

## GLOBAL VARIATIONS IN THE CHEMISTRY OF GROUND WATER

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### Summary

The scientific and technological know-how to protect ground water is pretty universal and accessible to all those in charge of environmental management programs anywhere. What lacks in many cases is the political resolve to create the institutional and juridical framework to promote and implement effective ground-water quality management. Cost considerations often pose intractable obstacles to protect and remediate ground water. Time will tell how nations ultimately decide to reconcile their cultural and economic practices with the ever-increasing water needs of their citizens.

### 1. Introduction

Ground water provides about one half of all the freshwater used worldwide (Shiklomanov, 1996). This puts aquifers on an equal footing with rivers and lakes insofar as human water supply is concerned. It is no surprise then the widespread interest in the management of ground water (Loaiciga et al., 2000), in its natural availability (Zektser and Loaiciga, 1993; Vörösmarty et al., 2000), and in its physical, chemical, and biological properties (Freeze and Cherry, 1979; Matthes, 1982; Hem,

1985; Drever, 1988; Stumm and Morgan, 1996). The physical, chemical, and biological properties of water are generically referred to as water quality.

Water quality is the subject matter of this article. It is a vast subject, and, thus, the author presents herein a brief summary that condenses our current state of knowledge. In doing so, several objectives guided the preparation of this article. First, we strove to explain the pathways that result in the main natural chemical constituents found in ground water. Those pathways are primarily controlled by the geologic environment. Thus, an understanding of the natural chemical composition of ground water (i.e., not influenced by humans) relies on our knowledge of local and regional geochemical characteristics, and it is independent of political geographical units. The natural chemical composition of ground waters may, and does, pose concerns for human and crop health, and for this reason it is of paramount concern in the use of ground water as a supply source. The second guiding objective was to highlight the role of humans in altering ground water quality. To this end, the main anthropogenic (i.e., human-induced) pollutants that threaten and degrade ground water quality were identified. Unlike the natural constituents of ground water, anthropogenic pollutants are strongly associated with geographical political units, and they are the product of economic practices, geopolitical activities, and environmental protection regulations. The last guiding objective was to review policy options for the protection of ground-water quality. In this regard, the data on ground-water quality on a worldwide basis are sparse, specially in relation to anthropogenic pollutants. Reasons for the paucity of ground-water quality data are the lack of a centralized repository for such data, and the lack of consistent protocols and procedures for water-quality measurements that would ensure even quality assurance and data reliability across the myriad of data sources. In synthesis, this article was written for the purpose of providing the reader with answers to the questions: why is ground-water quality the way it is? how do humans impact ground-water quality? and what can be done to protect it?

## 2. The origin of common natural constituents in ground water

### 2.1 Classification of ground-water chemical constituents based on typical concentrations.

There is great geographical variability in the chemical composition of ground water. Such variability is a function of (1) the geologic substrate in which ground water is found, (2) the residence time of water in the subsurface, and (3) surface water/ground-water interactions. Table 1 lists the most common ground-water constituents and their typical concentration ranges.

Constituent name	Formula	Typical concentration range (mg l <sup>-1</sup> )
Major constituents		
Bicarbonate	HCO <sub>3</sub> <sup>-</sup>	> 5
Calcium	Ca <sup>2+</sup>	> 5
Chloride	Cl <sup>-</sup>	> 5
Magnesium	Mg <sup>2+</sup>	> 5

Silicon	Si <sup>4+</sup> (as H <sub>4</sub> SiO <sub>4</sub> or SiO <sub>2</sub> )	> 5
Sodium	Na <sup>+</sup>	> 5
Sulfate	SO <sub>4</sub> <sup>2-</sup>	> 5
Minor constituents		
Boron	B (various compounds)	0.01 to 10
Carbonate	CO <sub>3</sub> <sup>2-</sup>	0.01 to 10
Dissolved organic carbon	DOC (humic, fulvic acids)	0.01 to 10
Fluoride	Fl <sup>-</sup>	0.01 to 10
Iron	Fe <sup>2+</sup> , Fe <sup>3+</sup>	0.01 to 10
Nitrate	NO <sub>3</sub> <sup>-</sup>	0.01 to 10
Potassium	K <sup>+</sup>	0.01 to 10
Strontium	Si <sup>2+</sup>	0.01 to 10
Trace constituents		
Aluminum	Al <sup>3+</sup>	< 0.1
Arsenic	As <sup>+3</sup> , As <sup>5+</sup>	< 0.1
Cadmium	Cd <sup>2+</sup>	< 0.1
Lead	Pb <sup>2+</sup>	< 0.1
Lithium	Li <sup>+</sup>	< 0.1
Mercury	Hg	< 0.1
Radium	<sup>226</sup> Ra (radioactive isotope)	< 0.1
Selenium	Se	< 0.1
Uranium	<sup>238</sup> U (radioactive isotope)	< 0.1
Zinc	Zn <sup>2+</sup>	< 0.1

Table 1. Selected ground water constituents and typical concentration ranges.

The charges of the constituents shown in Table 1 are those most typically associated with the dissolved form of the elements in ground water. It is seen also that there is overlap in the typical concentration ranges listed in Table 1. This is testimony of the inherent variability in their concentrations from one location to another.

Many authors classify ground waters based not on particular constituents, but, rather, on the aggregate concentration of all dissolved substances, called total dissolved solids (TDS). Table 2 shows a classification of ground water based on its TDS content. TDS is a widely used water quality parameter.

