CHEMICAL PROPERTIES OF SOIL AND GROUND WATERS

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Summary

Subsurface (soil and ground) waters are formed from atmospheric precipitation, seawater, and evaporite brines. Their chemical composition depends on the combined effect of several factors, of which the water source, the composition of enclosing rocks, climate, and biotic processes are the most important. The content of salt in subsurface waters varies between $n \cdot 10 \text{ mg/l}$ (ultrafresh waters) to $n \cdot 100 \text{ g/l}$ (concentrated brines). (The typical salt content of brackish water is 2,000 to 10,000 mg/L and for seawater over 35,000 mg/L. WHO guidelines recommend no more than 500 mg/L for drinking water, i.e. there must be a reduction in salt content of between 75 % and 99 %, depending on the raw water).

Two types of zonality are observed in the distribution of subsurface waters. Climatic zonality is typical for soil waters and waters of the upper water-bearing horizon. Partial decomposition of organic remains and removal of a major part of pedogenesis products...
from the soil profile are inherent to the natural zones with low mean annual temperatures, relatively high accumulation of biomass, and a percolative regime. This results in the formation of soil solutions with low salt content and predominance of metabolites of living organisms (carbonic and organic acids) in their composition. The content of organic acids in the soil waters of the arid zone is negligibly small because of the high degree of decomposition of organic remains. The mineralization of soil solutions depends on their bonding to ground waters. Deeply occurring ground waters hardly affect the composition of soil solutions. When the ground water table is shallow, the composition of the soil solution depends on capillary rise of water and transpiration of plants. The relatively high salt content is explained by the fact that the products of weathering, pedogenesis, and eolian transfer are not removed from the soil profile by scanty atmospheric precipitation, but they move within the profile and form various salt deposits. The distribution of salts in the soil profile depends on their solubility and direction of water flows: more soluble salts are moved further than less soluble salts.

The water composition in the upper water-bearing horizon largely depends on soil waters and is affected by the dissolution and hydrolysis of rocks in the water-bearing horizons by atmospheric precipitation with the participation of biota. The mean salt content varies from 0.25 g/l in humid conditions to 1.36 g/l in arid conditions; the reaction is near neutral.

A clear vertical hydrogeochemical zonality is manifested in the waters of deep water-bearing horizons. It is independent of climatic conditions and determined by the geological history of the Earth's crust areas. Waters of marine origin are predominant among deep-seated waters. Their salt content averages 30–35 g/kg; sodium and calcium chlorides are the predominant salts.

Bound forms of chemical elements predominate in soil and ground waters. In solutions of the upper soil horizons in the humid zone, most metals form complexes with organic acids, predominantly of a humic nature. In soil solutions of the arid zone, metals are capable of forming ionic pairs with mineral acid anions, the proportion increasing with the salt concentration. The increase in salt content of subsurface waters is determined by the increase in the content of readily soluble salts. The formation of various associates in subsurface waters favors increase in salt content in the soil solution. The ecological significance of subsurface waters is determined by their impact on plants and ground waters, including potable water.

1. Introduction

Water occurs in the Earth's crust in chemically and physically bound forms and as free moisture. The total mass of water in the Earth's crust is estimated at 0.73·10^{24} g. The estimated mass of chemically bound water is 0.42·10^{24} g; that of physically bound water is 0.11·10^{24} g, and the mass of free water is about 0.20·10^{24} g. Almost all sedimentary and crystalline rocks of the Earth's crust below the ground water table are saturated with water. Fracture water has been found in crystalline rocks even at a depth of 10 km.

Subsurface (soil and ground) waters play a vital role in the biological and geological cycles of chemical substances on Earth. The transformation of minerals from mountain
rocks and organic remains mainly proceeds through the liquid phase, as well as the formation of secondary mineral, organic, and organo-mineral products and the material composition of sedimentary rocks and soils. Water migration is the main mechanism of matter transfer in the Earth's crust. In the early twentieth century, V.I. Vernadsky called soil water the substrate of life. Soil water forms, along with living organisms, the mobile compounds of chemical elements in the surface layers of the Earth's crust. These substances ensure the unique ecological functions of soils, the most important of which is fertility.

Estimation of the state and stability of the biosphere, as well as prediction of environmental implications of human activity, is impossible without analysis of the chemical status of soil and ground waters and regularities of their formation.

