# Wells and Words

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**Some simple and helpful observations on basic inorganic groundwater chemistry**

Review of perhaps hundreds or even thousands of inorganic groundwater quality analyses reported by many different laboratories and tabulated by consultants have provided certain easily observable and important relationships among the various analytes and physical properties. To assist in these observations, rather than simply list the analytes and physical properties in alphabetical order, it is far more useful and revealing to list the results by meaningful and associated groups. One such tabulation is shown on Table 1, which lists the measured constituents by the five categories: major cations, major anions, minor ions, physical properties, and trace ions.

1. Major cations and major anions in groundwater are detected in concentrations ranging generally from 1 to 1,000 milligrams per liter (mg/L). The major cations include calcium, magnesium, sodium, and potassium; the major anions include bicarbonate, chloride, and sulfate. The major cations represent 11.4 percent (%) by mass of the elements in the earths crust, while oxygen (46.6%), silicon (27.7%), alumina (8.1%), and iron (5.0%) make-up nearly the rest.

2. The ionic balance or reaction error (RE) between the major cations and anions should be less than 5%. All aqueous solutions must be stable and ionically balanced. The RE is defined as the difference between the total cations and total anions divided by the sum of the ions in milliequivalents per liter (meq/L). If the RE is greater than 5% then the analytical analysis for the individual ions may be in error or an important constituent of the solution may not have been included in the RE calculation.

3. The stoichiometric or chemical equilibrium equation between bicarbonate and carbonate is $HCO_3^- = CO_3^{2-} + H^+$. Because bicarbonate and carbonate are on opposite sides of the equilibrium equation, they are not often detected in the same groundwater sample. However, they can occur simultaneously at defined temperatures, pressures, and hydrogen ion concentrations (pH). Bicarbonate and carbonate can coexist in groundwater at alkaline pH conditions. These conditions can be caused in the vicinity of wells by contamination and leaching from high-pH materials, including cement surface seals, cement backfill, and some types of drilling mud.

4. Minor ions (iron, manganese, fluoride, boron, nitrogen species, strontium, and carbonate) have concentrations typically ranging from 0.01 to 10 mg/L. Generally, elevated concentrations of iron (> 0.3 mg/L) or manganese (> 0.05 mg/L) separately or a combination of these concentrations > 0.3 mg/L will tend to precipitate from the solution, staining laundry and porcelain fixtures red or gray; excess fluoride will stain teeth and reduce bone strength, while elevated boron is harmful to plants.

5. Electrical conductivity (EC or specific conductance) is commonly measured in micromhos per

centimeter (µmhos/cm). It is a convenient and easily measured surrogate property for the total ionic concentration often referred to as total dissolved solids (TDS). TDS can be estimated from EC with an accuracy of less than 100 mg/L. For most groundwater, an approximate relationship between EC and TDS is 1 µmho/cm = 0.55 to 0.75 mg/L.

6. A fuzzy relationship exists between the observed turbidity in groundwater and (1) the number of trace ions or metals detected in the sample, and (2) elevated concentrations of those trace ions. Increased turbidity usually results in increases in the number of trace ion detections and their concentrations. Typically, these trace ions range from 0.0001 to 0.1 mg/L, or less than 100 micrograms per liter (µg/L). Elevated turbidity does not appear to impact the concentrations of major cations, anions, and EC, but be wary of all samples having elevated turbidity concentrations.

Because of the very slow velocities of subsurface waters, groundwater is usually turbid-free. Water collected from a pumping well should be "crystal-clear" and free of any turbidity to truly represent groundwater from the aquifer. Even collecting a crystal-clear sample of water (no turbidity) cannot ensure that the groundwater you have collected -- particularly from confined aquifers -- represents the water quality in the aquifer because of changes in the geochemical environment, especially pressure and temperature changes. Results from analytical methods represent both the dissolved and colloidal fractions of the solution. The colloidal fraction may be caused by improper well design, insufficient well development, and/or operational parameters. Filtering the sample helps; however, even the filtered groundwater sample may not represent the quality of water in the aquifer. A 30 micron filter still allows colloidal fractions to pass into the sample. Preserving the sample by acidizing only exacerbates the dissociation of the colloids into the solution creating elevated trace ion (metal) concentrations. It is not surprising that elevated-turbidity samples usually show elevated aluminum concentrations since most geologic materials, and thus colloids, are composed of aluminosilicates. The best way to prevent ambiguous laboratory results is to avoid turbidity and collect clear and turbid-free groundwater samples (< 0.1 NTU) from properly designed and fully developed wells. Every groundwater analysis must include turbidity measurements to correctly evaluate detected trace ion concentrations.

