

# Determination of metals in sea water of the Baltic Sea in Międzyzdroje

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## ABSTRACT

The present research work deals with the quantification of toxic heavy metals in the water samples collected from sea water in Międzyzdroje. While the annual average concentration of Cadmium was calculated as 0.44 ppm in 2008 of the year and 0.46 ppm in 2009 of the year. The values obtained were found to be below the permissible limit of 2.0 ppm set for inland surface water. While the annual average concentration of Chromium was calculated as 2.67 ppm in 2008 of the year and 2.64 ppm in 2009 of the year. Which was very much above the permissible limit of 0.1 ppm set for inland surface water. The observed annual average concentration of Copper in the water was 0.08 ppm in 2008 of the year and 0.05 ppm in 2009 of the year, which was below the permissible limit of 3.0 ppm set for inland surface water. While the annual average concentration of Mercury was calculated as 0.05 ppm in 2008 of the year and 0.05 ppm in 2009 of the year, which was very much above the maximum limit of 0.01 ppm set for inland surface water. The annual average concentration of Nickel in the water samples was observed to be 2.47 ppm in 2008 of the year and 2.70 ppm in 2009 of the year, which is close to the limit of 3.0 ppm set for inland surface water. The annual average concentration of Lead in the water samples was observed to be 0.06 ppm in 2008 of the year and 0.05 ppm in 2009 of the year, which is above the permissible limit of 0.1 ppm set for inland surface water. The results of the present investigation indicate that the annual average concentration of Zinc in water samples was 3.45 ppm in 2008 of the year and 3.73 ppm in 2009 of the year, which is above the permissible limit of 5.0 ppm set for inland surface water.

**Keywords:** Toxic Heavy Metals; sea water; Baltic Sea

## 1. INTRODUCTION

Urbanization is the cause of many changes which are taking place in the environment, including those found in the catchment. With this in mind, it is an important issue to properly protect water reservoirs and also take action to counter the adverse effects of human activities on the natural environment, including water bodies [1-5,16-21,62-70].

To address the increasing degradation of surface waters in the European Union, the approach to the evaluation and protection of water resources was changed [1-5,16-21,62-70]. This approach was formulated in the European Union Water Framework Directive

(2000/60/EC), which calls for the protection of water, as well as an environment-friendly and comprehensive approach to water assessment [1-5,16-21,62-70]. The ecological status of surface waters and groundwater is assessed on the basis of the ecological potential of the biological and physico-chemical and hydromorphological indicators [1-5,16-21,62-70].

Heavy metal pollution is an ever increasing problem of our lakes [1-8,52-61]. These toxic heavy metals entering in 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 [9-17,22-35,52-57,61]. The increase in residue levels of heavy metal content in water, sediments and biota has resulted in decreased productivity and increase in exposure of humans to harmful substances [61].

## 2. EXPERIMENTAL

The Baltic Sea is a mediterranean sea located between Central and Northern Europe, from 53°N to 66°N latitude and from 10°E to 30°E longitude. It is bounded by the Scandinavian Peninsula, the mainland of Europe, and the Danish islands [73-77]. It drains into the Kattegat by way of the Øresund, the Great Belt and the Little Belt. The Kattegat continues through Skagerrak into the North Sea and the Atlantic Ocean [73-75]. The Baltic Sea is connected by artificial waterways to the White Sea via the White Sea Canal, and to the North Sea via the Kiel Canal. The Baltic Sea might be considered to be bordered on its northern edge by the Gulf of Bothnia, on its northeastern edge by the Gulf of Finland, and on its eastern edge by the Gulf of Riga. These various gulfs can also be considered part of the Baltic Sea [73-77].



Fig. 1. Map of the Baltic Sea.

Międzyzdroje (German: *Misdroy*) is a town and a seaside resort in northwestern Poland on the island of Wolin on the Baltic coast. Previously in the Szczecin Voivodeship (1975-1998), Międzyzdroje has been in Kamień Pomorski County in the West Pomeranian Voivodeship since 1999. Międzyzdroje has a population of 6000 [78-79].

The samples were concentrated to tenfold on a water bath and subjected to nitric acid digestion [14,42]. 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) are added [48,61]. The solution in separating funnel was shaken vigorously for 2 min and was 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 [13,61]. 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 the sea water of the Baltic Sea in Międzyzdroje from the month of April to October 2008 - 2009 is presented in Table 1 and 2.

