

## **WATER POLLUTION AND ITS IMPACT ON FISH AND AQUATIC INVERTEBRATES**

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### **Contents**

- 1. Heavy Metals
- 2. Organic Compounds
- Glossary
- Bibliography
- Biographical Sketch

### **Summary**

This chapter describes the influence of heavy metals on hydrobionts, presenting generalized information on heavy metal distribution in the atmosphere, atmospheric precipitation, bottom sediments of rivers and lakes of different regions of the world. Data on metal concentrations in water of a number of water bodies in Russia are compared, and some water quality criteria for heavy metals in different countries are discussed. Special attention is given to the danger of mercury. It is shown that the most globally widespread organic pollutants are oil and oil products, chlorinated organic hydrocarbons and polycyclic aromatic hydrocarbons. The highest levels of hydrocarbon content are typical for inland seas as well as for near-coastal, and shelf zones, and for seas where oil production and transportation are carried out. A general scheme is presented for development of biologic effects of oil pollution, including acute and chronic impact on hydrobionts. It is noted that chlorinated hydrocarbons, as well as oil products and heavy metals, have become toxicants of global abundance.

### **1. Heavy Metals**

Of the many different toxic compounds present in aquatic ecosystems, the heavy metals are considered by some to be the most hazardous. It is clear that the anthropogenic input of heavy metals is much higher than the natural input. For example, anthropogenic input is almost double the natural input of mercury, and for copper, lead, and zinc it is greater by an order of magnitude. This is typical for the global distribution of heavy metals in the hydrosphere. Thus, compared to other toxicants, they are of prime interest, particularly in view of their high toxicity in relation to aquatic organisms (hydrobionts). The environmental impact of metals is of particular concern because, unlike organic compounds, they cannot be subject to chemical degradation beyond the elemental state; they can only be redistributed between abiotic and biotic components and interact with their components.

Freshwater bodies always contain small quantities of heavy metals (e.g. zinc, copper,

mercury, cadmium, cobalt, chrome, iron, manganese, and arsenic). On average, metal concentrations are higher in river water than in sea water because in the sea the metals are adsorbed by colloids and organic substances. Tables 1 to 3 present generalized data on distribution of some heavy metals in the atmosphere, in atmospheric precipitation, and in water and bottom sediments of rivers and lakes in various regions in the world.

The natural sources of the metals entering the aquatic environment are rocks. Presently, the levels of metal ingress from the anthropogenic and natural sources are comparable.

Region	Pb	Cd	As	Hg (gaseous)
Europe (without USSR)	2 – 107	0.01 – 3.0	0.23 – 5.4	6.5 – 49
European part of Former USSR	2.9 – 17	0.1 – 0.9	0.19 – 3.4	4.9 – 26
Asia	1.2 – 43	0.06 – 0.92	0.2 – 8.8	5.1 – 34
North America	3.6 – 72	0.17 – 2.0	0.3 – 2.5	0.5 – 50
South America	1.9 – 11	0.02 – 1.1	0.9 – 1.6	-
Atlantic ocean (northern part)	0.05 – 64	0.003 – 0.6	0.12	0.4 – 3.5
Pacific ocean: (northern part)	0.17 – 1.9	-	0.02–0.14	1.5 – 2.0
Arctic	0.2 – 4.9	0.05 – 0.39	0.2 – 0.6	-
Antarctica	0.1 – 0.6	0.001–0.024	0.008	-

Table 1. Background concentrations of lead, arsenic, cadmium, and mercury in the atmosphere (ng/m<sup>3</sup>) in the various regions of the planet (Izrael *et al*, 1989)

Region	Pb	Cd	As	Hg
Europe (without USSR)	0.3 – 69	0.07 – 1.2	0.7 – 3.9	0.1 – 0.4
Asia	0.5 – 9.3	0.1 – 4.9	0.4 – 6.1	0.02 – 1.8
North America	0.6 – 39	0.15 – 1.0	0.03 – 4.0	0.01 – 2.2
Atlantic ocean: (northern part)	1.5 – 9.0	-	-	-
Pacific ocean: (northern part)	0.006–0.11	-	0.019–0.032	-
Arctic	0.013–0.62	0.0004 – 0.8	0.019–0.021	0.005 – 0.12
Antarctica	0.005–0.23	0.003 – 0.032	0.008–0.025	0.026– 0.033

Table 2. Background concentrations of lead, arsenic, cadmium, and mercury in atmospheric precipitation (µg/l) in the various regions of the planet (Izrael *et al*, 1989)

For example, on a global scale, the annual increment of lead to the World Ocean comprises a value of the order of  $6.7 \times 10^{-7}$  mg/l. This rate of growth does not present a serious threat to the global ocean ecosystem. The real threat comes from local sources of pollution. Comparison of the metal concentrations in a number of water bodies and the biologically efficient concentrations, shows that some metals are already present in natural water bodies in concentrations capable of causing adverse biological effect. This is particularly apparent in water bodies that receive wastes from big cities, industrial centers, pulp and paper mills, and metallurgical works. For example, mercury concentration in muscles of bream (*Abramis*) from the river Severnaya Dvina, i.e. in the

zone affected by wastes from the Arkhangelsk pulp and paper mill (PPM), exceed the allowable norm.