## 2.2 Gases in ground water.

Various gases are found dissolved in ground water. A few are listed in Table 3. Table 3 shows the solubilities of several gases when their partial pressure is 1013.24 mbar (1 atmosphere) and the water temperature is 0 °C (273.15 °K). The solubilities are expressed in mg of dissolved gas per kg of pure water. These theoretical solubilities are not achievable in ground water because the partial

TDS (in mg l <sup>-1</sup> )	Category
0 - 10 <sup>3</sup>	Fresh water
10 <sup>3</sup> - 10 <sup>4</sup>	Brackish water
10 <sup>4</sup> - 10 <sup>5</sup>	Saline water
> 10 <sup>5</sup>	Brine water

Table 2. Classification of ground water based on its total dissolved solids (TDS).

pressures of the gases in air differ among themselves and are a fraction of one atmosphere. In addition, most ground waters are found at temperatures larger than 0 °C and other constituents are dissolved in ground water also. Gas solubility in ground water decreases with increasing water temperature and with increasing concentrations of solutes. The latter three factors, i.e., partial pressure of a gas, water temperature, and solutes militate to render actual gas solubilities that are much lower than those reported in Table 3. For example, the solubility of oxygen in ground water at sea level does not exceed 13 mg l<sup>-1</sup> under most field conditions. In ground water not in contact with air (i.e., closed ground-water systems), the concentrations of gases such as oxygen and carbon dioxide may be negligible. Other gases are produced under anaerobic conditions in ground-water systems. Examples are methane and hydrogen sulfide. The theoretical solubilities in Table 3 are provided as a means of comparison among gases under identical thermodynamic conditions. The estimation of the solubility of a gas in ground water in contact with air is approximated using Henry’s law, which is written as  $C = K_H P$ . C is the (equilibrium) concentration of the gas dissolved in groundwater,  $K_H$  is Henry’s constant, and P is the partial pressure of the gas in air. Henry’s constant varies with the type of gas, and with the temperature and ionic strength of groundwater. Henry’s constants for various gases (air, carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), hydrogen (H<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S), methane (CH<sub>4</sub>), nitrogen (N<sub>2</sub>), and oxygen (O<sub>2</sub>)) are tabulated in Tchobanoglous and Schroeder (1987) for dilute ground water whose temperature ranges from 0 to 50 °C.

Gas	Formula	Theoretical solubility (mg kg <sup>-1</sup> ) <sup>A</sup>
Ammonia	NH <sub>3</sub>	1000
Carbon dioxide	CO <sub>2</sub>	3350
Hydrogen sulfide	H <sub>2</sub> S	7100
Methane	CH <sub>4</sub>	39.6
Nitrogen	N <sub>2</sub>	28.8
Nitrous oxide	N <sub>2</sub> O	not available
Oxygen	O <sub>2</sub>	69.5
Radon	<sup>222</sup> Rn (radioactive gas)	not available

<sup>A</sup> The theoretical solubility is expressed in mg of dissolved gas per kg of pure water at a water temperature of 0 °C (273.15 °K) and a partial pressure of the gas equal to 1013.24 mbar (1 atmosphere). Theoretical solubilities obtained from Matthes (1982).

Table 3. Selected gases in ground water and their theoretical solubilities.

### 2.3 Microbes in ground water.

Data on microbial pathogens in ground water systems are rare. Of particular concern in this regard is biologically contaminated surface water that percolates to shallow unconfined aquifers. Leachate from septic wells, dry wells, and seepage in contaminated streams and lakes are the principal sources of microbial pathogens to ground water systems. Microbial pathogens of concern are classified as bacterial, viral, and protozoan. Many of the involved species or pathogenic strains cause acute

intestinal disease in humans (e.g., gastroenteritis) and other debilitating symptoms that are potentially lethal and/or handicapping. Table 4 provides a summary of selected pathogenic taxa and related illnesses.

Little is known about the survivability, fate, and transport of microbial pathogens in ground water. Many authors (Bower, 1978) have contended that the soil environment deprives pathogens from hosts and exposes them to an adverse environment that effectively eliminates them within hours. Thus, soils and aquifers have been thought as attenuating media with respect to microbes. This hypothesis may not be universally valid. Some pathogens can remain viable during sufficiently long-periods of time in hostile environments so as to constitute a threat to wells and springs. Examples are the protozoan *Cryptosporidium* and facultative anaerobic species (i.e., which thrive in oxygenated and anoxic waters) in the Enterobacteriaceae, Micrococcaceae, and Streptococcaceae families of bacteria. The genus *Cryptosporidium* includes species that can remain viable in a hardy cyst form. Well-known indicator microorganisms in the Streptococcaceae and Enterobacteriaceae families are enterococci and *Escherichia coli*, respectively, both of which are facultative anaerobic.

Pathogenic taxa	Disease
Bacterial	
Campylobacter spp.	Gastroenteritis
Escherichia coli	Gastroenteritis, bacteremia
Leptospira spp.	Leptospirosis
Pasteurella spp.	Turalemia
Salmonella spp.	Salmonellosis
Salmonella typhosa	Typhoid fever
Vibrio cholera	Cholera
Viral	
Hepatitis A virus	Hepatitis A
Poliovirus	Polio
Coxsackie A and B, Norwalk virus, parvovirus	Gastroenteritis
Protozoan	
Entamoeba spp.	Amebiasis
Giardia lamblia	Giardiasis
Cryptosporidium spp.	Gastroenteritis

Table 4. Selected pathogenic taxa and related illnesses in ground water.

#### 2.4 Sources and pathways of chemical constituents in ground water.

There are multiple biochemical processes or pathways that yield common dissolved constituent in ground water. Next, a few examples of reactions leading to common anions, cations, elements and gases in ground water are presented.

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