1

Composition, Chemistry, and Regulatory Framework

Much water goeth by the mill
That the miller knoweth not of.

John Heywood (1497–1580)

1.1 Water Composition

Water is composed of two parts hydrogen and one part oxygen. It is not the materials of the water but the contaminants in it that make it important. If we look at a chemical reaction, we would be extremely satisfied with a reaction yield of 99% purity, as many reactions are in the 70–90% range. However, for water, even a 1% level of impurity is unacceptable. The levels of contaminants that we often consider insignificant in many products and foods can prevent us from using water. Impurities in water at the 1% level are equivalent to 10 000 ppm or $mg\,l^{-1}$. At that level, even things like sodium chloride, table salt, in the water will render it undrinkable or harmful if consumed. In other instances, even a few milligrams of the right compound can render the water unpalatable or unusable for many aquatic purposes.

From another standpoint, the challenges that are presented to a wastewater treatment plant can be formidable. From a process standpoint, the reaction yields we look for produce a treated effluent with contamination levels of less than $10\,mg\,l^{-1}$, and in a number of instances under $2\,mg\,l^{-1}$ of particular contaminants. That is pretty good for a waste stream which may start out at $500\,mg\,l^{-1}$ or more – it represents a 99.6% removal efficiency.

The usability of the water depends upon the compounds either dissolved in it or suspended in it. Contaminants can be organic or inorganic, solids or liquids. The usability of the water also depends upon the purpose of the use. For example, water used for cooling does not necessarily need to be of the same quality (purity) as that used for drinking or food preparation. Fecal and bacterial contamination of cooling water is often unavoidable in cooling towers, and

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tower water is treated with chemicals to reduce corrosion and inhibit excessive bacterial growth. In all cases, this water quality is not suitable for food preparation, nor for drinking. The sterility, turbidity, and dissolved constituents in the water are important quality control issues, but not all three are necessary for a specific use.

Water can also be too pure for a specific use. As an example, there are a number of locations worldwide that have their drinking water from thermal desalination sources. At one specific facility in the Middle East, the water is slightly above 43 °C, which is a bit uncomfortable for drinking, but because it is from a thermal desalination plant, it is *distilled*. Hence the water is aggressive because it is so low in carbonates and minerals that it has the effect of leaching the calcium from the asbestos-cement piping, thus weakening it. Similarly, distilled water will corrode iron and steel piping, and drinking distilled water can also cause health problems such as diuresis, and a change in the electrolyte concentration in the body[1].

1.2 Water Characteristics and Physical Properties

Water (H_2O) is dense, weighing in at 999.972 kg m^{-3}, boiling at 99.98 °C (212.96 °F), and melting at 0.0 °C. It is the standard for viscosity, at 1 centipoise (cp) at 20 °C, and has a vapor pressure which is temperature-dependent, from 611 Pa (0.180 in. of Hg) at 0 °C to 101 901.3548 Pa at 100 °C. The formula for vapor pressure of water in that range is

$$P_w = 10^{A-B/(C+T)}$$

where A = 8.07131, B = 1730.63, and C = 233.426 and the temperature T is in Celsius between 0 °C and 100 °C. P_w is in pascals; for reference, 1 atmosphere is 101 325 Pa, or 764.2602 mm of Hg, and 1 mm of Hg is equal to 133.333 Pa.

Pure water is an excellent insulator, but water is seldom, if ever, pure, and contains small quantities of dissolved salts and many materials. The known maximum resistivity of pure water is 182 KΩ m^{-1} at 25 °C, (or 5.4945×10^{-6} S m^{-1} or 0.054945 μS cm^{-1}).[2] Very small levels of contaminants, sometimes in the parts per trillion (ppt) range (10^{-12} g l^{-1}), can cause large increases in its conductivity. The conductivity of water is dependent not only on the quantity of contaminant, but on the type of contaminant. If the contaminant has an interaction with the water, and a secondary and/or tertiary ionization constant, it is much harder to relate conductivity to concentration.

When water has salts (ionic material) in it, it can become an excellent conductor. The electrical conductivity of water can be used to estimate the dissolved

Table 1.1 Approximate conductivity of various chemicals in water where the substance is the principal contaminant.

Salt	Conductivity equivalent	TDS/conductivity
Sodium chloride	1.00 ppm TDS = 2.04 μS cm^{-1}	0.49
Sodium sulfate	1.00 ppm TDS = 1.49 μS cm^{-1}	0.67
Calcium sulfate	1.00 ppm TDS = 1.36 μS cm^{-1}	0.74
Sodium bicarbonate	1.00 ppm TDS = 1.06 μS cm^{-1}	0.91

solids concentration in water if that value is less than about 1500 mg l^{-1}. Above that point, the conductivity to dissolved solids curve flattens out and becomes unreliable. Most conductivity meters use a formula of:

$$\text{Total dissolved solids, TDS (mg/l)} = C \times 1000 \times \text{conductivity in microsiemens/cm}$$

Depending upon the water source and components, the value of C can vary anywhere from 0.51 to 0.83.[3] At higher levels of dissolved solids, the coefficient changes. Table 1.1 illustrates the difference in conductivity of certain soluble materials in water. It should be noted that the conductivity is a function of the molecular structure of the solid or gas, and in some cases, substances that have second ionization constants or which react with water have substantially different values for conductivity which will not follow the formula shown above. Multiple ions in solution will have a nonlinear relationship to the values given in the table.

Conductivity can also be used to measure the amount of calcium carbonate in water, if that is the principal dissolved salt. Calcium carbonate and its forms are referred to as hardness, and represent the ability of the water to leave $CaCO_3$ deposits in piping, on heat exchangers, cooling towers, and so on. We will cover hardness in later chapters.

If an electric current is passed through water, it will generate hydrogen and oxygen in the ratio of 2:1 by volume. If there are salts such as sodium chloride in the water, a quantity of chlorine gas (Cl_2) will be generated along with the hydrogen and oxygen. If large concentrations of high purity salt are dissolved in the water, and the positive and negative electrodes are separated by a membrane, the electric current becomes the basis for an electrolytic cell used in the chemical industry for the generation of chlorine gas and caustic soda (NaOH). With water having a conductivity less than 1200 μ℧, the voltage requirements increase as the salt concentration becomes proportionally less.

1.2.1 Solubility of Gases in Water

The most important dissolved gas is oxygen, and the second most important gas is nitrogen, because it comprises approximately 79% of our atmosphere, and is a potential source of nutrients for certain aquatic plants.

The solubility of various gases in water is given in many tables found in chemical and analytical handbooks, and on many commercial websites, including www.engineeringtoolbox.com, and in handbooks and analytical reference materials.[4]

Table 1.2 is a listing of the solubility of oxygen in water at temperatures between 0 °C and 30 °C, for various values of salts in the water. Table 1.2 shows the solubility of selected gases in water.

L.E. Geventman published a research paper on the solubility of selected gases in water.[5] Geventman's paper states that the solubility of the selected gases can be calculated by the following formula:

$$\ln X_1 = \mathrm{A} + \mathrm{B}/T^* + \mathrm{C} \ln T^*$$

where $T^* = T/100$ K, and X_1 is the solubility of the gas. A, B, and C are determined experimentally from chemical data. His paper provides a list of the coefficients. All values refer to a partial pressure of the gas of 101.325 kPa (1 atm).

The concentration of oxygen in water at any temperature is given by the following equation found in *Standard Methods*:[6]

$$\begin{aligned}\mathrm{Ln\,O_2} = {} & -139.34411 + (1.575701 \times 10^5/\mathrm{T}^2) - (6.642308 \times 10^7/\mathrm{T}^2) \\ & + (1.243800 \times 10^{10}/\mathrm{T}^3) - (8.621949 \times 10^{11}/\mathrm{T}^4) \\ & - \mathrm{Chl}((3.1929 \times 10^2) - (1.9428 \times 10/\mathrm{T}) + (3.8673 \times 10^3/\mathrm{T}^2))\end{aligned}$$

where Chl is the chlorinity measured in grams/kilogram and is defined as chlorinity = salinity/1.80655, and salinity is approximately equal to total solids in water after carbonates have been converted to oxides and after all bromide and iodide have been replaced by chloride.

Figure 1.1 illustrates the solubility of oxygen in water at varying temperatures and values of chlorinity of zero and 1000 mg l^{-1}.

1.2.1.1 Nitrogen

Nitrogen is soluble in water, but in the gaseous or N_2 form is essentially inert. Principal forms of nitrogen in water are ammonia, nitrate, and nitrite. The only time one has to worry about the solubility of nitrogen is in its ionized forms, as ammonia nitrite, or nitrate (to be discussed later) or when one is designing a pressure flotation system.

Figure 1.2 illustrates the solubility of nitrogen gas (N_2) in water at temperatures between 0 °C and 60 °C.

Table 1.2 Solubility of oxygen in mg l^{-1} in water exposed to water-saturated air at atmospheric pressure (101.3 kPa).

Temperature	Chlorinity					
	0	**5**	**10**	**15**	**20**	**25**
0	14.621	13.728	12.888	12.097	11.355	10.657
1	14.216	13.356	12.545	11.783	11.066	10.392
2	13.829	13.000	12.218	11.483	10.790	10.139
3	13.460	12.660	11.906	11.195	10.526	9.897
4	13.107	12.335	11.607	10.920	10.273	9.664
5	12.770	12.024	11.320	10.656	10.031	9.441
6	12.447	11.727	11.046	10.404	9.799	9.228
7	12.139	11.442	10.783	10.162	9.576	9.023
8	11.843	11.169	10.531	9.930	9.362	8.826
9	11.559	10.907	10.290	9.707	9.156	8.636
10	11.288	10.656	10.058	9.493	8.959	8.454
11	11.027	10.415	9.835	9.287	8.769	8.279
12	10.777	10.183	9.621	9.089	8.586	8.111
13	10.537	9.961	9.416	8.899	8.411	7.949
14	10.306	9.747	9.218	8.716	8.242	7.792
15	10.084	9.541	9.027	8.540	8.079	7.642
16	9.870	9.344	8.844	8.370	7.922	7.496
17	9.665	9.153	8.667	8.207	7.770	7.356
18	9.467	8.969	8.497	8.049	7.624	7.221
19	9.276	8.792	8.333	7.896	7.483	7.090
20	9.092	8.621	8.174	7.749	7.346	6.964
21	8.915	8.456	8.021	7.607	7.214	6.842
22	8.743	8.297	7.873	7.470	7.087	6.723
23	8.578	8.143	7.730	7.337	6.963	6.609
24	8.418	7.994	7.591	7.208	6.844	6.498
25	8.263	7.850	7.457	7.083	6.728	6.390
26	8.113	7.711	7.327	6.962	6.615	6.285
27	7.968	7.575	7.201	6.845	6.506	6.184
28	7.827	7.444	7.079	6.731	6.400	6.085
29	7.691	7.317	6.961	6.621	6.297	5.990
30	7.559	7.194	6.845	6.513	6.197	5.896

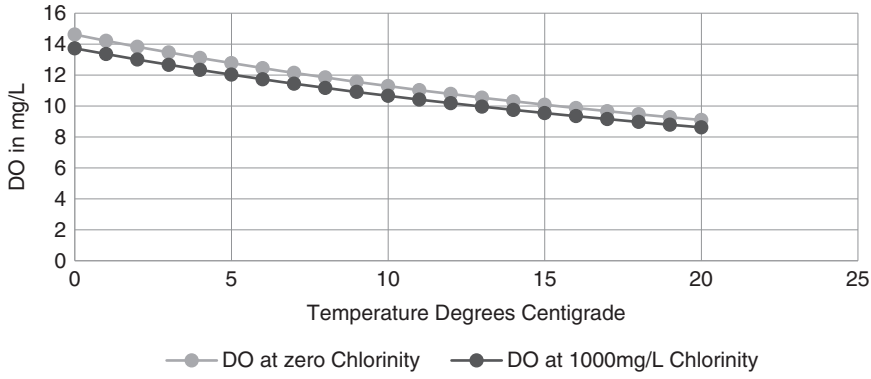

Figure 1.1 Solubility of oxygen in water at varying temperatures, and values of chlorinity of zero and 1000 mg l^{-1}.