**Table 1.** Heavy metals content in water samples collected from of the Baltic Sea in Międzyzdroje (April to October 2008).

Heavy Metals (ppm)	Cd	Cr	Cu	Hg	Ni	Pb	Zn
<b>Apr. 2008</b>	0.42	2.81	0.09	0.04	2.46	0.06	3.53
<b>May 2008</b>	0.48	2.29	0.08	0.04	2.37	0.05	3.55
<b>June 2008</b>	0.46	2.63	0.08	0.05	2.51	0.05	3.41
<b>July 2008</b>	0.44	2.68	0.09	0.05	2.43	0.03	3.46
<b>Aug. 2008</b>	0.52	2.82	0.08	0.04	2.39	0.04	3.34
<b>Sept. 2008</b>	0.39	2.75	0.07	0.04	2.56	0.04	3.56
<b>Oct. 2008</b>	0.41	2.72	0.09	0.05	2.61	0.06	3.31
<b>Average</b>	0.44	2.67	0.08	0.05	2.47	0.06	3.45

**Table 2.** Heavy metals content in water samples collected from of the Baltic Sea in Międzyzdroje (April to October 2009).

Heavy Metals (ppm)	Cd	Cr	Cu	Hg	Ni	Pb	Zn
<b>Apr. 2008</b>	0.43	2.73	0.06	0.05	2.87	0.05	3.79
<b>May 2008</b>	0.47	2.81	0.07	0.04	2.78	0.05	3.64
<b>June 2008</b>	0.45	2.54	0.08	0.06	2.81	0.06	3.83
<b>July 2008</b>	0.44	2.59	0.09	0.05	2.49	0.07	3.73
<b>Aug. 2008</b>	0.46	2.54	0.07	0.06	2.65	0.07	3.77
<b>Sept. 2008</b>	0.46	2.59	0.06	0.03	2.73	0.05	3.89
<b>Oct. 2008</b>	0.45	2.71	0.08	0.04	2.59	0.06	3.47
<b>Average</b>	0.46	2.64	0.08	0.05	2.70	0.06	3.73

In the present investigation, it was observed that the maximum concentration of Cd was 0.45 ppm and the minimum was 0.19 ppm (Table 1 and 2). While the annual average concentration was calculated as 0.45 ppm in 2008 of the year and 0.29 ppm in 2009 of the year. The values obtained were found to be below the permissible limit of 2.0 ppm set for inland surface water [61]. There are a few recorded instances Cadmium poisoning in human beings following consumption of contaminated fishes [61]. Cadmium it is less toxic to plants than Cu, similar in toxicity to Pb and Cr [61]. It is equally toxic to invertebrates and fishes [40,61]. In aquatic systems, cadmium is most readily absorbed by organisms directly from the water in its free ionic form Cd(II) [5,61].

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 [5,61]. Cadmium interacts with the calcium metabolism of animals [5,61]. In fish it causes lack of calcium (hypocalcaemia), probably by inhibiting calcium uptake from the water [5,61]. Effects of long-term exposure can include larval mortality and temporary reduction in growth [5,61].

In the present investigation, it was observed that the maximum concentration of Cr was 2.98 ppm and the minimum was 2.19 ppm (Table 1 and 2). While the annual average concentration was calculated as 2,78 ppm in 2008 of the year and 2.50 ppm in 2009 of the year. Which was very much above the permissible limit of 0.1 ppm set for inland surface water [61]. For invertebrates and fishes, its toxicity is not much acute [61]. Chromium is generally more toxic at higher temperatures and its compounds are known to cause cancer in humans [49,61]. The toxic effect of Chromium on plants indicate that the roots remain small and the leaves narrow, exhibit reddish brown discoloration with small necrotic blotches [30]. Symptoms of Chromium phytotoxicity include inhibition of seed germination or of early seedling development, reduction of root growth, leaf chlorosis and depressed biomass [50,61].

