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Chapter 48. Mercury in living organisms – sources and forms of occurrence, bioaccumulation, determination methods

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Abstract

Mercury (Hg) is a heavy metal with well-known and broadly tested toxicity. Since Hg pollution and its impacts on human health is of global concern, it has become necessary to develop analytical methodologies that will provide tools to obtain reliable analytical information about the levels of Hg in samples, which very often have a complex matrix composition. This chapter summarizes key information on Hg and its chemical forms, sources of its emission to the environment and the global Hg cycle. In addition, the concepts of bioaccumulation and biomagnification of Hg along the food chain are characterized. The chapter also describes the analytical methods used in the determination of Hg and its compounds.

Keywords

Mercury; Methylmercury; Bioaccumulation; Biomagnification; Analytical methods; Organomercury compounds;

48.1. Introduction

Mercury (Hg) is a heavy metal with known and widely studied toxicity. The toxicity of mercury depends on the chemical form of the element. Methylmercury (MeHg) is considered to be the most toxic form of mercury, which, when ingested, is bioaccumulated and biomagnified in organisms found on successive links in the food chain. In aquatic ecosystems, microorganisms convert inorganic forms of mercury into methylmercury. This organometallic form can easily penetrate cell membranes and accumulate in the blood, thus affecting the central

nervous system; it also blocks enzyme binding sites and impedes protein synthesis. Due to the fact that mercury poses a serious threat to human life and health, it has become necessary to develop analytical methodologies that will constitute tools for obtaining reliable analytical data.

This chapter presents the most important information on mercury and its chemical forms, sources of this element's emissions to the environment and the global mercury cycle. Additionally, the concepts of mercury bioaccumulation and biomagnification along the food chain were characterized based on the results of determination of total mercury and its compounds. The chapter also describes the analytical methods used in the determination of mercury and its compounds.

48.2. Properties of mercury

Due to intensive development of various industries, chemicalization of agriculture and growth of human population large amounts of various xenobiotics, such as mercury and its organic forms, are emitted to individual elements of ecosystems. Mercury is considered, by specialists from various organizations, including the United States Environmental Protection Agency (EPA), as one of the most toxic elements [1]. The American Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) lists mercury and its compounds in the third place of the "priority list of hazardous substances", and the European Water Framework Directive; 2000/60/EG) classifies it as one of thirty "hazardous pollutants of uncertain nature". Mercury is a transition metal in the periodic table and the only metal that is liquid at room temperature. It is also one of the most chemically and biologically active metals. The toxicity, biochemical properties and the environmental cycle of mercury depend on the concentration and chemical form of this element. Mercury occurs in the environment in three chemical forms – as:

- elemental mercury in liquid or vapor form;
- inorganic mercury salts and minerals;
- organic mercury compounds.

Each of these forms can be transformed in the environment, changing its form from one form to another [2]. In the aquatic environment, this metal can undergo the process of biomethylation, thus creating an organomercury compound – methylmercury, which is a strong neurotoxin and undergoes the process of bioaccumulation. The permanent nature of this

compound in organisms and the environment has an impact on the health and development of people and nature [1].

48.3. Sources of mercury in aquatic organisms

Although natural geochemical and geothermal processes related to rock weathering, volcanic activity and evaporation from the surface of land and water can be a source of mercury in the environment, much of the mercury is released into the environment as a result of various human activities. Among the anthropogenic sources the dominating ones are: combustion of coal and petroleum products, combustion of municipal and medical waste, gold and mercury production, non-ferrous metallurgy, as well as metallurgy processes related to the production of e.g. iron, lead and zinc. In recent years, an important source of mercury was the use of plant protection products in agriculture, mainly fungicides. However, it is believed that the main source of mercury pollution are combustion processes, which account for more than half of the global mercury emission [3, 4].

Historically, mercury has been used in the production of dyes and medications. Currently, it is used in the electrotechnical, electrochemical, paper and chloro-sodium industries, in the production of lamps, measuring devices, dry batteries, plastics and weapons, as well as in dentistry [5].

Modeling mercury transformation processes in nature is a complex problem because many components of the environment must be considered, e.g. hydrodynamics of waterbodies, sedimentary processes, transport of mercury in the atmosphere, chemical reactions and many others. The rate of mercury circulation in nature is also influenced by weather conditions such as temperature and humidity [3].