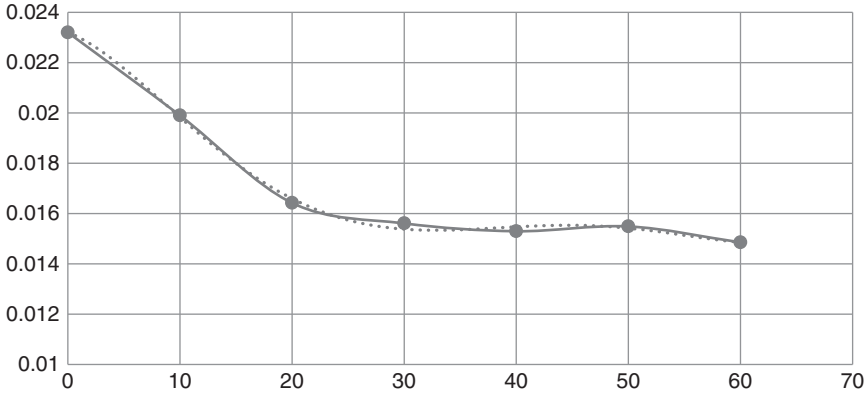

Figure 1.2 Solubility of nitrogen gas (N_2) in water at temperatures between 0 °C and 60 °C (liters per kg of water).

Other common gases soluble in water are shown in Table 1.3 in terms of millimols. This enables calculation of the volume of the listed gases as a function of pressure. There is an example below.

1.2.2 Henry's Law

Henry's law gives us some idea of the solubility of other gases. In 1803, William Henry stated: "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid."

$$P = K'_C C$$

Table 1.3 Molar Henry's law constants for aqueous solutions at 25 °C.

Gas	Constant (Pa (mol dm^{-3})$^{-1}$)	Constant (atm (mol dm^{-3})$^{-1}$)
He	282.7×10^6	2865.0
O_2	74.68×10^6	756.7
N_2	155×10^6	1600.0
H_2	121.2×10^6	1228.0
CO_2	2.937×10^6	29.76
NH_3	5.69×10^6	56.9

where P is the partial pressure of the gas, C is its molar concentration, and K'_C is the Henry's law constant. This is universally true for almost all liquids. However, as the concentrations and partial pressures increase, deviations from Henry's law become noticeable. This behavior is very similar to the behavior of gases, which deviate from the ideal gas law as pressures increase and temperatures decrease. Solutions that obey Henry's law are sometimes called ideal dilute solutions. Values of the Henry's law constants for many gases in many different organic compounds and gases have been measured. The inverse of the Henry's law constant, multiplied by the partial pressure of the gas above the solution, is the molar solubility of the gas.

Henry's law does not hold for gases that react with water and which have secondary and tertiary ionization constants. Some of those gases include hydrogen sulfide, chlorine, and carbon dioxide. The reactions of these gases are often pH-dependent, and the free molar form of the gas is directly related to the inverse of the pH at which it is most soluble. For example, ammonia tends to form NH_3OH in water, which is ammonium hydroxide, and is a strongly ionized base. As the pH of the water increases, the equilibrium reaction of:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

shifts leftward, releasing more free ammonia into the solution. At a value of pH 12, the reaction is essentially complete and there is essentially no ionic ammonia left in aqueous solution. This relationship is shown in Figure 1.3.

The value of the Henry's law constant is temperature-dependent. The value generally increases with increasing temperature. As a consequence, the solubility of gases generally decreases with increasing temperature. One example of this can be seen when water is heated on a stove. The gas bubbles appearing on the sides of the pan well below the boiling point of water are bubbles of air, which evolve due to the lowered solubility from hot water. The addition of boiled or distilled water to a fish tank will cause the fish to die of suffocation unless the water has been allowed to re-aerate before addition.

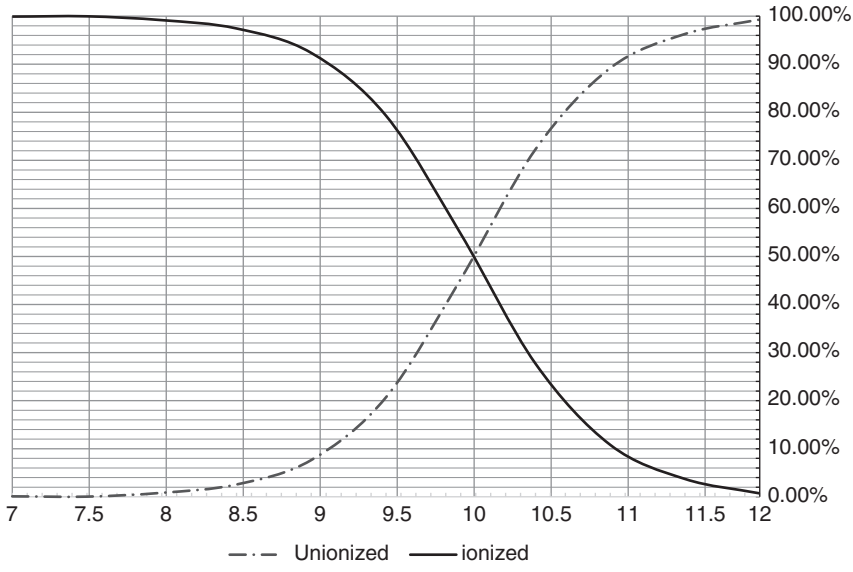

Figure 1.3 Ionized vs. free ammonia (%) at various pH levels at 0 °C.

A very complete listing of many Henry's law constants can be found at http://www.henrys-law.org/henry.pdf. The US Environmental Protection Agency (USEPA) has "Guidance for Reporting on the Environmental Fate and Transport of the Stressors of Concern in Problem Formulations," which has a section on calculation of Henry's law coefficients: http://www.epa.gov/pesticides/science/efed/policy_guidance/team_authors/endangered_species_reregistration_workgroup/esa_reporting_fate.htm.

The US Geological Survey lists many Henry's law coefficients for organic compounds starting on page 16 of their Survey Professional Paper: *Transport, Behavior and Fate of Volatile Organic Compounds in Streams*. This can be found at http://www.books.google.com/booksid=uVLwAAAAMAAJ&pg=RA5-PA16&lpg=RA5-PA16&dq=allintext:+Calculating+Henry%27s+Law+Coefficients&source=bl&ots=Dshx6nVwbi&sig=DNbPSdFW4rXGdLYznU0MdRQNm5w&hl=en&sa=X&ei=ZS9RVMfXFYSYgwTKsoCoAg&ved=0CFQQ6AEwCQ#v=onepage&q=allintext%3A%20Calculating%20Henry's%20Law%20Coefficients&f=false. And, there is a Henry's gas law calculator on the Internet at http://www.webqc.org/henry_gas_law.html.

A computer program for calculating Henry's law coefficients can be found at http://www.srcinc.com/what-we-do/environmental/tools-and-models.html. The program is called the EPI Suite, which was developed for the USEPA, and it can also be found at http://www.epa.gov/opptintr/exposure/pubs/episuite.htm. The program is used for predicting chemical values of spilled substances, but is not limited to those applications.

If you have one value for a Henry's coefficient at a given set of conditions (m^3 atm/mol) it can be transformed to another set of conditions by the equation:

$$H_{TS} = H_R \times \exp[-H_{V,TS}/\{R_c(1/T_S - 1/T_R)\}]$$

where H_{TS} is the coefficient at temperature T_S, and T_R is the reference temperature in degrees kelvin. The term $H_{V,TS}$ is the enthalpy of vaporization at T_S in units of cal/mol, and R_c is the gas constant, which has a value of 1.9872 cal $(\text{mol K})^{-1}$. The enthalpy can be obtained either from steam tables for water or chemical engineering tables for other fluids, or by using an alternative procedure for estimating the enthalpy of vaporization from the USEPA website: http://www.epa.gov/athens/learn2model/part-two/onsite/esthenry.html. Henry's coefficients may not really be considered as constants, but will vary with temperature and pressure.[7]

The study of Henry's law gained renewed interest in the environmental field when the remediation of benzene, toluene, ethylbenzene, xylene, and MTBE from leaking underground gasoline storage tanks became a US government funded program through a tax-supported trust fund. The study of Henry's law led to various remediation options, including vacuum stripping of volatile organics that were trapped in the soil above the water table.

Henry's law is useful in a number of ways, as illustrated below.

Example 1.1 ***Oxygen in Water*** Oxygen at 1 atm would have a molar solubility of (1/756.7) mol dm^{-3}, or 1.32 mmol dm^{-3}. The following examples will help in understanding this concept.

The amount of oxygen dissolved in air-saturated water under normal atmospheric conditions at 25 °C can be calculated as follows:

Normal atmospheric condition is 20.948 mol% oxygen, which makes the partial pressure of oxygen 0.20948 atm or 20.67 kPa. Using Henry's law, the concentration of oxygen is 0.20948 atm/(756.7 atm $(\text{mol dm}^{-3})^{-1}$), which is 0.2768 mmol dm^{-3}; given the weight of 32 g mol^{-1}, that comes out to be 0.0000088576 g dm^{-3} or about 8.85 mg l^{-1}, which is to be compared with the value of 8.263 mg l^{-1} from Table 1.2.

Example 1.2 ***Dissolved Air Flotation Systems*** If we want to run a dissolved air flotation (DAF) system at 50 psig (pounds per square inch gauge, or 115.23 ft of water pressure or 3.4473785 bar) for the pressure for flotation, how much nitrogen and oxygen will be produced when we release the pressure back to atmospheric?

The density of water is about 1 kg dm^{-3} or 1000 kg m^{-3}. The basic pressure on the water from the DAF system (50 psig) is approximately equal to a column of water 34.474 m high. A column of water 34.47 m high would exert a pressure of 344.737 kg dm^{-2} on its base, which converts to 344.73748 kPa pressure. The total system pressure is atmospheric pressure plus compression

or 101.325 kPa + 344.7375 kPa or a total of 446.0625 kPa. (This is equivalent to 446.0625/101.325 = 4.4023 atm.) The pressure change of 3.4023 atm (4.4023 atm total − 1 atm = 3.4023 atm) will produce a concentration change of 3.4023/1600 = 0.0021264375 mol dm^{-3}. (The pressure change of 344.738 kPa will cause a concentration change of 2.12644 mmol dm^{-3}.) For each gallon of water the amount of nitrogen generated is 3.785 × 2.12644 mmol = 8.418 mmol of nitrogen per gallon, or about 189 ml of nitrogen per cubic foot.[8]

For oxygen, the change is about 4.496 mmol dm^{-3} or about 89.2 ml of O_2 per cubic foot. (Note that the proportionality is approximately equal to the ratio of the Henry's constants for each of the gases.) The total volume for flotation is about 89.2 + 189 = 278.2 ml of gas per cubic foot.

