

# Natural Variations in the Composition of Groundwater

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## Abstract

It is commonly believed that the composition of groundwater does not change naturally. So if a change is recognized through taste and/or odor, many may think that something bad has happened. Perhaps the aquifer has become contaminated, or something is wrong with the well. However, a common cause of changes in water quality is through natural variations within the aquifer.

What gives groundwater its taste is the amount and type of dissolved minerals within it. Pure water, i.e., water having no dissolved minerals, doesn't occur naturally. Factors that control the dissolved minerals in groundwater include (1) the types of minerals that make up the aquifer, (2) the length of time that the water is in contact with the minerals, and (3) the chemical state of the groundwater.

Virtually all groundwater comes from precipitation that soaks into the soil and passes down to the aquifer. Rainwater has a slightly acidic pH, therefore it tends to dissolve solid minerals in the soil and in the aquifer. Different rocks, e.g., sandstone, limestone and basalt, all have different minerals; therefore, groundwater in contact with these materials will have different compositions (factor [1] above). Some of the constituents found in groundwater, however, are not abundant in common rocks and minerals, for example, chloride (Cl) and sulfate (SO<sub>4</sub>). The probable source for these chemicals is the infiltrating precipitation.

Factor (2) above is called the residence time of the groundwater in the aquifer. The longer the groundwater is in contact with the minerals, the greater the extent of its reaction with those minerals and the higher will be the content of dissolved minerals. The chemical state of groundwater (factor [3] above) is usually defined in terms of pH, temperature and oxidation-reduction potential. These parameters control and are influenced by chemical reactions. As temperatures change seasonally, as the water table rises and falls, or as recharge rates vary, the chemical state will change and, as a result, so will the composition of groundwater.

## Introduction

If you have a groundwater source for drinking water, you've probably heard or asked one or both of the following questions: "Why does our well water taste different from that of the people across the street?" or "How come our water tastes different than it did a few months ago?" Most people don't pay much attention to their drinking water quality until it changes. Maybe it is a sudden rotten egg smell ( $H_2S$ ), discolored water or perhaps a musty odor, but it is definitely different than it used to be.

There is a common misconception that the composition of groundwater does not change naturally. So, if it does change, many think that it must mean that something bad has happened. Perhaps the aquifer has become contaminated or something is wrong with the well. However, a common cause of changes in water quality is through natural variations within the aquifer. It is important that we understand these natural variations so that we can properly ascertain whether an actual problem exists.

## Total dissolved solids in groundwater

Groundwater tastes different in different places or at different times of the year for several reasons. In exploring those reasons, we'll first consider why groundwater from one well may be different from another well, even one that is close by.

What gives groundwater its taste is the amount and type of dissolved minerals within it. We've all seen the ads extolling "pure" water. But pure water, i.e., water having no dissolved minerals, doesn't occur naturally, and if it did, it would have no taste. So it is not pure water people want, it is water that tastes good and is safe to drink.

The amount and type of dissolved minerals in water is what gives waters their individual taste. Factors that control the dissolved minerals in groundwater include (1) the types of minerals that make up the aquifer, (2) the length of time that the water is in contact with the minerals, and (3) the chemical state of the groundwater. Below, we'll concentrate on factors (1) and (2), then we'll discuss the chemical state.

**Differences between wells.** Virtually all groundwater comes from precipitation that soaks into the soil and passes down to the aquifer. Within the aquifer, groundwater moves not as an underground stream, but rather it seeps between and around individual soil and rock particles. Rainwater has a slightly acidic pH, therefore it tends to dissolve solid minerals in the soil and in the aquifer. Sandstone, limestone and

basalt all have different minerals. Therefore, it is logical to expect groundwater in contact with these different geologic materials to have different compositions (factor [1] above) and therefore different tastes.

Factor (2) above is called the residence time of the groundwater in the aquifer. The longer the groundwater is in contact with the minerals, the greater the extent of its reaction with those minerals and the higher will be the content of dissolved minerals.

Table 1 illustrates typical natural water compositions, from rainwater to seawater, groundwater in different aquifers, to groundwater that has been in contact with the aquifer for different periods of time.

