicolumn packed with C18 modified with sodium diethyldithiocarbamate. Elution of mercury species with 500 cm^3 5 % thiourea in 0.5 % HCl from minicolumns.	-	-	-	-	HPLC – ICP - MS	5.6 ng/dm^3 (for MeHg)	[134]
Sediments, zoobenthos, water	Microwave assisted extraction 0.5– 4 g of a sample with the extraction agent containing 3 mol /dm^3 HCl + 0.2 mol/dm^3 citric acid + 50 % methanol (10 cm^3). Acidity of the filtrated extracts was adjusted to pH 3 by NaOH. Addition of 2-mercaptophenol.	The Speed C18 SPE stationary phase (Applied Separations, Allentown, PA, USA) was used for preparation of SPE microcolumns that also enabled countercurrent-flow elution.	Method of standard addition (certified reference material CRM 580)	-	>95	-	HPLC – CV - AFS	4.3µg/dm^3(for MeHg) 1.4 µg/dm^3(for EtHg) 0.8 µg/dm^3(for PhHg)	[20]
Soils, earthworm tissue, fungi	Addition to the samples of 5 % H_2SO_4, 18% KBr and 1.0 cm^3 1M $CuSO_4$	Derivatization of MeHg with 50 cm^3 1 % $NaBEt_4$ for 15 min in a buffer	Method of standard addition (certified reference materials:	89-103	-	-	GC – CV - AFS	0.05 µg/kg (for MeHg)	[19]

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	solution and vigorous shaking for 15 min. Addition of 1 cm^3 CH_2Cl_2 and the samples shaken again for 15 min. Centrifugation for 5 min at 3200 rpm. Separation of the organic phase (CH_2Cl_2) from the aqueous phase. Extraction repeated with an additional 5 cm^3 CH_2Cl_2. Addition of 35 cm^3 of Milli-Q water to the combined CH_2Cl_2. Evaporation on a water bath at about 90°C. Samples purged with N_2 for 5 min to remove remaining CH_2Cl_2.	solution at pH 4.6. Ethylmethyl-Hg was purged onto a Tenax trap for 15 min with Hg-free N_2.	DORM-2, TORT-2)						
Periphyton	Replicate MeHg extractions carried out by immersing three freeze-dried filters in 10 cm^3 of 25 % KOH in methanol solution in a screw-cap bottle. The bottles were mounted on a wrist shaker overnight at room temperature.	0.25 cm^3 of the extract transferred to a glass reaction vessel, and diluted with 50 cm^3 of mains tap water. pH was adjusted to 4.9 with acetate buffer. Derivatization of MeHg with 100 µl of 1 % sodium tetraethylborate solution. The volatile alkylmercury derivatives were trapped on a Tenax column.	Analysis of reference material (DORM-2)	98	-	-	GC – CV - AFS	10.8 pg (for MeHg)	[128]
Zooplankton	Digestion of 2-5 mg (d.w.) plankton aliquots in 0.5 ml KOH/MeOH (1g /4 cm^3) solution for 8 h.						GC - AFS	9.9 pg (for MeHg)	[55]
Microorganisms	Alkaline digestion of 2 to 5 mg d.w. of powder in 0.5 ml of KOH/MeOH (1g /4 cm^3) solution during 8 h at 6°C.	MeHg converted to MeEtHg with sodium tetraethylborate in a buffer solution at pH 4.5. MeEtHg trapped on a Tenax column.	Analysis of reference material (TORT-2 and DORM-2)	88-102	-	90.4-110	GC – CV - AFS	2 ng/g (for meHg)	[87]