Mercury in the atmosphere is found in the form of gas, elemental mercury vapors (Hg^0 – approx. 80%) and methylmercury (MeHg). Due to the high volatility of mercury vapors and their very slow process of oxidation to Hg(II), they remain in the air for a long time and their impurities can be transported over long distances. Under the influence of photochemical (oxidation) and biochemical reactions, mercury is converted to the Hg^{2+} ionic form. Mercury ions combine with water droplets in the atmosphere, fall to the earth's surface and into the aquatic environment.

Depending on the type of soil, mercury can be present in the form of Hg^{2+}, Hg_2^{2+}, HgS, HgS_2^{2-}, CH_3HgS^- and other alkyl compounds. Mercury enters the aquatic environment with rainfall or it is leached from soil and rocks. Depending on the redox potential of the water phase, mercury is present in the form of hydroxides $Hg(OH)^+$, $Hg(OH)_2$, $Hg(OH)_3^-$, or chlorides: $HgCl^+$, HgClOH, $HgCl_2$, $HgCl_3^-$, $HgCl_4^{2-}$. In oxygen-poor waters, mercury forms compounds with sulfur, such as: HgS_2H_2, HgS_2H^-, HgS_2^{2-}, CH_3HgS^-. It also exhibits the ability to combine with humic acids. It is estimated that about 95% of mercury in well-oxygenated waters is bound to organic matter. It can be in elemental form on the water surface, while high concentrations of methylmercury are noted near sediments. The speciation of mercury in the water environment and in soils is influenced by the bacterial microflora that participates in methylation processes [5].

Some anaerobic bacteria that reduce sulphates(IV) and iron(III) have the ability to methylate mercury in the second oxidation state (Hg^{2+}) and elemental mercury (Hg^0). The production of methylmercury occurs mainly under anaerobic conditions in sediments of inland, coastal and oceanic waters, as well as in peatlands and wetland soils. Methylation and demethylation are the two most important processes determining the methylmercury cycle in aquatic and terrestrial ecosystems. Methylmercury, the most common form of mercury in waterbodies, is highly toxic, accumulates in organisms and is incorporated into food chains associated with the aquatic environment. It undergoes the process of evaporation from the surface of soils and waters, thus returning to the atmosphere [3, 5].

Mercury in the environment occurs in many forms, which differ in their physicochemical properties determining its distribution, toxicity and mobility in the natural environment.

48.4. Forms of mercury in organisms

Mercury in organisms can be found in the form of methylmercury (MeHg), inorganic (InHg) and elemental (Hg^0). The main source of mercury intoxication in animals and humans is food, especially of marine origin. From the gastrointestinal tract of warm-blooded vertebrates, approximately 90% of methylmercury is absorbed, while in the case of inorganic mercury it only a few percent. Elemental mercury in the form of vapor is inhaled through the lungs; it is estimated that about 85% of mercury collected in this way will be absorbed in the body in vertebrates [6, 7].

In living organisms, mercury is accumulated in various tissues and internal organs; the highest concentrations are found in the liver, kidneys, brain, and then in muscles. The remaining internal organs accumulate this element to a lesser extent. A significant pool of mercury is also stored in the hair, or – in the case of birds – in feathers. A cluster analysis of different concentrations of mercury in organs and tissues on the example of a cormorant, a piscivorous bird associated with the marine environment of the Gulf of Gdańsk and the Vistula Lagoon, are shown in Figure 48.1 [8]