It is clear, then, why groundwater from different wells may taste different. The wells may be in different geologic units or of significantly different depths. Groundwater at greater depths (residence time from 10s to 1000s of years) usually has been in contact with the aquifer for much longer than shallow groundwater (residence time from months to 10s of years) (Heath, 1989). A check of the well reports (well logs) for the wells in question may help determine which of the above reasons may apply.

Some of the constituents found in groundwater, however, are not abundant in common rocks and minerals, for example, chloride (Cl) and sulfate (SO<sub>4</sub>). Given that they are found in almost all natural waters, including groundwater, where do these chemicals come from? The probable source for these chemicals is rainwater. Although not in high concentrations of rainwater, particularly inland from the ocean, Cl and SO<sub>4</sub> are found in virtually all precipitation (analyses 1 and 2, table 1). Because neither Cl nor SO<sub>4</sub> take part in typical biological or chemical reactions like other chemicals, they tend to concentrate in shallow groundwater over time.

	1	2	3	4	5	6	7	8
Calcium	0.8	0.65	241	400	144	6.5	3.11	4540
Magnesium	1.2	0.14	7200	1350	55	1.1	0.7	160
Sodium	9.4	0.56	83,600	10,500	~27	~37	3.03	2740
Potassium	-	0.11	4070	380	~2	~3	1.09	32.1
Bicarbonate	4	-	251	28	622	77	20	55
Sulfate	7.6	2.2	16,400	185	60	15	1.0	1
Chloride	17	0.57	140,000	19,000	53	17	0.5	12,600
Silica	0.3	-	48	3	22	103	16.4	8.5
TDS	38	4.7	254,000	35,000	670	222	36	20,338
pH	5.5	-	7.4	-	-	6.7	6.2	6.5

Table 1. Examples of the composition of natural water from a variety of locations and environments (all concentrations in milligrams/liter). TDS is total dissolved solids. A dash (-) indicates that the component was not detected or the water was not analyzed for this constituent. A tilde (~) indicates that the analysis is approximate only.

Key to Analyses: (1) Rainwater from Menlo Park, California; (2) Average rainwater from sites in North Carolina and Virginia; (3) Great Salt Lake, Utah; (4) Average seawater; (5) Groundwater from limestone of the Supai Formation, Grand Canyon; (6) Groundwater from volcanic rocks, New Mexico; (7) Groundwater from a spring, Sierra Nevada Mountains: short residence time; (8) Groundwater from metamorphic rocks in Canada: long-residence time.

Sources of Analyses: Analyses 3, and 7 (Drever, 1982); Analyses 1, 2, 4, 5 and 6 (Hem, J.D., 1985); Analysis 8 (Frape, S.K., Fritz, P., and McNutt, R.H., 1984.)

**Compositional variations with time.** Seasonal changes produce the most discomfort among consumers, primarily because the aesthetic quality of the water has changed from what they are used to. Table 2 lists the more common water quality “symptoms” and their causes. It is interesting to note that the water quality symptoms that are most noticeable by the public are the result of fairly innocuous constituents, i.e., ones that are not particularly harmful to health, while constituents that may cause harm are often not readily detected by the senses.

Characteristics or Symptoms	Cause(s)
Hardness: Low suds production with soap, mineral scale developed in water heater and plumbing	High concentrations of calcium and magnesium
Color: Water has a color other than clear	Red/Brown: iron Black: manganese or organic matter Yellow: dissolved organic matter such as tannins
Taste: Metallic or mineral taste	Metallic: dissolved metals such as iron and manganese Mineral taste: high concentration of common minerals such as sodium, chloride, sulfate, calcium, etc.
Odor: Musty or rotten egg smell	Musty: algae or bacterial growth in pipes or well Rotten egg: hydrogen sulfide
Appearance: Cloudy with or without color	Suspended mineral matter or microorganisms

Table 2. Natural substances that may reduce the aesthetic quality of groundwater.

