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# Heavy metals in water of Miedwie Lake (West Pomeranian, North-West Poland) and their potentiality in health risk assessment

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**ABSTRACT**

Miedwie Lake is the biggest post-glacial lake of the West-Pomeranian Voivodeship. At the same time it is the fifth of the largest lakes in Poland. Miedwie Lake is situated centrally between three big agglomerations, *i.e*. Szczecin, Stargard Szczecinski, and Pyrzyce. Miedwie Lake has been since 1976, the potable water source for the City of Szczecin. The reservoir is used not only for municipal purposes, but also for fishing, tourist and recreation purposes. Unfortunately, heavy metal pollution is an ever-increasing problem. The toxic heavy metals on entering into the aquatic environment are adsorbed onto particulate matter, although they can form free metal ions and soluble complexes that are available for uptake by biological organisms. Many of these metals tend to remain in the ecosystem and eventually move from one compartment to the other within the food chain. The increase in residue levels of heavy metal content in water, sediments and biota has resulted in decreased productivity and an increase in exposure of humans to harmful substances. Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water, soil, sediment, and air. The present research work deals with the quantification of toxic heavy metals in the water samples collected from Miedwie Lake (North-West Poland).

***Keywords:*** Heavy metal pollution, metals in water, Miedwie Lake (North-West Poland), pollution, environment

## 1. INTRODUCTION

The term "heavy metals" refers to any metallic element that has a relatively high density and applies to the group of metals and metalloids with atomic density greater than 4 $g \cdot cm^{-3}$. Heavy metals are well known to be toxic to most organisms when present in high concentration in the environment. In the last decades, human activities have continuously increased the levels of heavy metals circulating in the environment. Anthropogenic activities such as agriculture, industry and urban life increase content of these elements in soils and waters.

Many of these metals tend to remain in the ecosystem and eventually move from one compartment to the other within the food chain. Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water, soil, sediment and air.

Heavy metals, diluted in water, are usually in ionic or colloidal form. They are partly taken in by water organisms into their cells and tissues and partly absorbed by inorganic particles in suspension. Organic matter, released into water after the decay of bacteria, plants and animals containing a certain amount of heavy metals absorbed earlier can additionally absorb more metals from the water. With time, organic and inorganic suspension falls down forming bottom sediments. Although a certain amount of heavy metals can be released into water in this process, a considerable amount of them is deposited in bottom sediments permanently [1-37].

Hence, in the present investigation, efforts are made to quantify the accumulation of toxic heavy metals in water of Miedwie Lake of North-West Poland. The study was carried out with an objective to generate the pollution load data from scientific study so as to gauge the extent of pollution due to toxic heavy metals in the lake water.

## 2. EXPERIMENTAL

Miedwie Lake is the biggest post-glacial lake of the West-Pomeranian Voevodeship. At the same time it is the fifth of the largest lakes in Poland. As regards the geographical situation, Miedwie Lake is situated centrally between three big agglomerations, *i.e*. Szczecin, Stargard Szczecinski, and Pyrzyce. The lake lies on the territory of three municipalities: Pyrzyce and Warnice in the District of Pyrzyce as well as Stargard Szczecinski in the District of Stargard (**Figure 1**).

At the moment, the reservoir is characterized with the regular, prolonged shape resembling an ellipse. Banks are shallow, regular, and sometime very wet. The lake has the belt of the near-shore reaching locally tens meters far from the lake bank, what is the reason, together with the fact that the wind blows always here, that it is convenient for practising the various kinds of water sports.

The lake area amounts to 3 527 ha; maximal depth – 43.8 m; average depth – 19.3 m; water capacity – 681.7 mln $m^3$; shore-line length – 38.8 km; water level datum 14.1 m above sea level; maximal width 3.16 km; maximal length 16.2 km. The lake's bottom is the lowest situated area on the territory of Poland. Miedwie Lake is used since 1976 as the potable water source for the City of Szczecin. The reservoir is used not only to the municipal purposes, but also for fishing, tourist, and recreation purposes.


