The Chemistry of Natural Waters

- Measures of amount of organics/biological species in water
- Oxidation and Reduction Chemistry in Natural Waters
- pE scale, sulfur and nitrogen compounds
- Acid Mine drainage
- Acid-Base Chemistry in Natural Waters

http://www.youtube.com/watch?v=a-x0AJQ5zHQ&feature=fvw
88 Pounds of Plastic Found in Dead Whale in the Philippines

A post-mortem on a beached whale that died in Mabini, the Philippines, revealed 88 pounds of plastic inside its stomach. Mary Gay Blatchley

By Daniel Victor

March 18, 2019

A beached whale found in the Philippines on Saturday died with 88 pounds of plastic trash inside its body, an unusually large amount even by the grim standards of what is a common threat to marine wildlife.
The Water Resources of Earth

- Over 70% of our Earth's surface is covered by water.

- 97.5% of all water on Earth is salt water, leaving 2.5% as fresh water.

- Nearly 70% of this fresh water is frozen in the icecaps. Most of the remainder is present as soil moisture, or lies in deep underground aquifers as groundwater not accessible to human use.

- < 1% of the world's fresh water (~0.007% of all water on earth) is accessible for direct human uses.
  - Lakes, rivers, reservoirs and underground sources.
  - Only this amount is regularly renewed by rain and snowfall, and is therefore available on a sustainable basis.

Where Does **Potable** (fit for consumption) Drinking Water Come From?

**Surface water**: from lakes, rivers, reservoirs

**Ground water**: pumped from wells drilled into underground aquifers
Access to safe drinking water varies widely across the world.
Water is an important constituent in our body and our survival depends on natural waters.

In the environment:

- Water can transport toxic substances into, within, and out of living organisms.
- Water-soluble toxic substances, such as some pesticides, lead ions, and mercury ions, can be widely distributed.
- Water may reduce the concentrations of pollutants to safe levels by dilution or by carrying them away (or both).
- Rainwater carries substances, including those responsible for acid rain, from the atmosphere down to Earth.
Different Representations of Water

Lewis structures

Charge-density

Region of partial negative charge

Regions of partial positive charge

Space-filling

Charge-density
A difference in the electronegativities of the atoms in a bond creates a polar bond.

<table>
<thead>
<tr>
<th>Electronegativity value (EN)</th>
<th>3.5</th>
<th>2.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN difference</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

Partial charges result from bond polarization

A polar covalent bond is a covalent bond in which the electrons are not equally shared, but rather displaced toward the more electronegative atom.
Polarized bonds allow **hydrogen bonding** to occur.

A **hydrogen bond** is an electrostatic attraction between an atom bearing a partial positive charge in one molecule and an atom bearing a partial negative charge in a neighboring molecule. The H atom must be bonded to an O, N, or F atom.

Hydrogen bonds typically are only about one-tenth as strong as the covalent bonds that connect atoms together *within* molecules.

H–bonds are intermolecular bonds. Covalent bonds are intramolecular bonds.
Concentration of O$_2$ in water is quite low
(~10 ppm average or ~10 mg/L)

For 1 atm O$_2$:
At 25$^\circ$C, $[O_2\,_{aq}] = K_H \times (pO_2) = 1.3 \times 10^{-3}$ mol L$^{-1}$ atm$^{-1}$ x 1 atm

In air:
At 25$^\circ$C, $[O_2\,_{aq}] = 1.3 \times 10^{-3}$ mol L$^{-1}$ atm$^{-1}$ x 0.21 atm
= $0.26 \times 10^{-3}$ mol L$^{-1}$ for 1 atm air
= 8.7 mg L$^{-1}$ = 8.7 ppm

At 0$^\circ$C 14.7 ppm

*Thermal pollution decreases oxygen concentration*
Oxidation and Reduction Chemistry in Natural Waters

\[ \text{O}_2 \text{ is reduced from 0 to -2 state in H}_2\text{O or OH}^- \]

Acidic solution
\[ \text{O}_2 + 4\text{H}^+ + 4e \rightarrow 2 \text{H}_2\text{O} \]

