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Studies of Heavy Metal Pollution in Water River Odra Estuary (North-West Poland)

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The present research work deals with the quantification of toxic heavy metals in water samples collected from the lakes of river Odra estuary (North-West Poland). In present investigation, it was observed that the concentration range of cadmium was 0.41-0.59 ppm, chromium ranged 0.57-0.97 ppm, copper ranged 0.04-0.09 ppm, mercury ranged 0.03-0.09 ppm, nickel ranged 2.38-2.98 ppm, lead ranged 0.05-0.09 ppm and zinc ranged 2.65-3.96 ppm.

Keywords: Toxic heavy metals, Lake water, River Odra Estuary (North-West Poland).

INTRODUCTION

Urbanization is the cause of many changes which are taking place in the environment, including those found in the catchment[1-8]. 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[2,5,9-15].

Heavy metal pollution is an ever increasing problem of our lakes[1-4,9,16-20]. 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[5,6,10-12,17,20-28]. 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[15,16,28].

Many of these metals tend to remain in the ecosystem and eventually move from one compartment to the other within the food chain[13,14,16-20,29-35]. 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[13,14,18-20].

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[17-20,29-36]. 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[5-8,10-12,14-36]. 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[5-8,10-12,14-36].

Hence in the present investigation, efforts are made to quantify the accumulation of toxic heavy metals in water in the lakes of the river Odra Estuary (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 water river Odra Estuary.

EXPERIMENTAL

The Odra Estuary includes, as its major part, the brackish Szczecin Lagoon which consists of two parts: the Kleines Haff (located in Germany) and the Wielki Zalew located in Poland (Fig. 1). The Lagoon receives the river Odra water supplied from the south; prior to being discharged into the Lagoon, part of the Odra flow passes through Lake Dabie[58-60]. In its northern part, the Lagoon connects-*via* three straits (the Peene, Swina and Dziwna) with the Pomeranian Bay, a Baltic embayment[37,38].

The Odra (German: Oder) Estuary is located at the southern Baltic Sea (German-Polish border). It consists of the Szczecin (Oder-) Lagoon and the Pomeranian Bay. The Szczecin Lagoon (687 km^2) can be subdivided into the "Large Lagoon" (Polish: Wielki Zalew) on the Polish territory and the "Small Lagoon" (German: Kleines Haff) on the German side. The Lagoon is connected to the Pomeranian Bay *via* 3 outlets[37,38].

The entire estuary is dominated by the discharge of the river Odra (Oder) into the Lagoon. With its length of 854 km and basin area of 120,000 km², the Odra is one of the most

important rivers in the Baltic region. The average annual Odra discharge is 17 km^3 (530 m^3 s 1) and it contributes at least 94 % to the lagoon's water budget[37,38] (Fig. 1).

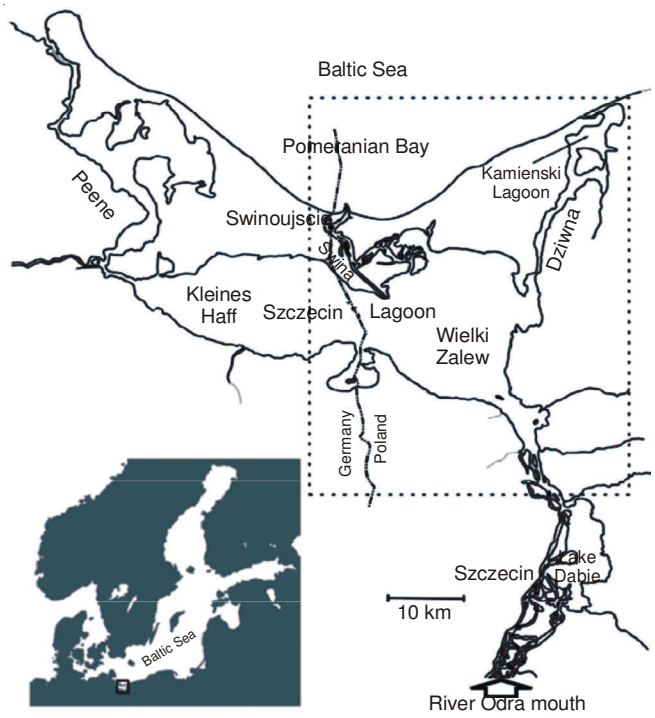

Fig. 1. River Odra Estuary and sampling figure sites location

Research was carried out in the years 2008-2012 (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[20].

The samples were concentrated to tenfold on a water bath and subjected to nitric acid digestion[33]. 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[20,39]. 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[13,14,20]. 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, chromium, copper, mercury, nickel, lead and zinc was done by atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

The experimental data on toxic heavy metals in water samples collected along the in lakes of the river Odra Estuary from the month of 2008-2012 (april to october) is presented in Table-1.