### Chemical state of groundwater

Much of the natural and seasonal water quality variations we observe are the result of small but significant changes in the chemical state of groundwater. The chemical state of groundwater is generally defined in terms of three parameters: the temperature, pH, and oxidation-reduction potential (redox potential). These factors are often influenced by chemical reactions between the groundwater and aquifer materials or mixing with different waters, and these factors in turn control the chemical composition of groundwater. For example, the total dissolved solids (TDS) in groundwater, largely derived from aquifer minerals that dissolve in groundwater, will change significantly as a function of temperature and pH.

**Temperature.** At any given temperature, there is a specific concentration of a dissolved mineral's constituents in the groundwater that is in contact with that mineral. The actual concentration is temperature dependent, e.g., at higher temperatures, groundwater can dissolve more of the mineral. Even changes in groundwater

temperature of only 5 to 10 ° C can cause detectable changes in TDS. To some individuals, an increase in the temperature of their drinking water alone can be perceived as a different, and generally less palatable, taste.

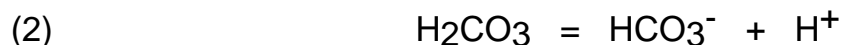
For groundwater deeper than 50 to 75 feet, seasonal changes are generally less than one degree (Heath, 1989) and temperature variations do not play a significant role in groundwater composition. For shallow groundwater, larger seasonal variations, related to warming of or cooling at the surface are common, and may be on the order of 5 to 10 degrees or more. Another source of temperature change in shallow groundwater, and occasionally deeper water, is the introduction of water from the surface during high-recharge time periods. For shallow groundwater, seasonal temperature-driven fluctuations in groundwater TDS may occur.

**The natural pH of groundwater.** The pH is a measure of the acidity of groundwater: the lower the pH, the more acidic is the water. At the typical temperature of groundwater, a pH of 7 is considered neutral. Therefore, a pH less than 7 is acidic and a pH greater than 7 means the water is alkaline. The pH is actually a measure of the hydrogen ion (H<sup>+</sup>) availability (activity). The hydrogen ion is very small and can enter and disrupt mineral structures so that they contribute dissolved constituents to groundwater. Consequently, the greater the H<sup>+</sup> availability (i.e., the lower the pH) the higher the TDS in the water.

Natural rainwater is slightly acidic (Krauskopf, 1994) because it combines with carbon dioxide (CO<sub>2</sub>) in the atmosphere, forming carbonic acid (H<sub>2</sub>CO<sub>3</sub>) according to reaction (1):



Some of the carbonic acid in the rainwater disassociates or breaks down according to reaction (2), producing bicarbonate (HCO<sub>3</sub><sup>-</sup>) and H<sup>+</sup>.



The hydrogen ion produced by reaction (2) lowers the pH of rainwater. How far it lowers it from the neutral value of 7 depends on how much carbonic acid is in the water, which in turn depends on how much carbon dioxide is in the atmosphere. The more CO<sub>2</sub> present, the more acidic is the water. For the amount of CO<sub>2</sub> in the Earth's atmosphere (~0.3%), the pH of rainwater is about 5.7.

**Oxidizing-reducing (redox) reactions.** Oxidizing-reducing reactions result in a change of the charge of an ion as it gains or loses an electron. These reactions are almost always facilitated by bacteria that can gain energy from the reactions. The solubility of some elements in water depends on whether they are oxidized or reduced. The redox potential can be correlated with the amount of dissolved oxygen. As the oxygen content drops, the environment becomes more reducing (the redox potential drops). The natural environment, therefore, may control in which state the element occurs. For example, iron (Fe) can exist in either as reduced (Fe<sup>2+</sup>) or oxidized (Fe<sup>3+</sup>) iron (note the different charge).

Iron is more soluble in the reduced state than it is in the oxidized state, where it often forms an iron oxide mineral (Fe<sub>2</sub>O<sub>3</sub>) or iron hydroxide mineral (Fe[OH]<sub>3</sub>). Therefore, if the local environment produces the reduced iron form, the water will have higher concentrations of iron.

The most common cause of reducing reactions is organic matter, either in solid form or as dissolved organic carbon (DOC). The oxidation of an organic molecule (contributing electrons) can result in iron, in a solid iron oxide mineral (Fe<sub>2</sub>O<sub>3</sub>), being dissolved into the water as reduced iron (Fe<sup>2+</sup>) (accepting electrons). Manganese (Mn) behaves in a similar manner to iron.

