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MERCURY IN THE ENVIRONMENT

RTEĆ W ŚRODOWISKU

Key words: Mercury, environment, environmental pollution.

Słowa kluczowe: rtęć, środowisko, zanieczyszczenie środowiska.

Rtęć jest pierwiastkiem, który zajmuje jedno z pierwszych miejsc na liście najbardziej niebezpiecznych zanieczyszczeń środowiska. Wraz z decyzją UNEP z 2009 r. przygotowywana jest konwencja międzynarodowa, która od roku 2013 będzie obligować wszystkie państwa na świecie do ograniczenia emisji rtęci w skali globalnej [UNEP 2008].

Rtęć nie pełni żadnej znanej roli biologicznej, jest natomiast toksyczna dla wszystkich żywych organizmów. Pierwiastek ten w warunkach naturalnych występuje w stanie ciekłym, jak również w fazie gazowej oraz w postaci jonów w środowisku wodnym. Przeprowadzone liczne badania wskazują, że główny problem stanowią:

1) uwalnianie się związków rtęci w środowisku,

2) ich przemiany

oraz

3) rozprzestrzenianie się na znaczne odległości.

Prowadzący badania naukowcy, coraz częściej zwracają uwagę na zjawisko reemisji rtęci z powierzchni wód i gleb, wskazując na istotność tego źródła rtęci w atmosferze.

Toksyczne działanie rtęci i jej związków zależy głównie od formy, w jakiej występuje (rtęć elementarna oraz nieorganiczne i organiczne związki rtęci), od drogi wnikięcia do organizmu, dawki oraz czasu ekspozycji. Najbardziej groźne dla człowieka (zwłaszcza dla

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plodu i małych dzieci) są organiczne związki metylortęciowe, ponieważ uszkadzają one przede wszystkim ośrodkowy układ nerwowy.

Rtęć nie ulega w środowisku biodegradacji i tworzy wiele toksycznych połączeń, zarówno nieorganicznych, jak i organicznych. Uwzględniając te właściwości należy pamiętać, że zanieczyszczenie środowiska przyrodniczego tym pierwiastkiem występujące w obecnych czasach, będzie stanowiło problem również w przyszłości.

1. INTRODUCTION

Mercury rarely occurs free in the nature and it is mainly found in cinnabar ore (HgS) in Spain and Italy. The highest contents of this element (40–400 $\mu\text{g}\cdot\text{kg}^{-1}$) were found in sedimentary rocks, argillaceous sediments and, in particular organic-rich shales [Kabata-Pendias and Pendias 2001; Winter 2007].

The natural release of mercury to environment occurs as a result of weathering of rocks and volatilization from the surface of seas and oceans. However, the main source of mercury, in the environment is anthropogenic activity like hard coal and brown coal mining, coal combustion, metallurgy and cement production [Pacyna 2008]. The significant influence on the mercury content in the environment has a presence of this element in industrial wastes, sewage as well as sediments.

Mercury (Hg) pollution demands attention because of the toxicity, mobility and long residence period of the metal in the environment, and its ability to be transformed to methyl mercury (MeHg) in soil, a bioaccumulative compound that can readily cross the blood–brain barrier.

Data originating from European Union indicate that in the first decade of the 21st century from 3 to 15 million people in Europe are exposed to the exceeded levels of mercury in the environment [Hlawiczka 2008]. Therefore, reduction of mercury emission to the environment is of prime importance in activities carried out in order to protect the environment.

In the paper there is a brief overview of the state of pollution of Hg in the air, soils, waters, sediments, plants and organisms of animals and people, indicating the potential risk to the environment coming from natural and re-emitted mercury emissions.

2. MERCURY IN THE AIR

As mercury is a very volatile element, dangerous levels are readily attained in air. Mercury vapour should not exceed 0.1 $\text{mg}\cdot\text{m}^{-3}$ in air. Air saturated with the vapour at 20°C contains mercury in a concentration far greater than that limit. The danger increases at higher temperatures [Winter 2007].

In Poland Regulation of Environmental Ministry regarding emission standards originate from installations [2005]. The aforementioned regulation concerns, among others, stand-

ards of air pollution emission from the combustion of installations. Hg is the only one element occurring separately with the maximum value of 0.05 mg/m³, whereas for other metals the standards are given for to the sum of two or more metals.

Data given by the National Centre for Emissions Management approved by the Ministry of Environment the total emission of Hg given in Table 1 indicate the gradual decrease of Hg within the period of 2000–2008 [Statistical... 2010].