**Figure 1.** Miedwie Lake, Poland

Research was carried out in the years 2008-2012, in the period from April to October. The water samples collected from different sampling stations were filtered using 0.45 μm pore-size filter paper to remove suspended particles. Filtrates were preserved in polythene bottles. In order to prevent the precipitation of metals, 2 mL nitric acid was added to the filtrate.

The samples were concentrated to tenfold on a water bath and subjected to nitric acid digestion. About 400 mL of the sample was transformed into clean glass separating funnel in which 10 mL of 2% ammonium pyrrolidine dithiocarbamate, 4 mL of 0.5 M HCl, and 10 mL of methyl isobutyl ketone (MIBK) were added. The solution in separating funnel was shaken vigorously for 2 min and then left undisturbed for the phases to separate.

The MIBK extract, containing the desired metals, was then diluted to give final volumes depending on the suspected level of the metals. The sample solution was then aspirated into air acetylene flame in an atomic absorption spectrophotometer. The analysis for the majority of the trace metals, like Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Nickel (Ni), Lead (Pb), and Zinc (Zn) was done by Atomic Absorption Spectrophotometer.

## 3. RESULTS AND DISCUSSION

The experimental data on toxic heavy metals in water samples, collected along in water of the Miedwie Lake for the months of 2008 – 2012 (April to October), are presented in **Tables 1** through **5**.

**Table 1.** Heavy metals content in water samples collected from Miedwie Lake (April to October 2008)

| Heavy Metals (ppm) | Cd | Cr | Cu | Hg | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|
| **April 2008** | 0.45 | 0.71 | 0.07 | 0.04 | 2.36 | 0.04 | 3.31 |
| **May 2008** | 0.31 | 0.69 | 0.06 | 0.02 | 2.47 | 0.07 | 2,54 |
| **June 2008** | 0.36 | 0.83 | 0.08 | 0.04 | 2.21 | 0.04 | 3.25 |
| **July 2008** | 0.38 | 0.88 | 0.06 | 0.05 | 1.83 | 0.06 | 3.43 |
| **August 2008** | 0.43 | 0.72 | 0.06 | 0.04 | 1,79 | 0.04 | 3.35 |
| **September 2008** | 0.39 | 0.85 | 0.07 | 0.05 | 2.26 | 0.04 | 3.54 |
| **October 2008** | 0.43 | 0.82 | 0.05 | 0.03 | 2.41 | 0.06 | 3.29 |
| **Average** | 0.45 | 0.78 | 0.06 | 0.04 | 2.19 | 0.06 | 3.25 |

**Table 2.** Heavy metals content in water samples collected from Miedwie Lake (April to October 2009)

| Heavy Metals (ppm) | Cd | Cr | Cu | Hg | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|
| **April 2008** | 0.25 | 0.19 | 0.04 | 0.05 | 1.87 | 0.04 | 2.65 |
| **May 2008** | 0.27 | 0.41 | 0.08 | 0.05 | 1.78 | 0.05 | 2,59 |
| **June 2008** | 0.19 | 0.35 | 0.06 | 0.03 | 2.81 | 0.06 | 3.43 |
| **July 2008** | 0.32 | 0.52 | 0.07 | 0.05 | 2.49 | 0.07 | 3.75 |
| **August 2008** | 0.39 | 0.84 | 0.05 | 0.06 | 2,65 | 0.05 | 2.67 |
| **September 2008** | 0.32 | 0.39 | 0.04 | 0.03 | 2.73 | 0.05 | 2.91 |
| **October 2008** | 0.29 | 0.84 | 0.05 | 0.04 | 2.59 | 0.06 | 2.67 |
| **Average** | 0.29 | 0.50 | 0.05 | 0.04 | 2.42 | 0.05 | 2.95 |

