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Ecological Rating of Mercury Ions in Water Bodies

1. Introduction

Heavy metal compounds in industrial waste waters are one of the most harmful pollutants discharged to surface water. The ions of mercury, leads, copper and cadmium are toxic for human health and water biota. Furthermore the metal salts can inhibit the process of photosynthesis and biochemical oxidation of organic substances in water that brings to the violation of ecological equilibrium and degradation of water ecosystem.

Table 1. Concentrations of heavy metals in Baltic Sea and North Sea

Water area	Concentrations, μg/l			
	lead	copper	mercury	cadmium
Neva Bay	2.0–24.0	3.0–28.0	0.05–0.30	0.5–2.0
Baltic Sea	5.0–30.0	3.0–17.0	0.05–0.15	0.5–5.0
North Sea	1.0–3.0	1.0–2.0	0.02–0.10	0.03–0.1

In comparison to unpolluted waters almost all water basins in Europe are characterized by increased concentrations of heavy metals. The Baltic Sea is one of the most polluted sea, as compared to other marine ecosystems, e.g. North Sea or Atlantic Ocean (Tab. 1) [1].

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The most affected area of the Baltic Sea is the Gulf of Finland heavily polluted by waste water from the Neva river. The other area polluted by heavy metal is the Bay of Gdansk. According to Helsinki Commission, more than 50% of heavy metal loads to the Baltic Sea is discharged with river outflows (Tab. 2) [2].

Table 2. Heavy Metal Loads to the Baltic Sea

Metals	Heavy metal loads, kg per year
Mercury	11 580
Cadmium	16 410
Zinc	3 584 180
Copper	1 469 200
Lead	300 500

In the 60s mercury compounds brought to serious environmental problems and its content is still increasing. In 40% of the Swedish lakes pike have mercury contents exceeding 0.5 mg/kg w.w. (wet weight) which is the limit for human consumption recommended by United Nations Codex Alimentarius [2]. The level of organic mercury compounds in offshore areas of the Baltic Sea are normally low, but in predatory fish bodies in some local near-shore areas this level exceeds the permissible contents. Mercury content in fish of Neva Bay, the Gulf of Finland and eastern part of the Gulf of Finland several times exceeds this limit.

The increase of mercury concentration in the course of time in chosen parts of the Baltic Sea is presented in table 3 [3].

Table 3. Mercury concentration in fish body in different areas of the Baltic Sea

Period of time	Sea area	Mercury concentration in predatory fish body, mg/kg w.w.
1967–1974	Neva bay Eastern part of the Gulf of Finland Gulf of Finland	0.6 0.92 4.70
1989–1992	Neva Bay Eastern part of the Gulf of Finland	2.52 2.40

Sea food with high concentrations of heavy metals can be harmful to human health. Prenatal and children are most sensitive and high concentrations of mercury in their brains can bring to blindness, deafness and paralysis. Lower level of mercury can lead to visual field, retarded mental development and learning problems [2].

2. Results of the Researches

Heavy metals are accumulated not only in the body of water animals and fish but also in water bottom sediments and under some conditions it can be the source of secondary pollution of water.

All European countries established the permissible concentrations of mercury in water for different types of water usage (water supply, fishery, recreation). Frame Water Directive suggests the following permissible concentrations of mercury and its compounds: 0.05 μg/l in inland surface waters and other surface waters (for annual average values) [4]. The standards of United Nations Economic Commission for Europe are not so strict – 1,0 μg/l for the needs of water supply [5]. In Poland the permissible levels of mercury content in surface water depends on the type of water usage: 1.0 μg/l – for water supply; 0.5–1.0 μg/l – for general classification of surface waters and 5,0 μg/l – for recreation purposes [6–8].

The established water quality standards not always take into account the interest of water ecosystems and provide the ecological security for surface water. It was established that in the Gulf of Finland the violation of photosynthesis process begins at mercury concentration of 0.5 μg/l. This phenomenon can bring to the disturbance of the biotic balance, self-purification processes, deterioration of water quality [1].

Therefore in order to solve the ecological problems, some theoretical and applied tasks must be solved in the field of ecological ration and monitoring of surface water state. Such tasks are the following:

- elaboration of theoretical conception, which adequately reflects the concept of ecological equilibrium as the normative ecological status of water ecosystems, and the main functional characteristics of them;
- elaboration of numerical integral criteria describing the ecological status of water ecosystems;
- elaboration of ecological standards of surface water quality, i.e. the standards which provide the preservation of self-regulation capacity of different water ecosystems;
- elaboration of wide-available express methods of ecological monitoring of natural water systems.

Hence, in order to provide the ecological equilibrium of surface waters it is necessary to elaborate the ecological standards of water quality. The solution of this task requires the elaboration of quantitative criteria which indicate the ecological state of waters.