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Starfish, polychaetes	-	-	Adding known amounts of mercury to samples -method of standard addition (DORM-l)	87	-	94	GC - ECD	0.003 µg/g (in an averaged 1.5 g sample) (for MeHg)	[93]
Mollusks	Dissolution of the tissue in an alkaline medium.	Ethylation with sodium tetraethylborate. Volatile ethylated forms of mercury were then subjected to a flow of nitrogen and trapped on a Tenax column.					GC - AFS	-	[95]
Mussels	Separation of MeHg from the homogenized mussel samples using two techniques: a water vapor distillation technique (1.0 g of homogenized sample in a mixture of H_2S0_4/NaC1/H_20 at 150° C), and an ion exchange method (Dovex 1X8, Cl-form, 100-200 mesh), followed by UV decomposition of methylmercury.	Ionic mercury reduction by tin (II) chloride (10 % $SnCl_2$ in 20 % H_2S0_4) to elemental mercury	-	-	-	-	CV - AAS	-	[99]
Cephalopod tissue	Addition of 2 cm^3Milli-Q water and 3 cm^3 6 mol/dm^3 KOH solution to 200 mg of dried sample. The mixture was shaken for 2 h, after which 3 cm^3 6 mol/dm^3 HCl and 4 cm^3KBr/CuSO4 (3:1) solution was added. After 10 minutes of shaking, 5 cm^3 dichloromethane (DCM) was added, the mixture centrifuged and the organic	A weak sulfide solution was used to extract MeHg from the organic phase, thenMeHg was back-extracted to DCM.	Method of standard addition (certified reference materials: DORM-2, TORT-2)	92-103	-	-	GC - AFS	0.01 µg/g (for Hg)	[96,173]

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	phase separated.								
Fish tissue	Drying, cryogenic grinding and addition of potassium bromide and hydrochloric acid solution (1 mol/dm^{3}KBr in 6 mol/ dm^3 HCl) to the samples. Centrifugation.	Extraction of organomercury compounds from KBr solution using chloroform. Back-extraction with 1 % m/v L-cysteine. Mercury vapor generation from extracts was performed using 1 mol/dm^{3}HCl and 2.5 % m/v $NaBH_4$ solutions and a batch chemical vapor generation system.	-	-	-	-	CVG - ETAAS	5 ng/g (for MeHg)	[6]
Fish tissue	Acidic digestion with HCl–H_2O (1+1) and triple extraction with 10 cm^3 of benzene. Extracts were diluted to 25 cm^3 with benzene and mixed with 5g Na_2SO_4.	-	-	-	-	-	GC - ECD	-	[101]
Fish tissue	Alkaline digestion with KOH – ethanol solution at 100° C in a water bath containing ethylene glycol.	Extraction of MeHg with 0.01 % dithizone–toluene solution, clean up and purification of the Dz-Tol extract.	-	-	-	-	GC -ECD	-	[102]
Fish tissue	Acidic digestion with 2 ml of 14.25 mol/dm^3 H_2SO_4 (saturated with copper(II) sulfate), 2 ml of 4 mol/dm^3 KBr, and 2.5cm^3 of toluene solution and shaking for 35 min.	Organic extract back-extracted with 1 ml cysteine solution (1.5% *w/v)*. Shaking and centrifugation (2200 rpm) for 10 min.	Analysis of reference material (CRM 463)	98.6	-	96.5	GC - ECD	7 ng/g (for MeHg)	[27]
Fish tissue	Acidic digestion with 11.3 cm^3 37 % HCl. Incubation at 100° C for 10 min. Addition of 15 cm^3 toluene. Sonication for 20 min and centrifugation for 25 min.	Extraction of supernatant with 5 ml 0.1 % cysteine solution. Shaking for 10 min and centrifugation for 25 min	Analysis of two certificate reference material (DORM-2 and NIES CRM 13)	97 ± 5-98 ± 6	-	-	RPC - CVG - AFS	18 pg (for MeHg) 18 pg (for EtHg) 20 pg (for PhHg)	[174]