**Table 3.** Heavy metals content in water samples collected from Miedwie Lake (April to October 2010).

| Heavy Metals (ppm) | Cd | Cr | Cu | Hg | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|
| **April 2008** | 0.41 | 0.53 | 0.04 | 0.05 | 2.41 | 0.03 | 3.12 |
| **May 2008** | 0.37 | 0.31 | 0.06 | 0.04 | 2.24 | 0.05 | 2,74 |
| **June 2008** | 0.39 | 0.17 | 0.04 | 0.04 | 2.35 | 0.04 | 3.43 |
| **July 2008** | 0.35 | 0.42 | 0.06 | 0.03 | 2.39 | 0.05 | 3.15 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **August 2008** | 0.37 | 0.35 | 0.05 | 0.04 | 2,15 | 0.04 | 3.22 |
| **September 2008** | 0.35 | 0.13 | 0.07 | 0.04 | 2.57 | 0.06 | 3.34 |
| **October 2008** | 0.36 | 0.42 | 0.04 | 0.06 | 2.32 | 0.05 | 3.47 |
| **Average** | 0.37 | 0.33 | 0.05 | 0.04 | 2.35 | 0.04 | 3.21 |

**Table 4.** Heavy metals content in water samples collected from Miedwie Lake (April to October 2011)

| Heavy Metals (ppm) | Cd | Cr | Cu | Hg | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|
| **April 2008** | 0.29 | 0.64 | 0.07 | 0.05 | 2.47 | 0.03 | 2.36 |
| **May 2008** | 0.27 | 0.36 | 0.04 | 0.06 | 1.79 | 0.06 | 2,51 |
| **June 2008** | 0.39 | 0.59 | 0.06 | 0.05 | 1.85 | 0.06 | 3.17 |
| **July 2008** | 0.37 | 0.34 | 0.05 | 0.05 | 2.42 | 0.03 | 3.35 |
| **August 2008** | 0.33 | 0.76 | 0.05 | 0.07 | 2,61 | 0.05 | 2.83 |
| **September 2008** | 0.34 | 0.52 | 0.07 | 0.04 | 2.76 | 0.07 | 2.47 |
| **October 2008** | 0.36 | 0.67 | 0.05 | 0.04 | 2.52 | 0.06 | 2.91 |
| **Average** | 0.33 | 0.55 | 0.05 | 0.05 | 2.34 | 0.05 | 2.80 |

**Table 5.** Heavy metals content in water samples collected from Miedwie Lake (April to October 2012)

| Heavy Metals (ppm) | Cd | Cr | Cu | Hg | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|
| **April 2008** | 0.31 | 0.85 | 0.04 | 0.05 | 2.51 | 0.07 | 3.19 |
| **May 2008** | 0.25 | 0.43 | 0.06 | 0.07 | 2.75 | 0.03 | 3,68 |
| **June 2008** | 0.29 | 0.56 | 0.08 | 0.04 | 2.49 | 0.05 | 3.45 |
| **July 2008** | 0.33 | 0.63 | 0.05 | 0.06 | 2.86 | 0.03 | 3.36 |
| **August 2008** | 0.34 | 0.89 | 0.06 | 0.04 | 2,79 | 0.06 | 3.73 |
| **September 2008** | 0.27 | 0.75 | 0.08 | 0.07 | 2.24 | 0.04 | 3.61 |
| **October 2008** | 0.34 | 0.48 | 0.03 | 0.04 | 2.52 | 0.08 | 3.57 |
| **Average** | 0.30 | 0.65 | 0.06 | 0.05 | 2.59 | 0.05 | 3.51 |

In the present investigation, in water in the Miedwie Lake, it was observed that the maximum concentration of Cd was 0.41 ppm and the minimum was 0.19 ppm, while the annual average concentration was calculated as 0.45 ppm in 2008 of the year, 0.29 ppm in 2009 of the year, 0.37 ppm in 2010 of the year, 0.33 ppm in 2011 of the year and 0.30 ppm in 2012 of the year.