The study of soil and ground waters began almost 200 years ago. Current investigations cover the following areas: (1) the theory of formation of the chemical composition of soil and ground waters; (2) the history of a specific subsurface water body—the initial source and subsequent merging of waters of different genesis; (3) the changes in water composition during interaction with solid phases and living substance; (4) the development and perfection of analytical methods for determination of material composition of subsurface waters; (5) the development of calculation methods and the physicochemical and mathematical simulation of processes in subsurface waters; (6) the changes and mechanisms of formation of subsurface water composition in different natural zones; and (7) the anthropogenic changes in the chemical status of soil and ground waters. Of practical importance are soil waters, because they are available to plants, as well as fresh subsurface waters in the upper soil horizons, because they are used as a source of water supply.

2. Approaches to the study of chemical properties of soil and ground waters

The study of chemical properties of subsurface waters is based on several theoretical approaches: (1) Soil and ground waters are components of a united natural water system, which combines all natural waters. (2) Subsurface waters are heterogeneous; they contain true solutions, suspensions, and colloids. Subsurface waters include various physical and chemical forms of elements. Water in soil exists in both bound (sorbed, film, capillary, etc.) and free states. (3) The chemical and physical properties of natural waters develop regularly, which is determined by processes composing a hierarchy and characterized by the specific interaction mechanisms among their components, the rate of processes, and the transfer range of the products formed. The stability of soil and ground water properties is related to the dynamic equilibrium of these processes. Different water kinds are related hydraulically. The chemical composition of waters is formed under the effect of precipitation–dissolution, sorption–desorption, and ion exchange processes. The distribution, migration, and accumulation of solutes in the landscape, as well as the formation of horizontal and vertical zonalities of subsurface waters, are affected by the climate, relief, vegetation, rock composition and history, and other conditions. (4) The chemical status of subsurface waters is characterized by the total content of chemical elements and the composition of their compounds. Theoretical analysis and experimental data show that most elements are present in subsurface waters in the chemically bound state.
The methods of studying soil and ground waters should provide reliable information on their properties. General requirements for methods of studying subsurface waters include accuracy, precision, and sensitivity. A list of methods widely used in study of soil and ground waters is given below. Dialysis, filtration, ultrafiltration, and centrifugation are used to separate suspensions and colloids from the truly soluble fraction. The analysis of solid residue and the measurement of solution electroconductivity are used for the determination of total salts in waters. The content of simple (unbound) ions is determined by photometric, ionometric, polarographic, and kinetic methods. The portion of bound chemical elements is determined using electrodialysis, electrophoresis, and gel filtration. Ion exchange and electrodialysis are used to determine the sign of charge of the element-containing particles. Theoretical (calculation) methods of date acquisition on the chemical composition of soil and ground waters are based on the concepts of equilibria in a heterogeneous system described by the equations of the mass action law and material balance, and thermodynamic constants or free formation energies of chemical compounds present in solutions.

3. Origin and occurrence of soil and ground waters

Subsurface waters vary according to their location in the Earth's crust, the depth and conditions of occurrence, and their chemical composition. They impregnate the soil, fill the pores of loose sedimentary rocks, and fractures in the upper crystalline basement. Subsurface waters are conventionally classified into soil and ground waters. Soil water is the part of subsurface water that impregnates the topmost Earth's crust. It is separated into a separate group because of the effect of living matter, which forms the soil (a peculiar bio-abiotic formation), in this part of the Earth's crust.

Subsurface (soil and ground) waters are formed from atmospheric precipitation, seawater, evaporite brines, and deep-seated (endogenic and regenerated) waters. Atmospheric precipitation (rains and ice water) is the main source of soil waters and ground waters in the upper water-bearing horizons. The ratio between free and bound waters varies across a wide range. Chemically bound water enters the structure of minerals and the solid phase of soils and sediments. Physically bound water includes adsorbed, film, and capillary water. The surface of soil and sediment particles retain adsorbed and film moisture by the forces of molecular attraction; this water is not subjected to the action of gravity and acts as a buffer, protecting the solid phase from external impacts. These waters are low in dissolved substances as compared to free water.

Capillary moisture constitutes the major part of the soil solution. Water in capillaries of different diameters varies in chemical composition. Soil capillary moisture is bound to ground waters and forms the capillary fringe over their level. During the evaporation of capillary water, it is regenerated due to the rise of ground water. Soil water also includes the gravitation moisture of the pore space (known as lysimetric water). This remains in the soil after rains, snow melt, or irrigation. Capillary moisture can move down the soil profile under the action of gravity to replenish ground water reserves. The amount of water in soils varies significantly, the mean value being 15 to 25% of the soil mass.
Soil water composition is affected by the type of water source, the depth of ground waters, lithology (mineralogical composition of enclosing rocks), relief (confinement of soils to automorphic or hydromorphic landscape elements), climate (evaporation-to-precipitation ratio), water regime (permeable and impermeable), air regime (intake of gases from the atmosphere, absorption of gases from soil air by the liquid soil phase and their emission, and condensation of water vapor), vegetation (consumption of water and nutrients and transpiration), consumption of substances from the soil solution, and their release by other living organisms. Physical and chemical properties of soils affect the dissolution of minerals; the decomposition of organic remains; and the formation of new mineral, organic, and organo-mineral substances in solid, liquid, and gaseous phases, as well as the biological activity of soils.

