

WATER CHEMICAL COMPOSITION OF RIVERS, LAKES AND WETLANDS

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Summary

In the present article we consider an extensive range of problems associated with the

formation of the natural chemical composition of land surface waters in the Earth's hydrological cycle. From the perspective of water's significance for human life and human economic activity, the priority problem of the world population's supply of pure water, the importance of making consolidated decisions by all states associated with water protection, and the creation of a Global Environment Monitoring System are discussed briefly.

A modern presentation of knowledge about basic groups of water chemical composition (main ions, dissolved gases, nutrients, microelements), and natural water classification and methods for assessment of their quality, are expounded in a systematized form.

Hydrochemical peculiarities of land surface waters, e.g. rivers and lakes, and the defining natural factors directing chemical composition, including physical, chemical and biological processes occurring in water bodies, are considered.

A description of the hydrochemical appearance of two largest water bodies of the world, the Amazon River and Lake Baikal, the basins of which are as yet lightly exposed to anthropogenic impact, is presented in detail.

Considerable attention is paid to the wetlands formed at the boundary of water and land. Among the existing systems of wetlands, swamps and waterlogged soils occupy almost 3% of the land and are of the utmost interest. By way of the example of swamp systems, the Urals region in Russia, and the various conditions of formation of their chemical composition (mineral, organic components and heavy metals) are discussed.

1. Introduction

The most important substance for humans in their surrounding material world is natural water. It is one of the most wonderful, not yet completely understood, combinations on the Earth. It possesses a complex of anomalous properties distinguishing it from all other substances, (e.g. anomalously high values for the temperature of melting, boiling, and evaporation, and heavy dissolving capacity).

Chemically pure water should be considered an extremely complex substance consisting of atoms of various isotopes of hydrogen and oxygen, which can form up to 18 isotope varieties of water. Under natural conditions, water corresponding to the known H₂O formula is not found in a chemically pure form.

In the processes of the hydrological cycle on the Earth, connecting hydrosphere with atmosphere, lithosphere and biosphere, the chemical composition of water is formed. Interacting with all the components of the natural landscape and being influenced by natural and man-made factors, water, a universal solvent, is enriched by a wide gamut of various substances in gaseous, solid and liquid states that create an enormous variability of natural water types from the perspective of their chemical composition.

Natural water is a dynamic chemical system containing in its composition a complex group of gases, mineral and organic substances in the form of true solutions, and suspended and colloidal matters as well.

The variety and complexity of natural water composition is defined not only by the occurrence of a large number of chemical elements in it, but also by the difference of forms and the values and presence of each of them. Almost all known chemical elements occur in natural water, proving academician's V.I. Vernadsky statement that in each water drop the composition of the macrocosmos is reflected as in a microcosm. About 90 stable chemical elements contained in the Earth's crust are found in natural waters.

We can now be certain that the negative consequences of human economic activity upon the planet have a cumulative impact of enormous scope, on a scale of impact comparable with the natural processes happening on the planet. Practically all the natural components of the biosphere are exposed to direct or indirect anthropogenic impacts. The destabilizing effect of this on the most vulnerable part of the biosphere, the hydrosphere, has given rise to many problems, among which the problems of "pure water" has become the most urgent. This is due to the necessity to fulfill the human need for pure water in all manifestations of vital activity including everyday life, industry, and recreation. The urgency of the problem is associated with the poor quality of water and its shortage in some regions of the Earth (especially in the developing countries) in spite of sufficiency of fresh water on a global scale.

The significance of the water situation necessitates solving various problems at the state level, including assessment and prediction of water quality (with due account of pollution), the monitoring of national and transboundary water bodies, observance of international agreements, and promotion and creation of national monitoring systems of surface water quality in the majority of the developed countries.

An event of world importance in the 1970s was creation of the Global Environmental Monitoring System [GEMS] (according to the decision of the Stockholm Conference on Environmental Protection 1972), whose mission is to determine the key trends and ensure the fulfillment of works in the field of natural environment use and protection. In 1976 UNEP and WHO supported by UNESCO and WMO initiated the GEMS/WATER program with the aims of creating a global monitoring system of surface water quality (with the world's observation data bank in Canada), improvement of water monitoring in the countries participating in the program, detection of new priorities for investigations at global and regional levels, and also improvement of interaction and decision-making in water quality management.