Region	Medium	Pb	Cd	As	Hg
Western Europe	water	0.07 – 9.0	0.05 – 2.0	0.02 – 3.6	0.01 – 6.5
	sediments	3 – 100	0.4 – 5.7	6 – 13	0.01 – 11
Eastern Europe (within the former USSR)	water	0.06 – 7.5	0.07 – 1.9	0.2 – 6.3	0.02 – 0.5
	sediments	2 – 110	0.04 – 1.7	0.4 – 11	0.01 – 0.45
Asia (within the former USSR)	water	0.02 – 9.0	0.02 – 1.9	0.2 – 9.0	0.01 – 0.5
	sediments	18 – 76	0.18 – 2.1	3.0 – 11	0.01 – 0.02
North America	water	0.5 – 6.2	0.01 – 3.5	0.08 – 7.5	0.01 – 5.0
	sediments	2 – 78	0.2 – 2.7	1 – 13	0.004 – 2.1
Australia	water	–	0.02 – 0.08	–	0.01 – 0.31
	sediments	–	–	–	0.13

Table 3. Background concentrations of lead, arsenic, cadmium, and mercury in water and bottom sediments ( $\mu\text{g/l}$ ) in the various of the planet (Izrael *et al*, 1989)

The water bodies of Karelia, Lakes Onega, Ladoga, and Vychozero, and the Toma and Yanis-Ioki rivers are exposed to the heaviest pollution from PPM, and as a result of this, the catches of valuable fish species have been drastically decreased.

The regular active sources of heavy metal pollution of the Black and Azov Seas include coastal sites where dredgings are discharged. This results in silting of the spawning grounds (breeding sites) for fish and damage to sessile filter feeders. The maximum allowable concentrations (MAC) of heavy metals and other pollutants in the water are often exceeded by tens and hundreds of times. In most years high levels of concentration of heavy metals and other toxicants are observed in the lower reaches of the river Don. This sometimes results in the mass death of fishes, especially in periods when the water temperature rises. In the delta (mouth) of the river Volga, pollution of bottom sediments and water by toxic substances results in the development of oncologic diseases in fish.

In the river Moskva, within the city boundaries and downstream, the concentrations of metals (zinc, lead, cadmium) exceed the environmental standards by factor of two or three. A great number of anomalies and deformities in the fishes are reported; and this number increases downstream. The most frequent defects are in the structure of the cranium, the eyes and associated neural pathways, the gills, and internal organs (especially the liver). The Kuibyshevskii water reservoir demonstrates preferential accumulation of metals in different organs of the same fish species, and by individuals of different species, depending on their level within the trophic chain, e.g. sabrefish (plankton-feeder) (*Pelecus cultratus*) - bream (*Abramis*) and roach (benthos-feeder) (*Rutilus rutilus*) - perch (mixed feeding) (*Perca fluviatilis*) - zander (*Stizostedion lucioperca*) and pike (*Esox lucius*) (predators). The lowest levels of manganese occur in

the muscles and gills of sabrefish and roach; that of copper is contained in bream muscles. The skin of bream and pike contain low amounts of zinc, and low levels of lead are present in muscles of sabrefish, roach, and bream, and in bream liver.

Analysis of fish from the river Oka basin has revealed irregularity of metal distribution in fish organs. In all species except bream and white-eyed bream (*Abramis sapa*), copper was absent in the muscles, while in the liver of silver bream (*Blicca bjorkna*) its content exceeded the allowable amount by 1.3 times, and in the livers of bream, sabrefish, and white-eyed bream, this level was exceeded by a factor of 3.1, 5.5 and 17.8, respectively. Spawn of silver bream and white-eyed bream contained significant amounts of copper. Unlike organic substances which are all in due course degraded, adsorbed or assimilated in the water body, metal compounds retain their toxicity virtually indefinitely, since during their transformation the basic component of the compound, i.e. the metal, does not change.

The toxicity of a metal is determined by many factors including concentration and duration of action, ambient temperature, oxygen content in water, pH, hardness of the water, and presence of compounds with which the metal may complex. Rise of water temperature, oxygen deficit, decrease of pH, and hardness usually enhance the metal toxicity for hydrobionts. Simultaneous presence of organic compounds or other metals in water can have different effects on the toxicity. Coefficients of metal accumulation by hydrobionts, calculated in relation to their concentration in the water, differ greatly between organisms of different taxonomic status, as well as for different organs and metals. Basically, the values vary within a range from a few tens to tens of thousands.