Example 1.3 ***Benzene Concentration*** In a remediation situation, the client has spilled gasoline. You use a calibrated portable ionization detector and determine that the concentration of benzene in the soil gas is 20 ppm. What is the concentration of benzene in the groundwater?

First, let's look at the Henry's law coefficient for benzene. A good source of data is the USEPA Superfund Guidance section.[9] The tabular values for that reference list the following parameters:

CAS No.	Name	Sol. (mg l^{-1})	K_c (atm-M^3 mol^{-1})	K_c' (dimensionless)
71-43-2	Benzene	1.75E+03	5.55E-03	2.28E-01

where K_c' is a dimensionless value for the Henry's law coefficient.

Assuming that the soil vapor and the water are in equilibrium, what is the concentration in the water? The mol. wt of benzene is 78.114 g mol^{-1}.

20 ppm in air is a volume measurement; in order to get mg m^{-3} we need to multiply the gram molecular weight by the concentration and divide it by 23.235 (which is the volume of a mole (22.41 l) at 0 °C corrected for the temperature of the ground which is approximately 10 °C). So concentration C in mg m^{-3} = 20 × 78.114/23.235 = 67.238 mg m^{-3} in air. The molar concentration is then 67.238/78.114 = 0.8608 mmol m^{-3} or 0.0008608 mol m^{-3}. Then C = 0.00555/0.0008608 or 0.00645 mol m^{-3} or 0.503 g m^{-3} = 0.503 mg l^{-1}.

1.3 Solution Chemistry: Salts and Ions in Water

Water is the universal solvent. Everything dissolves in water to a greater or lesser extent. Depending upon the various elements and their combinations, organic and inorganic compounds are more or less soluble in water. Chemists use the *solubility product* as an indication of the solubility of a substance. In a

later chapter we will discuss the practical uses of solubility product manipulation for the purposes of wastewater and drinking water treatment.

The solubility product is calculated by the following:

$$\text{Ksp} = [\text{Cation}^+][\text{Anion}^-]$$

If we call the substance AC, the formula is then

$$\text{Ksp}_{(\text{AC})} = [\text{C}][\text{A}]$$

Or if the substance is A_2C_3 then

$$\text{Ksp} = [\text{C}^+]^2[\text{A}^-]^3$$

where the substances in brackets are the molar concentrations.

But if one wants to calculate the solubility of the compound AC in water, make the substitution [A] = [C] and that would give you either $[A]^2$ or $[C]^2$ and the concentration of the compound would be $[A] = [C] = \sqrt{\text{Ksp}}$ or the square root of the solubility product. If the compound is more complex and has the general formula of A_2C_3, then

$$\text{Ksp} = [\text{C}]^2[\text{A}]^3$$

The appropriate substitution to get the solubility of the compound would be:

$$[2\text{C}]^2[3\text{A}]^3 = \text{Ksp}$$

where C or A represent moles of ion in solution, and we get 1.5 mole of A for every mole of C at equilibrium.

These equations assume that the substance does not react with water to form a weak acid or a weak base. It is also useful to note that the solubility product can be used to manipulate the solubility of specific compounds in water. If one adds or subtracts selected ions from the water, the solubility will be increased or decreased until equilibrium is restored.

Example 1.4 ***Copper Chloride*** Copper (cuprous) chloride (CuCl) has a $\text{Ksp} = 1.2 \times 10^{-6}$. If one had a saturated solution of CuCl, at equilibrium, the concentration of copper would be equal to the quantity of chloride in solution or $[\text{Cu}] = \sqrt{1.2} \times 10^{-6} = 1.0954 \times 10^{-3}\ \text{mol l}^{-1} = 0.06961\ \text{g l}^{-1}$, or $69.1\ \text{mg l}^{-1}$.

If we need to get copper in the solution down to $1\ \text{mg l}^{-1}$ or less, that can be done by adding chloride: $1\ \text{mg l}^{-1} = 0.000015737\ \text{mol l}^{-1} = 1.5737 \times 10^{-5}\ \text{mol l}^{-1}$. Back-calculating to the Ksp: $1.2 \times 10^{-6} / 1.5737 \times 10^{-5} = 0.07626\ \text{mol l}^{-1}$ of chloride in solution to reduce the Cu concentration to $1\ \text{mg l}^{-1}$ or less. $0.07626\ \text{mol l}^{-1}$ of chloride required is $35.453 \times 0.07626 = 2.703\ \text{g l}^{-1}$.

A list of metals and their solubility products will be presented in a later chapter on precipitation.

Hydroxide precipitation is also to be covered later, but it represents an exception to the general principles of solubility. Some metals form hydroxyl precipitates, which have optimum pH precipitation ranges. Outside those ranges, the solubility of the metal is higher. An example is aluminum hydroxide $Al(OH)_3$, which has an optimum precipitation range at approximately pH = 5.5.[10]

1.4 Disassociation Constants for Weak Acid and Bases

Strong acids and bases fully disassociate in water. HCl, NaOH, HNO_3, and others completely disassociate in water to form acids and bases. Weak acids or bases partially disassociate, and the equation used to describe that disassociation is similar to the one used for solubility. It is called an *ionization constant,* and if the compound is an acid, it would generally be expressed as

$$HA = H^+ + A^-$$

where H^+ represents the cation (generally hydrogen) and A is the acid portion of the compound, for example, H_2SO_4 or HCl.

For bases, the base would be written

$$MOH = M^+ + OH^-$$

where M is generally a metal and OH^- is the hydroxyl ion from water, for example, NaOH or $Ca(OH)_2$.

The equilibrium constant is written slightly differently from the solubility product:

$$Keq = \frac{(H)(A)}{(HA)}$$ for the HA acid and a similar formulation for the MOH base.

As a convention, the square brackets are used to express solids in solution, and the round brackets are used for weak acids and bases.

Take for an example:

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

and

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

The first and second ionization constants are:

$$K_1 = \frac{(H^+)(HCO_3^-)}{(H_2CO_3)} \text{ and } K_2 = \frac{(H^+)(CO_3^{2-})}{(HCO_3^-)}$$

So for H_2CO_3, which is obtained when CO_2 is bubbled through water, $K_1 = 4.45 \times 10^{-7}$, and $K_2 = 4.65 \times 10^{-11}$.

The equations can be simplified and combined so that for CO_2 bubbled through water the overall reaction may be combined into $K_1 \times K_2 = (H^+)^2 (CO_3^{2-})/(H_2CO_3)$ which gives a combined value of K_{1-2} of 2.06925×10^{-17}.

Another way of expressing the disassociation constant is similar to the way in which we express the acidity or alkalinity of a liquid, or pH. For water, pH is defined as the negative logarithm (to the base 10) of the concentration of ions in the water, or $pH = -1 \log_{10} (H^+)$ or $-\log_{10} (1/(H^+))$. Since $K_{water} = (H^+) \times (OH^-) = 10^{-14}$, the pH of a neutral solution is approximately 7 at 25 °C.[11] For a 0.1 M concentration of hydrochloric acid, pH = 1.0, and for a 0.1 M concentration of sodium hydroxide, pH = 14. Chemists often express the values of the ionization constant of acids and bases in terms of **p** notation, and for compounds with multiple ionization constants, the ionization constants are listed in order as K_1, K_2, etc. for the specific compound.

For example, consider the reactions of chlorine with water.

$$Cl_2 + H_2O \leftrightarrow HOCl + HCl$$

which further resolves into

$$HOCl \leftrightarrow H^+ + OCl^-$$

The HCl completely ionizes into $H_3O^+ + Cl^-$.

Ammonia is another substance that partially disassociates in water. The reaction is:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

The equilibrium reaction is:

$$K = (NH_4^+)(OH^-)/(NH_3) = 1.65 \times 10^{-5}$$

A few disassociation constants are listed in Table 1.4. A more complete list of disassociation constants for weak acids and bases in water can be found at: http://chemwiki.ucdavis.edu/Reference/Reference_Tables/Equilibrium_Constants/E1%3A_Acid_Dissociation_Constants_at_25°C, and their page E2 contains data for bases. Another source is: http://www.csudh.edu/oliver/chemdata/data-ka.htm.

Question: Where or how is this knowledge useful?

Answer: Given a waste with emulsified oils and suspended solids, one can remove most of the oil by breaking the emulsion with salts of iron or aluminum and sulfuric acid. Reduce the pH to about 2 with H_2SO_4, and then attack the oily wastewater with aluminum sulfate ($Al_2(SO_4)_3$) until the emulsion breaks. When that occurs the oil will float to the surface and can be skimmed off. To reduce the dissolved solids in the system, add a small amount of a suspension of milk of lime ($Ca(OH)_2$) to the mix. The lime will react with and neutralize the acid, raising the pH and precipitating the

Table 1.4 Aqueous disassociation constants.

Name	Formula	First disassociation constant (K_a)	Second disassociation constant		
			pK_1	pK_2	pK_3
Acetic acid	CH_3CO_2H	1.75×10^{-5}	4.765		
Boric acid	H_3BO_3	5.4×10^{-10}	9.27	>14	
Carbonic acid	H_2CO_3	4.5×10^{-7}	6.35	10.33	
Hydrogen sulfide	H_2S	8.9×10^{-8}	7.05	19	
Hypochlorous acid	HClO	4.0×10^{-8}	7.40		
Phosphoric acid	H_3PO_4	6.9×10^{-3}	2.16	7.21	12.32
Sulfuric acid	H_2SO_4	Strong	Strong	1.99	
Ammonia	NH_3	1.8×10^{-5}	4.75		
Magnesium hydroxide	$Mg(OH)_2$	2.6×10^{-3}	2.56		
Bases					
Ammonia	NH_3	1.8×10^{-5}	4.75		
Calcium hydroxide	$Ca(OH)_2$	3.72×10^{-3}	2.43		
Ethylamine	C_2HyNH_3	4.5×10^{-4}	3.35		
Magnesium hydroxide	Mg(OH)2	2.6×10^{-3}	2.58		
Sodium hydroxide	NaOH		0.2		

aluminum as $Al(OH)_3$, and will react with and precipitate the calcium as a sulfate ($CaSO_4$), and both will fall out of the system. The remaining water will have a slight yellow color and will be almost free of suspended solids. At near-neutral pH, the aluminum concentration will be in the low mg/l range and the calcium sulfate will be soluble at between 1200 and 1600 mg l^{-1}. At that point, most of the other remaining cations will be precipitated to within most regulatory limits for discharge to a wastewater treatment plant.