This chapter uses information from observations of land surface water chemical composition (rivers, lakes, wetlands) obtained within the framework of the GEMS/WATER program and also comprehensive scientific investigations, including international ones carried out in natural water bodies not subjected to human's activity (or not being under direct anthropogenic impact).

2. Chemical Composition of Natural Waters.

The chemical composition of natural water (rivers, lakes, seas, wetlands and other) is usually classified under six headings:

1. Main ions
2. Dissolved gases
3. Biogeneous substances
4. Organic substances
5. Microelements
6. Pollutants

All components contained in natural waters give them certain properties—salinity, alkalinity, hardness, acidity, corrosivity, etc. Knowledge of water chemical composition and its properties is necessary for the solution of scientific and applied problems concerned with water use for human domestic and other activity—water supply (drinking, hygiene, public, industrial, agricultural), fish-breeding, recreation, hydropower and hydraulic engineering, reclamation, exploration and exploitation of mineral deposits, etc.

Knowledge of the absolute magnitude of the concentrations of the components of water and their interactions, permits specialists, for example:

- to classify water according to chemical composition, dominant ions, total content of all substances;
- to characterize water provision with nutrients (compounds of nitrogen, phosphorus, silicon and other) necessary for growth of hydrobionts;
- to assess water pollution, and
- to register cases of sudden rise in concentration of pollutants,
- to reveal pollution sources, and
- to make predictions about the future condition of water bodies.

The components of water chemical composition are the main characteristics of water quality that define its fitness for particular kinds of water use. Water quality assessment is performed according to certain parameters of water properties and composition, including concentrations of polluting harmful and toxic substances, which are categorized according to a harmfulness index. The standards of pollutant concentrations adopted in various countries are variously known as quality criteria, concentration standards, maximum allowable concentrations (MAC), maximum allowable levels (MAL), etc. Other measures of chemical substances dangerous for biota include classifications based on their type of effect—toxicity, carcinogenicity, mutagenity, etc. Different requirements specified for water quality are regulated by state normative documents, regulations on surface water protection from pollution, and standing standards. For this reason and also because of natural differences in chemical composition of water bodies in different regions, establishment of common, strict norms for water quality is extremely problematic.

In practical and scientific activity as applied to land surface water, the term *mineralization* is used. This is the total concentration of all mineral substance found during water analysis, or the sum of ions (\sum_i)—the arithmetic sum of the mass of all ions determined during analysis. Mineralization of fresh waters is usually expressed in $\text{mg}\cdot\text{eq}\cdot\text{l}^{-1}$ ($\text{g}\cdot\text{kg}^{-1}$ when mineralization is more then $1000 \text{ mg}\cdot\text{l}^{-1}$), and saline waters and brines, in “practical salinity units” (PSU), which are equivalent to ppm.

2.1. Main ions

Mineral substances contained in natural waters in the dissolved state (in the form of ions, complex ions, undissociated compounds and colloids) are conventionally subdivided into macrocomponents and microcomponents. The macrocomponents comprise the so-called main ions that determine water chemical type and account for the bulk of natural water mineral content (up to 95% for fresh water and up to 99% for highly mineralized waters). The microcomponents comprise substances occurring only under certain conditions and in very small concentrations ($\mu\text{g}\cdot\text{l}^{-1}$ and $< 1 \text{ mg}\cdot\text{l}^{-1}$). An intermediate position is occupied by ions of hydrogen, compounds of nitrogen, phosphorus, and silicon dissolved in water.

The concentrations of all minerals is related to two main factors—the abundance of chemical elements in the Earth's crust and the solubility of their compounds.

The main anions contained in natural water are Cl^- , SO_4^{2-} , HCO_3^- , and CO_3^{2-} and the main cations are Ca^{2+} , Na^+ , Mg^{2+} and K^+ .

Chloride ions (Cl^-) have a large migratory ability in connection with the very high solubility of chloride salts of sodium, magnesium and calcium. Their presence in water is naturally associated with the processes of leaching from minerals (e.g. gallite, sylvite, carnallite, bischofite), from rocks (e.g. nephelines), and from saline deposits. It is also present in atmospheric precipitation, and today it is particularly associated with industrial and municipal wastes. Chloride ions occur in all types of water in concentrations from parts of $\text{mg}\cdot\text{l}^{-1}$ to hundreds of $\text{g}\cdot\text{kg}^{-1}$ (in brines).