Basic solution
\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e \rightarrow 4\text{OH}^- \]
Oxygen Demand

The most common substance oxidized by dissolved oxygen in water is organic matter of biological origin (plant debris, dead animals etc.)

\[
\text{CH}_2\text{O} \text{ (aq)} + \text{O}_2 \text{ (aq)} \rightarrow \text{CO}_2 \text{ (g)} + \text{H}_2\text{O} \text{ (aq)}
\]

The oxidation state of carbon increases from 0 to +4 and that of oxygen reduces from -2 to 0
Similarly dissolved oxygen is consumed by ammonia and ammonium ion in the nitrification process.

Water in streams and rivers are constantly replenished with oxygen
Stagnant water and deep lakes can have depleted oxygen
Measures of amount of organics/biological species in water

Biochemical Oxygen Demand (BOD)
Chemical Oxygen Demand (COD)
Total Organic Carbon (TOC)
Dissolved Organic Carbon (DOC)

(TOC)-(DOC) = Suspended carbon in water
Biochemical Oxygen Demand - BOD

The capacity of the organic and biological matter in a sample of natural water to consume oxygen, a process usually catalyzed by bacteria, is called Biochemical Oxygen Demand or BOD.

Oxygen concentration is measured in a sealed sample before and after 5 days at constant temperature and neutral pH.

BOD equals the amount of oxygen consumed as a result of the oxidation of the dissolved organic matter in the sample.

**BOD5** corresponds to about 80% of the actual value. It is not practical to measure the BOD for an infinite period of time. The surface water has a BOD of 0.7 mg/L –significantly lower than the solubility of O₂ in water (8.7 mg/L).
**Humic acid** is a fraction of the complex mixture known as humic substances or Natural Organic Matter (NOM). Humic substances make up a large portion of the dark matter in humus and are complex colloidal supramolecular mixtures that have never been separated into pure components.

- Humic substances have been designated as either humic acid, fulvic acid or humin.
- Humic substances arise by the microbial degradation of biomolecules (lipids, proteins, carbohydrates, lignin) dispersed in the environment after the death of living cells.
- A modern structural description regards humic material as a supramolecular structure of relatively small bio-organic molecules.
Humic acid is a chemical ring structure that incorporates lots of carbon, hydroxyl, carbonic and nitrogen compounds. All around the outside are places for micronutrients to bond.
Chemical Oxygen Demand -COD

\[ O_2 + 4H^+ + 4e \rightarrow 2H_2O \]

Dichromate ion, \( \text{Cr}_2\text{O}_7^{2-} \) dissolved in sulfuric acid is a powerful oxidizing agent. It is used as an oxidant to determine COD.

\[ \text{Cr}_2\text{O}_7^{2-} + 14H^+ + 6e \rightarrow 2\text{Cr}^{3+} + 7 \text{H}_2\text{O} \]

Excess dichromate is added to achieve complete oxidation. Back titration with \( \text{Fe}^{2+} \) gives the desired endpoint value.

\[
\text{# moles of } O_2 \text{ consumed} = \frac{6}{4} \times (\text{#moles } \text{Cr}_2\text{O}_7 \text{ consumed})
\]

*Note: \( \text{Cr}_2\text{O}_7^{2-} \) is a powerful oxidizing agent and can oxidize species that are not usually oxidized by \( O_2 \) ---hence gives an upper limit*
Decomposition of Organic Matter under Anaerobic Conditions

In the absence of O₂ bacteria present in water can induce chemical transformations,

\[ 2\text{CH}_2\text{O} \xrightarrow{-\text{bacteria}} \text{CH}_4 + \text{CO}_2 \]

.... Example swamp gas

1966-Michigan Swamp Gas Case

March 14-20, 1966: Southeastern Michigan. From about 3:50 a.m. on March 14 and for 2-1/2 hours thereafter, Washtenaw County sheriffs and police in neighboring jurisdictions reported disc-shaped objects moving at fantastic speeds and making sharp turns, diving and climbing, and hovering. At one point, four UFOs in straight-line formation were observed.