The values obtained were found to be below the permissible limit of 2.0 ppm set for inland surface water. There are a few recorded instances of Cadmium poisoning in human beings following consumption of contaminated fishes. Cadmium is less toxic to plants than Cu, similar in toxicity to Pb and Cr. It is equally toxic to invertebrates and fishes. In aquatic systems, cadmium is most readily absorbed by organisms directly from the water in its free ionic form Cd(II).

The acute toxicity of cadmium to aquatic organisms is variable, even between closely related species, and is related to the free ionic concentration of the metal. Cadmium interacts with the calcium metabolism of animals. In fish it causes lack of calcium (hypocalcaemia), probably by inhibiting calcium uptake from the water. In the present investigation in water in the Miedwie Lake, it was observed that the maximum concentration of Cr was 0.89 ppm and the minimum was 0.19 ppm, while the annual average concentration was calculated as 0.78

ppm in 2008 of the year, 0.50 ppm in 2009 of the year, 0.33 ppm in 2010 of the year, 0.55 ppm in 2011 of the year, and 0.65 ppm in 2012 of the year.

That was very much above the permissible limit of 0.1 ppm set for inland surface water. For invertebrates and fishes, its toxicity is not much acute. Chromium is generally more toxic at higher temperatures, and its compounds are known to cause cancer in humans. The toxic effect of Chromium on plants indicates that the roots remain small and the leaves narrow, exhibiting reddish brown discoloration with small necrotic blotches. Symptoms of Chromium phytotoxicity includes inhibition of seed germination or of early seedling development, reduction of root growth, leaf chlorosis, and depressed biomass.

From the results it appears that the Cu content in water in the Miedwie Lake was minimum of 0.04 ppm and maximum of 0.08 ppm. The observed annual average concentration of Copper in the water was 0.06 ppm in 2008 of the year, 0.05 ppm in 2009 of the year, 0.05 ppm in 2010 of the year, 0.05 ppm in 2011 of the year and 0.06 ppm in 2012 of the year. That was below the permissible limit of 3.0 ppm set for inland surface water. It is important here to note that Copper is highly toxic to most fishes, invertebrates and aquatic plants, more than any other heavy metal, except mercury. It reduces growth and rate of reproduction in plants and animals. The chronic level of Cu is 0.02–0.2 ppm.

Aquatic plants absorb three times more Copper than plants on dry lands. Excessive Copper content can cause damage to roots, by attacking the cell membrane and destroying the normal membrane structure, inhibit root growth and formation of numerous short, brownish secondary roots. Copper is highly toxic in aquatic environments and has effects in fish, invertebrates, and amphibians, with all three groups equally sensitive to chronic toxicity. Copper also causes reduced sperm and egg production in many species of fish.

In the present investigation in water in the Miedwie Lake, it was observed that the maximum concentration of Hg was 0.07 ppm and the minimum was 0.02 ppm, while the annual average concentration was calculated as 0.04 ppm in 2008 of the year, 0.04 ppm in 2009 of the year, 0.04 ppm in 2010 of the year, 0.05 ppm in 2011 of the year and 0.05 ppm in 2012 of the year. That was very much above the maximum limit of 0.01 ppm set for inland surface water. Mercury is generated naturally in the environment from the degassing of the earth's crust from volcanic emissions.

The organic form is readily absorbed in the gastrointestinal tract (90-100%), lesser but still significant amounts of inorganic mercury are absorbed in the gastrointestinal tract (7-15%). Previous study had reported that Mercury in dissolved form enter the fish through the gills. Further studies have indicated that inorganic Mercury gets adsorbed to the suspended particulate matter and settles down. Further it gets methylated and ultimately enter the food chain, resulting in bioaccumulation.

The monthly concentration of Ni in the water in Miedwie Lake samples was found to be in the range of 1.78 ppm – 2.86 ppm. The annual average concentration of Nickel in the water samples was observed to be 2.19 ppm in 2008 of the year, 2.42 ppm in 2009 of the year, 2.35 ppm in 2010 of the year, 2.34 ppm in 2011 of the year and 2.59 ppm in 2012 of the year.