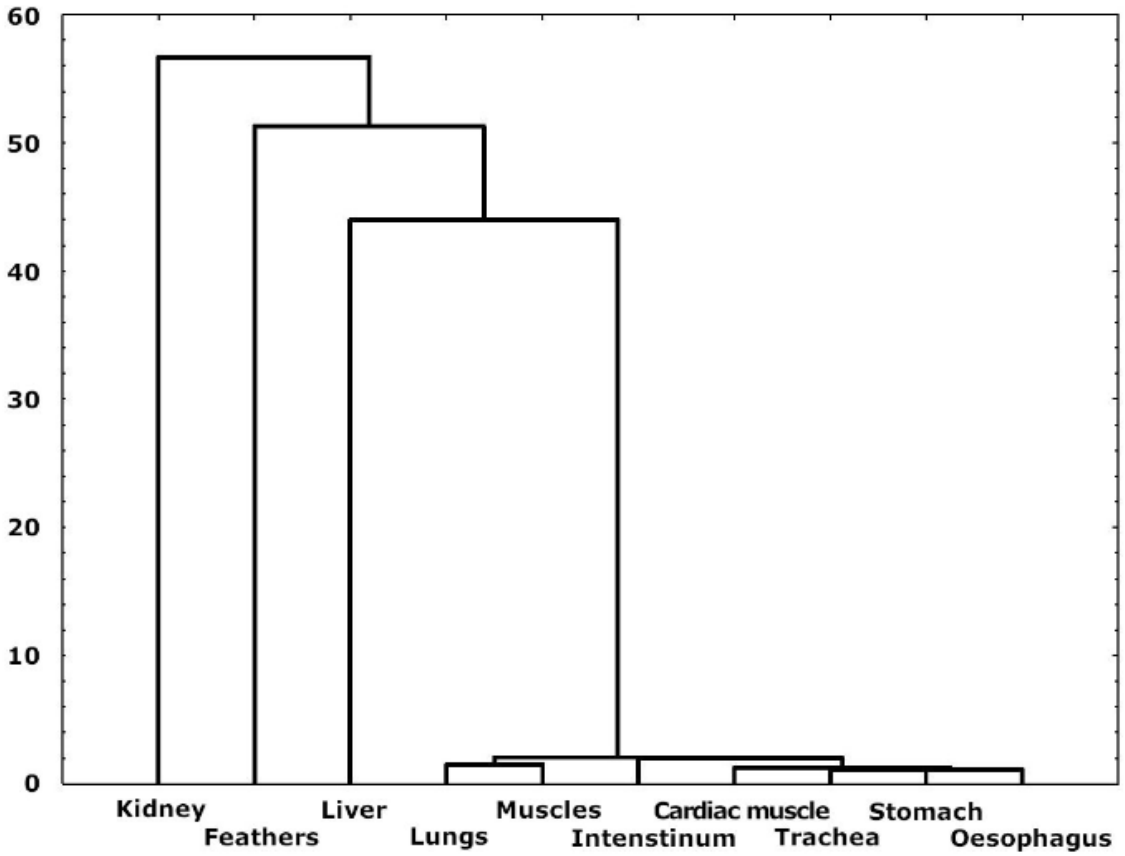
Increased Hg concentration in birds may diminish their breeding success, cause nervous system disorders (including poor coordination and muscle tension), difficulties in moving and weight loss [7, 9]. In adult birds, the concentration of MeHg exceeding 50 μg/g of dry matter (DM) in various tissues, especially in the brain, shows a strong intoxication leading to their death [7].

In the case of piscivorous birds, which are at the top of the trophic pyramid, mainly inorganic mercury Hg (InHg) is detected in the liver and kidneys. The most efficient enzymatic demethylation of MeHg takes place in these organs, and the resulting InHg is gradually removed by the excretory system. In the case of seabirds, the hepatic mercury concentration is estimated to be below 3 μg Hg/g DM reflects the geochemical background, while at a concentration exceeding 16.7 μg Hg/g DM toxic effects are observed [10, 11]. Hepatic mercury concentrations up to 40 μg/g DM have a negative impact on the growth and development of the individuals, their reproduction, metabolism and behavior [12, 13]. Increased concentrations in the organisms of aquatic birds in the liver and kidneys, respectively 67 and 133 μg/g DM, are lethal for them [14, 15].

In muscle tissue, mercury is deposited mainly in the methyl form. It is estimated that approximately 50% of the total mercury can be found there, not taking into account the MeHg immobilized in feathers [16]. Birds also eliminate excess MeHg by incorporating it into forming feathers, where methylmercury is permanently bound to keratin, a protein containing sulfhydryl groups (–SH), to which mercury has a strong affinity. It is estimated that the level of mercury contamination in feathers reflects the element's blood level in birds approximately 3 weeks before formation [17, 18]. Bird feathers can be used as biomonitors of environmental pollution with this metal. They constitute easy, non-invasive material for collection and the Hg concentrations in them correlate with the concentrations in internal tissues. Mercury bound in feathers is stable and does not undergo any further transformations – when it binds, its level in internal tissues does not change. In some species of piscivorous birds, including the cormorant,

