BASIC CHEMICAL PRINCIPLES OF GROUNDWATER

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Summary

Water is a highly reactive substance having a great capacity to dissolve solids, liquids and gases. Physical and chemical characteristics of natural waters depend on several factors such as the lithology of the geological strata in which groundwater is flowing (i.e. the aquifer), time of residence of water in the aquifer, and environmental conditions. Normally, a small number of substances constitute the chemical composition of water (major ions), but other ions (minor ions) can also be found in low concentrations. Other substances (pollutants) can be present in water as a consequence of pollution processes.

Evaluation and discrimination between natural and anthropogenic origin of solutes requires a multi-parametric approach in which sampling methods and chemical analysis have to be reliable enough to permit consistent data interpretation.

1. Introduction

The purpose of this chapter is to describe the geochemical properties and principles that control the behavior of dissolved constituents in the groundwater environment. The interest of this topic is not only to know the hydrogeochemical history of water but also to provide some tools to identify pollution sources.

2. Properties and structure of water

Water is a chemical compound of hydrogen and oxygen with the formula H_2O. The principal reason for the unusual properties of water can be discerned from the structure of the H_2O molecule. The two bonds between the oxygen and the hydrogens form an angle of 105º. Therefore, both hydrogens are on the same side of the molecule and that side has a net positive charge relative to the other side, giving a polar characteristic to the molecule.

Liquid water is a weak ionic compound, having the following dissociation:

$$H_2O \Leftrightarrow H^+ + OH^-$$
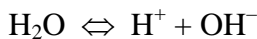
Where the symbols + and – indicate the charge of ionic species.

Three isotopes of hydrogen and three of oxygen exist in nature, but our interest will be only concerned with the isotopes that provide useful hydrological and geochemical information, such as $^2H_2^{16}O$, $H_2^{18}O$, $^3H_2^{17}O$, $H_2^{16}O$ being the most common form. All of the six isotopes are stable, and one, known as tritium (^3H), is radioactive with a half life of 12.4 years (see Table 1).

Isotope	Relative abundance (%)
^1H	99.984
^2H deuterium	0.016
^3H tritium	$0\text{-}10^{-15}$ radioactive
^{16}O oxygen	99.76
^{17}O oxygen	0.04
^{18}O oxygen	0.20
^{14}C carbon	<0.01 radioactive

Table 1. Natural isotopes in water and relative abundance

Water is a solvent for many salts, gases and some types of organic matter. Water is effective in dissolving salts because it has a very high dielectric constant and because its molecules tend to combine with ions to form hydrated ions. Species that occur in groundwater can be in an ionic or molecular form, the first being the most important. The chemical composition of natural water is derived from many sources of solutes from the atmosphere, weathering of rocks and soil, chemical reactions occurring below the land surface and effects resulting from human activity.

In general, major constituents (concentration in water greater than 5 mg/l) are commonly referred to as major ions: Na^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^-, SO_4^{2-} (table 2). The total concentration of these six major ions normally comprises more than 90% of the total dissolved solids (TDS) in the water, regardless of whether the water is dilute or has salinity greater than seawater. The TDS in groundwater is determined by weighing the solid residue obtained by evaporating a measured volume of filtered sample to dryness and it consists of inorganic constituents and a very small amount of organic matter. Organic compounds are those that have carbon and usually hydrogen and oxygen as the main elemental components in their structural framework. Their concentrations in groundwater are generally low compared to the inorganic constituents. The most abundant dissolved gases are N_2, O_2, CO_2, CH_4, H_2S and N_2O, and they can have a significant influence in the subsurface environment.

Major constituents (greater than 5mg/l)		Minor constituents* (0.001 - 5.0 mg/l)	
bicarbonate	silicon	boron	nitrate
calcium	sodium	carbonate	potassium
chloride	sulfate	fluoride	strontium
magnesium	carbonic acid	iron	

*trace constituents are those present in a concentration lower than 0.001 mg/l

Table 2. Dissolved inorganic constituents in groundwater

3. Expression of concentration units

Various terms and units are commonly employed in the expression of data obtained in the chemical analysis of water. An understanding of those more frequently used is required for the interpretation of analysis.

For many years, it has been known that most inorganic salts in solution are dissociated into ions. In accordance with the dissociation concept, water analysis is expected in concentrations of individual ions. The two most common types of concentration units are those which report weights of solute per weight of solution (ppm or parts per million) and those which report weights of solute per unit volume of solution (mg/l or milligrams per liter). If TDS is less than 5000 ppm and water density is approximately 1, then 1 ppm= 1 mg/l. When concentrations are low, it is used to express it in ppb or parts per billion, equivalent to μg/l.

Also chemical expressions of ions can be used in order to indicate the chemical behavior of dissolved material. The molality (weight expression), molarity (volume expression) or equivalents per liter (meq/l) are the most important units. One mole of substance is the equivalent of one molecular weight. Equivalents per liter, is the number of moles of solute multiplied by the valence of the solute species, in 1 liter of solution. In an analysis expressed in meq/l, unit concentrations of all ions are chemically equivalent; the total milliequivalents per liter of anions should exactly equal the total milliequivalents per liter of cations.

$$meq/l = \frac{moles\ of\ solute}{liter\ of\ solution} \qquad ppm = \frac{grams\ of\ solute}{10^6\ g\ of\ solution}$$
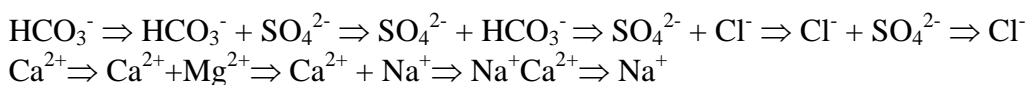
4. Groundwater chemical composition

Nearly all groundwater originates as rain or snowmelt that infiltrates through soil into flow systems in the underlying geologic materials. In recharge areas, the soil zone undergoes a net loss of mineral matter to the flowing water. As flow lines move from recharge to discharge areas, its chemistry is altered by the effects of a variety of geochemical process and due to the long residence time of groundwater in the aquifers. Groundwater chemical composition is the result of the composition of water that enters groundwater reservoirs and the reactions with minerals present in the rock that may modify the composition.