That is close to the limit of 3.0 ppm set for inland surface water. Short-term exposure to Nickel on human being is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart, liver damage, and skin irritation.

In the present investigation in water in the Miedwie Lake, it was observed that the maximum concentration of Pb was 0.07 ppm and the minimum was 0.03 ppm. The annual average concentration of Pb in the water samples was observed to be 0.06 ppm in 2008 of the year, 0.05 ppm in 2009 of the year, 0.04 ppm in 2010 of the year, 0.05 ppm in 2011 of the year and 0.05 ppm in 2012 of the year. That is above the permissible limit of 0.1 ppm set for inland surface water. Acute toxicity generally appears in aquatic plants at concentration of 0.1–5.0 ppm. In plants, it initially results in enhanced growth, but from a concentration of 5 ppm onwards this is counteracted by severe growth retardation, discoloration, and morphological abnormalities. There is an adverse influence on photosynthesis, respiration and other metabolic processes. Acute toxicity of Lead in invertebrates is reported at concentration of 0.1–10 ppm. Higher levels pose eventual threat to fisheries resources. A number of studies have investigated effects of prolonged Lead exposure on freshwater fish. These studies report a wide range of effects induced by chronic exposure to elevated Lead concentrations, oocyte growth, including effects on pituitary function, gonadosomatic index.

In the present study in water in the Miedwie Lake, the monthly concentration of Zinc was in the range from 2.37 ppm to 3.75 ppm. The results of the present investigation indicate that the annual average concentration of Zn in water samples was 3.25 ppm in 2008 of the year, 2.95 ppm in 2009 of the year, 3.21 ppm in 2010 of the year, 2.90 ppm in 2011 of the year and 3.51 ppm in 2012 of the year.

That is above the permissible limit of 5.0 ppm set for inland surface water. Zn may result in ne crosis, chlorosis, and inhibited growth of plants. Previous studies have reported toxic effect of Zinc on some aquatic organisms such as fish. Although there is a low toxicity effect of Zn in man, however, the prolonged consumption of large doses has been reported to show some health complications such as fatigue, dizziness, and neutropenia.

## 4. CONCLUSIONS

The pollution of the aquatic environment with heavy metals has become a worldwide problem during recent years, because they are indestructible and most of them have toxic effects on organisms. Heavy metals in water refer to the heavy, dense, metallic elements that occur in trace levels, but are very toxic and tend to accumulate, hence are commonly referred to as trace metals. The major anthropogenic sources of heavy metals are industrial wastes from mining sites, manufacturing and metal finishing plants, domestic waste water and run off from roads. In the present investigation in water in the Miedwie Lake, it was observed that:

- maximum concentration of Cd was 0.41 ppm and the minimum was 0.19 ppm (the values obtained were found to be below the permissible limit of 2.0 ppm set for inland surface water), maximum concentration of Cr was 0.89 ppm and the minimum was 0.19 ppm (which was very much above the permissible limit of 0.1 ppm set for inland surface water),
- minimum concentration of Cu was 0.04 ppm and maximum of 0.08 ppm (which was below the permissible limit of 3.0 ppm set for inland surface water),
- maximum concentration of Hg was 0.07 ppm and the minimum was 0.02 ppm (which was very much above the maximum limit of 0.01 ppm set for inland surface water),
- minimum concentration of Ni was 1.78 ppm and maximum of 2.86 ppm (which is close to the limit of 3.0 ppm set for inland surface water),
- maximum concentration of Pb was 0.07 ppm and the minimum was 0.03 ppm (which is above the permissible limit of 0.1 ppm set for inland surface water),

- minimum concentration of Zn was 2.37 ppm and maximum 3.75 ppm (which is above the permissible limit of 5.0 ppm set for inland surface water).

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