Swamp Gas Mystery Solved
Bohannon, Science NOW 24 August 2005: 2
In the same lake aerobic and anaerobic condition may exist

**Aerobic vs. Anaerobic Conditions**

Fe$^{3+}$ in sediments gets converted into soluble Fe$^{2+}$ under reductive conditions

\[
\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}
\]

Insoluble Fe(III)  Soluble Fe(II)

<table>
<thead>
<tr>
<th>Aerobic conditions (warm water)</th>
<th>CO$_2$</th>
<th>H$_2$CO$_3$</th>
<th>HCO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>Fe(OH)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anaerobic conditions (cold water)</td>
<td>CH$_4$</td>
<td>H$_2$S</td>
<td>NH$_3$</td>
<td>NH$_4^+$</td>
<td>Fe$^{2+}$(aq)</td>
<td></td>
</tr>
</tbody>
</table>
The \( pE \) Scale

Defined as negative (base-10) logarithm of the effective concentration or activity of electrons (reduction equivalent) in water. ....in analogy to \( pH \) scale

- Low \( pE \) values signify that electrons are readily available and hence the medium is reducing in nature
- High \( pE \) values signify dominance of oxidizing agents and few electrons are available for reduction.

When \( O_2 \) is dissolved in significant amount, the dominant reduction in water

\[
\frac{1}{4} O_2 + H^+ + e \rightarrow \frac{1}{2} H_2O
\]

Under such circumstances, the \( pE \) of the water is related to its acidity and to the partial pressure by

\[
pE = 20.75 + \log([H^+]P_{O_2}^{\frac{1}{4}}) \quad OR \quad pE = 20.75 - pH + \frac{1}{4} \log(P_{O_2})
\]
A convenient approach is to use Nernst Equation of electrochemistry

\[ E = E^0 - \frac{RT}{F} \ln \left( \frac{[\text{products}]}{[\text{reactants}]} \right) \]

...for 1 electron redox process

\[ E = E^0 - 0.0591 \ln \left( \frac{[\text{products}]}{[\text{reactants}]} \right) \]

where \( E^0 \) is the standard electrode potential for a one electron reduction

One can equate \( pE \) to the Electrode Potential \( E \)

\[ pE = \frac{E}{0.0591} \text{ or } pE^0 = \frac{E^0}{0.0591} \]

\[ \frac{E}{0.0591} = \frac{E^0}{0.0591} - \ln \left( \frac{[\text{products}]}{[\text{reactants}]} \right) \]

\[ pE = pE^0 - \ln \left( \frac{[\text{products}]}{[\text{reactants}]} \right) \]
\[ \frac{1}{4} \text{O}_2 + \text{H}^+ + e \rightarrow \frac{1}{2} \text{H}_2\text{O} \]

\[ E^0 = 1.23 \text{ V} \]
\[ pE^0 = 1.23/0.0591 \]

\[
pE = pE^0 - \log \left\{ \frac{1}{[\text{H}^+][\text{O}_2]^{1/4}} \right\} \\
= pE^0 + \log ([\text{H}^+][\text{O}_2]^{1/4}) \\
= 20.75 - \text{pH} + \frac{1}{4} \log(\text{P}_{\text{O}_2})
\]

Note: \( \text{pH} = -\log[\text{H}^+] \)

For a neutral sample of water that is saturated with oxygen from air (\( p\text{O}_2 = 0.21 \text{ atm} \)) that is free from \( \text{CO}_2 \) (\( \text{pH} = 7 \)) the \( pE \) value corresponds to 13.9

\[ pE \text{ value decreases with decrease in } \text{O}_2 \text{ and increase in } \text{pH} \]
Example

\[ \frac{1}{8} \text{NO}_3^- + \frac{5}{4} \text{H}^+ + e \rightleftharpoons \frac{1}{8} \text{NH}_4^+ + \frac{3}{8} \text{H}_2\text{O} \quad E^0 = +0.836 \text{ V} \]

\[ pE = pE^0 - \log\left(\frac{[\text{NH}_4^+]^{1/8}}{[\text{NO}_3^-]^{1/8}[\text{H}^+]^{5/4}}\right) \]

\[ = 14.15 - \frac{5}{4}p\text{H} - \frac{1}{8}\log\left(\frac{[\text{NH}_4^+]}{[\text{NO}_3^-]}\right) \]