The forming conditions and chemical composition of soil waters in the humid and arid zones differ significantly, as do soil solutions in automorphic and hydromorphic landscapes within the same zone. The leading factor affecting the composition of the soil solution is the predominant percolative water regime in the humid zone, and the exudative (or periodically exudative) water regime in the arid zone. The specific character of subsurface waters in hydromorphic landscapes is determined by the interaction of soil and ground waters.

Atmospheric precipitation is a source of water in water-bearing subsoil horizons, where it penetrates from the soil. The profile of sedimentary rocks includes water-bearing horizons, which are readily penetrable for water, and waterproof layers. Within the water-bearing horizons, subsurface waters are hydraulically bound, and their movement is ordered. The movement of subsurface waters is due to (a) the force of gravity along the slope of water-bearing horizons (non-artesian ground water), (b) hydraulic pressure head from the areas of supply to the discharge areas (artesian water), and (c) rock compaction under the load of overlying strata (elision water). The displacement rate of subsurface waters in the Earth's crust decreases with depth. In deep water-bearing horizons, waters can occur without displacement over hundreds of millions of years.

In sloped beds or fractures of crystalline rocks, these waters can move to significant depths. The zone with subsurface waters of predominant atmospheric supply is usually several hundreds meters (or, rarely, a few kilometers) thick in flat landscapes. In highlands, it frequently cover the whole scorable depth. Meteogenic (caused by atmospheric precipitation) subsurface waters are almost always fresh, but their salt content can increase in the presence of readily soluble minerals in the rocks of water-bearing horizons.

Seawater entered the pores of sedimentary rocks during their formation on the bottom of a Jurassic basin. Taking into account that the major portion of sedimentary rocks in the Earth's crust is of marine genesis, this source is essential for subsurface waters. However, sedimentation waters buried in the pores do not always remain there indefinitely. During mountain formation, water-bearing horizons in uplifted areas are usually subjected to leaching by waters of atmospheric supply. Thus, sedimentation waters can be displaced and/or mixed with atmospheric waters. Nonetheless, the lower sedimentary cover on platforms is generally filled with saline subsurface waters of marine origin.
Concentrated brines are frequently observed in deep water-bearing horizons. These brines were formed during halogenesis—the formation of natural salts. Natural salts can be formed in semi-isolated lagoons, sabkhas, and lakes during the intensive evaporation of water. Evaporite lagoons periodically appearing on vast areas were an essential part of the Earth’s history. During the Miocene (25 to 6 millions years ago), a vast evaporite basin almost completely occupied the Mediterranean region. Immense volumes of concentrated brines were simultaneously accumulated in evaporite basins. These brines saturated all sediments, both formed in the basin and occurring under the basin bottom. The latter phenomenon was favored by the fact that brines are denser than less saline waters and can displace them from water-bearing horizons because of gravity. As a result, all subsalt water-bearing horizons are filled with brines in the regions where salts are present in the Earth's crust profile.

Deep-seated sources of subsurface waters are significantly more problematic. Waters of endogenic ("juvenile") origin are probably formed due to the condensation of gases evolved from magmatic melts. Volcanic eruptions are always accompanied by significant gas releases, and the appearance of endogenic subsurface waters could be expected in modern volcanism areas. However, geochemical studies, including isotopic ones, demonstrated atmospheric supply of subsurface waters in these regions, and the juvenile component was not found. "Regenerated" metamorphogenic water, which is released from the bound state upon heating of sedimentary rocks, can be another possible deep-seated source. No reliable indicators of this water have been found so far. At the same time, the presence of deep-seated metamorphogenic components in natural waters is evident in some instances, e.g. when elevated levels of carbon dioxide are found in water from deep horizons of many young folded mountains.

Human economic activity changes the reserves of subsurface waters (water withdrawal), moisture regime (irrigation), and chemical composition (application of chemicals and contamination of soils and sediments from various sources).

4. General characterization of chemical properties of soil and ground waters

Chemical elements occur in natural waters as suspensions, colloids, dissolved gases, and true solutions. The colloidal and suspended fractions are of minor importance for ground waters. The composition of the truly soluble fraction is classified in different ways—charged and uncharged particles, free particles and those associated with organic and mineral components, mono- and poly-atomic particles, and labile (capable of dissociation) and non-labile forms can be distinguished.