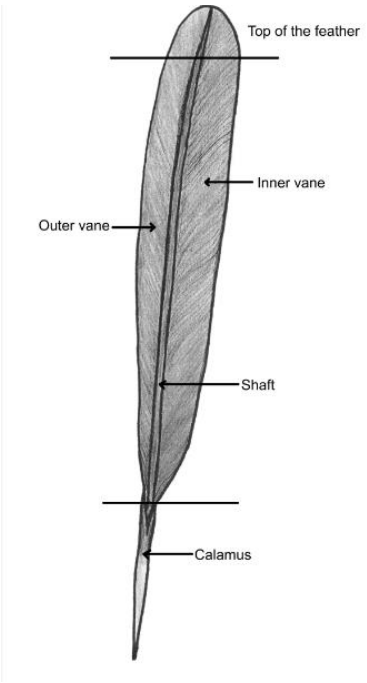
statistically significant differences are found in Hg concentrations between different types of feathers, i.e. tectrices > down > rectrices > remiges (Kruskal-Wallis ANOVA, $p < 0.001$) [19]. In the case of the cormorant, the distribution of the contamination within a single feather is also interesting. In the studies by Misztal-Szkudlińska et al. [19] slight differences were found between the tip of the feather, external and internal vanes, calamus and rachis – Figure 48.2 shows a schematic structure of the feather. It is estimated that mercury concentrations between 5 and 40 μg/g DM in bird feathers have an adverse effect related to reduced reproduction and brood reduction [17].

The concentration of Hg in the tissues of piscivorous birds is influenced by many factors, especially its supply in food, the bird's age, and according to some researchers also sex, the rate of demethylation processes, the living environment and its contamination [8, 9, 16, 20, 21]. Higher concentrations of this metal are observed in piscivorous birds [17] than in omnivorous or herbivorous species [22]. A concentration of 0.53 μg/g DM was considered a safe, threshold dose that can be taken by a piscivorous animal occurring in nature, which consumes whole fish individuals [22]. In addition to the elements discussed above that affect the concentration of pollutants in organisms there is another factor – the rate of detoxification processes. Mercury in birds is eliminated by three main routes, i.e. through excrement (InHg), feather shedding (MeHg), and egg laying (MeHg). The half-life of Hg in the bird's body is approximately 100 days.



Ryc. 48.1. Analysis of mercury concentrations per wet weight [µg/g] in selected tissues of the black cormorant

[Source: based on 8]



Ryc. 48.2. Schematic structure of a feather

[Source: based on 12]

48.5. Bioaccumulation of mercury in the trophic chain

Chemical elements, such as heavy metals, may undergo bioaccumulation processes in the natural environment, i.e. bioconcentration and biomagnification [23]. **Bioconcentration** is defined as the absorption of pollutants by an organism directly from the abiotic environment as a result of exposure to toxic substances found in non-living elements of nature, such as soil, air, water, etc. [23]. Toxic substances can also be carried along the subsequent links in the food chain, and their concentration increases at each higher trophic level. This phenomenon is known as **biomagnification**. Mercury in the natural environment, especially in aquatic ecosystems, undergoes bioconcentration and biomagnification along marine and freshwater trophic chains. Consequently, the highest levels of contamination are found in predatory organisms, which are at the top of food chains. This phenomenon may pose a serious toxicological risk and lead to the appearance of adverse effects related to limitations in growth and development, reproduction, and disturbances in metabolic processes and behavior.

The bioconcentration of mercury in ecosystems is described by the concentration factor, expressed as the ratio of the concentration of this pollutant in the organism to the concentration in an abiotic element of the natural environment [24]:

$$CF = \frac{C_x}{C_s}, \qquad [48.1]$$

where: CF is the concentration factor, C_x – concentration in a living organism [μg/g DM], C_s – concentration in the abiotic element of the ecosystem [μg/g DM].

Biomagnification is determined by the ratio of mercury concentrations in individuals standing lower in the trophic relation to individuals standing above [8, 23, 24]:

$$BMF = \frac{C_d}{C_o}, \qquad [48.2]$$

where: BMF is the biomagnification factor, C_d - concentration in the organism of the predator [μg/g DM], C_o – concentration in the organism of the prey [μg/g DM].

According to the definition of BMF provided in the literature [23, 25], if the concentration ratio is higher than one, it can be assumed that the biomagnification process takes place in the studied ecosystem. Mercury biomagnification is well described for many aquatic ecosystems, both marine and inland [23, 25, 26]. The lower the trophic relation, the less intense this process is. For example, the value of BMF in the lowest trophic relations, plankton-benthos-fish, is about one, whereas in the next link (benthophagic fish-predatory fish) a several-fold increase is observed.