TABLE-1
HEAVY METALS CONTENT IN WATER SAMPLES COLLECTED FROM RIVER ODRA ESTUARY

Heavy Metals (ppm)	Cd	Cr	Cu	Hg	Ni	Pb	Zn
2008							
Apr.	0.49	0.77	0.05	0.06	2.49	0.07	3.76
May	0.56	0.72	0.06	0.05	2.58	0.08	3.51
June	0.48	0.79	0.04	0.05	2.67	0.09	3.77
July	0.54	0.84	0.07	0.04	2.81	0.07	3.62
Aug.	0.45	0.83	0.07	0.05	2.43	0.09	3.84
Sept.	0.41	0.79	0.06	0.04	2.39	0.08	3.81
Oct.	0.53	0.86	0.08	0.04	2.61	0.09	3.94
Average	0.42	0.80	0.06	0.05	2.57	0.08	3.75
2009							
Apr.	0.49	0.76	0.07	0.06	2.76	0.06	3.47
May	0.57	0.68	0.08	0.07	2.98	0.07	3.75
June	0.45	0.73	0.06	0.03	2.59	0.07	3.59
July	0.48	0.68	0.09	0.07	2.77	0.06	3.81
Aug.	0.47	0.79	0.07	0.06	2.68	0.08	3.46
Sept.	0.52	0.67	0.09	0.05	2.85	0.05	3.87
Oct.	0.49	0.79	0.08	0.05	2.67	0.08	3.59
Average	0.49	0.73	0.07	0.05	2.75	0.07	3.65
2010							
Apr.	0.59	0.75	0.07	0.06	2.67	0.07	3.51
May	0.46	0.57	0.05	0.03	2.74	0.06	3.24
June	0.57	0.74	0.08	0.07	2.88	0.08	3.71
July	0.51	0.67	0.06	0.05	2.75	0.06	2.65
Aug.	0.45	0.79	0.08	0.08	2.56	0.07	3.49
Sept.	0.46	0.86	0.07	0.05	2.83	0.05	3.75
Oct.	0.49	0.69	0.09	0.05	2.68	0.07	3.69
Average	0.50	0.72	0.07	0.05	2.73	0.06	3.43
2011							
Apr.	0.43	0.86	0.07	0.08	2.91	0.07	3.57
May	0.49	0.74	0.05	0.06	2.76	0.08	3.94
June	0.56	0.88	0.07	0.05	2.84	0.05	3.68
July	0.42	0.71	0.06	0.07	2.38	0.06	3.96
Aug.	0.46	0.85	0.06	0.09	2.85	0.08	3.79
Sept.	0.57	0.79	0.04	0.07	2.47	0.07	3.91
Oct.	0.49	0.81	0.08	0.08	2.63	0.09	3.64
Average	0.49	0.80	0.06	0.07	2.69	0.07	3.78
2012							
Apr.	0.46	0.72	0.08	0.06	2.66	0.06	3.47
May	0.41	0.95	0.06	0.05	2.83	0.07	3.74
June	0.45	0.82	0.07	0.07	2.47	0.08	3.41
July	0.58	0.67	0.05	0.05	2.65	0.05	3.76
Aug.	0.53	0.75	0.07	0.08	2.37	0.09	3.34
Sept.	0.49	0.97	0.06	0.06	2.64	0.07	3.69
Oct.	0.56	0.74	0.05	0.07	2.78	0.05	3.56
Average	0.49	0.80	0.07	0.06	2.63	0.07	3.57

In the present investigation in water in the river Odra Estuary, it was observed that the maximum concentration of copper was 0.59 ppm and the minimum was 0.41 ppm. While the annual average concentration was calculated as 0.42 ppm in 2008 of the year, 0.49 ppm in 2009 of the year, 0.50 ppm in 2010 of the year, 0.49 ppm in 2011 of the year and 0.49 ppm in 2012 of the year.

The values obtained were found to be below the permissible limit of 2 ppm set for inland surface water[20]. There are a few recorded instances cadmium poisoning in human beings following consumption of contaminated fishes[13,14,20]. Cadmium it is less toxic to plants than Cu, similar in toxicity to Pb and

Cr[13,14,20]. It is equally toxic to invertebrates and fishes[16,17]. In aquatic systems, cadmium is most readily absorbed by organisms directly from the water in its free ionic form Cd (II)[2,13,14,20].

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[10,13,14,20]. Cadmium interacts with the calcium metabolism of animals[10,13,14,20]. In fish it causes lack of calcium (hypocalcaemia), probably by inhibiting calcium uptake from the water[10,13,14,20].

In the present investigation in water in the river Odra Estuary, it was observed that the maximum concentration of Cr was 0.97 ppm and the minimum was 0.57 ppm. While the annual average concentration was calculated as 0,80 ppm in 2008 of the year, 0.73 ppm in 2009 of the year, 0.72 ppm in 2010 of the year, 0.80 ppm in 2011 of the year and 0.80 ppm in 2012 of the year.

Which was very much above the permissible limit of 0.1 ppm set for inland surface water[20]. For invertebrates and fishes, its toxicity is not much acute[20]. Chromium is generally more toxic at higher temperatures and its compounds are known to cause cancer in humans[13,14,20]. 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[8]. Symptoms of chromium phytotoxicity include inhibition of seed germination or of early seedling development, reduction of root growth, leaf chlorosis and depressed biomass[13,14,20].

