BASIC CHEMICAL PRINCIPLES OF GROUNDWATER

L. Candela  
*Department of Geotechnical Engineering and Geo-Sciences. Technological University of Catalonia. Spain*

I. Morell  
*Department of Experimental Sciences. University Jaume I. Castellón. Spain.*

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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 \( \text{H}_2\text{O} \). The principal reason for the unusual properties of water can be discerned from the structure of the \( \text{H}_2\text{O} \) molecule. The two bonds between the oxygen and the hydrogens form an angle of 105°. 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:

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-
\]

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 \( ^2\text{H}_2^{16}\text{O} \), \( ^2\text{H}_2^{18}\text{O} \), \( ^3\text{H}_2^{17}\text{O} \), \( ^3\text{H}_2^{18}\text{O} \) being the most common form. All of the six isotopes are stable, and one, known as tritium (\( ^3\text{H} \)), is radioactive with a half life of 12.4 years (see Table 1).

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Relative abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\text{H})</td>
<td>99.984</td>
</tr>
<tr>
<td>(^2\text{H}) deuterium</td>
<td>0.016</td>
</tr>
<tr>
<td>(^3\text{H}) tritium</td>
<td>0-10(^{-15}) radioactive</td>
</tr>
<tr>
<td>(^{16}\text{O}) oxygen</td>
<td>99.76</td>
</tr>
<tr>
<td>(^{17}\text{O}) oxygen</td>
<td>0.04</td>
</tr>
<tr>
<td>(^{18}\text{O}) oxygen</td>
<td>0.20</td>
</tr>
<tr>
<td>(^{14}\text{C}) carbon</td>
<td>&lt;0.01 radioactive</td>
</tr>
</tbody>
</table>

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: $\text{Na}^+$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{Cl}^-$, $\text{HCO}_3^-$, $\text{SO}_4^{2-}$ (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 $\text{N}_2$, $\text{O}_2$, $\text{CO}_2$, $\text{CH}_4$, $\text{H}_2\text{S}$ and $\text{N}_2\text{O}$, and they can have a significant influence in the subsurface environment.

<table>
<thead>
<tr>
<th>Major constituents (greater than 5mg/l)</th>
<th>Minor constituents* (0.001 - 5.0 mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bicarbonate</td>
<td>silicon</td>
</tr>
<tr>
<td>calcium</td>
<td>carbonate</td>
</tr>
<tr>
<td>chloride</td>
<td>sulfate</td>
</tr>
<tr>
<td>magnesium</td>
<td>caronic acid</td>
</tr>
<tr>
<td>calcium</td>
<td>carbonate</td>
</tr>
<tr>
<td>chloride</td>
<td>fluoride</td>
</tr>
<tr>
<td>magnesium</td>
<td>iron</td>
</tr>
</tbody>
</table>

*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 $\mu$g/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.
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 CO₂ 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 H₂CO₃ derived from the reaction of CO₂ and H₂O. CO₂ 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 CO₂.

Carbon dioxide-charged water infiltrating through the soil zone commonly encounters minerals that can be dissolved (mainly Ca²⁺, Mg²⁺, Na⁺ and K⁺) under the influence of H₂CO₃ which is consumed by the mineral-water reactions. As H₂CO₃ is consumed in the soil zone, oxidation of organic matter and root respiration is a source of replenishment of CO₂ 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 (FeS₂) 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

\[ \text{HCO}_3^- \Rightarrow \text{HCO}_3^- + \text{SO}_4^{2-} \Rightarrow \text{SO}_4^{2-} + \text{Cl}^- \Rightarrow \text{Cl}^- + \text{SO}_4^{2-} \Rightarrow \text{Cl}^- \]
\[ \text{Ca}^2+ + \text{Mg}^{2+} \Rightarrow \text{Ca}^2+ + \text{Na}^+ \Rightarrow \text{Na}^+ \text{Ca}^2+ \Rightarrow \text{Na}^+ \]

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.

Bibliography


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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 Geoscience 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.