The process of mercury bioaccumulation depends on the quantitative balance between the uptake of pollutants from the abiotic environment and food, and their elimination in organisms that constitute various links in the trophic chain.

48.6. Concentration levels of mercury and its compounds

The toxicity, biochemical properties and the cycle of mercury in the environment depend on the concentration and chemical form of this element. Contrary to other heavy metals, which accumulate in bacteria and microalgae but are not biomagnified, mercury is absorbed by microorganisms at the base of the food chain, and its concentration in the tissues of animals constituting the subsequent links in the trophic chain is increased [27]. Therefore, each organism from a given link in the food chain has a higher level of mercury, which results in high concentrations of this xenobiotic in animal tissues at subsequent levels of the food chain,

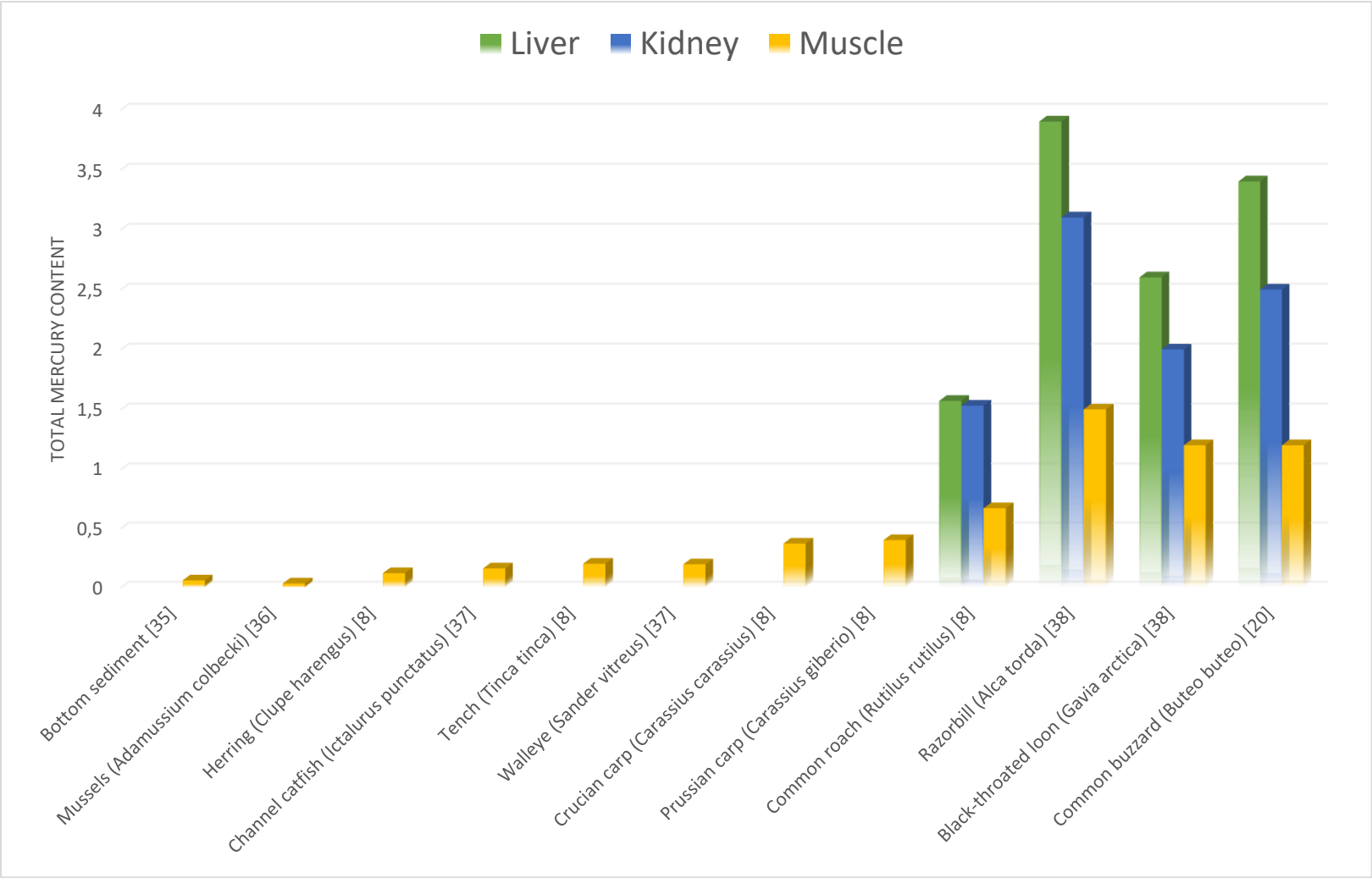
in relation to the initial concentration in water, bottom sediment or soil [28]. Therefore, the most important factor influencing the level of mercury and its organic forms in the tissues of a given animal seems to be the diet [3]. The type and variety of food consumed are therefore closely related to the level of mercury in tissues and organs of organisms. Figure 48.3. shows compiled literature information on the levels of mercury and its organic compounds in sediment samples and tissues of organisms at different levels of the trophic chain.

