VARIATION IN THE CHEMICAL COMPOSITION OF RIVERS, LAKES AND WETLANDS

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Contents

Summary

This chapter considers the deleterious changes in the state of natural water bodies under impact of anthropogenic factors. There is great concern about pollution with toxic substances, acidification and eutrophication. The global problem of drinking water supply directly depends on the integration of national initiatives in ecological politics.

Among the various kinds of impact on surface waters, much attention is paid to anthropogenic pollution. The main sources of this pollution are industrial waters, domestic/municipal wastewater, surface runoff from urban areas, and agricultural wastes. The ways of entering, distribution and transformation of pollutants in water bodies are described as are their effects on chemical composition of river waters, lakes, and wetlands including processes of eutrophication and acidification.

Changes in the chemical composition of the Rhine River waters, the use of which for numerous economic needs has given rise to some serious ecological problems, are examined in some detail. The effectiveness of the international co-operation of western

European countries in implementing comprehensive measures for the improvement of the condition of the Rhine is demonstrated.

The character of changes in the state of large lakes is traced, using the example of the American Great Lakes which have suffered great anthropogenic impacts. The joint measures undertaken by the USA and Canada have made it possible, in particular, to decrease phosphates entering the lakes, and to reverse the process of eutrophication.

The effect of anthropogenic impact on the state of wetlands is illustrated by the swamp systems of the Ural region in Russia. Heavy metal pollution of wetlands in industrially developed regions are compared with background levels in comparatively pure districts not subject to direct anthropogenic impact.

1. Introduction

Humankind has entered the third millennium burdened with global ecological problems accumulated during previous centuries. The scales of human economic activity caused by the increase of population, rise in the consumption of natural resources, and intensification of manufacture have increased many times. The rates of development of negative changes in the global environment (degradation of natural ecosystems, increase of land area disturbed by economic activity, deforestation, changes in biogeochemical cycles of some elements, overall pollution, etc.) have reached such levels that, in the opinion of some scientists, a manifestation of irreversible effects is threatening the stability of the biosphere itself.

Pollution of the hydrosphere with anthropogenic toxic substances, including xenobiotics, raises particular alarm. It is universally recognized that humankind has already discharged into the biosphere about 5·million different compounds (from about 10 million known today), and about 3000 new compounds are released annually. A part of these substances enters the natural environment and remains there for a very long time, becoming involved in food chains in the aquatic ecosystems. These persistent compounds accumulate in individual components (suspended matter, hydrobionts, and bottom sediments).

Even for substances not entering directly into water bodies but discharged into soil or atmosphere, there is a strong probability of their subsequent entry into the hydrosphere. Human health directly depends on the availability of pure water of suitable quality for drinking and sanitary/hygienic use. According to WHO, about half of the world population is forced to use water of poor quality. The people of the developing countries of North Africa, the Middle East, and Asia suffer most of all from water shortage. The UN efforts during the international decade (1981-1990) on drinking water supply and improvement of sanitary conditions were practically without result, mainly due to the overwhelming increase of population. Three billion people in 50 countries are expected to experience water shortage by 2005. Another important problem is the acidification of surface waters—a problem connected with atmospheric precipitation containing high concentration of acid-forming combinations of sulfur and nitrogen as a result of mineral fuel combustion and transport of gaseous emissions by transboundary air masses.

Accumulation of nutrients and organic substances is exacerbated by construction of reservoirs that reduce the flow of running water, eventually leading to eutrophication of water bodies—an extremely unfavorable and dangerous phenomenon. Solution of the planet’s aquatic problems requires strong and effective measures based on modern scientific principles and strict water protection, totally stopping waste discharge into water bodies.

The global character of the above-mentioned problems has led to the necessity to consolidate efforts of all countries towards the formation of an ecological policy and realization of its aims to ensure ecological safety of the Earth in the light of the strategy for sustainable development proposed by the United Nations Environment Programme (UNEP). The UN has an important role to play in the integration of national initiatives, organization of various levels, and coordination of scientific activity in the field of ecological problems. Under the aegis of the UN, the United Nations Educational, Scientific and Cultural Organization (UNESCO), European Economic Community (EEC), UNEP, WHO, and the World Meteorological Organization (UMO), together with the Worldwide Fund for Nature (WWF) and International Union for the Conservation of Nature and Natural Resources (IUCN), are active in this field.