*Note: Express the reactions as one electron reduction process*

….. Follow the examples given on page 435
pE-pH Diagrams

Zone dominance of various oxidation states

- For example, Fe$^{2+}$/Fe$^{3+}$ is important for only pH below 3 as both exists in dissolved form.
- At higher pH Fe$^{3+}$ is present as Fe(OH)$_3$. Fe(OH)$_2$ does not precipitate until solution becomes significantly basic.
- Under extreme conditions pE-pH combination result in the participation of H$_2$O in the reduction process (shaded region).
Sulfur compounds in natural waters

Highly reduced -2 state as found in H₂S and highly oxidized +6 state as encountered in SO₄²⁻.

<table>
<thead>
<tr>
<th>Oxidation state of S</th>
<th>Increasing levels of sulfur oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>−2</td>
</tr>
<tr>
<td>Aqueous solution and salts</td>
<td>H₂S</td>
</tr>
<tr>
<td></td>
<td>HS⁻</td>
</tr>
<tr>
<td></td>
<td>S²⁻</td>
</tr>
<tr>
<td>Gas phase</td>
<td>H₂S</td>
</tr>
<tr>
<td>Molecular solids</td>
<td></td>
</tr>
</tbody>
</table>

Similar to the oxidation in air (recall from acid rain chapter), H₂S in water is oxidized by O₂ first to SO₂ and then to H₂SO₄.

H₂S + 2O₂ → H₂SO₄
Acid Mine Drainage

Conversion of soluble Fe$^{2+}$ to insoluble Fe$^{3+}$

$$4\text{Fe}^{2+} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}^{3+} + 4\text{OH}^-$$

$$4\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 \text{ solid}$$

*Ground water that contain Fe$^{2+}$ forms orange colored deposit when gets oxidized by air!*

- Mines (e.g., coal mines) that contain Ferrite (FeS$_2$) often leach out iron in water as a result of air oxidation.
- Under anaerobic condition FeS$_2$ is insoluble in water, but undergoes oxidation when comes in contact with air to form S$^2$ (-1 oxidation state).

$$2\text{S}_2^{2-} + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{SO}_4^{2-} + 4\text{H}^+$$

- Since the sulfate of the Fe$^{2+}$ is soluble in acidic water, the iron pyrite effectively becomes solubilized.
- The reaction produces H$^+$ ions some of which is consumed in air oxidation to form Fe$^{3+}$

$$4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$$
Overall Reaction

\[4\text{FeS}_2 + 15\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}^{3+} + 8\text{SO}_4^{2-} + 4\text{H}^+\]

In other words the insoluble FeS$_2$ produces soluble iron(III) sulfate and sulfuric acid
(Note: acidic conditions are required for the dissolution of Fe$_2$(SO$_4$)$_3$)

- If gets diluted with the natural water Fe$_2$(SO$_4$)$_3$ gets deposited as Fe(OH)$_3$
- On the other hand, concentrated acid can also liberate toxic heavy metals from the ores in the mines

\[\text{Fe}^{3+}\text{ can also serve as an oxidant for the oxidation of } \text{S}_2^{2-}\]

\[\text{S}_2^{2-} + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 14\text{Fe}^{2+} + 16\text{H}^+\]

The phenomenon of acid drainage is currently of importance in abandoned mines
Nitrogen compounds in natural waters

Highly reduced -3 state as found in NH₃ or NH₄⁺ and highly oxidized +5 state as encountered in NO₃⁻