Sulfate ions (SO_4^{2-}) are contained in all surface waters, and their content is limited by the presence of calcium ions together with which they form a slightly soluble CaSO_4 . The main source of sulfate in water is various sedimentary rocks which include gypsum and anhydrite. Water enrichment by sulfates takes place both by the process of oxidation of sulfide, which is abundant in the Earth's crust, and oxidation of hydrogen sulfide which is created during volcanic eruption and is present in atmospheric precipitation. The processes of decompositions and oxidation of substances of vegetable and organic origin containing sulfur, and also human economic activity, have an effect on sulfur content in water bodies. The sulfate content of waters of rivers and freshwater lakes reaches several tens of $\text{mg}\cdot\text{l}^{-1}$.

Hydrocarbonate and carbonate ions (HCO_3^- and CO_3^{2-}) occur in natural waters in dynamic equilibrium with carbonic acid in certain quantitative proportions and form a carbonate system of chemical equilibrium connected with the pH of water. When the pH of a water system is 7 to 8.5 the predominant ion is hydrocarbonate. When pH is less than 5, the content of hydrocarbonate ions is close to zero. Carbonate ions dominate when $\text{pH} > 8$. The sources of HCO_3^- and CO_3^{2-} are various carbonate rocks (limestones, dolomites, magnesites), from which dissolution takes place with the participation of carbon dioxide.

Hydrocarbonate ions always dominate in water with low mineralization, and often in waters with moderate mineralization. Accumulation of hydrocarbonate ions is limited

by the presence of calcium ions, forming with HCO_3^- , a poorly dissolved salt. Usually in surface fresh waters HCO_3^- content does not exceed $250 \text{ mg}\cdot\text{l}^{-1}$ (with the exception of soda alkaline waters in which HCO_3^- and CO_3^{2-} content can reach grams and even dozens of grams per kilogram).

Ions of sodium (Na^+). The migratory ability of sodium as an element is rather high, as all its salts have high solubility. In waters with low mineralization Na^+ is third in concentration. With higher mineralization, the content of sodium rises, and in waters having mineralization of some $\text{g}\cdot\text{kg}^{-1}$ it becomes a dominant ion. A high proportion of the sodium ions is balanced by chlorine ions, forming a stable mobile combination that migrates with high velocity in a solution.

The sources of Na^+ in waters are deposits of various salts (rock-salt), weathering products of limestone rocks, and its displacement from the absorbed complex of rocks and soils by calcium and magnesium.

Ions of potassium (K^+). Potassium, in terms of the magnitude of its content in the Earth's crust and the solubility of its compounds, is very similar to sodium. However, it occurs in lower concentrations in surface waters as it has weak migratory ability. This is due to its active participation in biological processes, e.g. absorption by living plants and micro-organisms.

Ions calcium. (Ca^{2+}). The basic sources of calcium are carbonate rocks (limestones, dolomites) that are dissolved by carbonic acid contained in water. When the availability of carbon dioxide (with which it is in a balance), is low, however, the reaction begins to proceed in a reverse direction, accompanied by precipitation of CaCO_3 . Another source of Ca^{2+} in natural waters is gypsum, is common in sedimentary rocks. Calcium ions dominate in the cation composition of low-mineralized waters.

Ions of magnesium (Mg^{2+}). Magnesium is less abundant than calcium in the Earth's crust. It enters surface water as a result of the processes of chemical weathering and dissolution of dolomites, marls, and other rocks. Magnesium ions occur in all natural waters, but very seldom dominate. Its concentration in river waters ranges from one to tens of $\text{mg}\cdot\text{l}^{-1}$. The weaker biological activity of magnesium, as compared with calcium, and also the higher solubility of magnesium sulfate and hydrocarbonate as compared the equivalent compounds of calcium, favor increase of Mg^{2+} concentration in water. With higher water mineralization, the ratio between calcium and magnesium begins to change towards predominance of the latter.