There are several examples of successes of international ecological programs. We will consider the long-term activity of the International Commission for Protection of the Rhine, the international Danube Commission, the agreements between the USA and Canada directed to the decrease of anthropogenic load on the Great Lakes, and interstate agreements between Russia and the USA in the field of environment protection.

Considering the variety of anthropogenic impacts on the Earth’s hydrosphere, the complexity of the effects is noted and the changes in chemical composition of land surface waters, mainly due to anthropogenic pollution, are considered in this chapter,.

2. Anthropogenic Impact on Land Surface Waters.

Among the various anthropogenic impacts on natural waters (e.g. quarrying, mining, intensification of agriculture, agricultural amelioration/drainage, irrigation and water supply, construction and operation of hydraulic structures, thermal, nuclear and hydroelectric power stations, etc) water pollution by municipal wastes, industrial effluents, and agricultural practices has acquired a dominant character, having aggravated the ecological situation at local, regional and global levels. The growing shortage of pure water mainly due to pollution, is becoming, to a certain degree, a deterrent to industrial development and one that seriously affects human society.

Some countries having scanty water resources are forced to solve the problems of water supply by drawing and transferring water from remote regions. For example the city of Karaghanda, Russia, receives it water from the Irtish River by a channel 457 km long. The water sources for Los Angeles are at distances of 300-400 km, and New York city obtains water from the Hudson River, 225 km away. Some countries have to go outside their own borders (Germany – from Switzerland, the USA – from Canada), and some countries have to use water that has transited through other countries, e.g. the Netherlands taking water from the Rhine River, and Hungary and Romania using the

Danube. The high level of development achieved in these countries would not have been possible if their water resources were limited to just local runoff.

Water bodies are used today as sources of water supply (drinking, domestic, agricultural, industrial), recreation zones, fishery areas, and hydropower resources. Sometimes they are used as receivers of waste waters (taking advantage of natural self-purification).

2.1. Anthropogenic Pollution of Surface Waters.

As a result of anthropogenic activities, surface waters receive pollutants that do not occur in unpolluted waters under natural conditions. Industry, in particular, is a major contributor to natural water pollution. If the types of industry are arranged according to decreasing order of quantity of substances discharged with their wastes, the sequence would be: paper and pulp, chemical, non-ferrous metal industry, ferrous metal industry, coal, mechanical engineering, petrochemicals, and electrical energetics. Industrial waste waters account for approximately 70 to 80% of total wastes entering surface waters; they are distinguished by their wide variety of composition of mineral and organic substances, depending on the process of manufacture, the technology and raw materials used, their system of treatment, and drainage. The basic pollutants in industrial wastewaters are: suspended matter, oil and oil-products, phenols, cyanides, compounds of heavy metals (copper, lead, arsenic, mercury and other), and detergents (synthetic surfactants).

With the emergence of new branches of industry, there is an increase in the development of new chemicals and this is inevitably accompanied by increased amounts of wastewater, and increased complexity and intensification of their effect on natural waters.

Entry of oil-products into water bodies has serious impacts on spawning and fry of food-fish. An oil film on the surface greatly decreases the self-purifying ability of a water body. The presence of detergents causes considerable increase in phosphates, and heavy metals retard self-purification processes with reference to toxic organic matter, etc.

Crude waste waters from the oil industry require dilution by a factor of about 300,000, something which is difficult to achieve even with such rivers as the Volga, with its abundance of water. According to approximate estimates, in 1980 the world volume of industrial wastewater was 290 km^3. The volume of river discharge being polluted by these wastewaters was 5800 km^3, i.e. 7.6% of the total annual volume of world river discharge.

Domestic (household, municipal) wastewaters, which account for about 20% of total wastes, contain large quantities of nutrients, organic, and mineral substances in dissolved and suspended states, including pathogenic organisms (e.g. helminth eggs, coliform bacteria, etc.). Detergents in these wastes can create a heavy foam, decreasing oxygen concentrations and paralyzing the activity of micro-organisms which destroy organic matter.

Great harm is done to water bodies by wastes conducted away from agricultural land, formed in the process of their irrigation or drainage and containing compounds of nitrogen, phosphorus, pesticides, and readily soluble salts washed out from soils. With prolonged use of high doses of fertilizers and crop protection agents, up to 100-180 $kg \cdot ha^{-1}$ nitrogen, 20-50 $kg \cdot ha^{-1}$ phosphorus, 200 $t \cdot ha^{-1}$ of mineral salts, and up to 10% of the quantity of applied pesticides, can penetrate with these wastes into surface and ground waters each year.