Along with the total content and above-mentioned parameters, the chemical composition of subsurface waters is also characterized by pH and redox potential.

Suspensions in soil and ground waters include finely dispersed particles of primary and secondary minerals, the composition of which is determined by the local lithology. The colloidal fraction is composed of polymerized macromolecules of mineral hydroxy acids (such as meta- and orthosilicic acids), hydrolysis products of metal (aluminum and iron) ions, and associates of organic acids and organo-mineral complexes.
According to the total concentration of dissolved substances (mineralization), subsurface waters are subdivided into ultrafresh (mineralization of n·10 mg/l), fresh (<1 g/l), slightly saline (1–10 g/l), and saline waters (10–50 g/l) and brines (>50 g/l). The dissolved substances are classified into macroelements, the portion of which generally exceeds 1% of total dissolved substances, and microelements. Macroelements include Na, Mg, K, Ca, Cl, S, and C. The two latter elements exist in water as oxy anions $\text{HCO}_3^-$, $\text{CO}_3^{2-}$ and $\text{SO}_4^{2-}$. Carbon is present in various organic substances and dissolved CO$_2$.

Microelements include Si, Fe, Mn, Cu, Zn, Pb, As, Se, Sr, F, Br, Li, B, P (as phosphate ion and organic compounds), and N (as NH$_4^+$, NO$_3^-$ and organic compounds).

Macroelements of subsurface waters belong to the elements that are most abundant in the Earth's crust (from 2.7% for Ca to 0.02% for Cl). At the same time, such important elements as Al, Fe, and Ti are present in waters in very low concentrations. This incomplete correspondence between the elemental compositions of rocks and waters is explained on the basis of the principle advanced by M.G. Valyashko: "The accumulation of components in natural waters is limited by the solubility of their compounds with other major components of natural waters". The limiting factor for the above elements is the low solubility of their oxides and hydroxides, the low solubility of barium sulfate for Ba, etc. Although the content of fluorine in the Earth's crust is 2.5 times higher than that of chlorine, its concentration in natural waters is lower because of the formation of the hardly soluble minerals, fluorite and fluor-apatite. The subdivision of subsurface waters into hydrochemical types is based on the predominance of certain ions.

The total salt content in water correlates with the total of the composing elements. The sodium–calcium sulfate–hydrocarbonate composition is typical for fresh waters of soils and upper water-bearing horizons, chloride or hydrocarbonate–chloride for saline waters, and sodium or calcium–sodium chloride for brines.

Only a few elements exist in natural waters as simple free ions. These are elements with small ionic radii and low positive charges (such as Li, Na, K, Rb, and Cs) and elements with relatively large ionic radii and low negative charges (F, Cl, and Br). Transitional elements occupying the place from Sc to Zn in the periodic table predominantly occur as complexes with organic and mineral ligands. Such elements as S, P, As, and Mo exist in waters as oxy anions resulting from the dissociation of the corresponding acids. Carbon occupies a special place; it enters into the composition of carbonic acid and various organic acids. The dissociation products of these acids exist in waters in both free and bound states.

The concentration and composition of soil and ground waters are controlled by a dynamic equilibrium in the water/solid precipitation–exchange complex–gas phase–living substance system. The processes of ion exchange to a greater extent affect the composition of slightly saline soil waters in the humid zone. The composition of highly saline soil waters of the arid zone and deep-seated subsurface waters is largely formed by dissolution/precipitation of salts.

Calculation methods for the determination of the total concentration of different chemical elements in waters are based on suppositions about the local chemical
equilibrium in the system, connecting substances in the solution and substances on the surface of different solid phases. The last can be presented by soil absorbing complex or mineral salts of soils and sediments. The calcium carbonate system, which includes the solid-phase CaCO$_3$, Ca$^{2+}$ ions of the exchange complex in solid soil phases, gas-phase CO$_2$, H$_2$CO$_3$ and products of its ionization, and solution Ca$^{2+}$, is of environmental importance. The interference of all components is complicated by the impact of living substance. In most cases, the calcium carbonate system determines the acid-base conditions of the soil solution.

Acid-base and redox conditions affect the course of all reactions in soil solutions. The formation of these conditions is largely related to the activity of living organisms, the water/air regime, and the gas-phase composition. Some gases arrive enter the soil air and soil solution from the atmosphere (N$_2$ and O$_2$); other gases result from the chemical decomposition of mineral compounds (CO$_2$ and H$_2$S). Living soil organisms consume oxygen for respiration and release carbon dioxide, which forms carbonic acid when dissolved in water. In addition, carbon dioxide is formed during the complete decomposition of organic remains by soil microorganisms. N$_2$, H$_2$S, CH$_4$, H$_2$, NH$_3$, and various organic acids are also microbial metabolites.