2.2. Ions of Hydrogen

In the composition of natural waters hydrogen ions H^+ take an especially important place, though their absolute content as compared with other ions is very low. Ions of hydrogen are always present in water as they arise during electrolytic dissociation of water itself: $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$. Concentration of hydrogen ions in water solution is determined by the so-called ionic product of water $K_w = [\text{H}^+][\text{OH}^-]$. It follows that the product of concentrations (in gram molecules) of hydrogen ions and hydroxyl at a temperature of 22°C , is always equal to a constant value, $K_w = 1 \cdot 10^{-14}$. Concentrations

of hydrogen and hydroxyl ions are very small, which is why it is customary to present it in the form of their logarithm with the reversed sign of $\text{pH} = -\lg[\text{H}^+]$; $\text{pOH} = -\lg[\text{OH}^-]$.

Water reaction is usually expressed as concentration of hydrogen ions. When $\text{H}^+ = 10^{-7}$, water reaction is neutral; if $\text{pH} > 7$ or $\text{pH} < 7$, then the reaction shifts in the alkaline or acid direction respectively. In natural waters, the concentration of hydrogen ions depends on the dissociation and hydrolysis of the combinations occurring in it (see Table 1).

Water type	Water characteristics	pH
Acid	Waters of volcanic exhalation	> 2
Acid	Mine waters	3 - 4
Acid	Swamps	4 - 6
Acid	Groundwaters	5 - 7
Alkaline	Rivers	6.8 - 7.8
Alkaline	Fresh lakes	7.3 - 9.2
Alkaline	Ocean	7.8 - 8.3
Alkaline	Salt (soda) lakes	up to 10.5

Source: Tsytsarin G.V. (1988) Introduction to water chemistry. M.: MGU Pub. H. p.104.

Table 1. pH values of natural waters of various types.

2.3. Dissolved Gases

All natural waters containing dissolved gases but they differ in their origin.

The composition of gases connected with the exchange processes between water and atmosphere depends mainly on their content in the atmosphere. In terms of abundance of gases in the Earth's atmosphere, nitrogen, oxygen, argon and carbon dioxide account for 99.9% of the composition. These are the most important in determining the composition of natural water.

Processes that take place in water bodies, including biochemical ones, require the presence of oxygen (which is formed during photosynthesis), carbon dioxide, methane, and, to a lesser extent, hydrogen sulfide, ammonia, heavy hydrocarbons, and nitrogen.

Volcanic processes and degassing of the Earth's mantle supply oxides and dioxides of carbon, methane, ammonia, hydrogen sulfide, hydrogen, hydrogen chloride, sulfurous gas and others into natural waters. Some other gases can appear and dissolve in water as a result of ultra-violet irradiation (ozone), thunderstorm discharges (nitric oxide), and anthropogenic pollution (sulfurous gas, vapors of iodine, ammonia, carbonic oxide, etc.).

2.4. Biogenous Substances.

Substances that are connected by their origin with the vital activity of aquatic organisms, which determine the possibility for their existence in a water bodies, are called *biogenous*. These include compounds of silicon, nitrogen, phosphorus and iron.

Silicon (Si) is a constant component in natural waters. Its content in natural waters relative to the total salt composition is low (in land surface waters up to $10\text{-}20\text{ mg}\cdot\text{l}^{-1}$) due to the low solubility of silicate minerals and their consumption by some organisms. Silicon belongs to the anionogenic elements; it occurs in waters in a fully dissolved state in the form of meta- and ortho-silicic acids H_2SiO_3 and H_4SiO_4 and in colloidal form of $x\text{ SiO}_2 \cdot y\text{ H}_2\text{O}$ type.

Nitrogen (N) occurs in natural waters in the form of various inorganic ions (ammonium NH_4^+ , nitrite NO_2^- and nitrate NO_3^-) and organic compounds (in the amino acids and proteins of organisms, and the products of their vital activity and decomposition). These occur in water in the form of suspended and colloidal substances, and dissolved molecules. Transformation of complex organic forms into mineral ones happens in the process of biogenous element regeneration, the result of which is ammonia formation. Under oxidizing conditions with bacterial action, ammonia is oxidized into nitrites and nitrates. With oxygen deficiency the process runs in a reverse direction. Nitrogen compounds cycle in water bodies: vegetation \rightarrow animals \rightarrow decomposition products \rightarrow $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^- \rightarrow$ vegetation.

Nitrate content in water bodies is determined by the balance between their input and their consumption by plants. The content of nitrite ions is small (hundredths and thousandths of $\text{mg}\cdot\text{l}^{-1}$), and the content of nitrate ions is from tenths to unities of $\text{mg}\cdot\text{l}^{-1}$.