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Sea food	Oxidation of the organomercury species permitted the determination of total mercury. Mercury species separated by the selective retention of inorganic mercury on the chelating resin. The inorganic mercury was removed on-line from the microcolumn with 6 % (m/v) thiourea.	Mercury cold vapor generation was performed on-line with 0.2 % (m/v) sodium borohydride and 0.05 % (m/v) sodium hydroxide as reducing solution.	Method of standard addition (certified reference materials: (DOLT-1 , TORT-1)	98-110	-	94-110	FI CV-AAS	10 ng/dm^3 (forMeHg) 6 ng/dm^3 (forMeHg)	[23]
Seafood tissue	Addition of water (1.0 cm^3) and KOH (1.5 cm^3, 6 mol/dm^3) solution to each of the samples, shaken for 12 h. Addition of HCl (3 cm^3, 3mol/dm^3) to each vial for neutralization. Once the effervescence and heat had subsided, acidic KBr and $CuSO_4$ mixture at 3:1 ratio (v/v, 3 cm^3) were added. Then, 10 cm^3 of toluene was added, and the mixture was shaken for 3 min and set aside for 10 min.	Centrifugation at 8000 rpm for 2 min. Subsequently, 5 cm^3 of $Na_2S_2O_3$ (0.01 mol/dm^3) was added to 5 cm^3 of toluene and the mixture was shaken for 3 min and set aside for 10 min. Addition of acidic KBr/CuSO4 in 3:1 ratio (v/v, 0.4 cm^3) to 2 cm^3 of the aquatic layer. After the addition 0.2 cm^3 of toluene, the mixture was shaken for 2 min, then set aside for 10 min.	Method of standard addition (certified reference material: DORM-2)	-	88-106	-	GC – ICP - MS	0.5 pg (for MeHg) 1.0 pg (for EtHg)	[113]
Seafood	Addition of 3 cm^3 25 % (m/v) KOH (in methanol) to 1.0–2.0 g wet samples with mechanical shaking overnight. Addition of 3 cm^3 6 mol/dm^{3}HCl, 4 cm^3 acidic KBr/$CuSO_4$ (3:1) and 5 cm^3 CH_2Cl_2 were added to the tube in sequence, shaking for 2 h to extract organic mercury into the CH_2Cl_2 phase.	Centrifugation at 2000 rpm for about 10 min, the CH_2Cl_2. Extraction with 1 cm^3 sodium thiosulfate. Shaking for 45 min.	-	-	-	-	HPLC – CV - AFS	0.2 ng(forMeHg) 0.17 ng(forEtHg) 0.14 ng(forPhHg)	[175]
Seafood tissue	Acid digestion with H_2SO_4 + $CuSO_4$ + KBr.						INNA	0.02 mg/kg (for MeHg)	[98]

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	Extraction with toluene.								
Bird tissue (pectoral muscle, intestines, liver and kidney)	Microwave assisted extraction 0.2-1.0 g of sample with 6 mol/dm^3 HCl + 0.1 mol/dm^{3}NaCl for 10 min in an Ethos SEL high-pressure microwave digestion unit.	After filtration and dilution, the supernatant with acetate buffer (pH = 5) was made up to the final volume of 50 cm^3.	Analysis of reference material (DORM-2)	95-107			HPLC – CV - AFS	0.2 ppb (for MeHg) 0.06 ppb (for PhHg) 0.12 ppb (for EtHg)	[7]
Ringed seal tissue	Homogenization with an aqueous solution of acidic sodium bromide (5 cm^3 of 30 % in 4 N H_2SO_4) and copper(II) sulfate (7.5 cm^3 of 2.5 % in 4 N H_2SO_4). Extraction MeHg and other forms of organic mercury by vortexing the tissue homogenate with a 3:2 v/v mixture of dichloromethane - hexane (5-10 cm^3).	A fraction of the organic layer was withdrawn and extracted with (3 - 4 cm^3) aqueous thiosulfate (0.005 N) by vortexing for 1 min and centrifuging. Separation by adding an aliquot of thiosulfate (1-2 cm^3), KI (0.5 cm^3, 3 mol/dm^3). Back-extraction with toluene (1.5 - 3.0 cm^3). Separation with toluene by centrifuging for 2 min at 2500 rpm. The extract was dried over anhydrous sodium sulfate.	Using marine mammal liver tissue with a relatively high organic mercury and MeHg content to test recovery and extraction efficiencies for MeHg.	92	90	-	GC - ECD	10-80 ng/g Hg ww. pg (for MeHg)	[134]
Biological tissues	Extraction of mercury species into 10 g/dm^3 EDTA and 0.2 % (v/v) 2-mercaptoethanol solution.		Method of standard addition (certified reference materials: (DORM-2 , DOLT-3)	93-99			HPLC – ICP - MS	0.2–0.3 µg/dm^3 (for MeHg)	[122]
Biological samples	Acidic extraction with hydrochloric acid.	Decantation and the re-extraction. Neutralization with 10 mol/dm^3 sodium hydroxide. Dilution of extracts in the mobile phase and filtration.	-	-	-	-	HPLC – ICP - MS	0.08 µg/dm^3 (for MeHg)	[176]
Sediment, biological tissue	Water vapor distillation technique for the isolation of methylmercury		Method of standard addition (certified reference materials: IAEA 356, CRM 463, CRM 464,	>95	-	-	HPF/HHPN ICP - MS	0.025 mg/kg (for MeHg)	[177]