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TABLE 1

| | | TW-11 | TW-5 | H-14P | BNMW-1 |
|---|---|---|---|---|---|
| MAJOR CATIONS mg/L | | | | | |
| Calcium | Ca[1] | 51 | 16 | 10 | 39 |
| Magnesium | Mg | 44 | 7 | 2 | 22 |
| Sodium | Na | 140 | 92 | 80 | 484 |
| Potassium | K | 4 | 5 | 2 | 4 |
| Sum of Cations meq/L | | 12.363 | 5.504 | 4.195 | 24.912 |
| MAJOR ANIONS mg/L | | | | | |
| Bicarbonate | $HCO_3$ | 230 | 190 | 160 | 322 |
| Chloride | Cl | 79 | 65 | 17 | 620 |
| Sulfate | $SO_4$ | 210 | 13 | 35 | <1 |
| Sum of Anions meq/L | | 10.371 | 5.169 | 3.831 | 22.789 |
| MINOR IONS mg/L | | | | | |
| Iron | Fe | 0.120 | 0.310 | 0.710 | 0.948 |
| Manganese | Mn | 0.003 | 0.180 | 0.025 | 0.172 |
| Fluoride | F | 0.20 | 0.27 | 8.00 | 0.10 |
| Boron | B | <0.5 | <0.05 | <0.05 | 8.22 |
| Nitrate as $NO_3$ | | <2 | <2 | 11 | 1 |
| Nitrite as nitrogen | | <0.4 | <0.4 | <0.06 | <0.02 |
| Carbonate | $CO_3$ | <1 | <1 | <2 | 13 |
| PHYSICAL PROPERTIES mg/L | | | | | |
| Total Hardness as $CaCO_3$ | | 310 | 68 | 36 | 188 |
| Total Alkalinity as $CaCO_3$ | | 230 | 160 | 130 | 335 |
| Total Dissolved Solids | TDS | 690 | 340 | 270 | 1,410 |
| Electrical Conductivity µmhos/cm | EC | 1,100 | 550 | 430 | 2,600 |
| pH Units | | 8.1 | 7.6 | 7.9 | 8.4 |
| Apparent Color | | <2 | 6 | <2 | >70 |
| Odor Units | | <1 | 2 | <1 | <1 |
| Turbidity NTU | | 0.21 | 0.88 | 9.10 | 12.70 |
| TRACE IONS mg/L | | | | | |
| aluminum | Al | <0.05 | <0.05 | 0.67 | 0.614 |
| antimony | Sb | <0.006 | <0.006 | <0.002 | <0.002 |
| arsenic | As | 0.0028 | <0.002 | 0.0038 | 0.0110 |
| barium | Ba | <0.1 | 0.100 | 0.041 | 0.339 |
| beryllium | Be | <0.001 | <0.001 | <0.001 | <0.001 |
| cadmium | Cd | <0.001 | <0.001 | <0.0005 | <0.001 |
| chromium | Cr | <0.01 | <0.01 | 0.012 | <0.01 |
| copper | Cu | <0.05 | <0.05 | 0.0074 | <0.05 |
| lead | Pb | <0.0002 | <0.005 | 0.0013 | <0.005 |
| mercury | Hg | <0.001 | <0.001 | <0.001 | <0.001 |
| nickel | Ni | <0.01 | <0.01 | <0.002 | <0.01 |
| selenium | Se | 0.0046 | <0.005 | <0.005 | <0.005 |
| silver | Ag | <0.01 | <0.01 | <0.01 | <0.01 |
| thallium | Tl | <0.001 | <0.001 | <0.001 | <0.001 |
| zinc | Zn | <0.05 | <0.05 | <0.01 | 0.082 |
| 1. Common abbreviation. | | SSCWD | VOMWD | MWD | SBCWD |