The reaction of soil waters is usually within a pH range of 3 to 8. The acidity of soil waters is mainly due to H$^+$ ions released during the ionization of carbonic and organic acids, as well as of boric, silicic, and hydrosulphuric acids, the role of which varies depending on the origin of the water. As a result of partial dissociation, these acids are capable of forming acid–base buffer systems. This permits partial neutralization of acid fallouts, which arrive to the soil with technogenic discharge. The dissolution of carbonates contributes even more to the capacity of soil waters for resisting acidification, as well as the uptake of H$^+$ ions by solid soil phases via adsorption and ion exchange. The reactions of sorption/desorption, ion exchange, and precipitation/dissolution ensure the capacity of resisting to concentration changes of various chemical elements in soil waters. They are responsible for the buffer capacity of soil solutions with respect to contaminants.

The reaction of subsurface waters is usually near neutral (pH between 6 and 8.5). Anomalously acid waters are found in specific situations of modern volcanism: in fumarole condensates and crater lakes (to pH 0) and in the oxidation zones of sulfide deposits (pH < 2). The most alkaline waters are found in alkaline rocks (to pH 12.5).

The redox potential of soil and ground waters varies between +700 and −200 mV. The redox potential of waters depends on a number of potential-determining systems. Electron transitions in the systems composed of elements with different degrees of oxidation proceed successively in accordance with the content of each component in the conjugated redox pairs of different chemical elements and their capacity for oxidizing or reducing. In the presence of sufficient amounts of iron and manganese oxides, these can operate as potential-determining systems. At the low content of other oxidized compounds, except sulfates, the redox potential can be determined by the sulfate-to-sulfite ratio. As SO$_4^{2-}$ ions are removed, H$_2$S, CH$_4$, and even H$_2$ can appear in waters (the redox potential of these waters is lower than 200 mV and can be in the range between −100 and −400 mV). All these reactions proceed with the active participation
of microorganisms.

The redox potential of waters affects the ratio between elements with different degrees of oxidation and the solubility of their compounds; e.g. the oxidized forms of Fe and Mn are less soluble and the oxidized forms of Hg, Cr, Se, Te, V, As, and Mo are more soluble than their reduced forms.

The redox potential of subsurface (soil and upper water-bearing horizon) waters in the zone of sustainable development of oxidation processes, which is depleted in organic matter, usually exceeds +200 mV and attains 450 mV on average. It predominantly depends on the amount of free oxygen, which is released during photosynthesis and is dissolved in water at 1 to 15 mg/l, and is available to participate in oxidation reactions.

Reducing conditions are generally created in deep water-bearing horizons. The reducing environment is mainly determined by the oxidation and decomposition of organic matter. The problem of the potential-determining pair for the reducing conditions in subsurface waters is far from being definitively solved. It has been shown that this is the H₂S–S⁰ pair in some cases.

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Biographical Sketches

Galina V. Motuzova graduated from the Faculty of Soil Science, Moscow State University after M.V. Lomonosov in 1962. She received her Ph. D. (1973) and Doctor of Biology (1992) in soil science and chemistry of chemical elements’ search at Moscow State University, Faculty of Soil Science. Since 1973 she has held the positions of Staff Junior, Senior Scientist and Staff Associate Professor of Soil Science, from 1995- Staff Professor Soil Science at the Faculty of Soil Science, Moscow State University after M.V. Lomonosov, Moscow, Russia. Prof. G. Motuzova is the author of more than 240 scientific publications. Her research interests are in the fields of soil science, ecology, soil chemistry, interactions of soils with pollutants and their influence on neighboring media. She is dealing now with the ability of soils to protect ground water from pollutants.

Dmitry V. Grichuk graduated from the Geological Faculty of Moscow State University after M.V. Lomonosov in 1971. He received his Ph.D. (1976) at the Geological Faculty of Moscow State University and Doctor of Geology (1998) at Vernadsky Institute of Geochemistry and Analytical Chemistry of RAS, Moscow, Russia in hydro chemical processes’ search and their modelling. 1974 he hold the positions of Staff Junior, Senior Scientist and Staff Associate Professor of Geochemistry, from 2000 – Staff Professor, Department of Geochemistry, Geological Faculty, Moscow State University. His research interests are in the fields of geochemistry of natural waters, and thermodynamic modelling of hydrothermal processes. He is the author about 130 publications. He is currently working in ecological geochemistry.