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			DORM – 1)						
Biological tissue, sediment	Hydrolyzed with HBr (47–49 %). Shaking, addition of 20 cm^3 toluene to the samples. Mixed for 20 min. Centrifugation at 2400 rpm for 20 min. Collecting the supernatant, containing organomercuryspecies in falcon tubes.	Back-extraction with 6 cm^3 of 1 % (v/w) l-cysteine aqueous solution to strip methylmercury from toluene.	Analysis of certificate reference materials (CRM-580, IAEA-405, DORM-2, DOLT-3, SRM-2976 and SRM – 2977)	-	> 80 (except DOLT 3 - 74)	-	Direct Mercury Analyzer DMA - 80	0.04 ng (for MeHg)	[197]

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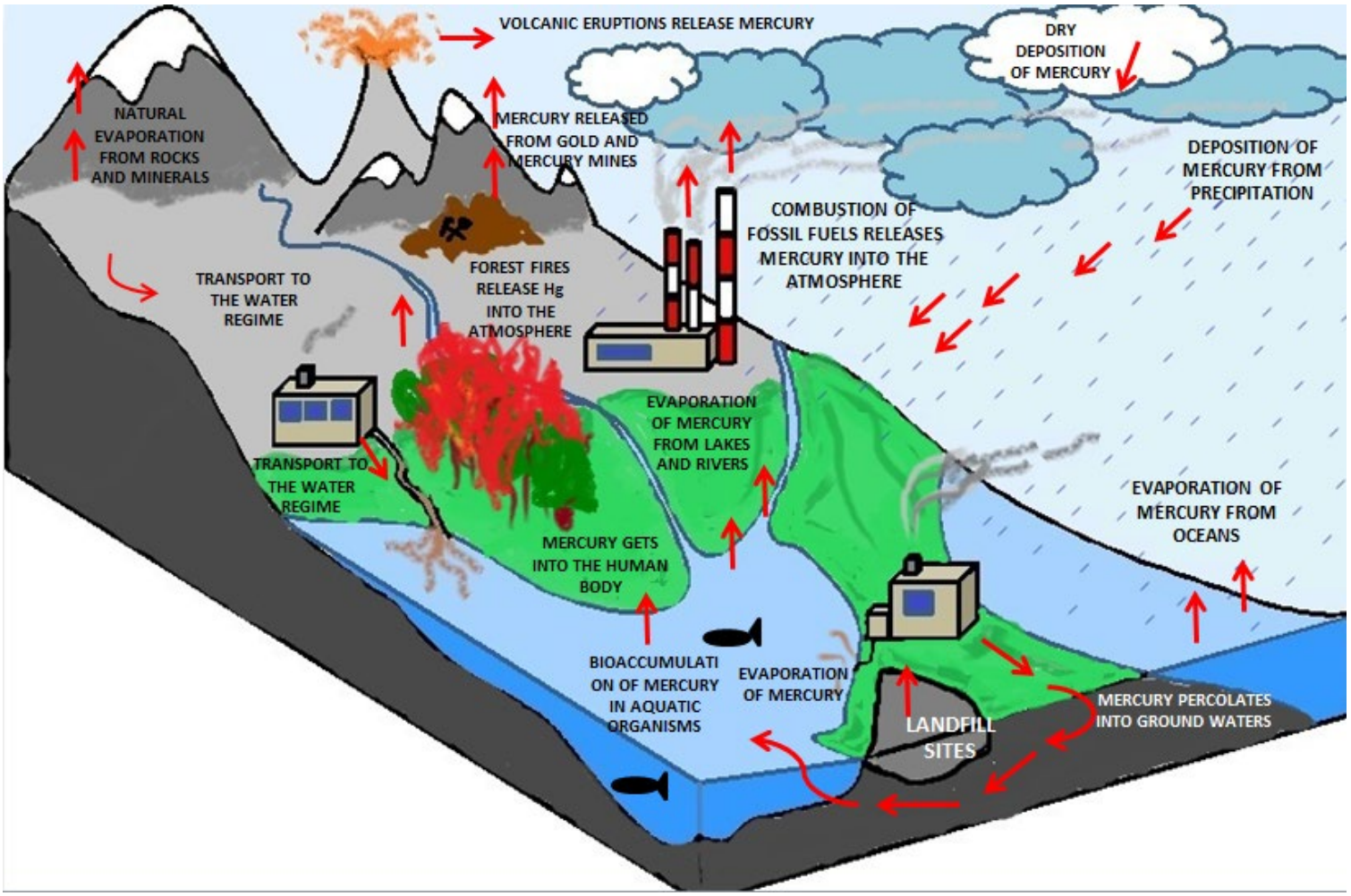