Example 1.5 Chromium exists in two forms, Cr^{3+} and Cr^{6+}. The Cr^{3+} form is much less toxic than the Cr^{6+} form.[12] The higher valence form is sometimes used in cooling towers and industrial applications because it is a passivator (protects metals from corrosion) and a powerful disinfectant, but it is lethal to bacterial and many aquatic organisms. Hexavalent chromium is also used in chromium plating of metallic parts. The wastes can be highly toxic.
In order to remove chromium from the water, it is best reduced in valence from the 6+ to the 3+ form with sulfur dioxide (SO_2) at low pH, or sodium bisulfite ($NaHSO_3$) or sodium meta-bisulfite ($Na_2S_2O_5$) or H_2S, or ferric sulfate. The solubility product for the hydroxide is 6.3×10^{-31}. At a pH of

about 7.5, the solubility of Cr^{3+} in water is approximately 0.18 mg l^{-1}, as will be shown later. However, if nickel is also present in the water, as is a common occurrence, sulfide is added to the water, the reaction will proceed to Cr_2S_3, and with precipitation and simple filtration the chromium concentration remaining in solution is between 2 and 7 ppb (μg l^{-1}).[13]

1.4.1 Common Minerals Dissolved in Freshwater and Seawater

There are a variety of compounds dissolved in water. The most abundant is sodium chloride, which represents about 3.5% by weight, and it is followed by salts of calcium and magnesium chloride and various sulfates. Table 1.5 shows the approximate concentrations of the principal dissolved elements in freshwater, and Table 1.6 shows the approximate concentrations of dissolved minerals in seawater.

Calcium and magnesium salts are the most abundant in freshwater, and the interactions between carbon dioxide and limestone (calcium carbonate and magnesium carbonate formations) also play a significant role in water and water treatment. In some areas, and depending upon the geological formations, some groundwaters may contain high enough concentrations of certain

Table 1.5 Solubility of common minerals in freshwater.

	1	2	3	4	5	6	7	8	9	10	11	12
Calcium	0.8	0.65	40.7	1.68	14	22	241	400	144	6.5	3.11	4540
Magnesium	1.2	0.14	7.2	0.24	13	17	7200	1350	55	1.1	0.7	160
Sodium	9.4	0.56	1.4	0.16	8	14	83 600	10 500	~27	~37	3.03	2740
Potassium	–	0.11	1.2	0.31	–	0.5	4070	380	~2	~3	1.09	32.1
Bicarbonate	4	–	114	5.4	104	129	251	28	622	77	20	55
Sulfate	7.6	2.2	36	1.3	4.7	1.3	16 400	185	60	15	1.0	1
Chloride	17	0.57	1.1	0.06	8.5	33	140 000	19 000	53	17	0.5	12 600
Silica	0.3	–	3.7	0.7	24	30	48	3	22	103	16.4	8.5
TDS	38	4.7	207	10	120	180	254 000	35 000	670	222	36	20 338
pH	5.5	–	–	6.9	7.7	7.0	7.4	–	–	6.7	6.2	6.5

Key to analyses: (1) rainwater from Menlo Park, California; (2) average rainwater from sites in North Carolina and Virginia; (3) composition of the Rhine River as it leaves the Alps; (4) stream draining igneous rocks in the Washington Cascades; (5) Jump-Off Joe Creek, southwestern Oregon, wet season, November 1990; (6) Jump-Off Joe Creek, southwestern Oregon, dry season, September, 1991; (7) Great Salt Lake, Utah; (8) average seawater; (9) groundwater from limestone of the Supai Formation, Grand Canyon; (10) groundwater from volcanic rocks, New Mexico; (11) groundwater from a spring, Sierra Nevada Mountains: short residence time; (12) groundwater from metamorphic rocks in Canada: long residence time.
Source: http://www.waterencyclopedia.com/En-Ge/Fresh-Water-Natural-Composition-of.html#ixzz3Nxvp1Kpk.

Table 1.6 Some of the most common elements dissolved in seawater.

Element	Concentration in mg l^{-1}	Element	Concentration in mg l^{-1}	Element	Concentration in mg l^{-1}
Oxygen	8.57×10^5	Potassium	380	Argon	0.6
Hydrogen	1.08×10^5	Bromine	65	Nitrogen	0.5
Chlorine	1.9×10^4	Carbon	28	Lithium	0.18
Sodium	1.05×10^4	Strontium	8.1	Rubidium	0.12
Magnesium	1.35×10^3	Boron	4.6	Phosphorus	0.07
Sulfur	8.85×10^2	Silicon	3	Iodine	0.06
Calcium	4.0×10^2	Fluorine	1.3	Barium	0.03

Source: *Handbook of Chemistry and Physics,* 66th ed., CRC Press.

cations, including arsenic and radium, to make drinking the groundwater harmful to health.[14]

The solubility of materials in water is largely determined by the types of ion forms.

1.5 Sources of Water

1.5.1 Groundwater

Groundwater serves the majority of the smaller inland communities in the United States and elsewhere in the world. It is a source of drinking water, agricultural water, industrial water, and just about anything else. Groundwater is characterized by natural minerals in moderate to low concentrations.

Flow regimens in groundwater are linear, and flow through porous media is analogous to heat transfer through a solid medium. The overall equations used to calculate flow regimens are the Darcy equations, and they are laminar flow equations. The one noticeable exception is flow through fractured rock and some limestone. The limestone may develop solution cavities; the fractured rock (including granite and other highly crystalline rocks) are often of low porosity, and the movement of water takes place primarily in the cracks.

Groundwater quality is highly variable as it depends upon the rocks and minerals with which it is in contact. In some areas, calcium, magnesium, and iron salts comprise the greatest contaminant. In other areas, sulfates and dissolved salts of toxic metals such as arsenic and cadmium can be found in the groundwater, sometimes rendering it non-potable. Where the underlying rock formations are limestone-rich ($CaCO_3$) or have magnesium carbonate ($MgCO_3$), and even iron (Fe^{2+}) in them, the waters are often considered to be "hard waters." The waters may contain varying amounts of dissolved minerals which can cause

discoloration or deposits in heat exchangers, sinks, on cooling towers, and in boilers and hot water heaters. These deposits, with time, act as an insulator and reduce the thermal transfer efficiency of the heat exchangers and hot water heaters, and also cause unsightly deposits.

1.5.2 Groundwater Quality

The quality of the groundwater in a particular area is dependent upon a number of factors, including the following general factors.

1. First and foremost, the quality of the water is dependent upon the formation and characteristics of the aquifer and its geology.
2. The geology includes aquifer chemistry, pore and grain size, fractures, organic materials in the soil, clays, and soil structure and profile.
3. The movement and age of the water in the aquifer. The older the water, the more likely it is to be in chemical equilibrium with the rocks in the aquifer.
4. The source and quality of the water that enters the aquifer. Often the source of groundwater is rainwater. In order to get to the aquifer, the water must pass through the soil, and it will pick up some of the minerals in the soil. Note that in recent years the presence of sulfur dioxide in the atmosphere has created acid rain, as very weak sulfuric acid in the rainwater. This acid tends to dissolve more of the minerals in the rocks of the aquifer, resulting in higher mineral content in the waters.
5. The number and kinds of aquifers and aquicludes. There are often multiple aquifers, which may or may not be hydraulically connected, and it is not uncommon to have a shallow aquifer that is contaminated from surface sources, and a deeper aquifer that is pristine, with an aquiclude separating the aquifers.
6. Mixing of groundwaters with other sources. This is entirely dependent upon hydraulic gradients in the ground. In most instances, the groundwater moves very slowly, in terms of a few meters per year, and the flow regimen is laminar. Mixing will occur very, very slowly, and given the tens or perhaps thousands of years of age of the groundwater, diffusion of contaminants and dissolution of rocks is an important parameter.
7. Anthropogenic factors such as surficial contamination or infiltration from various sources. Runoff from roadways and sidewalks contains lead, rubber, and oils. Sanitary sewers leak, while asphalt parking areas contribute to groundwater contamination through the leaching of the asphalt solvents during precipitation. Storm and sanitary sewers and septic tanks contribute their share of contaminants, and agricultural application of pesticides and fertilizers are potential and actual huge sources of groundwater contamination. Industrial discharges and waste disposals, and residential and industrial landfills can be a potent source of contamination.

1.5.3 Other Principal Contaminants in Groundwater

The largest single group of organic contaminants soluble in water is found in petroleum. It is even more remarkable that the contamination is so widespread when petroleum has been around as a fuel only since 1859 when the first commercial well struck oil in Pennsylvania. Initially, the fire marshalls and insurance companies mandated that gasoline tanks and certain types of chemical tanks be placed underground to reduce fire and release hazards. In the late 1980s the US started a program to identify, register, and test underground storage tanks (USTs). Leaking tanks were to be removed or replaced, and leaks and spills from leaking tanks were remediated.

When the UST regulation, testing, replacement, cleanup and remediation program began in the US, there were over 2.1 million tanks which were suspected to be leaking petroleum into the groundwater. In New York and New Jersey alone (USEPA Region 2), the Federal and State actions closed over 1.5 million (old and leaking) substandard tanks, cleaned up more than 300 000 petroleum leaks, and reduced the number of new releases from these regulated tanks from a high of over 66 000 in 1990 to roughly 7000 in 2008. EPA Region 2 still has approximately 50 246 federally regulated USTs and 37 579 leaking underground storage tanks (LUSTs), but cleanups have been initiated at 36 569 of the LUST sites and 30 432 cleanups have been completed.[15] When a leak occurs into the soil from a LUST, approximately 75% of the leak is retained in the soil, about 24% can be found floating on the soil and water interface, and about 1% is dissolved in the groundwater.

Contaminants such as benzene, toluene, ethylbenzene, and xylene (BTEX) are of the greatest concern because they have a direct exposure link to development of cancer in humans (see Table 1.7).[16]

Table 1.7 Principal groundwater contaminants found in petroleum.

Element	Avg. amount in petroleum % by weight	Range of concentrations in crude oil	Solubility in H_2O @ 20–25 °C(mg l^{-1})	Henry's law constant
Benzene	0.16	0.04–0.41	1800	0.228
Toluene	0.67	0.08–2.5	530	0.272
Ethylbenzene	0.17	0.056–0.31	170	0.323
M-Xylene	0.66	0.08–2.0	407	160
O-Xylene	0.26	0.033–0.092	31	0.0198
p-Xylene	0.26	0.090–0.68	190	0.314
Napthalene	0.069	0.033–0.092	31	0.0198
Acenapthalene	0.057	0.057–0.057	4.2	0.00636

Source: Table 1, Fate and transport of petroleum hydrocarbons in soil and groundwater at Big South Fork National River and Recreation Area, Tennessee and Kentucky, 2002–2003, available at http://pubs.usgs.gov/sir/2005/5104 and http://pubs.usgs.gov/sir/2005/5104/PDF/SIR20055104.pdf.

1.5.4 Movement of Groundwater

The ground is a porous medium but the groundwater moves very slowly. The principal factor that causes groundwater movement is a hydraulic gradient. The velocity of groundwater movement is measured in feet or meters per day, or per year, or in centimeters per second. The rate of fluid movement through the ground varies with the reciprocal of the viscosity of the fluid. The rate of fluid movement ranges between 10^{-3} cm s^{-1} for gravels or very coarse gravels (86.4 ft/day), to 10^{-12} cm s^{-1} (8.64×10^{-8} ft/day) for very tight clays. By comparison, new uncracked concrete has a permeability of 10^{-11} to 10^{-12} cm s^{-1} (0.0000316 ft/year), and impermeable clay layers to be used in landfills must be compacted to 10^{-9} cm s^{-1}.

A later chapter in this book will discuss groundwater movement further.