The discharge, over 25 years, of collector-drainage waters from irrigated land into the Syr Daria River has caused a rise of its mineralization by a factor of 2.5 (from 400 $mg \cdot l^{-1}$ to 1.0 $g \cdot kg^{-1}$) and a change of its water chemistry type from hydrocarbonate-calcium to sulfate-sodium. Pesticides entering water bodies have adverse effects on the vital capacity of aquatic plants, plankton, and fish, and through the food chain to land animals as well.

Large cattle-breeding farms (commercial production of meat and milk) are serious sources of water pollution by nutrients and organic substances (20-35% in dissolved form and 65-80% in suspended form). According to the quantity of organic matter and nutrients contained in wastes, one fattening complex for 10 000 livestock is equivalent to the pollution from a city of 100 000 people.

Surface runoff (stormwater, snowmelt, running waters, etc.) from settlements, industrial enterprises, lands treated by chemicals, and eroded areas, is an intermittent but very severe cause of pollution of water bodies. Surface urban runoff has a different composition from domestic waste waters. Suspended matter, oil-products, oils, heavy metals, and synthetic chemicals dominate in them. Runoff from eroded land carries a heavy load of mineral particles into water bodies and can cause silting of reservoirs and ponds.

Warm cooling water from thermoelectric and nuclear power stations, and some industrial enterprises contribute to “thermal” pollution, which causes serious biological changes in water bodies (e.g. stimulation of phytoplankton growth, particularly, diatoms and blue-green algae).

Discharges from mines have high mineralization, acidic reaction, and a great number of mineral elements (in dissolved and suspended state).

Increasing threat of negative impact upon water body state is associated with periodically occurring emergency situations at industrial enterprises, oil-pipe-lines, water transport (oil-tankers) accompanied by accidental discharges of pollutants and oil into water.

Irrespective of the character of anthropogenic pollution (physical or chemical, in dissolved or suspended form) the common ways in which pollutants enter a water body are:

- direct or non-point discharge of wastewaters and solid wastes;

- with dry or wet fall-out from atmosphere;
- with waters of surface discharge from the catchment area and with ground waters;
- entering from bottom sediments;
- wastes entering as a result of water transport, floating of timber, etc.

All pollutants under the effect of physical, chemical and biological processes occurring in freshwater ecosystems, are subject to dilution, concentration, transfer, assimilation by hydrobionts, adsorption by suspended matter, deposition on the bottom, or various transformations (see Figure 1).