Figure 1. The mercury cycle in the biosphere.

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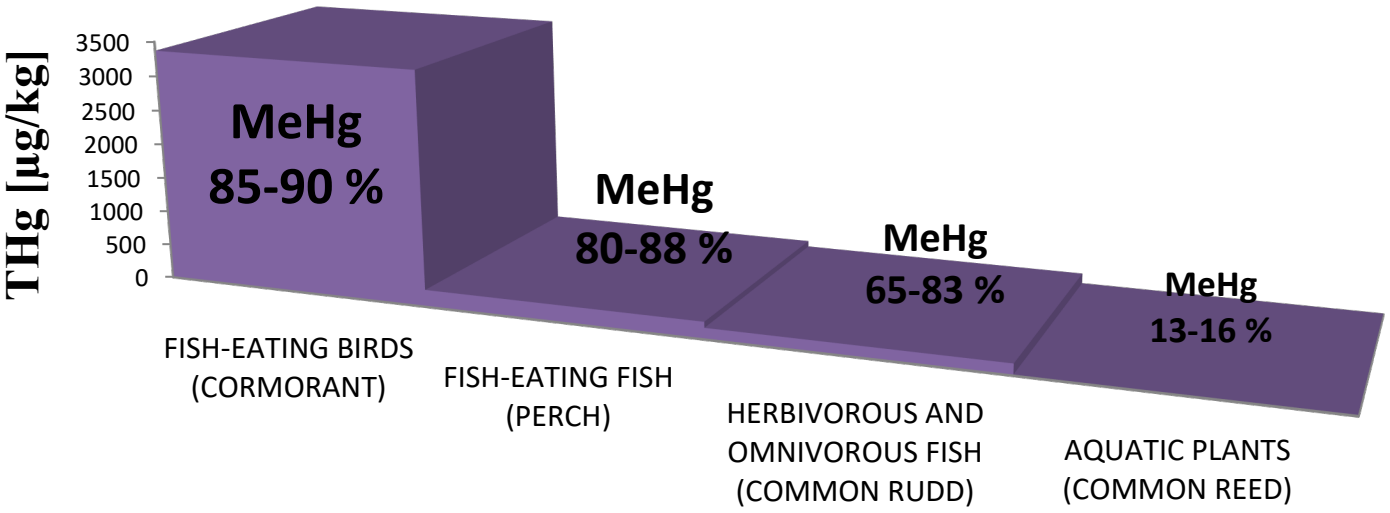

Figure 2. Levels of total mercury in organisms/samples [µg/kg] and the percentage of methylmercury in the total mercury content [7].