From the results it appears that the Cu content in water in the river Odra Estuary was minimum of 0.04 ppm and maximum of 0.09 ppm. The observed annual average concentration of copper in the water was 0.06 ppm in 2008 of the year, 0.07 ppm in 2009 of the year, 0.07 ppm in 2010 of the year, 0.06 ppm in 2011 of the year and 0.07 ppm in 2012 of the year.

Which was below the permissible limit of 3 ppm set for inland surface water[20]. 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[20]. It reduces growth and rate of reproduction in plants and animals[20]. The chronic level of Cu is 0.02-0.2 ppm[20,40]. Aquatic plants absorb three times more Copper than plants on dry lands[20]. 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[20,40]. Copper is highly toxic in aquatic environments and has effects in fish, invertebrates and amphibians, with all three groups equally sensitive to chronic toxicity[13,14,20,25]. Copper also causes reduced sperm and egg production in many species of fish[13,14,17,20,41].

In the present investigation of water of the river Odra Estuary, it was observed that the maximum concentration of Hg was 0.09 ppm and the minimum was 0.03 ppm. While the annual average concentration was calculated as 0.05 ppm in 2008 of the year, 0.05 ppm in 2009 of the year, 0.05 ppm in 2010 of the year, 0.07 ppm in 2011 of the year and 0.06 ppm in 2012 of the year.

Which was very much above the maximum limit of 0.01 ppm set for inland surface water[20]. Mercury is generated naturally in the environment from the degassing of the earth's crust from volcanic emissions[20].

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 %)[20]. Previous study have reported that mercury in dissolved form enter the fish through the gills[13,15,16,28]. Further studies have indicated that inorganic mercury get adsorbed to the suspended particulate matter and settles down[15,16,28,40]. Further gets methylated and ultimately enter the food chain, resulting in bioaccumulation[20].

The monthly concentration of Ni in the water of river Odra Estuary samples was found to be in the range of 2.38 ppm-2.98 ppm. The annual average concentration of nickel in the water samples was observed to be 2.57 ppm in 2008 of the year, 2.75 ppm in 2009 of the year, 2.73 ppm in 2010 of the year, 2.69 ppm in 2011 of the year and 2.63 ppm in 2012 of the year.

Which is close to the limit of 3 ppm set for inland surface water[20]. 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[13,14,20,40].

In the present investigation in water in the river Odra Estuary, it was observed that the maximum concentration of Pb was 0.09 ppm and the minimum was 0.05 ppm. The annual average concentration of Pb in the water samples was observed to be 0.08 ppm in 2008 of the year, 0.07 ppm in 2009 of the year, 0.06 ppm in 2010 of the year, 0.07 ppm in 2011 of the year and 0.07 ppm in 2012 of the year.

Which is above the permissible limit of 0.1 ppm set for inland surface water[20]. Acute toxicity generally appears in aquatic plants at concentration of 0.1-5.0 ppm[20,40]. 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[20]. There is an adverse influence on photosynthesis, respiration and other metabolic processes[20]. Acute toxicity of lead in invertebrates is reported at concentration of 0.1-10 ppm[15,16,28,63]. Higher levels pose eventual threat to fisheries resources[20]. A number of studies have investigated effects of prolonged Lead exposure on freshwater fish[28]. 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[13,14,20,35].

In the present study in water in the River Odra Estuary, the monthly concentration of zinc was in the range of 2.65 ppm to 3.96 ppm. The results of the present investigation indicate that the annual average concentration of Zn in water samples was 3.75 ppm in 2008 of the year, 3.65 ppm in 2009 of the year, 3.43 ppm in 2010 of the year, 3.78 ppm in 2011 of the year and 3.57 ppm in 2012 of the year.

Which is above the permissible limit of 5 ppm set for inland surface water[20]. Zinc may result in ne crosis, chlorosis and inhibited growth of plants[20]. Previous studies have reported toxic effect of zinc on some aquatic organisms such as fish[13,14,20]. 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[13,14,20,24].

Conclusions

In the present investigation, river water Odra Estuary, it was observed that:

• Maximum concentration of cadmium was 0.59 ppm and the minimum was 0.41 ppm (the values obtained were found to be below the permissible limit of 2. ppm set for inland surface water)

• Maximum concentration of chromium was 0.97 ppm and the minimum was 0.57 ppm (which was very much above the permissible limit of 0.1 ppm set for inland surface water)

• Minimum concentration of copper was 0.04 ppm and maximum of 0.09 ppm (which was below the permissible limit of 3 ppm set for inland surface water)

• Maximum concentration of mercury was 0.09 ppm and the minimum was 0.03 ppm (which was very much above the maximum limit of 0.01 ppm set for inland surface water)

• Minimum concentration of nickel was 2.38 ppm and maximum of 2.98 ppm (which is close to the limit of 3.0 ppm set for inland surface water)

• Maximum concentration of lead was 0.09 ppm and the minimum was 0.05 ppm (which is above the permissible limit of 0.1 ppm set for inland surface water)

• Minimum concentration of zinc was 2.65 ppm and maximum 3.96 ppm (which is above the permissible limit of 5 ppm set for inland surface water).

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