Dangerously high levels of organic mercury have been found in the tissues of fish, birds, and also aquatic and terrestrial mammals that eat fish. Fish are an essential element in the biological cycle of organic mercury compounds in nature. This is due to the fact that they are an important link in the trophic chain, being the basis of the diet of not only many aquatic organisms, but also people [29]. Another reason is that, the tissues and organs of piscivorous birds, such as cormorants, which are predators of aquatic ecosystems, significant amounts of MeHg accumulate, while other species, such as the great crested grebe, whose diet consists of insects and crustaceans as well as small fish, accumulate significantly lower amounts of the toxic form of mercury [20].

Marine mammals have the most varied diets, as they are at the top of the food chain. Therefore, these animals, consuming fish, molluscs and other aquatic organisms of various sizes , are at risk of poisoning with MeHg, which is present in their food, and accumulation of this toxic compound in significant amounts in their tissues [30]. High levels of mercury are determined especially in the liver. Based on the results of studies aimed at determining toxic forms of mercury in tissues of various marine mammals, it was found that their livers contain much higher concentration levels of mercury than the kidneys [31]. It is related to the process of storing and transforming toxic forms of mercury in the liver. The results of studies conducted in various centers indicate that organic forms of mercury, and in particular methylmercury, are transformed into its less toxic forms (e.g. HgSe) in marine mammals' livers [32], since the liver is an organ where metals are accumulated and detoxified, and in which metabolic processes related to metals take place.

Multiple studies have also been carried out to investigate the relationship between the body length or size of marine mammals and the mercury level in their liver and kidneys. Concentration of organic mercury in the liver generally increases with the age of animals [32, 33].

The level of pollution of individual elements of the environment with organic mercury compounds is not only a problem for aquatic ecosystems. It also applies to terrestrial ecosystems, especially to animals that are at higher levels of the food chain [34].



Ryc. 48.3. Literature data on total mercury content [mg/kg DM] in environmental samples.

[Source: based on 35–38]

48.7. Analytical methods used in the determination of mercury and its compounds

Due to specific properties of mercury and the possibility of creating compounds that exhibit the ability to bioaccumulate and biomagnify along the food chain, it has become necessary to obtain detailed information on the sources of emissions to the environment and the environmental fate of mercury. In addition, growing awareness of the dependence of mercury's toxicity on its chemical form has led to an increase in interest in determining specific mercury forms in environmental samples. The determination of the content of contaminants deposited in the tissues and organs of individual organisms throughout their life cycle can provide valuable information about the quality of the environment of which they are part. The study of mercury speciation has therefore become extremely important due to the determination of mercury's biogeochemical cycle, as well as the scale of the analytical challenge – taking into account the need to develop appropriate analytical procedures and the production of reference materials that will constitute tools for obtaining reliable analytical information.

To determine the total mercury content, a number of methods have been developed using analytical techniques such as: atomic fluorescence spectrometry (AFS) [39], various forms of atomic absorption spectrometry (AAS), and inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) [40]. One of the most commonly used techniques for determining total Hg content in environmental samples is cold vapor atomic absorption spectrometry (CV-AAS). This technique is primarily characterized by high selectivity, high precision and repeatability, as well as reproducibility, and therefore it is widely used in biomonitoring of environmental pollution [29].