1.6 Analytical Methods

In order to know what is in the water, we must also know something about how the medium is sampled and preserved, and how the contaminants are measured. This is not a text on analytical chemistry, but merely a brief mention of some of the methods of detecting the most common compounds dissolved in water. It is imperative that the sample for analysis be representative of the conditions or fluid being sampled, and often this is not as straightforward as it may at first appear. It is almost impossible to obtain representative samples of two-phase flows (consider water with an oil layer floating on it) or suspended solids in a channel or stream. Both are difficult to sample unless the samples are extremely well mixed in an area of very high turbulence.

Once the material is sampled, it must be preserved until it can be shipped to the laboratory and analyzed. Even after the sample is transmitted to the laboratory, the lab will have some holding times before the analyses can be scheduled. Some sampling protocols require preservatives to be added, and others prohibit the use of certain containers because of the chance of contamination or because the material in the liquid could adhere to the sides of the sampling container.

In the water industry there are two principal references on methods. The first and one of the oldest is *Standard Methods for the Examination of Water and Wastewater*, published by the American Water Works Association (AWWA .org), the Water Environment Federation (WEF.org), the American Public Health Association (APHA.org), the American Society of Civil Engineers, and others. The second principal reference has become important not only because of its publisher (USEPA), but also for many of the methods that are applicable to groundwater and wastewater: SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, Office of Solid Waste Research, principally for hazardous waste analyses. It has also become a de facto standard in the United States and elsewhere because of the many references in EPA-issued permits to the manual. The manual can be viewed and downloaded at http://www.epa.gov/epaoswer/hazwaste/test/main.htm. However, it often does not

include as thorough an explanation of the methods, and it often relies on methods that focus on the issue of the analysis of hazardous wastes, and occasionally relies on methods that use advanced and expensive analytical equipment not generally available in many laboratories. SW-846 often includes specialized analytical methods that are not covered by *Standard Methods*.

Table 1.8 briefly lists some of the more common analytical methods used in a modern laboratory.

Inorganic contaminants in water generally follow specific rules that are determined based upon the valence of the compounds and the reaction between the cations and anions, as cited above and in the following materials. The rules for predicting solubility of an inorganic compound are shown in Table 1.9.

A caveat is appropriate. Most chemistry texts, handbooks, and common definitions of solubility define insoluble compounds as those which are less than 1% soluble (solubility $< 0.1\ \text{mol}\,\text{l}^{-1}$). However, for the environmental

Table 1.8 Principal analytical methods for contaminants in water.

Element	Measurement method	Element *n*	Measurement method
Aluminum	Flame ionization	Carbonate (CO_3)	Calculation
Antimony	Flame ionization	Chloride (Cl)	Gravimetric
Arsenic	Flame ionization	Cyanide (CN)	Colorimetric
Calcium	Flame ionization	Fluoride (F)	Gravimetric
Chromium	Flame ionization	Hydronium (OH)	pH
Copper	Flame ionization	Hypochlorite ($HClO_2$)	pH
Hydrogen	pH	Hypochlorous (ClO_2)	pH
Iron	Flame ionization	Nitrate (NO_3)	Colorimetric
Lead	Flame ionization	Nitrite (NO_2)	Colorimetric
Magnesium	Flame ionization	Sulfate (SO_4)	Colorimetric
Manganese	Flame ionization	Sulfite (S)	Colorimetric
Mercury	Flame ionization	*Other*	
Potassium	Flame ionization	Alkalinity	Colorimetric
Silica	Flame ionization	Total org. carbon	Gravimetric
Silver	Flame ionization	Diss. O_2	Azide titr or probe
Sodium	Flame ionization	Org. nitrogen	Kjelldahl
Zinc	Flame ionization	Chem O_2 demand	Digestion/titration
Ammonia	Kjelldahl or Nesslerization	Biochemical. O_2 demand	Difference in oxygen uptake
Bicarbonate (HCO_3)	Calculation		

Table 1.9 Solubility rules for simple inorganic compounds in water.

Rule number	Rule
1	Periodic Table Group 1 elements (Li, NA, K, Cs, Rb) are soluble.
2	Salts containing NH_4 ammonium ion and nitrate and nitrite ions (NO_3 and NO_2) are generally soluble
3	Most salts of Cl, Br, and I (halide salts) are soluble. Except for Ag, Pb^{+2} and Hg_2
4	Silver salts of $AgNO_3$ and Ag ($C_2H_3O_2$) are soluble. All other silver salts are insoluble
5	$CaSO_4$, $BaSO_4$, $PbSO_4$, Ag_2SO_4, and $SrSO_4$ are insoluble, but most other Sulfate salts are soluble
6	Hydroxides: Group 1 metals are soluble; Group II metals are slightly soluble; Salts of transition metals and Al^{+3} are insoluble. Reactions of $Al(OH)_3$, $Fe(OH)_3$, and $Co(OH)_2$ are also insoluble
7	Group II carbonate salts are insoluble, as are most other carbonates
8.	Sulfide salts are insoluble: CdS, FeS, Ag_2S, As_2S_3, Bi_2S_3 PbS are also insoluble
9	Reactions of chromates with cations often yield insoluble salts.
10	Fluoride reactions with Group II metals will often yield insoluble salts, except Calcium
11	Phosphates are also frequently insoluble.

Note: Insoluble is considered as less than 1% molar concentration of the salt.
Source: http://chemwiki.ucdavis.edu/Physical_Chemistry/Equilibria/Solubilty/Solubility_Rules and http://www2.ucdsb.on.ca/tiss/stretton/Database/solubility.htm.

engineer and chemist, 1% solubility represents 1000 mmol l^{-1}. The aquatic contaminants that turn water into sewage rarely exceed 400 mg l^{-1} of solids, and waste with 1000 mg l^{-1} of almost any contaminant would be considered extremely strong. Most of the waste treatment operations are required to meet a permit limit on oxygen-consuming substances (as measured by biochemical oxygen demand (BOD)) of less than 20 mg l^{-1}, and in certain circumstances the limit is less than 5 mg l^{-1}. Additional information on solubility for inorganic compounds can be found at the following website: http://sites.chem.colostate.edu/diverdi/all_courses/CRC%20reference%20data/solubility%20of%20inorganic%20compounds.pdf.

When examining old data generated prior to the 1970s, some caution should be exercised with regard to the presence or absence of compounds. Until about 1970, it was uncommon to have environmental data reporting for metals under 5 mg l^{-1}, and highly unusual to have organic compounds reported at levels less than 10 mg l^{-1}. The development of new and better computer techniques and analytical instruments has improved accuracy ranges. For gas chromatographic analysis, a chemist can get concentrations to 1 mg l^{-1} and sometimes lower.

For analysis by gas chromatograph/mass spectrography, the analytical limits are now down to the parts per billion ranges, micrograms per liter, and for many compounds, the analytical range is in nanograms per liter or ppt.

Inorganic analysis has also improved with new techniques. The modern laboratory uses inductively coupled plasma techniques for analysis, and the reporting limits are micrograms per liter.[17] The analytical techniques for metals often incorporate the need for a standards curve where known concentrations of substances are analyzed to develop a spectrum absorbance curve versus concentration for a particular set of samples to be analyzed.[18] There are often problems with interferences in the analysis from either competing elements with similar absorption spectra or similar emission spectra. Mercury and lead analyses use cold emission spectra, and the same general concerns about calibration apply.

If one is having samples analyzed for the purpose of submitting them to a regulatory agency, state, national, or regional certification of the laboratory is a must if the results are to be accepted. The same applies to samples analyzed in another country, and the quality control data should always accompany the results.

1.7 Laboratory Guidance

When you examine water analyses, quality control in the laboratory is as important as the detection limits of the analytical equipment. One has to be familiar with the measurement techniques and some of the quality control procedures in order to understand the analyses. The equipment, the detection limits, the analytical methods, and interferences for specific analytes are always important. In most cases, the result one gets from the laboratory is sufficient, but there are cases, especially when one looks at low detection limits, and especially with organic chemical analyses, when the detection equipment can become an important part of the answer. If the equipment cannot detect the compound, or if the wrong compound is analyzed, the analysis can be useless in solving a water quality puzzle or in understanding the analysis.

For all samples delivered to the laboratory, strict protocols for sampling, preservation and transportation must be followed. Chain of evidence/custody protocols must be observed for all samples collected and submitted to a regulatory agency.[19] Some of those protocols include:

1. Packing the samples in ice and making sure that they are delivered to the laboratory before the ice melts.
2. All samples must be collected in thoroughly cleaned glassware (most often specially cleaned glassware).
3. Samples must be delivered within a specific timeframe (generally 48 hours).
4. The samples must have a completed chain of custody form for each sample.

5. The sample container must be sealed and be tamper-proof, or have seals that indicate whether it has been opened and examined prior to receipt.[20]

An aside is necessary here to indicate the manner in which planning for all contingencies is necessary. In 2004 my team was collecting water and soil samples in Ecuador under the supervision of the Ecuadorian Court. Initially, a laboratory with the required equipment to analyze soil and water samples at very low detection limits required for the project was not available.[21] So, we chose a US-based laboratory which had the required equipment, and which had a US Department of Agriculture soils permit for our analyses. (The soils permit was required to allow the samples to enter the US, ensuring that they would be sent to a laboratory or other location which would prevent foreign disease and insect vectors from entering the US, and to prevent the USDA from destroying the samples.)

The samples were to be delivered by Federal Express, and we were assured that the samples should be in the laboratory within the allowable holding times.

We packed the samples in a lot of ice, sealed the sample containers (big blue coolers) and executed the chain of custody forms, and placed a note in the paperwork indicating that the samples were for analyses and included the Soil Permit Number of the designated laboratory, along with a copy of their permit.

The Department of Agriculture placed a three days hold on the samples, causing the cooling ice to melt, raising the temperature of the samples beyond the protocol temperature limits, and the delay also caused the samples to exceed the protocol's holding times. Because of the protocol violations, we could not use the analyses. The point is that we should have planned better and accompanied the samples.

It is also important to decide in advance, especially in a regulatory situation, how non-detects and below quantification limits are to be handled and reported.[22]

The laboratory must have a quality control/quality assurance manual that includes use of duplicate and matrix spike samples. This is especially important in the analyses of organic compounds.

For specific information on sample holding times and preservation techniques for US regulatory programs, and most other countries' analytical protocols,[23] see the US Code of Federal Regulations, Chapter 40, Part 136, (http://www.epa.gov/region9/qa/pdfs/40cfr136_03.pdf), and analyses involving hazardous wastes are specified in SW-846, Chapter 2, starting at about page 60: (http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/chap2.pdf). It is important to recognize that detection limits between various programs and analytical methods are substantially different, and what is invisible

(non-detectable) in one set of analyses may be measured to two or three significant places with other methods. In general, *Standard Methods* is most often used for water analyses, and the methods are direct and often require less expensive equipment.

The analytical procedures in the EU are sufficiently different from the procedures in the US that the EU procedures follow ISO-9000 series standards.[24]

1.8 Regulatory Framework of Water Regulations

1.8.1 What Is Quality Water?

Defining quality water is difficult because the perception of water quality depends upon who is asking, and the uses for the water. The simplest definition of quality water would be a lack of contaminants, often equated with pure water. However, pure water is difficult and expensive to obtain. The perceived quality of water depends upon the types of contaminants it contains. The removal of contaminants from water is an expensive process, and the cost of that removal is directly related to the requirements for purity or the perceived quality of the water. For practical purposes, we have to compromise about the contaminants that we can accept in the water, regulating or eliminating those that are harmful, and ignoring those that are too difficult, impractical or expensive to regulate or remove.