Table 1. Total emission of Hg [Statistical... 2010]

Tabela 1. Całkowita emisja rtęci [Ochrona Środowiska 2010]

| Hg | 2000 | 2005 | 2007 | 2008 |
|----|------|------|------|------|
| | Mg | | | |
| | 25,6 | 20,1 | 16,2 | 15,7 |

Table 2 shows that main emission of Hg comes from combustion in energy production and transformation industries [Statistical... 2010].

Table 2. Total emission of Hg by kinds of activity in Poland in 2008 [Statistical... 2010]

Tabela 2. Całkowita emisja Hg według rodzajów działalności w Polsce w 2008 [Ochrona Środowiska 2010]

| Specification | Hg |
|---|--------------|
| Mg | |
| Total | 15,69 |
| Combustion in energy production and transformation industries | 8,81 |
| Combustion in municipal and housing sector | 1,36 |
| Combustion in industry | 4,63 |
| Production processes | 0,84 |
| Road transport | – |
| Other vehicles and machinery | – |
| Waste management | 0,04 |

Note: – not found.

According to data presented by Zyśk et al [2011] Poland is one of the highest mercury emitters in Europe mainly because its power sector is based on coal. The total mercury emission in Poland in 2005 was 20 Mg, of which 18.5 Mg were emitted from coal combustion. The mercury content of Polish coal reported in the literature was in the range of 0.013 – 0.302 mg·kg⁻¹ in hard coal and 0.08 to 1.03 mg·kg⁻¹ in brown coal, respectively [Bojakowska, Sokołowska 2001; Bojarska 2006; Wojnar, Wisz 2006].

3. MERCURY IN SOILS

Soils play an important role in the biological cycle of mercury acting both as a sink and as a source of this metal to biota, atmosphere and hydrological compartments.

Total concentration of Hg in the soils results from the content of this element in parent rocks as well as from atmospheric input, of both natural and human-made origin. Since the beginning of industrialization Hg has been deposited to terrestrial systems, even in remote areas. In spite of reducing contents of this element in the environment as a result of decrease of production fungicides containing Hg, considerable amounts of Hg are still released from manufacturing industries [Kabata-Pendias and Pendias 2001; Camargo 2002; Rémy et al. 2003].

There were carrying out a lot of researches in order to determine impact of mercury from an industrial plant on the nearby environment and potential risks to the local population.

Total mercury concentration in the 0–15 cm layer of soil from north-western Portugal was found to be highly variable, ranging between 0.010 and 91 mg·kg⁻¹ [Reis et al. 2009].

Deng et al. [2011] conducted the research on the mercury concentration in soils from farmland near a Pb–Zn mine and ore concentrating facility built in the 1950's in the karst area of Guangxi Zhuang Autonomous Region, China. The results shows that the concentrations in dry land and in paddy fields ranged 0.06–1.94 mg·kg⁻¹ and 0.36–5.68 mg·kg⁻¹ respectively, exceeding permissible value for Hg in soil stated by Chinese law (0.3 mg·kg⁻¹).

The soil pollution by mercury in Poland is an object of many researches. Results of research led by Florencka and Wojtanowicz [2007] on areas of meadows and forests indicate higher pollution of upper layer of the soil in forests (0,003–0,248 mg·kg⁻¹) than meadows (0,004–0,086 mg·kg⁻¹) on account of the accumulation of mercury bound by the organic substance in the form of leaves of trees. According to the Regulation of the Environment Minister [Regulation] the soil is regarded as polluted by mercury if the mercury content in the upper layer of the soil exceeds 2 mg·kg⁻¹ on agricultural lands and 30 mg·kg⁻¹ on industrialized areas. It is why Florencka and Wojtanowicz [2007] could state that soils examined by them were not polluted with mercury.

Szopka et al. [2011] stated that Hg has accumulated mainly in the litter (with the highest concentrations) and in the layer 0–10 cm. Hg concentrations in all samples were in the range of 0.04–0.97 mg·kg⁻¹, with mean values of 0.38 mg·kg⁻¹ for litter and 0.28 mg·kg⁻¹ (in the layer 0–10 cm) and 0.14 mg·kg⁻¹ (in the layer 10–20 cm), respectively.

Mercury being found in a soil causes limitation of: the growth and the development of plants as well as reduction the yield even by the 25%, what on the example of the maize is presenting Ciećko et al. [2007]. Therefore, introducing restrictions through the proper regulations in using the soil up to agricultural cultivations about ecological character is correct action. Regulation of the Agriculture and Rural Development Minister [2002] determines that

on ecological farms the acceptable mercury content for light, average and heavy soils is 0.5 mg·kg⁻¹ 1.0 and 2.0, respectively.