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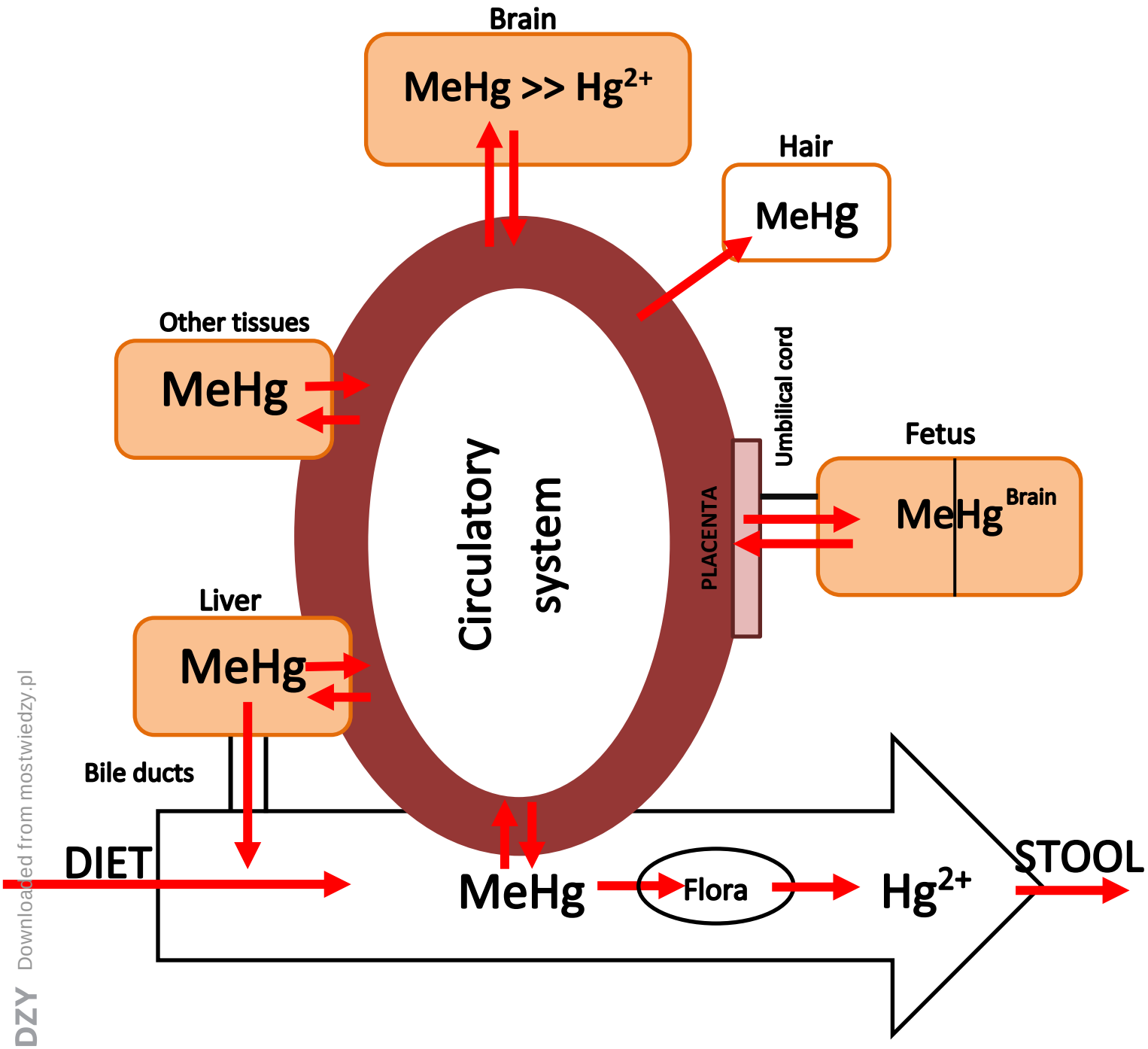

Figure 3. The circulation of methylmercury in the maternal and fetal organisms [73].