Typically in groundwater, sulfur exists as sulfate (SO<sub>4</sub><sup>2-</sup>). In this form, it generally has little impact on the potability of groundwater (an exception is at much higher concentrations, i.e., at 250 mg/L, sulfate may have a laxative effect on some individuals). If, however, the sulfur is in the form of hydrogen sulfide (H<sub>2</sub>S), the distinct and unpleasant rotten egg odor occurs even at concentrations below 10 mg/L. Redox reactions can change sulfate to hydrogen sulfide in oxygen-poor environments in the presence of organic matter or DOC.



It is important to note that oxidizing and reducing reactions must take place simultaneously; i.e., for a reducing reaction (accepting electrons) to occur, an oxidizing reaction (giving up electrons) must also take place. Also, not all molecules are oxidized or reduced at the same redox potential. With decreasing redox potential, the following reducing reactions will occur: nitrate to nitrogen gas,  $\text{Fe}^{3+}$  (insoluble) to  $\text{Fe}^{2+}$  (soluble), sulfate to hydrogen sulfide and, at very low redox potential, methane formation (Drever, 1982).

### **Changing the chemical state of groundwater**

It is common to observe seasonal variations in dissolved iron or in detectable hydrogen sulfide. From what has been said above, these changes may reflect variations in the chemical state of groundwater. So how might changes in the chemical state of groundwater occur?

If we focus on iron and sulfur, we note that the reduction in aesthetic water quality results from these constituents being in their reduced form ( $\text{Fe}^{2+}$  and  $\text{H}_2\text{S}$ ). At a given temperature, changing from the oxidized form ( $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$ ) to the reduced form requires a decrease in redox potential (or dissolved oxygen) or a decrease in pH (becoming more acidic), or both.

There are a number of ways in which this change in chemical state of the groundwater could occur. We will consider just two.

1. Consider an aquifer in which groundwater is in a mildly oxidized state and a near neutral pH. Under such conditions, the Fe will likely be  $\text{Fe}^{3+}$  and tied up in solid phases and the sulfur will occur as sulfate. If the soil zone above the aquifer contains appreciable organic carbon, the soil moisture will likely have elevated DOC. Further, under conditions of high biologic activity, elevated  $\text{CO}_2$  will be given off during respiration, leading to a decrease in the pH. If, during the onset of recharge, this lower pH, high DOC water is flushed to the aquifer, there may be a shift in the pH and redox conditions such that Fe is dissolved and, if the redox potential become low enough, sulfate is transformed to hydrogen sulfide. With time this situation will return to the normal state of groundwater in the aquifer. This scenario is more likely to occur during the winter and in a shallow aquifer that is screened at shallow depths.

2. Consider an aquifer containing groundwater that is naturally reducing, i.e., containing dissolved  $\text{Fe}^{2+}$  and  $\text{H}_2\text{S}$ . Seasonal recharge may result in a situation where the groundwater in the aquifer is layered, with oxygenated groundwater occurring above the reduced groundwater below. After recharge occurs, routine pumping may result in the bulk of the water coming from the upper oxygenated groundwater. As pumping continues throughout the summer, the shallow oxygenated water may become depleted and more and more of the water comes from the deeper reduced groundwater. As the deeper groundwater dominates, the elevated Fe and  $\text{H}_2\text{S}$  may become noticeable. This condition may be reversed when recharge occurs (and pumping is reduced) during the winter season. This scenario may be more likely in a well in late summer that is open hole or is screened throughout.

## Summary

Groundwater may vary in composition from one well to another because of the respective groundwaters being in contact with different aquifer materials or having been in contact with the aquifer minerals for significantly different periods of time.

Seasonal variations in the composition of groundwater from a single well generally results in a change in the chemical state of groundwater, i.e., temperature, pH and redox potential. These parameters influence the amount and character of the dissolved constituents and therefore may produce changes in the taste, odor, appearance, etc. Possible causes of changes in the chemical state include different water levels and annual recharge events.

The variations described above are the result of natural causes. It is important to recognize this so as not to attribute these changes in water potability to anthropogenic causes.

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