From the results it appears that the Cu content in the lake water was minimum of 0.04 ppm and maximum of 0.08 ppm (Table 1 and 2). The observed annual average concentration of Copper in the water was 0.06 ppm in 2008 of the year and 0.05 ppm in 2009 of the year, which was below the permissible limit of 3.0 ppm set for inland surface water [61]. It is important here to note that Copper is highly toxic to most fishes, invertebrates and aquatic plants than any other heavy metal except mercury [61]. It reduces growth and rate of reproduction in plants and animals [61]. The chronic level of Cu is 0.02-0.2 ppm [61,67]. Aquatic plants absorb three times more Copper than plants on dry lands [61]. Excessive Copper content can cause damage to roots, by attacking the cell membrane and destroying the normal membrane structure, inhibited root growth and formation of numerous short, brownish secondary roots [61,67]. Copper is highly toxic in aquatic environments and has effects in fish, invertebrates, and amphibians, with all three groups equally sensitive to chronic toxicity [29,61]. Copper also causes reduced sperm and egg production in many species of fish [53-56,61,66].

In the present investigation, it was observed that the maximum concentration of Hg was 0.06 ppm and the minimum was 0.03 ppm (Table 1 and 2). While the annual average concentration was calculated as 0.04 ppm in 2008 of the year and 0.04 ppm in 2009 of the year, which was very much above the maximum limit of 0.01 ppm set for inland surface water [61]. Mercury is generated naturally in the environment from the degassing of the earth's crust from volcanic emissions [61].

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 %) [61]. Previous study have reported that Mercury in dissolved form enter the fish through the gills [15,61]. Further studies have indicated that inorganic Mercury get adsorbed to the suspended particulate matter and settles down [33,61]. Further gets methylated and ultimately enter the food chain, resulting in bioaccumulation [61].

The monthly concentration of Ni in the lake water samples was found to be in the range of 1.78 ppm – 2.81 ppm (Table 1 and 2). The annual average concentration of Nickel in the water samples was observed to be 2.19 ppm in 2008 of the year and 2.42 ppm in 2009 of the year, which is close to the limit of 3.0 ppm set for inland surface water [61]. 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 [61,67].

In the present investigation, it was observed that the maximum concentration of Pb was 0.07 ppm and the minimum was 0.04 ppm (Table 1 and 2). The annual average concentration of Pb in the water samples was observed to be 0.06 ppm in 2008 of the year and 0.05 ppm in 2009 of the year, which is above the permissible limit of 0.1 ppm set for inland surface water [61]. Acute toxicity generally appears in aquatic plants at concentration of 0.1-5.0 ppm [61,67]. 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 [61]. There is an adverse influence on photosynthesis, respiration and other metabolic processes [61]. Acute toxicity of Lead in invertebrates is reported at concentration of 0.1-10 ppm [61,67]. Higher levels pose eventual threat to fisheries resources [61]. A number of studies have investigated effects of prolonged Lead exposure on freshwater fish [61]. 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 [47,61].

In the present study, the monthly concentration of Zinc was in the range of 2.54 ppm to 3.75 ppm (Table 1 and 2). 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 and 2.95 ppm in 2009 of the year, which is above the permissible limit of 5.0 ppm set for inland surface water [61]. Zn may result in ne crosis, chlorosis and inhibited growth of plants [61,67]. Previous studies have reported toxic effect of Zinc on some aquatic organisms such as fish [3,61]. Although there is 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 [28,61].

#### **4. CONCLUSION**

1. While the annual average concentration of Cadmium was calculated as 0.44 ppm in 2008 of the year and 0.46 ppm in 2009 of the year.
2. While the annual average concentration of Chromium was calculated as 2.67 ppm in 2008 of the year and 2.64 ppm in 2009 of the year.
3. The observed annual average concentration of Copper in the water was 0.08 ppm in 2008 of the year and 0.05 ppm in 2009 of the year.
4. While the annual average concentration of Mercury was calculated as 0.05 ppm in 2008 of the year and 0.05 ppm in 2009 of the year.
5. The annual average concentration of Nickel in the water samples was observed to be 2.47 ppm in 2008 of the year and 2.70 ppm in 2009 of the year.
6. The annual average concentration of Lead in the water samples was observed to be 0.06 ppm in 2008 of the year and 0.05 ppm in 2009 of the year.
7. The results of the present investigation indicate that the annual average concentration of Zinc in water samples was 3.45 ppm in 2008 of the year and 3.73 ppm in 2009 of the year.

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