4. MERCURY IN WATERS AND SEDIMENTS

In aquatic environment Hg appears as elemental, inorganic, and organic forms [Wang, 2004]. Elemental mercury (Hg⁰) has high volatility and relatively low water solubility and it is the only metal in liquid form at room temperature. Aqueous inorganic mercury with valence +2 is more widely spread in the environment; usually HgII is used as a substitute for inorganic mercury. HgII consists of both Hg₂C free ions and Hg₂C complexes such as, chloride, hydroxide, sulfide, dissolved organic matter (DOM), and other chemicals. Aqueous organic mercury may be divided into two groups:

- 1) covalently-bonded organomercurials, such as MeHg and dimethyl mercury (dimethyl mercury being less important than MeHg in mercury transport and transformation),
and
- 2) mercuric complexes with organic matter, such as humic substances [Ambio 2007]. As it was mentioned, organic mercury compounds are important - and dangerous. Methyl mercury is a lethal pollutant found in rivers and lakes.

The main source of Hg pollution is industrial wastes settling to the river and lake bottoms [Winter 2007]. The results show that the most important anthropogenic sources of mercury pollution in aquatic systems are: atmospheric deposition, erosion, urban discharges, agricultural materials, mining, and combustion and industrial discharges (Wang 2004).

In the Regulation of the Environment Minister [2008] regarding the way of classification of the state of the uniform parts of surface waters the permissible value of Hg is equal to 0.07 µg·l⁻¹.

In Polish Law pursuant to the Regulation of the Health Minister [2002] highest permissible concentration of mercury in the surface waters in rivers and lakes used for recreation should not be higher than 0.005 mg·l⁻¹.

According to the Regulation of the Environment Minister [2002] in Poland the highest permissible concentration of mercury in the surface waters used for the supply into water intended for the consumption is 0.001 mg·l⁻¹. The recommended value according to this regulation is 0.0005 mg of Hg·l⁻¹.

Mercury is a global contaminant and a potent neurotoxin, affecting human health and wildlife reproductive potential. The very therefore among others the water intended for the human consumption ought to contain very little mercury. According to the Regulation of the Health Ministry [2010] in Poland the highest permissible concentration of mercury in the water intended for the human consumption is 0.001 mg·l⁻¹.

Geochemical sediment concentration is very useful in estimation of quality of surface waters. Geochemical concentration of mercury (Hg) in sediments does not exceed 0.05 mg·kg⁻¹.

Wastewater coming from plants producing chlorine (mercury method), plants producing artificial fibers (mercury compounds are used as catalyzes) celluloses plants are major sources of pollution with Hg. English river sediments contained as much as $32.9 \text{ mg}\cdot\text{kg}^{-1}$ [Bubb 1991]. Mean Hg levels in different parts of the sediments of Lake Vänern varied from 0.18 to $5.3 \text{ mg}\cdot\text{kg}^{-1}$ [Lindeström 2001] while in other studies the median content of Hg $0.19 \text{ mg}\cdot\text{kg}^{-1}$ in sediments was found. Hg contents in Polish rivers sediments in 2006 were in the range of $0.004\text{--}32.4 \text{ mg}\cdot\text{kg}^{-1}$, whereas, in lakes sediments in 2007 Hg contents were in the range of $0.043\text{--}0.585 \text{ mg}\cdot\text{kg}^{-1}$ [Statistical... 2008].

Polish legislation demands, among others, control of Hg in dredged sediments that are excavated from the bottom of the rivers, channels and harbors mainly for navigation purposes with the maximal value of $1 \text{ mg}\cdot\text{kg}^{-1}$ [Decree of... 2002].

5. MERCURY IN PLANTS

As it was already stated mercury is a pollutant of global concern. It is largely due to its potential for biological transformation into harmful forms, bioaccumulation and biomagnification through the ecological food chains. Plants can take up Hg easily from soil solution. There is also much evidence that increasing soil Hg generally causes an increase in the Hg content of plants.

During research conducted by Reis et al. [2009] one predominant species of forage plant (*Lolium perenne*) were collected in fields surrounding the chlor-alkali plant. Its roots contained between 0.0070 and $2.0 \text{ mg}\cdot\text{kg}^{-1}$. Levels of mercury in the aerial parts of plants ranged between 0.018 and $0.98 \text{ mg}\cdot\text{kg}^{-1}$. Results of research shows that despite a production in chemical industrial complex were ceased in 2002, the environmental pollution with mercury is still significant.

The meadow flora examined on the area of Czarny Potok in Poland by Kopeć and Gondek [2009] was not much polluted with mercury as the content was in the range of $0.0120\text{--}0.0236 \text{ mg}\cdot\text{kg}^{-1}$.