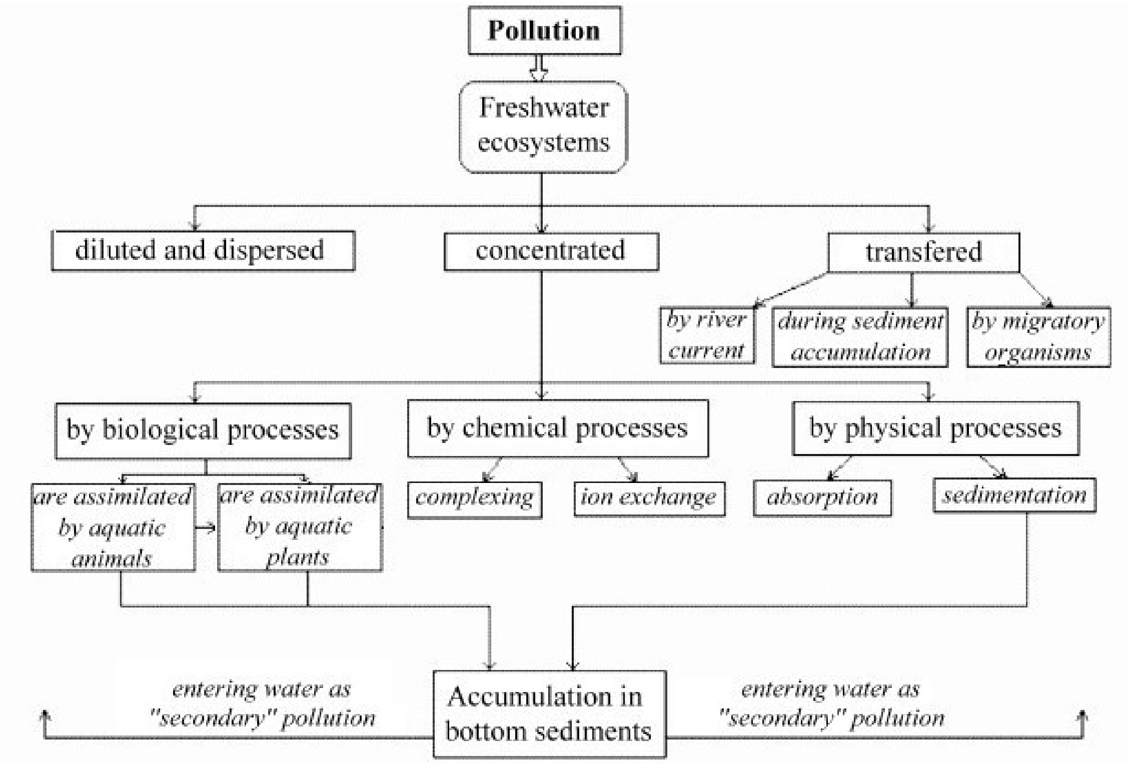

Figure 1. Fate of pollutants in freshwater ecosystems.

Various chemical and physical changes can occur as a result of entry of substances into natural waters, e.g:

- change in the content of chemical compounds already naturally present in the water;
- appearance of new specific components;
- change in mineralization value and water chemistry type;
- decrease of dissolved oxygen content;
- transformation of redox and acidic-alkaline conditions of medium (Eh and pH states);
- changes in complexing capacity with regard to heavy metals;
- formation of new migratory forms of chemical elements, and

- change in the intensity and trends of physico-chemical, chemico-biological, microbiological and other processes responsible for the buffering capacity of a water body and its self-purification.

The process of transformation of migratory forms of element occurring in water bodies are accompanied not only by geochemical but also ecological consequences. In particular, many heavy metals complexed with high molecular weight organic matter become less toxic. Under certain conditions of aquatic environment, however, the less toxic compounds can be transformed into more toxic ones (e.g. NO_3^{2-} into NO_2^- and NH_4^+). Heavy metal methylation, when compounds of mercury ($(CH_3)_2Hg$), arsenic ($(CH_3)_3As$), lead ($(CH_3)_2Pb$) and other metals, are formed, poses a great ecological hazard. These compounds are soluble and have high toxicity.

The complexing capacity of dissolved organic matter of fresh waters and the concentrations of complexing substances (organic carbon, humic substances, humic and fulvic acids) differ greatly for water bodies in different physico-geographical zones (for example, 40 times for the Severnaya Dvina River as compared with the Don River).

2.2. Anthropogenic Eutrophication.

Changes in the chemical composition of water, under the effect of anthropogenic pollution, disturb the attained ecological equilibrium and affect species diversity and bioproductivity, which are indicators of the health of aquatic environments. Organic pollution of water bodies leading to eutrophication causes particular alarm. The natural process of eutrophication that occurs gradually in water bodies over hundreds and thousands of years, can be greatly accelerated under modern conditions, thereby causing conversion of water bodies from one trophic state to another in only 20 to 25 years (e.g. Lakes Erie, Tahoe, Ladoga)

The mechanism of this process of anthropogenic eutrophication, the negative consequences of which (e.g. water quality deterioration, disappearance of many hydrobionts including valuable food-fish) have become apparent on all continents of the world, is as follows.

When excess quantities of nutrients (mainly phosphorus) enter a water body with surface discharge and waste waters (mainly domestic, agricultural and industrial) its biological productivity begins to increase, stimulating an intensive phytoplankton growth and development of an algal bloom—accelerated growth of green and especially blue-green planktonic algae. As the phytoplankton dies, there is a large oxygen demand for oxidation of organic matter, accompanied by formation of anaerobic zones.

They first appear in bottom water layers and then little by little spread throughout the whole volume. In addition to increase in organic matter and nutrients in water bodies, another no less important matter, is retarding of water exchange. Particularly, as a result of the construction of reservoir and weirs, the running time of the Volga River runoff (from Rybinsk to Volgograd) has increased ten fold, and the Dnepr River (from the mouth of the Pripyat River to Kiev) from 2-3 days to 60 days. All these reservoirs as well as many others, are, to some extent, subject to eutrophication.