<table>
<thead>
<tr>
<th>Oxidation state of N</th>
<th>Increasing levels of nitrogen oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>−3</td>
<td>0</td>
</tr>
<tr>
<td>Aqueous solution</td>
<td>NH₄⁺</td>
</tr>
<tr>
<td>and salts</td>
<td>NH₃</td>
</tr>
<tr>
<td>Gas phase</td>
<td>NH₃</td>
</tr>
</tbody>
</table>

The equilibrium between the highly reduced and oxidized state is given by

$$\text{NH}_4^+ + 3\text{H}_2\text{O} \rightarrow \text{NO}_3^- + 10\text{H}^+ + 8\text{e}$$
**pE-pH Diagram**

\[
\text{NH}_4^+ + 3\text{H}_2\text{O} \rightarrow \text{NO}_3^- + 10\text{H}^+ + 8\text{e}
\]

For the diagonal line when \([\text{NH}_4^+] = [\text{NO}_3^-]\)

\[
pE = 14.15 - \frac{5}{4}\text{pH} - \frac{1}{8}\log(1) = 14.15 - \frac{5}{4}\text{pH}
\]

Nitrite ion (\(\text{NO}_2^-\)) dominates in relatively small field
Why we need to consider water chemistry seriously?

Business decisions that undermine science can have serious consequences.
How Lead Ended Up In Flint's Tap Water

Without effective treatment steps to control corrosion, Flint's water leached high levels of lead from the city's pipes.

http://cen.acs.org/articles/94/i7/Lead-Ended-Flints-Tap-Water.html
• The entire Flint water crisis could have been avoided if the city had just added orthophosphate.

• Cities such as Detroit add orthophosphate to their water as part of their corrosion control plans because the compound encourages the formation of lead phosphates, which are largely insoluble and can add to the pipes’ passivation layer.

• Some water utilities treat water so it has a high pH and high alkalinity. Such conditions decrease the solubility of lead carbonates.

• Another factor is corrosiveness due to its chloride concentration. The treated Detroit water’s average chloride level was 11.4 ppm and the treated Flint water had 85-ppm
A lake is stratified so that it has both aerobic and anaerobic conditions are present. The lake water contains several trace metals including copper. Copper(II) has a standard reduction potential of 0.16 V when reduced to copper (I).

(A) Calculate the ratio of Cu$^{2+}$ to Cu$^+$ ions available at a pE of -4 and at a pE of +14.

(B) What oxidation state of copper ions would you expect to dominate under anaerobic conditions?

(C) Assuming that oxygen determines the electron availability near the surface of a lake, how would the decrease in pH affect pE?

(D) Calculate the ratio of Cu$^{2+}$ to Cu$^+$ ions available at a pH of 5 near the surface.
8. A sample of lake water contains 0.72 ppb aluminum.

(A) What is the maximum pH at which this concentration of aluminum will stay in solution?

(B) Fish gills have a pH of about 7.3. What is the potential concern with fish and aluminum levels in water?

(C) Are fish safe in this lake? Explain your reasoning.
Acid-Base Chemistry in Natural Waters

The CO₂-Carbonate System

\[ \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) \]

\[ \text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \]

Calcium carbonate though insoluble, leaches out small amounts of CO₃²⁻

\[ \text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} \]

\[ \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^- \]

\[ \text{CaCO}_3(\text{s}) + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^- \]
Molar Solubility ($S$) of $\text{CaCO}_3$ in $\text{CO}_2$ free water versus pH

\[
\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}
\]

\[
\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-
\]

\[
S = \{K_{sp}(1+K_b/[\text{OH}])\}^{1/2}
\]