The metals get into the tissues of aquatic animals mainly via their food. In fish, metals can also come via mechanical capture of suspended particles of hydroxides in gills, and chemical absorption of ions on the mucous membrane. In decreasing order of toxicity for hydrobionts, the metals are arranged as follows:  $Hg > Cd = Cu > Zn > Pb > Co > Cr > Mn = Fe > Sn$ .

Water quality standards for heavy metals are not the same in different countries. Thus, the maximum allowable concentration for copper is 0.002 to 0.004 mg/l in Canada, 0.003 to 0.005 mg/l in Sweden, 0.006 to 0.021 mg/l in the USA, and 0.001 to 0.005 mg/l in Russia. There is a tendency for average metal concentrations to increase in fishes from inland seas as compared to ocean species. The average mercury concentrations in muscles of fishes from the Baltic, Black, and Caspian seas are higher by 2 to 4 times than in oceanic fish. Similar differences are noted for lead and cadmium, though these are smaller in value.

This agrees with the general trend of increase of the level of marine pollution when moving from the open ocean to the neritic zone and inland seas. One should also be aware, however, of the possibility of increase in heavy metal concentrations in the water and fish of inland seas and coastal waters as a result of natural processes, mainly surface run-off and coastal erosion. Lead concentrations are always higher in catadromous fishes as compared to oceanic species, while for cadmium such a relationship is not always observed.

Mercury accumulation in large oceanic predatory fishes, such as tuna (*Thunnus*), shark, and swordfish (*Xiphias*), as well as in cetaceans, is higher, by an order of magnitude, than in non-predatory marine fishes. Irreversible accumulation of mercury in predatory fishes takes place as a result of passage through the food chain.

Lead and cadmium are the metals most accumulated in the skin and scales of fishes.

Mercury is more concentrated in muscles and livers. This is connected with the ability of mercury to create strong complexes with functional groups of proteins. This results in creation of stable mercury-organic complexes with high capability of bioaccumulation. These compounds are slowly removed from animal organisms. Cases of mass poisoning of people and marine fish-eating mammals are known in Japan, Iraq, Pakistan, and Guatemala (Minimata disease). The mercury content in marine invertebrates is usually less than that in fishes. For example, the average concentration of mercury in muscles of 41 species of commercial (food) fishes in the North Atlantic shelf amounted to 0.154 mg/l while in the soft tissues of mollusks and invertebrates this did not exceed 0.1 mg/l. Similar data are typical for the Northern and Baltic seas and bays of Australia.

Hydrobionts can be arranged in the following order with respect to their sensitivity to mercury: bacteria, crustacea, algae, fishes, mollusks, insect larvae. Information on high mercury content in fishes, i.e. up to 7 mg/l of raw mass, was first obtained in the USA in the mid 1970s when studying water bodies in South Carolina. Elevated mercury content in fishes was later revealed both in Finnish water bodies and in those of North America. By the late 1980s in Sweden, concentrations of toxicant in fishes higher than the environmental standards were found in 10 000 lakes.

One of the reasons for this was of the lower pH of the water, as a result of acid rain. Lower pH increases the biological availability of mercury. Fecundity and productivity of hydrobionts can be used as a sensitive indicator of the toxic effects of metals.

Water hardness plays a key role in manifestation of metal toxicity. For the most fish species, increased water hardness reduces metal toxicity. The metal toxicity also depends on the degree of ionic dissociation. Ions of the metals are toxic as well.

It is very important to take into account the synergetic and antagonistic effects of metals on hydrobionts. Combinations of heavy metals, such as copper and zinc, copper and cadmium, nickel and zinc, are synergetic. Compounds of metals with cyanides create metal cyanide complexes, the toxicities of which are significantly lower than those of the cyanides and salts of heavy metals on their own.

The heavy metals have a high degree of accumulation through the food chain. This process can intensify the toxic effects, both directly on the hydrobionts and on humans eating marine products. Various combinations of metals and also metals and other ions and substances in domestic and industrial wastewaters, present a real and potential hazard for aquatic ecosystems. This problem needs to be thoroughly analyzed and studied.

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### **Biographical Sketch**

**Ivan Semenovich Shesterin** graduated from the biological-pedospheric faculty of the Lomonosov Moscow State University in 1968, with the speciality "aquatic toxicology and sanitary hydrobiology". In 1972 he finished the post-graduate course and defended a thesis devoted to inter-relations of plankton at the metabolite level. Since 1972, he has been head of the Laboratory of Ecological Toxicology in the All-Russian Research Institute of Freshwater Fish Culture. His scientific field covers investigation of the influence of toxicants on fishes and development of methods of improvement of toxic resistance in aquaculture, in polluted conditions. Recently he has been responsible for ecological monitoring of fish-culture water basins in Central and North-West regions of the Russian Federation.