However, there is an increasing trend to determine individual forms of mercury rather than the total content of this element in environmental samples. Determination of this type is possible because of the use of speciation analysis. Speciation as an area of research emerged only in the 1980s and it coincided with the development of many analytical procedures and techniques that allowed for the quantification of very small elements. Speciation was defined as the determination of various physicochemical forms of a given element in order to determine its level of toxicity, bioavailability, bioaccumulation and transport [41]. Contemporary speciation analysis chiefly consists in research on biologically active chemical elements. Speciation studies are used to determine the metabolism of various elements in living organisms and their biological activity. Additionally, they are used in food chemistry, pharmacy, biology, toxicology and environmental research, and even in the study of historic buildings [2]. Due to the fact that the analyzed samples are very often characterized by a complex matrix

composition, and the organic forms of mercury present in them are present at very low concentration levels, the use of selective separation techniques combined with sensitive and highly selective detection methods is required. Such connections are called coupled, hybrid or combined systems, and thanks to them, a significant improvement in the sensitivity of the system and shortening the analysis time is achieved [42].

As is the case with analyses aimed at determining total metal content, speciation analysis requires a series of carefully planned steps. Firstly, the issues related to sampling and preparation for analysis should be underlined. These steps need to be performed in such a way as to prevent decomposition and chemical transformations that could alter the composition of the compounds originally present in the sample, and should also meet the basic trace analysis requirements for analyte loss and risk of sample contamination [43]. A crucial step in the analytical process of speciation analysis is the process of extracting individual forms of mercury from a sample. It is required that the extraction is an efficient and effective process, which is why more and more often the process is supported by using such factors as: ultrasound (UAE, ultrasound-assisted extraction) [44, 45], increased pressure (PFE, pressurized fluid extraction) or microwaves (MAE, microwave-assisted extraction) [46].

Despite the use of multiple extraction techniques, it is impossible to determine some substances in an unchanged form in environmental samples. In such cases, the derivatization process is used, i.e. the process of converting the analyte into derivatives with properties that enable their determination using a given analytical technique. The derivatization process is very often used to separate various forms of mercury from a sample or to enrich an analyte, thus using the ability of this element to form mercury vapors in a reaction with a reducing agent [43].

Selecting an appropriate separation technique is related to the physicochemical properties of a measured substance. The most popular separation techniques in speciation analysis are gas chromatography (GC), high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE). While the choice of the sample preparation procedure depends on the type of matrix in which the analytes are present, the choice of the separation technique depends on the physicochemical properties of the analyte (i.e. volatility, charge, polarity). Therefore, thermally stable, inert and volatile compounds (or those that can be converted into volatile and stable derivatives) are separated using gas chromatography, whereas liquid chromatography is a suitable technique for separating other compounds.

The requirements for mercury speciation analysis can only be achieved using combined techniques, in which the separation technique is combined with detectors selective for mercury compounds.

First work on mercury speciation was done using GC in combination with an electron capture detector (ECD). However, the non-specific nature of this detector made other solutions more popular in the following years. In the late 1980s and 1990s, development of the relatively inexpensive, extremely sensitive and selective cold vapor atomic fluorescence spectrometry (CV-AFS) made this detector the most popular one used in laboratories working on the biogeochemical cycle of mercury. As a separation technique, gas chromatography has also been successfully combined with microwave induced plasma atomic emission spectrometry (MIP-AES), inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), furnace atomization plasma emission spectrometry (FAPES), and quartz furnace atomic absorption spectrometry (QF-AAS). Detection methods used in conjunction with HPLC can be broadly divided into three categories: photometry, plasma techniques (ICP-AES, ICP-MS), and cold vapor atomic absorption and fluorescence spectroscopy (CV-AAS, CV-AFS) [47].

Due to the large variety of environmental and biological samples, as well as the analytical methods themselves, appropriate analytical procedures should be selected that enable determination of the lowest possible levels of organic mercury compounds in the tested material.

48.8. Conclusions

Every day, huge amounts of xenobiotics, such as heavy metals, enter the environment, both as a result of natural processes and human activity. Mercury is characterized by significant environmental mobility and its chemical forms can be easily bioaccumulated and biomagnified, reaching in organisms on higher trophic levels concentrations a thousand times higher than in the environment. However, even small amounts of mercury in living organisms are mutagenic, teratogenic and highly neurotoxic. Due to the fact that the pollution of the environment with mercury and its compounds is a global problem, it has become necessary to obtain detailed information on the sources of emissions to the environment and the environmental fate of mercury. Since analytical measurements are aimed at identifying and determining environmental poisons, such as mercury and its compounds, which are present in samples with complex matrix compositions at increasingly lower concentration levels, it has become

necessary to develop appropriate analytical methodologies and reference materials with different metrological characteristics as tools to obtain reliable analytical information.

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