The function of water quality standards is to specify minima and maxima that can be used to protect the environment in accordance with overall objectives. Substances that are harmful are regulated, and specific water quality floors are set for those contaminants deemed to be beneficial. Note that this does not mean that criteria or regulations need to be meaningful, nor tied to controllable parameters – only that they can be measured and regulated.

Two good examples of this can be found in stream standards. First, in many areas, minimum dissolved oxygen (DO) concentrations are mandated for certain classes of aquatic life (trout streams) at 6.0 mg l^{-1} of DO, at all times. Given diurnal variations and seasonal variations in groundwater, runoff quality, and so on, it is functionally impossible to mandate that the DO concentration of 6.0 mg l^{-1} be achieved at all times because Mother Nature's activities upstream will govern the quality of the water and the oxygen content.

Secondly, turbidity standards (a measurement of the cloudiness of the water) have been imposed on many watercourses and streams. This is an attempt to control runoff from lands that are under development and which may have had their vegetative cover removed in preparation for earthwork. The regulation sets

limits on turbidity increases on runoff from a property with an active construction activity thereupon. Turbidity is measured in either Jackson Turbidity Units (JTUs, an older style measurement)[25] or nepthlometric units (NTUs),[26] where both measure light scattered in water, or the relative cloudiness of the water. The amount of light scattered depends upon particle size, shape, albedo, and color. For example, suspensions containing mica would have a higher albedo and thus a higher NTU than soils with a darker color for the same level of suspended solids in the water.[27] For low values of NTU, there is no calibration, and for soils, both measurements have a minimal relationship to suspended solids and the test has low repeatability.

In the first case, development can be restricted if the water quality is not maintained. In the second case, the property owner can be fined and his activity halted based upon the results of the test, even though the owner has done everything requested by the governing legal authority.

We often judge the environmental quality of water by its suitability to support aquatic life, and its suitability for public recreational and drinking water purposes, and freedom from contaminants that would prevent a specific use. For example, distilled water has high quality, but it is unsuitable for many purposes because it cannot support aquatic life, nor is it safe to use as drinking water. Freshwater is unsuited for saltwater organisms, and vice versa.

By comparison, the quality requirement for cooling water is much lower. The water has a tolerance for impurities because it is non-potable, and it is recirculated through process piping where it can pick up contaminants. The principal requirement for cooling water is its temperature, and it should be relatively free of suspended solids. Cooling tower water is often treated chemically to reduce corrosion in the plant piping, so it is generally non-potable and will require treatment before it is discharged to the environment.

1.8.2 Water Quality Standards

The next couple of sections will cover the US water quality standards and the EU and UK Water Quality Standards and effluent setting processes. The US Standards will be discussed in greater detail because: (i) the author is US-based and more familiar with the US regulations; (ii) the UK Regulations are set by a slightly different procedural basis which will be discussed in overview; (iii) the EU Regulations are set by policy which is then enforced by individual EU member countries; and (iv) because the US represents the largest single market in the world, with the exception of China, which at the time of writing, does not have a well-defined market nor structure.

1.8.3 Water Quality Standards in the United States

US surface water quality standards are established by classification and proposed use. The legal authority for the establishment of surface water quality standards is the Clean Water Act 1972 (CWA), and accompanying US regulations found in Chapter 40 of the Code of Federal Regulations Part 131. The CWA provided the authority for the Federal Government to establish standards for the navigable waters of the US.[28] These standards establish minimum concentrations of specific water quality parameters that must be met at all times. Depending upon the declared use for the waters, the provisions include temperature, dissolved oxygen, and other limits that are generally protective of aquatic life and protective of the proposed use. It is the water quality standards which drive effluent standards.

Water quality criteria are slightly different from standards as they express the intent to create water free from certain contaminants, but they do not have the force of law.

Groundwater in the US is generally regulated by the Clean Drinking Water Act. Because it is regulated by a different law, it is treated differently here. Drinking Water Quality Standards, are based on a requirement to protect health and the Water Quality Standards are requirements designed to protect aquatic life and river quality (and drinking water sources).

1.8.4 Establishing Water Quality Standards

In the US, waters are classified on a watershed basis or geographical area, and within that area, the individual rivers, streams, and water bodies are classified with regard to specific use. The use sets the water quality standards. An example of the classification and standards setting is shown in Section 1.8.10, taken from Georgia Environmental Law.

1.8.5 Effluent Standards and Guidance

Starting in the 1970s, the Federal and State and international communities started to publish water quality criteria (WQC). In the US, the earliest WQC can be tracked back to the Rivers and Harbors Act of 1899, where it was determined that unauthorized dumping of garbage or refuse matter of any kind into navigable waters of the US was a misdemeanor. The provisions of the Act were later used to control certain types of water pollution discharges, principally prior to the development of the Clean Water Act, and it is still used today to govern the discharge of dredge and fill materials to the "navigable waterways"[29] of the US.

The existence of water quality standards in the US dates back to the Ohio River Valley Sanitary Commission, formed in 1948 in an attempt to regulate

the discharge of industrial waters into the tributaries of the Ohio River. The compact was historic because any one state could bring an action against individual companies in other states, based on water pollution.

Later, when the Clean Water Act first became law in the early 1970s, the responsibility for discharge to waters of the Ohio and its tributaries was transferred from the Corps of Engineers to the agency that later became the US Environmental Protection Agency. The purpose of this bit of history is to set the stage for the next material in this chapter: regulations and their effect on water discharges and treatment.

We now live in a regulated environment and must comply with good practice and the appropriate regulations for treatment of water prior to discharge, in order to protect the environment. Many states and the Federal Government, the EU government, and almost every country have their own water quality standards that govern the discharge to surface waters. There are different ways of protecting the surface waters, depending upon the country and the philosophy with regard to protection. Section 1.8.10 contains an excerpt from the State of Georgia Code which describes the water quality standards and how they are established.

1.8.6 Mixing Zones

Before we go into stream quality and surface water quality standards, it is important to consider the definition of a mixing zone because it is generally an exception to the water quality standards and criteria.

> A mixing zone is a small area where water quality standards do not apply. It can be on a stream, a lake, or a river, but it is an area where the effluent from a process is allowed to mix with the receiving waters for the purpose of allowing the contaminants in the effluent to equalize into the water column.[30]

There are a number of qualifications to a mixing zone, and it can be a complex issue. The purpose of mixing zones is to allow the effluent to mix with the local water, and after a fashion, allow the effluent stream to mix fully with the receiving water body. The USEPA has developed a licensing and recommendation program with Mixzon, for their program called Cormix. The program constructs a detailed mathematical model of a mixing zone, and the diffusion and mixing that occurs when an effluent discharges into a body of water or stream. The Cormix program is available for a relatively expensive annual license fee.[31] Manually established mixing zones generally have a maximum width of a third to half of the stream width and a specified length where the effluent will be assumed to be fully diluted.[32]

If a wastewater discharge, legally permitted, is flowing into an intermittent stream, it can pose a significant industrial challenge. During dry weather, the only flow in the stream is the plant effluent. Since water quality standards are significantly lower than effluent standards, and are always applicable, the industry must achieve a higher level of treatment in order to comply with the water quality standards.

1.8.7 Discharge Permits

There are three prominent and distinct philosophies regarding effluent discharges and water quality protection. The US regulations characterize one type of approach, while the EU regulations characterize another approach, and the UK uses a third but similar approach. We will look at all three approaches, but will give the most attention to the US regulations. It should be noted that the EU regulations are set by a framework directive published by the EU governing body, but enforced individually and differently in each of the EU Member States.

The US approach is statistically based using a normal distribution (which will be covered in detail later), and sets limits on general pollutants, as well as individual chemical parameters. Most, if not all, US permits will have a daily maximum discharge quantity, and a monthly average discharge quantity, where the limits are derived from Stream Quality Standards, and Public Health Drinking Water Quality Criteria, with an adequate reserve or allowance for safety and expansion. In the vast majority of cases, the conventional and priority pollutants regulated will have mass-based quantity limits where the total daily average discharge mass limit is two times the monthly average figure. There is also a monthly average concentration where the daily maximum concentration cannot exceed the monthly average concentration by more than two times. Violation of either of these provisions can generate substantial fines. It is also not uncommon for the permits to have a biological monitoring component which requires aquatic testing of target organisms (usually *Daphnia magna*, or water fleas) for their survival rate in various concentrations of the facility effluent, as a check on the potential aquatic toxicity of the effluent stream.

1.8.8 US Penalty Policies – Enforcement of Permit Conditions

The US Water Pollution Control Penalty Policy starts at $10 000 per day, per violation. If the discharge is wilful or negligent, the fines can be quickly increased to between $37 500 and $50 000 per day of violation, plus a year in jail for each day of violation if the violation is found to be wilful or negligent, or fraudulent. The fine for spilling hazardous materials into public waterways is now set at $2100 per barrel or unit, plus administrative penalties starting at $137 000.[33] This regulatory approach is a huge hammer poised to be painful when dropped upon a violator. This, plus severe penalties for falsification of data, and a requirement

for self-monitoring and self-mandated reporting of all pollution permit conditions, plus any special circumstances, create a sometimes hostile relationship between industry and the EPA.[34] It is also a truism that while the EPA has been quick to bring suit against industry, even to the point of giving responsible parties prison time, it has been less enthusiastic about applying the same standards to municipal and governmental offices and locations. (The mayor does not go to jail over EPA violations, but the CEO of a company might!)

1.8.9 Water Quality Discharge Basics in the US

The following is a summary of the framework and the legal basis for development of Water Quality Regulations in the US.[35]

In the US, it is the State that must designate its waters with respect to the following objectives:

1. It is the national goal that the discharge of pollutants into the navigable waters be eliminated by 1985;
2. It is the national goal that wherever attainable, an interim goal of water quality which provides for the protection and propagation of fish, shellfish, and wildlife and provides for recreation in and on the water be achieved by July 1, 1983;
3. It is the national policy that the discharge of toxic pollutants in toxic amounts be prohibited;
4. It is the national policy that Federal financial assistance be provided to construct publicly owned waste treatment works;
5. It is the national policy that area-wide waste treatment management planning processes be developed and implemented to assure adequate control of sources of pollutants in each State;
6. It is the national policy that a major research and demonstration effort be made to develop technology necessary to eliminate the discharge of pollutants into the navigable waters, waters of the contiguous zone, and the oceans; and
7. It is the national policy that programs for the control of nonpoint sources of pollution be developed and implemented in an expeditious manner so as to enable the goals of this Act to be met through the control of both point and nonpoint sources of pollution.

Section 303 (c) (2) of the Clean Water Act further refines the requirements to require the States to issue and review triennially (once in every three years) water quality designations and standards which:

> (s)hall consist of the designated uses of the navigable waters involved and the water quality criteria for such waters based upon such uses. Such standards shall be such as to protect the public health or welfare, enhance the quality of water and serve the purposes of this Act. Such standards

Table 1.10 The 65 priority water pollutants according to the US code.