Solubility of $\text{CaCO}_3$ decreases as the hydroxide concentration increases.
FIGURE 13-6 Species diagram for the aqueous carbon dioxide–bicarbonate ion–carbonate system. [Source: S. E. Manahan, *Environmental Chemistry*, 6th ed. (Boca Raton, FL: Lewis Publishers, 2000), Figure 3.3, p. 54.]
<table>
<thead>
<tr>
<th>Ion</th>
<th>CaCO₃ single equation</th>
<th>CaCO₃ iterative</th>
<th>CO₂ and CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HCO₃⁻]</td>
<td>9.9 × 10⁻⁵ M</td>
<td>8.8 × 10⁻⁵ M</td>
<td>1.0 × 10⁻³ M</td>
</tr>
<tr>
<td>[CO₃²⁻]</td>
<td>—</td>
<td>3.7 × 10⁻⁵ M</td>
<td>8.8 × 10⁻⁶ M</td>
</tr>
<tr>
<td>[Ca²⁺]</td>
<td>9.9 × 10⁻⁵ M</td>
<td>1.25 × 10⁻⁴ M</td>
<td>5.2 × 10⁻⁴ M</td>
</tr>
<tr>
<td>[OH⁻]</td>
<td>9.9 × 10⁻⁵ M</td>
<td>8.8 × 10⁻⁵ M</td>
<td>1.8 × 10⁻⁶ M</td>
</tr>
<tr>
<td>[H⁺]</td>
<td>1.0 × 10⁻¹⁰ M</td>
<td>1.1 × 10⁻¹⁰ M</td>
<td>5.6 × 10⁻⁹ M</td>
</tr>
<tr>
<td>pH</td>
<td>10.0</td>
<td>9.9</td>
<td>8.3</td>
</tr>
</tbody>
</table>
The carbon dioxide in natural water creates an interesting phenomenon. Rainwater saturated with CO$_2$ dissolves lime stones. When CO$_2$ is lost due to temperature changes or escaping from water drops, the reverse reaction takes place.

The photograph here shows aragonite and calcite. The rain water carries the ions with it, sips through the crack of the rocks. When it reached the ceiling of a cave, the drop dangles there for a long time before fallen. During this time, the carbon dioxide escapes and the pH of the water increases. Calcium carbonate crystals begin to appear. Calcite, aragonite, stalactite, and stalagmite are four common solids found in the formation of caves.

http://www.science.uwaterloo.ca/~cchieh/cact/applychem/waternatural.html
Hard water contains high concentrations of dissolved calcium and magnesium ions. Soft water contains few of these dissolved ions.

\[
\text{Hardness} = [\text{Ca}^{2+}] + [\text{Mg}^{2+}]
\]

Hardness is expressed as milligrams of calcium carbonate that contains the same total number of divalent (2+) ions.

A pipe with hard-water scale build up
Because calcium ions, Ca$^{2+}$, are generally the largest contributors to hard water, hardness is usually expressed in parts per million of calcium carbonate (CaCO$_3$) by mass.

It specifies the mass of solid CaCO$_3$ that could be formed from the Ca$^{2+}$ in solution, provided sufficient CO$_3^{2-}$ ions were also present:

$$\text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \rightarrow \text{CaCO}_3(s)$$

A hardness of 10 ppm indicates that 10 mg of CaCO$_3$ could be formed from the Ca$^{2+}$ ions present in 1 L of water.
### Ion Concentrations in Natural Waters and Drinking Waters

#### TABLE 9-4
River Water Concentrations and Drinking Water Standards for Ions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Average for world</th>
<th>Average for U.S.</th>
<th>Average U.S.</th>
<th>Drinking water concentration in ppm</th>
<th>Maximum recommended concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO₃⁻</td>
<td>$9.2 \times 10^{-4}$</td>
<td>$9.6 \times 10^{-4}$</td>
<td></td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>$3.8 \times 10^{-4}$</td>
<td>$3.8 \times 10^{-4}$</td>
<td></td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>$1.6 \times 10^{-4}$</td>
<td>$3.4 \times 10^{-4}$</td>
<td></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Na⁺</td>
<td>$3.0 \times 10^{-4}$</td>
<td>$2.7 \times 10^{-4}$</td>
<td></td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>$2.3 \times 10^{-4}$</td>
<td>$2.2 \times 10^{-4}$</td>
<td></td>
<td>8</td>
<td>250</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>$1.1 \times 10^{-4}$</td>
<td>$1.2 \times 10^{-4}$</td>
<td></td>
<td>12</td>
<td>250</td>
</tr>
<tr>
<td>K⁺</td>
<td>$5.4 \times 10^{-5}$</td>
<td>$5.9 \times 10^{-5}$</td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>F⁻</td>
<td>—</td>
<td>$5.3 \times 10^{-6}$</td>
<td></td>
<td>0.1</td>
<td>$0.8–2.4$</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>$1.4 \times 10^{-5}$</td>
<td>—</td>
<td></td>
<td>0.1</td>
<td>$0.8–2.4$</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>$7.3 \times 10^{-6}$</td>
<td>—</td>
<td></td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>
Perchlorate