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Biographical Sketches

Nikanorov Anatoly Maximovich, was born in 1935 in Grozny. In 1958 he graduated from the geological prospecting faculty of Grozny Oil Institute. He worked from 1960 to 1972 in Stavropol branch of Groz SRI, North Cau SRPI –as an engineer, chief engineer, and laboratory manager. From 1972 to 1977 he was head of a faculty of hydrogeology, and dean of the geologo-geographical faculty of Rostov University. In 1977 Nikanorov was appointed director of the Hydrochemical Institute. In 1964 he defended a master's thesis "Hydrogeology of Post-Pliocene and Pliocene deposits of the East Pre-Caucasus", and in 1972 a doctor's thesis "Investigation in the sphere of hydrogeology of oil deposits (Mesozoic of the North-East Caucasus as an example)". In 1974 he became a Professor. Nikanorov's main spheres of interest are development of the general theory for formation of water chemical composition in the hydrosphere, the theory for in-water body processes for buffer capacity and resistance of freshwater ecosystems to pollution, and aspects of water chemistry of surface waters under conditions of anthropogenic impact. He has more than 250 scientific works devoted to the problems of hydrogeology and water chemistry including 30 monographs ("Biomonitoring of heavy metals in freshwater ecosystems", "Hydrochemical atlas of the USSR", "Monitoring systems for surface water quality", "In-water body processes and monitoring of natural water quality", "Water chemistry", "Ecology", etc.). Many of his works were published abroad. Dr. Nikanorov has the title "Honored Scientist of the Russian Federation" and "Honored Professor of Wisconsin University" (USA). He was elected as a corresponding member of RAS (1977), member of Engineering Academy of Russia (1993), and Ecological Academy (1994). Dr. Nikanorov was awarded Honored badges of the USA government (1987 and 1992) for successful participation in co-operation of USSR and USA in the field of water protection from pollution. At present he is director of the Hydrochemical Instituteand head of the South department of the Institute of Water Problems of RAS, and manager of the branch of a faculty "Geoecology, Environment protection" of Rostov state University. Dr. Nikanorov is in charge of post-graduate students; 18 master's and 2 doctor's thesis have been defended under his supervision. He was awarded an Order of the Badge of Honor, Friendship of People, jubilee medal for Valiant Labor. On the occasion of 100th anniversary of V.I. Lenin Dr. Nikanorov was awarded a medal of Labor – Veteran and honorary diploma of YCZ CC, Ministry of Oil Industry of the USSR, Goskomgidromet (Rosgidromet).

Brazhnikova Lidiya Valerianovna , was born in 1929 in the Novocherkassk, Rostov region of Russia.
In 1947 she finished at Rostov-on-Don secondary school, and in the same year entered Novocherkassk Polytechnical Institute of the chemico-technical faculty. After graduating from the Institute in August of 1952 she entered the Hydrochemical Institute where she worked as a senior laboratory assistant, junior research associate, scientific secretary, and head of laboratory. In 1973 she was appointed deputy director of the Institute and she worked at this post for twenty five years. Since 1998 she has been working as a senior research specialist. In 1962 she defended a master's thesis on "Ion runoff of the USSR rivers"; in 1967 the academic rank of senior research associate in "Water chemistry" was conferred on her. Her

scientific interests were connected with the problems of dissolved substances' outflow in rivers into seas, with the study of flows diverted from agricultural lands' and their effect on chemical composition of water bodies, with the problems of methodic and methodological provision creation, functioning and improvement of monitoring service for surface water state (pollution), processing and presentation of hydrochemical information gathered by network in the form of generalization of various kinds (Reviews, Year-books, reference information, reports, etc.). She authored/co-authored about 150 scientific works, among them some monographs ("Runoff of dissolved substances from the territory of the USSR", "Reference book on water chemistry", "Monitoring of water quality: an assessment of toxicity", "Reviews of surface water pollution", "Yearbooks of surface water quality", and others). Besides her scientific work she was chairman of the certifying Commission, secretary of specialized council for defence of master's and doctor's thesis, deputy editor of "Hidrohimicheskie Materialy" collection, and deputy chairman of the scientific Council of Hydrochemical Institute. She received several state awards: an order for Services to Fatherland of II degree, medal Labor-veteran, honored badges outstanding worker of Hidromet Service of the USSR, Honored scientific worker of Hidromet Service of Russia.