1. Acenaphthene	23. Cyanides	45. Mercury and compounds
2. Acrolein	24. DDT and metabolites	46. Naphthalene
3. Acrylonitrile	25. Dichlorobenzenes (1,2-, 1,3-, and 1,4-dichlorobenzenes)	47. Nickel and compounds
4. Aldrin/Dieldrin	26. Dichlorobenzidine	48. Nitrobenzene
5. Antimony and compounds	27. Dichloroethylenes (1,1-, and 1,2-dichloroethylene)	49. Nitrophenols (including 2,4-dinitrophenol, dinitrocresol)
6. Arsenic and compounds	28. 2,4-dichlorophenol	50. Nitrosamines
7. Asbestos	29. Dichloropropane and dichloropropene	51. Pentachlorophenol
8. Benzene	30. 2,4-dimethylphenol	52. Phenol
9. Benzidine	31. Dinitrotoluene	53. Phthalate esters
10. Beryllium and compounds	32. Diphenylhydrazine	54. Polychlorinated biphenyls (PCBs)
11. Cadmium and compounds	33. Endosulfan and metabolites	55. Polynuclear aromatic hydrocarbons (including benzanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenzanthracenes, and indenopyrenes)
12. Carbon tetrachloride	34. Endrin and metabolites	56. Selenium and compounds
13. Chlordane (technical mixture and metabolites)	35. Ethylbenzene	57. Silver and compounds
14. Chlorinated benzenes (other than dichlorobenzenes)	36. Fluoranthene	58. 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)

15. Chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane, and hexachloroethane)
16. Chloroalkyl ethers (chloroethyl and mixed ethers)
17. Chlorinated naphthalene
18. Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)
19. Chloroform
20. 2-chlorophenol
21. Chromium and compounds
22. Copper and compounds
37. Haloethers (other than those listed elsewhere; includes chlorophenylphenyl ethers, bromophenylphenyl ether, bis(dichloroisopropyl) ether, bis-(chloroethoxy) methane and polychlorinated diphenyl ethers)
38. Halomethanes (other than those listed elsewhere; includes methylene chloride, methylchloride, methylbromide, bromoform, dichlorobromomethane
39. Heptachlor and metabolites
40. Hexachlorobutadiene
41. Hexachlorocyclohexane
42. Hexachlorocyclopentadiene
43. Isophorone
44. Lead and compounds
59. Tetrachloroethylene
60. Thallium and compounds
61. Toluene
62. Toxaphene
63. Trichloroethylene
64. Vinyl chloride
65. Zinc and compounds

shall be established taking into consideration their use and value for public water supplies, propagation of fish and wildlife, recreational purposes, and also taking into consideration their use and value for navigation.

The State must, at a minimum, adopt the Federal Water Quality Regulations, and issue and adopt criteria for conventional and toxic pollutants which contain numerical standards, or which refer to biological monitoring or assessment methods. Table 1.10 contains the list of the 65 toxic pollutants that the EPA has identified.[36] The State must submit their Water Quality Standard to the Federal Government for approval, or certain portions of Federal revenues will be withheld from the non-compliant states. The Federal regulations represent a minimum floor for regulations and standards. The States are free to exceed the Federal requirements but must meet them as a minimum condition (44 FR 44502, July 30, 1979, as amended at 46 FR 2266, Jan. 8, 1981; 46 FR 10724, Feb. 4, 1981).

Other basic effluent standards are often specified by the type of industry and are regulated on a case-by-case basis. The CWA regulations at 40 CFR 401.16 identifies biochemical oxygen demand (BOD_5), total suspended (non-filterable) solids (TSS), pH, fecal coliform, and oil and grease as conventional pollutants which need to be regulated in discharge permits. 40CFR 401.17 contains limits on pH of the liquid discharged.

1.8.10 How Water Quality Standards Are Established

Water quality standards are established by watershed or geographical location and then by proposed use. All water quality standards have to be maintained at all times, even at very low flows. The definition of low flow is consistent in the US, as the lowest flow that occurs in a stream for seven consecutive days on an average of once in every 10 years. This is known as the "7Q10 Flow."

A sample of the classification and water quality standards follows. The regulations are similar in all the states in the US, and the specific samples of regulations are taken from the Georgia Code for protection of the environment. Specific references to Georgia have been removed, and the regulations have been edited to follow generally the appropriate sections of US Code.

In the following, ellipses and brackets are used to indicate comments or deleted sections of material that are largely irrelevant to the subject of water quality or development and promulgation of the Standards.

391-3-6-.03 Water Use Classifications and Water Quality Standards

(1) *Purpose*. The establishment of water quality standards.

(2) *Water quality enhancement:*

(a) The purposes and intent of the State in establishing Water Quality Standards are to provide enhancement of water quality and prevention of pollution; to protect the public health or welfare in accordance with

the public interest for drinking water supplies, conservation of fish, wildlife and other beneficial aquatic life, and agricultural, industrial, recreational, and other reasonable and necessary uses and to maintain

(b) and improve the biological integrity of the waters of the State.
   (i) Existing instream water uses and the level of water quality necessary to protect the existing uses shall be maintained and protected.
   (ii) Where the quality of the waters exceed levels necessary to support propagation of fish, shellfish, and wildlife and recreation in and on the water, that quality shall be maintained and protected unless the division finds, … that allowing lower water quality is necessary to accommodate important economic or social development in the area in which the waters are located.

(3) [is Irrelevant]

(4) *Water use classifications*. Water use classifications for which the criteria of this Paragraph are applicable are as follows:
   (a) Drinking Water Supplies
   (b) Recreation
   (c) Fishing, Propagation of Fish, Shellfish, Game and Other Aquatic Life
   (d) Wild River
   (e) Scenic River
   (f) Coastal Fishing

(5) *General criteria for all waters*. The following criteria are deemed to be necessary and applicable to all waters of the State:
   (a) All waters shall be free from materials associated with municipal or domestic sewage, industrial waste or any other waste which will settle to form sludge deposits that become putrescent, unsightly, or otherwise objectionable.
   (b) All waters shall be free from oil, scum, and floating debris associated with municipal or domestic sewage, industrial waste or other discharges in amounts sufficient to be unsightly or to interfere with legitimate water uses.
   (c) All waters shall be free from material related to municipal, industrial, or other discharges which produce turbidity, color, odor, or other objectionable conditions which interfere with legitimate water uses.
   (d) *Turbidity*. The following standard is in addition to the narrative turbidity standard … above: All waters shall be free from turbidity which results in a substantial visual contrast in a water body due to a man-made activity. [Note the vagueness of the standard.] The upstream appearance of a body of water shall be as observed at a point immediately upstream of a turbidity-causing man-made activity. That upstream appearance shall be compared to a point which is located sufficiently downstream from the activity so as to provide an appropriate mixing zone. For land disturbing activities, proper

design, installation, and maintenance of best management practices and compliance with issued permits shall constitute compliance ....

(e) All waters shall be free from toxic, corrosive, acidic, and caustic substances discharged from municipalities, industries, or other sources, such as nonpoint sources, in amounts, concentrations, or combinations which are harmful to humans, animals, or aquatic life.

(i) Instream concentrations of the following chemical constituents which are considered to be other toxic pollutants of concern in the State of Georgia shall not exceed the criteria indicated below under 7-day, 10-year minimum flow (7Q10) or higher stream flow conditions except within established mixing zones:

[List of specific chemicals with concentrations follows for both 1Q10 and 7Q10 flows but is omitted here.]

(6) *Specific criteria for classified water usage*. In addition to the general criteria, the following criteria are deemed necessary and shall be required for the specific water usages shown:

(a) *Drinking water supplies*. Those waters approved as a source for public drinking water systems permitted or to be permitted by the Environmental Protection Division. Waters classified for drinking water supplies will also support the fishing use and any other use requiring water of a lower quality.

(i) *Bacteria*. [The standard for bacterial quality is based on a geometric mean for May through October and a different level of quality for the months of November through April.]

(ii) *Dissolved oxygen*. A daily average of 6.0 mg l^{-1} and no less than 5.0 mg l^{-1} at all times for waters designated as trout streams by the Wildlife Resources Division. A daily average of 5.0 mg l^{-1} and no less than 4.0 mg l^{-1} at all times for water supporting warm water species of fish.

(iii) *pH*. Within the range of 6.0–8.5.

(iv) No material or substance in such concentration that, after treatment by the public water treatment system, exceeds the maximum contaminant level established for that substance by the Environmental Protection Division pursuant to the [Name of the State] Rules for Safe Drinking Water.

(v) *Temperature*. Not to exceed 90 °F. At no time is the temperature of the receiving waters to be increased more than 5 °F above intake temperature except that in estuarine waters the increase will not be more than 1.5 °F. In streams designated as primary trout or smallmouth bass waters by the Wildlife Resources Division, there shall be no elevation of natural stream temperatures. In streams designated as secondary trout waters, there shall be no elevation exceeding 2 °F of natural stream temperatures.

(b) *Recreation*. General recreational activities such as water skiing, boating, and swimming, or for any other use requiring water of a lower quality, such as recreational fishing. These criteria are not to be interpreted as encouraging water contact sports in proximity to sewage or industrial waste discharges regardless of treatment requirements:
  (i) *Bacteria*. [Fecal coliform standards for coastal and other recreational waters – omitted.]
  (ii) *Dissolved oxygen*. A daily average of 6.0 mg l^{-1} and no less than 5.0 mg l^{-1} at all times for waters designated as trout streams by the Wildlife Resources Division. A daily average of 5.0 mg l^{-1} and no less than 4.0 mg l^{-1} at all times for waters supporting warm water species of fish.
  (iii) *pH*. Within the range of 6.0–8.5.
  (iv) *Temperature*. Not to exceed 90 °F. At no time is the temperature of the receiving waters to be increased more than 5 °F above intake temperature except that in estuarine waters the increase will not be more than 1.5 °F. In streams designated as primary trout or smallmouth bass waters by the Wildlife Resources Division, there shall be no elevation of natural stream temperatures. In streams designated as secondary trout waters, there shall be no elevation exceeding 2 °F natural stream temperatures.

(c) *Fishing*. Propagation of Fish, Shellfish, Game and Other Aquatic Life; secondary contact recreation in and on the water; or for any other use requiring water of a lower quality:
  (i) *Dissolved oxygen*. A daily average of 6.0 mg l^{-1} and no less than 5.0 mg l^{-1} at all times for water designated as trout streams by the Wildlife Resources Division. A daily average of 5.0 mg l^{-1} and no less than 4.0 mg l^{-1} at all times for waters supporting warm water species of fish.
  (ii) *pH*. Within the range of 6.0–8.5.
  (iii) *Bacteria*. [Bacterial standards repeated and omitted.]
  (iv) *Temperature*. [Temperature standard repeated and omitted.]

(d) *Wild river*. For all waters designated in 391-3-6-.03(13) as "Wild River," there shall be no alteration of natural water quality from any source.

(e) *Scenic river*. For all waters designated as "Scenic River," there shall be no alteration of natural water quality from any source.

(f) *Coastal fishing*. This classification will be applicable to specific sites when so designated by the Environmental Protection Division. For waters designated as "Coastal Fishing," site specific criteria for dissolved oxygen will be assigned. All other criteria and uses for the fishing use classification will apply for coastal fishing.

(i) *Dissolved oxygen (D.O.)*. A daily average of 5.0 mg l^{-1} and no less than 4.0 mg l^{-1} at all times. [Qualifying statements omitted.]