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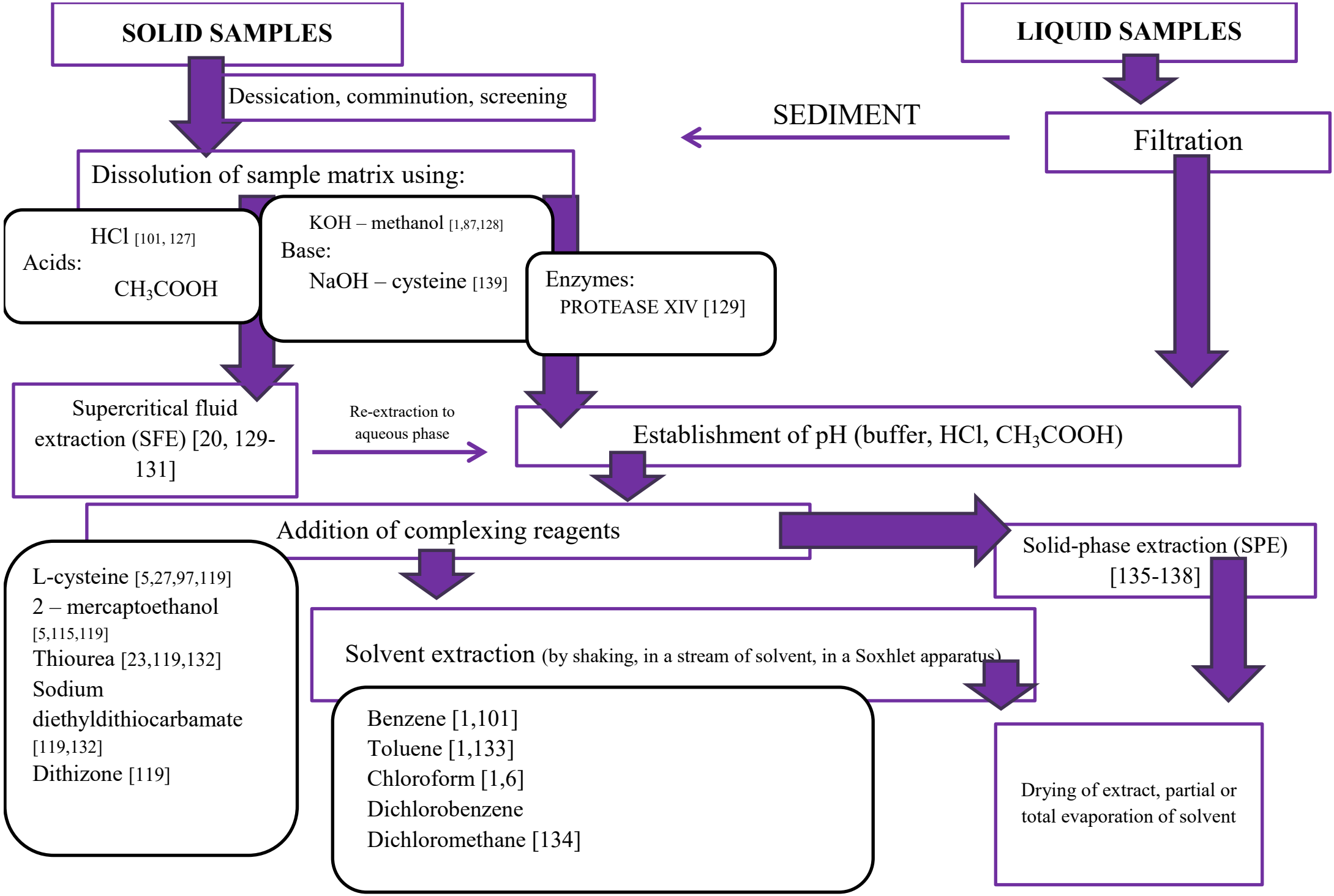

Figure 4. Scheme for preliminary sample preparation in the speciation analysis of mercury.