Mostly released as ammonium perchlorate – used as oxidizing agents, rocket fuels, fire works, airbags etc
Most of the release in the southwestern part
No federal limit has been set, although some states have set their limits
Temporary and permanent hard water
Due to the reversibility of the reaction,
\[ \text{CaCO}_3(s) + \text{H}_2\text{CO}_3 = \text{Ca}^{2+} + \text{HCO}_3^- \]
water containing Ca\(^{2+}\), Mg\(^{2+}\) and \(\text{CO}_3\)^{2-} ions is called temporary hard water, because the hardness can be removed by boiling.

- Boiling drives the reverse reaction, causing deposit in pipes and scales in boilers. The deposits lower the efficiency of heat transfer in boilers, and diminish flow rates of water in pipes. Thus, temporary hard water has to be softened before it enters the boiler, hot-water tank, or a cooling system.

- The amount of metal ions that can be removed by boiling is called temporary hardness. After boiling, metal ions remain due to presence of chloride ions, sulfate ions, nitrate ions, and a rather high solubility of MgCO\(_3\).

- Amount of metal ions that can not be removed by boiling is called permanent hardness. Total hardness is the sum of temporary hardness and permanent hardness.

- Thus, water conditioning is an important topic. The value of water treatment market has been estimated to be worth $30 billion.

http://www.science.uwaterloo.ca/~cchieh/cact/applychem/waternatural.html
Maximum Contaminant Level Goal (MCGL) and Maximum Contaminant Level (MCL)

Table 5.11
MCLGs and MCLs (in ppm) for Selected Pollutants in Drinking Water

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>MCLG</th>
<th>MCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium ((\text{Cd}^{2+}))</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>Chromium ((\text{Cr}^{3+}, \text{CrO}_4^{2-}))</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Lead ((\text{Pb}^{2+}))</td>
<td>0</td>
<td>0.015</td>
</tr>
<tr>
<td>Mercury ((\text{Hg}^{2+}))</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Nitrate ((\text{NO}_3^-))</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Benzene ((\text{C}_6\text{H}_6))</td>
<td>0</td>
<td>0.005</td>
</tr>
<tr>
<td>Trihalomethanes ((\text{CHCl}_3, \text{etc.}))</td>
<td>0</td>
<td>0.080</td>
</tr>
</tbody>
</table>
Water purification techniques:

Distillation

Reverse osmosis
**Complexation treatment**
Addition of complexing reagent to form soluble complexes with Ca$^{2+}$ and Mg$^{2+}$ prevents the formation of solid. One of the complexing agents is sodium triphosphate Na$_3$PO$_4$, which is marketed as Calgon, etc. The phosphate is the complexing agent. Other complexing agents such as Na$_2$H$_2$EDTA can also be used, but the complexing agent EDTA$^{4-}$ forms strong complexes with transition metals. This causes corrosion problem, unless the pipes of the system are made of stainless steel.

**Ion exchange**
Today, most water softeners are using zeolites and employing ion exchange technique to soften hard water. Zeolites are a group of hydrated crystalline aluminosilicates found in certain volcanic rocks. The tetrahedrally coordinated aluminum and silicon atoms form AlO$_4$ and SiO$_4$ tetrahedral groups. They interconnect to each other sharing oxygen atoms forming cage-type structures as shown on the right. This diagram and the next structural diagram are taken from an introduction to zeolites There are many kinds of zeolites, some newly synthesized.
As an invasive species with an endless appetite, they can decimate ecosystems and send species extinct...

Asian Carp??

Humans.