Ecological equilibrium of surface water can be estimated on the base of relationship between the rates of processes of production and destruction of organic matter which is the most fundamental functional characteristics of any ecosystem.

Integral criterion of ecological state of water ecosystem elaborated by the author reflects the state of biotic equilibrium in water. The elaboration of this criterion is based on the following theoretical thesis: the change of biotic balance (i.e. the balance of production-destruction processes) results in quantitative changes of oxygen content water pH value in water that is connected with carbonate equilibrium and CO_2 content.

On the base of the theoretical and empirical analysis it was established that in researched water bodies there is a linear correlation between oxygen saturation and the value of pH which can be described by the following equation (1)

$$pH = a_0 + a_1[O_{2\%}] \tag{1}$$

The obtained correlation allowed to calculate pH value under 100% oxygen saturation of water according to the equation:

$$pH_{100\%} = \sum_{i=1}^{n} \frac{pH_i}{i=1} + a_1\left(100 - \sum_{i=1}^{n} \frac{[O_{2\%}]}{n}\right) \tag{2}$$

where:

$pH_{100\%}$ – criterion of ecological state of water body,
pH_i – pH value in water body,
$[O_{2\%}]$ – oxygen saturation of water,
a_1 – empirical coefficient,
n – number of measurements of pH and $[O_{2\%}]$ values during investigation period.

On the base of theoretical and statistical analysis it was established that the value of the elaborated criterion $pH_{100\%}$ for waters of non-deteriorated ecological equilibrium is equal to 7.7 ± 0.3 [9].

Together with intensification of photosynthesis's processes the rate of productivity of surface waters increases and the value of this criterion also increases.

The researches conducted in the conditions of the Neva Bay showed that mercury ions even in concentrations lower than sanitary standards established for surface water in Russia (i.e. less than 0.5 μg/l) inhibited both the processes of photosynthesis and biochemical oxidation of organic matters that can brought to the disturbance of ecological equilibrium in this sea area. This was evidenced by close negative correlation between mercury ions, chlorophyll concentrations and the rate of organic matter oxidation in water:

$$Chl\ \text{“}a\text{”} = a_0 - a_1\ [Hg],\ r = 0.53 \tag{3}$$

$$k = a_0 - a_1\,[\mathrm{Hg}],\ r = 0.68 \tag{4}$$

where:

[Hg] – mercury ions concentration, μg/l,
k – constant of biochemical oxidation rate for organic matter in water,
Chl "a" – chlorophyll concentration in water,
a_0, a_1 – empirical coefficients,
r – Pearson coefficient.

It was also established very close negative correlation between the proposed criterion of ecological state of water and concentration of mercury ions (r = 0.96).

On the base of multifactor statistical analysis it is possible to formulate the mathematical regression model of investigated water ecosystem which takes into account the prior ecological factors. This model allows to determine ecologically permissible regional concentrations of mercury ions which provide the preservation of biotic balance in concrete water body and security for human health. Ecologically permissible concentrations, elaborated on the base of proposed methodology, allow to determine ecologically permissible loads of mercury to water body and estimate the level of wastewater purification in waste water treatment plants. The same approach can be applied for elaboration of regional ecologically permissible standards of other pollutions discharged to water bodies.

The regression model was elaborated for the conditions of the Neva Bay

$$\mathrm{pH}_{100\%} = a_0 + a_1 t + a_2 h + a_3 V + a_4[\mathrm{Hg}] \tag{5}$$

where:

$\mathrm{pH}_{100\%}$ – criterion of ecological state,
t – temperature of water,
h – depth of water body, m,
V – velocity of water flow, m/s,
[Hg] – mercury ions concentration, μg/l,
a_0, a_1, a_2, a_3, a_4 – empirical coefficients.

Ecologically permissible concentration calculated with the help of this statistical model for mercury ions amounted to 0.1 μg/l (Tab. 4) [1].

Data mentioned in table 4 show that regional ecologically permissible concentrations of pollutions can be different from established by different legislation documents: they can be more strict, less strict than generally established or equal to them.

Table 4. Ecologically permissible concentrations of mercury calculated on the base of the elaborated criterion of water ecological state for the Neva Bay

Ecologically permissible concentration, µg/l	State standards of water quality (Russia)	
	Water supply purposes	Fishery
0.1	0.5	0.1

Source: [1]

3. Summary

Ecologically permissible concentrations of pollutants are principally different from the standards elaborated for different types of water usage: water supply purposes, fishery and recreation. The ecological standards must be elaborated on local and regional level. Ecologically permissible concentrations of pollutions in water allow to preserve the homeostatic mechanisms of ecosystems' self--regulation. On the base of elaborated ecological standards the permissible loads of pollution can be estimated that do not exceed the ecological capacity of water ecosystem. Such approach enables the elaboration of ecologically and economically proved technical and organization measures aimed to the preservation of surface water good ecological state.

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