It is very important that fruits and vegetables contain Hg as less as it is possible. Therefore, in the Regulation of the Health Minister [2005] in Poland the highest permissible concentration of mercury in fresh fruits and fresh vegetables is equal to $0.01 \text{ mg}\cdot\text{kg}^{-1}$.

The mercury contents did not exceed permissible values in fruit and vegetables determined by Bartodziejska et al. [2010]. The mercury content in fruits was $0.001\text{--}0.003 \text{ mg}\cdot\text{kg}^{-1}$, while in vegetables ranged from 0.001 up to $0.003 \text{ mg}\cdot\text{kg}^{-1}$. Lettuce, in which the mercury content reached the level $0.011 \text{ mg}\cdot\text{kg}^{-1}$ constituted the only exception.

Summarizing results of their work, Pierzynowska et al. [2009] are pointing out the fact that cereals, vegetables, potatoes and meat were main sources of mercury in Polish diet. Authors stated that, depending on household type, mercury intake ranged from 35.63 to $50.97 \mu\text{g}/\text{person}/\text{week}$. In their opinion a risk of exaggerated charging mercury with the food eaten daily does not exist in the Polish population.

Determining contents of trace elements in such plants as mosses is being used for biomonitoring of the air quality for decades. Like mosses from many European countries, Polish mosses according to Migaszewski et al. [2010] were distinctly elevated in Hg, bearing a signature of cross-border atmospheric transport combined with local point sources. Hg concentration in the moss species *H. Splendens* and *P. Schreberi* collected by Migaszewski et al. [2010] from Poland (Kielce, Holy Cross Mountains-HCM) ranged between 28 and 97 $\mu\text{g}\cdot\text{kg}^{-1}$ in Kielce and from 67 to 101 $\mu\text{g}\cdot\text{kg}^{-1}$ in samples from HCM.

6. MERCURY IN ORGANISMS OF ANIMALS AND PEOPLE

Mercury occurs naturally within the environment in a variety of forms including elemental Hg, as Hg^{2+} dissolved in water, cinnabar (HgS), oxidized (HgO), and organometallic compounds, such as methyl mercury (CH_3Hg^+), the latter of which shows great potential for bioaccumulation, being recognized as the most toxic form to humans [Deng et al. 2011].

According to information presented by Leśniewska et al. [2009] 75–95% of mercury in fish and seafood is in the form of methylmercury, which is the strong neurotoxin. The amounts of mercury found in food products other than fish and seafood are not so worrying because in the case of these products mercury does not appear in the form of methylmercury, which poses less threat for human health. Results of the research on the total mercury content in the muscular tissue of fish available in the trade and coming from private breeding from surroundings of Łódź led by authors, indicates that fish contains from 0.092 (salmon) up to 0.359 (tuna) $\text{mg}\cdot\text{kg}^{-1}$.

Results of blood and urine mercury determination among children and adults were presented by Prokopoicz et al. [2010]. The concentration of mercury in the children's blood was 0.10–1.72 $\text{ng}\cdot\text{cm}^{-3}$, while adults' blood contain 0.11–5.82 $\text{ng}\cdot\text{cm}^{-3}$, respectively. The concentration of mercury in the urine of children and adults expressed in the creatinine was in the range of 0.01–11.54 $\text{ng}\cdot\text{cm}^{-3}$. Authors are pointing out to the fact that regular consumption of fish (over 3 meals per month) in children and (over 5 meals per month) in women increased the concentration of mercury in blood, on average twice.

Mercury can penetrate into the human body through inhaled air. It is very important so that the man in the place in which he/she is working is exposed like least to the negative influence of factors harmful for his health. Mercury, especially in organic compounds, is such a factor and therefore, according to Regulation of the Labour and Social Policy Minister [2002] the Hg concentration cannot be higher than 0.01 $\text{mg}\cdot\text{m}^{-3}$.

7. CONCLUSIONS

Mercury is a pollutant of global concern largely due to its potential for biological transformation into harmful forms, bioaccumulation and biomagnification through the ecological

food chains. Mercury is not able to biodegrade in the environment and it forms many toxic inorganic and organic complexes.

Researchers, more and more often pay attention to the occurrence of re-emission of mercury from the surface of waters and of the soil, indicating the gravity of this source of mercury in the atmosphere. On the one hand, given data prove the gradual decrease of Hg within the period of 2000–2008, but on the other, Poland is one of the highest mercury emitters in Europe mainly because its power sector is based on coal. Available data indicate diverse results of contamination of environment with Hg. Some of them show that Hg did not exceed permissible values. However, due to the human health safety the continuous monitoring of toxic metal levels in agricultural products is required.

To sum up, it should be pointed out that environmental pollution with Hg nowadays would also be a problem in the future.

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