Phosphorus (P) occurs in water in the form of inorganic and organic compounds in a dissolved state and in the form of suspended and colloidal substances. Phosphorus, being an anionogenic element, forms phosphorous acid H_3PO_4 of neutral strength that dissociates into some derivative forms: H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , the relation between which is determined by the pH value of water. The main factor defining its concentration, is its exchange between living organisms and inorganic forms. In natural waters phosphorus usually occurs in low concentrations (hundredth and tenths of $\text{mg}\cdot\text{l}^{-1}$) due to the low solubility of its compounds and intensive consumption by hydrobionts. Human economic activity is a factor causing increased phosphorus concentrations in water bodies.

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generalization and analysis of long-term information, regional levels of heavy metals (mercury, cadmium, lead, zinc and copper) in natural objects (water, suspensions, bottom sediments, hydromorphic soils and peat) of the main wetland classes in the territory of Russia are given].

Biographical Sketches

Nikanorov Anatoly Mazimovich, Russian, was born in 1935 in Grozny in the family of an oil-industry engineer. In 1958 he graduated from the geological prospecting faculty of Grozny Oil Institute. He worked in 1960-1972 in the Stavropol branch of Groz SRI, North Cau SRPII as an engineer, chief engineer, laboratory manager, in 1972-1977 as head of the faculty of hydrogeology, and dean of the geologo-geographical faculty of Rostov University. In 1977 he 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", in 1972 a doctor's thesis "Investigation in the sphere of hydrogeology of oil deposits (Mesozoic of the North-East Caucasus as an example)", and in 1974 an academic rank of professor was conferred on him. His sphere of scientific interests is development of a general theory of formation of water chemical composition in hydrosphere, the theory for in-water body processes for buffer capacity and resistance of freshwater ecosystems to pollution, specific and applied aspects of water chemistry of surface waters under conditions of anthropogenic impact. He has more than 250 scientific works devoted to problems of hydrogeology and water chemistry, including 30 monographs (e.g. "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"). Many works were published abroad. He has the title of "Honored Scientist of Russian Federation" and "Honored Professor of Wisconsin University" (USA). He was elected as a corresponding member of the RAS (1977), member of Engineering Academy of Russia (1993), and the Ecological Academy (1994). He was awarded Honored badges of the USA government (1987 and 1992) for successful participation in co-operation between USSR and USA in the field of water protection from pollution. At present he works as a director of the Hydrochemical Institute, as head of the southern department of the Institute of water problems of RAS, and a branch of the faculty "Geoecology. Environment protection" of Rostov state University. He is in charge of post-graduate students; 18 master's and 2 doctor's thesis were defended under his supervision. He was awarded the Order of the Badge of Honor, Friendship of People, jubilee medal for Valiant Labor. On the occasion of the 100th anniversary of V.I. Lenin he was awarded a medal of Labor – Veteran and honorary diploma of YCZ CC, Ministry of Oil Industry of the USSR, Goskondromet (Rosgidromet). He is married, with one son.

Brazhnikova Lidiya Valerianovna, Russian, was born in 1929 in Novocherkassk, Rostov region. In 1947 he finished Rostov-on-Don secondary school, and in the same year entered Novocherkassk Polytechnical Institute in the chemo-technical faculty. After graduating from the Institute in August 1952 he entered the Hydrochemical Institute where he worked as a senior laboratory assistant, junior research associate, scientific secretary, and head of laboratory.

In 1973 he was appointed deputy director of the Institute on scientific work and he has worked on this post for twenty five years. Since 1998 he has been working as a senior research specialist.

In 1962 he 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 him.

His scientific interests are connected with the problems of dissolved substances' drift –over by river flow 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), and processing and presentation of hydrochemical information gathered in the form of generalizations of various kinds (Reviews, Year-books, reference information, reports).

He has prepared and published about 150 scientific works including co-authorship. These include 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", etc.

Besides scientific work he has been heavily involved in organizational work, as chairman of the certifying Commission, secretary of specialized council for defence of master's and doctor's thesis, deputy editor of

the “Hidrohimicheskie Materialy” collection, and deputy chairman of the Scientific Council of the Hydrochemical Institute.

He has received the following state awards: order for Services to Fatherland of II degree, medal Labor-veteran, honored badges outstanding worker of Hydromet Service of the USSR, Honored scientific worker of the Hydromet Service of Russia.

He is married with two sons.

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