Generally, minerals are not soluble species, but their solubility may increase depending on the presence of CO_2 in water. The water which infiltrates through the soil has a capability to generate relatively large amounts of acid and to consume much or all of the available dissolved oxygen in the water that infiltrates it. Geochemically speaking, the most important acid produced in the soil zone is H_2CO_3 derived from the reaction of CO_2 and H_2O. CO_2 is generated by the decay of organic matter and respiration of plant roots.

Actually, the first hydrochemical characteristic is given to rainwater by the atmosphere where mineral particles coming from pollutant sources or marine spray in coastal areas can be dissolved. The atmosphere also supplies the oxygen which plays an important role in the soil where organic matter can be oxidized, generating CO_2.

Carbon dioxide-charged water infiltrating through the soil zone commonly encounters minerals that can be dissolved (mainly Ca^{2+}, Mg^{2+}, Na^+ and K^+) under the influence of H_2CO_3 which is consumed by the mineral-water reactions. As H_2CO_3 is consumed in the soil zone, oxidation of organic matter and root respiration is a source of replenishment of CO_2 to the soil air. As new water from recharge events passes through the soil, biochemical and hydrochemical processes in the soil are therefore capable of providing a continuing supply of acidity to promote mineral-water reactions. The reaction of free oxygen with reduced iron minerals such as pyrite (FeS_2) is another source of acidity. The soil zone can therefore be thought of as an acid pump operating in the very thin but extensive veneer of organic-rich material that covers most of the earth's surface.

As groundwater moves along its flowpaths in the saturated zone, increases of TDS and most of the major ions normally occur. It has been observed that shallow groundwater in recharge areas is lower in dissolved solids that water in shallow zones in the discharge areas. Groundwater tends chemically toward the composition of seawater

$HCO_3^- \Rightarrow HCO_3^- + SO_4^{2-} \Rightarrow SO_4^{2-} + HCO_3^- \Rightarrow SO_4^{2-} + Cl^- \Rightarrow Cl^- + SO_4^{2-} \Rightarrow Cl^-$
$Ca^{2+} \Rightarrow Ca^{2+} + Mg^{2+} \Rightarrow Ca^{2+} + Na^+ \Rightarrow Na^+ Ca^{2+} \Rightarrow Na^+$

where $\Rightarrow$ represents increasing age (residence time).

From a geochemical point of view, the evolution sequences described above can be explained in terms of two main variables: mineral availability and mineral solubility.

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Bibliography

Appelo, C.A.J. and Postma, D. (1993). *Geochemistry, groundwater and pollution*. 536 pp. Rotterdam. Balkema. [This book offers a wide treatment of hydrochemistry]

Domenico, P.A. and Schwartz, F.W. (1998). *Physical and chemical hydrogeology*. 506 pp. New York. John Wiley and Sons, Inc. [This book contains some hydrochemical information of great interest]

Drever, J.I. (1988). *The geochemistry of natural waters*. 437 pp. New Jersey. Prentice Hall, Inc. [The behavior of organic compounds is clearly treated]

Freeze, R. A. and Cherry, J.A. (1979). *Groundwater*. 604 pp. New Jersey. Prentice Hall, Inc. [This classic book provides a comprehensible approach to hydrochemistry]

Kehew, A.E. (2001). *Applied Chemical Hydrogeology*. 368 pp. New Yersey. Prentice Hall, Inc. [The chemical background in this book is very comprehensible and provides many cases studies]

Lloyd, J.W. and Heathcote, J.A. (1985). *Natural inorganic hydrochemistry in relation to groundwater*. 296 pp. Oxford. Oxford Science Pub. [This is a good book to start the study of water chemistry and data treatment]

Mazor, E. (1997). *Chemical and isotopic groundwater hydrology*. 413 pp. New York. Marcel Dekker, Inc. [This is an applied approach to hydrochemical studies]

Morell, I., Giménez, E., Esteller, M.V. (1996). Application of the Principal Components Analysis to the study of salinization of the Castellon Plain (Spain). *The Science of the Total Environment* 177: 161-171. 1996 [This work provides extensive examples of hydrochemical graphics]

Biographical Sketches

Ignacio Morell is a Professor of Hydrogeochemistry and Hydric Resources at University Jaume I of Castellón, Spain. He is the Leader of the Hydric Resources Research Group whose main activity consists of the study of pollution of groundwater mechanisms, with emphasis on salinization processes and the fate of agrochemicals in the environment. His work has been carried out in several European and American countries. He is the author of more than 100 scientific papers

Lucila Candela is a Professor in the Department of Geotechnical Engineering and Geosciece at the Technical University of Catalonia (Barcelona, Spain). She has over twenty years of research experience and expertise in groundwater hydrology. Her research concerns the nature and fate of contaminants in the subsurface (with particular interest in heavy metals and pesticides), laboratory process studies on contaminant transport, geostatistical applications to groundwater hydrology, and agricultural threats to groundwater. During her career she has published around 150 papers and books and has received national and international funding from a wide variety of industrial, regulatory and governmental bodies, and has participated as expert in numerous international expert panels.