(7) *Natural water quality*. It is recognized that certain natural waters of the State may have a quality that will not be within the general or specific requirements contained herein. These circumstances do not constitute violations of water quality standards. This is especially the case for the criteria for dissolved oxygen, temperature, pH and fecal coliform. NPDES permits and best management practices will be the primary mechanisms for ensuring that discharges will not create a harmful situation.

(8) *Treatment requirements*. Notwithstanding the above criteria, the requirements of the State relating to secondary or equivalent treatment of all waste shall prevail. The adoption of these criteria shall in no way preempt the treatment requirements.
[Definition of low flow conditions follows.]

(9) *Streamflows*. Specific criteria or standards set for the various parameters apply to all flows on regulated streams. On unregulated streams, they shall apply to all streamflows equal to or exceeding the 7-day, 10-year minimum flow (7Q10) and/or the 1-day, 10-year minimum flow (1Q10). All references to 7-day, 10-year minimum flow (7Q10) and 1-day, 10-year minimum flow (1Q10) also apply to all flows on regulated streams. All references to annual average stream flow also apply to long-term average stream flow conditions. Numeric criteria exceedences that occur under streamflows lower than 7Q10 or 1Q10, whichever applies, do not constitute violations of water quality standards as long as all current permit conditions are met.

(10) *Mixing zone*. Effluents released to streams or impounded waters shall be fully and homogeneously dispersed and mixed insofar as practical with the main flow or water body by appropriate methods at the discharge point. Use of a reasonable and limited mixing zone may be permitted on receipt of satisfactory evidence that such a zone is necessary and that it will not create an objectionable or damaging pollution condition. Protection from acute toxicity shall be provided within any designated mixing zone to ensure a zone of safe passage for aquatic organisms.

(11) *Toxic pollutant monitoring*. The Division will monitor waters of the State for the presence or impact of Section 307 (a)(l) Federal Clean Water Act toxic pollutants**,** and other priority pollutants. The monitoring shall consist of the collection and assessment of chemical and/or biological data as appropriate from the water column, from stream bed sediments, and/or from fish tissue. Specific stream segments and chemical constituents for monitoring shall be determined by the Director on the basis of the potential for water quality impacts from toxic pollutants from point or nonpoint waste sources. Singularly or in combination, these constituents may cause an adverse effect on fish propagation at levels lower than the criteria.

Additional toxic substances and priority pollutants will be monitored on a case specific basis using Section 304(a) Federal Clean Water Act guidelines or other scientifically appropriate documents.

(12) *Fecal coliform criteria*. The criteria for fecal coliform bacteria provide the regulatory framework to support the USEPA requirement that States protect all waters for the use of primary contact recreation or swimming… The assessment of streams, rivers, lakes, and estuaries in Georgia and other States is based on fecal coliform organisms….

(13) *Acceptance of data*. [The State will accept data for listing if it is sampled in accordance with the State's water quality assurance manual and analyzed by a Federal or State certified laboratory.]

(14) *Specific water use classifications*. Beneficial water uses assigned by the State to all surface waters … stream reaches not specifically listed are classified as Fishing. The specific classifications are as follows:
[What follows is a very abbreviated listing of some watersheds with their classifications excerpted directly from the Code and provided as an example of the type of classification system used and the classes of waters considered]:

Altamaha River Basin		*Classification*
All littoral waters on the ocean side of St. Simons, Sea, and Sapelo Islands		Recreation
Chattahoochee River Basin		*Classification*
Alexander Creek	Headwaters to confluence with Cedar Creek	Drinking water
Bear Creek	Headwaters to confluence with Chattahoochee River	Drinking water
Chattahoochee River	Soque River to White Creek	Recreation and drinking water
Jacks Creek	Waters within the Cohutta wilderness area	Wild and scenic

(15) *Specific criteria for lakes and major lake tributaries*. In addition to the general criteria, the following lake specific criteria are deemed necessary and shall be required for the specific water usage as shown. [Specific water quality criteria are not shown.]

1.8.11 UK Water Effluent Quality Standard[37]

The UK has a regulatory regime that is different from much of the rest of the EU. The water standards are set by the UKTAG group, and they have established a number of control parameters that are very similar to the priority pollutants in

Table 1.11 UK list of priority pollutants.

See the UK Water Quality Directive
ammonia, arsenic, chlorine, chromium(III), chromium(VI), copper, cyanide, cypermethrin, diazinon, 2,4-dichlorophenol, 2,4-dichlorophenoxyacetic acid (2,4-D), dimethoate, iron, linuron, mecoprop, permethrin, phenol, toluene, zinc, and the following recently added pollutants: benzyl butyl phthalate, carbendazim, chlorothalonil, 3,4-dichloroaniline, glyphosate, manganese, methiocarb, pendimethalin, tetrachloroethane and triclosan.

Source: http://www.wfduk.org/sites/default/files/Media/Environmental%20standards/UKTAG%20Environmental%20Standards%20Phase%203%20Final%20Report%2004112013.pdf.

the US. Briefly, the Water Quality Directive has identified the following pollutants shown in Table 1.11.

The UK government has determined that sampling and analyzing water quality 12–20 times per year will establish that river water quality standards have been met approximately 90–95% of the time. Table 4 of the UK standards establishes the number of permissible failures in a dataset that will lead to indicating that water quality standards have not been met, as shown in Table 1.12.

Most of the UK effluent standards have an "upper tier" (do not exceed limit) and an effluent value which must be achieved 95% of the time. The 95% effluent standard is established using river water quality modeling, where the BOD_5 and other minimum river water quality parameters should be achieved approximately 90% of the time. The 95% effluent limit is also based upon a log-normal statistical distribution, which will be discussed later. The exceedances to the permit limits are determined by a look-up table (presented above) which considers the accuracy of the test, and the likelihood that the reported values may actually be within permit parameters because of the test's accuracy.

Table 1.12 UK water quality sampling table for determining compliance with standards UK directive Table 4.

Look-up table for 95% confidence of failing a 95 percentile standard	
Number of samples	**Required number of samples exceeding standard**
4–7	>1
8–16	>2
17–28	>3
29–40	>4
41–53	>5
54–67	>6

The UK water quality standard is found here: http://www.wfduk.org/sites/default/files/Media/Environmental%20standards/UKTAG%20Environmental%20Standards%20Phase%203%20Final%20Report%2004112013.pdf.

There is a further complication, which seems to be used more in Scotland than England, Wales, or Northern Ireland. If one fails the 95-percentile requirement but meets a percentage removal of the influent load, the plant is determined to have been in compliance.[38]

> Prosecution of the violator is also not automatic. The EA (England/Wales) or SEPA (Scotland) may decide that there were exceptional circumstances, or they were warned in advance of the cause and what was being done to prevent it, or that they accept that measures are in place to prevent it from happening again. Should they decide to prosecute, the fine is still not fixed; it goes to court. There is an upper limit to the fine, but what is paid may be less – (if) the court decides. The maximum fine appears to be £20 000.[39]

The water quality standards are established on a watershed-by-watershed basis, by assessing what is ecologically acceptable to the river, and are enforced and compared with a set of standards designed to ensure that benefit of the doubt goes to the polluter.[40] The preference is to avoid prosecution, and the authorities will work with companies to ensure that steps are taken to avoid the problem in the future. If the case goes to court there is no control by the EA on the level of fine, but it will not exceed £20 000.

1.8.12 EU Water Quality Standards and Effluent Limits

The European Union approach to water pollution discharges is very different. There are a number of details involved in obtaining a permit, but the basic philosophy is very similar to an odometer. The permittee pays a fee for the right to discharge pollutants to the environment, based upon negotiated values and water quality criteria, and the permittee pays per kilogram of materials discharged.[41] It is analogous to an odometer because the meter is running and the higher the discharge amount, the faster the meter runs and the higher the fees.

When it comes to determination of individual water quality parameters and effluent standards, the EU is a bit of a mixed bag. Germany has national mass limits, a national consent value, with a multiplier of the mass discharged above the consent value. But, like the UK, "exceptional circumstances" is a defense, and, unlike the UK system, severe winter or heavy rainfall is accepted as an exceptional circumstance.[42] The discharge limits are based on the Water Framework Directive (WFD) (http://ec.europa.eu/environment/water/water-framework/index_en.html). This states that all water bodies are required to have a good ecological water quality by 2015.

If technical or financial circumstances make timely compliance prohibitive, an extension can be granted if there is sufficient excuse. The EU also has an Urban Wastewater Directive whose objective is to protect the environment from the adverse effects of urban wastewater discharges and discharges from certain industrial sectors.[43]

Every member state can then apply this directive as they wish, as long as they meet the standards set forth. In most countries, although the WFD allows for variable discharge limits, many still use fixed discharge limits. There are some exemptions, usually for industry where it does not make technical or financial sense.[44]

The EU also has a list of its own priority pollutants that member states must regulate (Table 1.13). That list of priority pollutants is very similar to the USEPA's priority pollutants, except that the enforcement is left to the member states.

1.8.13 Other Water Quality Requirements

We have seen how the stream and river water quality requirements for fish and for recreational activities are established. There are many other types of requirements for water: drinking water, agricultural water, industrial water (boiler and cooling water), to name but a few. In all of these categories, the water quality requirements are tailored to the use, and if the available water is not of sufficient quality for the intended use or purpose, it must be treated to conform to the requirements.

1.8.13.1 US Primary and Secondary Drinking Water Standards

One of the most important uses and highest classifications of use is for drinking water. The water must be free of any harmful substances or organisms.[45] Drinking water has some of the greatest restrictions on water contaminant levels (from USEPA)[46]: nitrate, NO_3-N 10 mg l^{-1}; benzene, 0.005 mg l^{-1}; bacterial contamination such as Cryptosporidium and *Giardia lamblia*, zero; uranium, 0.03 mg l^{-1}; pesticides such as Lindane, 0.0002 mg l^{-1}; chromium (total) 0.1 mg l^{-1}; cadmium 0.005 mg l^{-1}.

The USEPA uses a two-tier list of Primary and Secondary Drinking Water Standards, and Maximum Contaminant Levels and Treatment Technology Standards to establish the requirements for limitations on drinking water. The Treatment Technology Goals have been established for those contaminants that cannot be effectively removed. The EPA also has a more extensive list of microbiological contaminants than the EU, UK, or WHO.

Table 1.13 EU list of priority water pollutants.

	CAS number	EU number	Name of priority substance	Identified as priority hazardous substance
(1)	15972-60-8	240-110-8	Alachlor	
(2)	120-12-7	204-371-1	Anthracene	X
(3)	1912-24-9	217-617-8	Atrazine	
(4)	71-43-2	200-753-7	Benzene	
(5)	Not applicable	Not applicable	Brominated diphenyletheriv	X
	32534-81-9	Not applicable	Pentabromodiphenylether (congener numbers 28, 47, 99, 100, 153, and 154)	
(6)	7440-43-9	231-152-8	Cadmium and its compounds	X
(7)	85535-84-8	287-476-5	Chloroalkanes, C10-13 iv	X
(8)	470-90-6	207-432-0	Chlorfenvinphos	
(9)	2921-88-2	220-864-4	Chlorpyrifos (chlorpyrifos-ethyl)	
(10)	107-06-2	203-458-1	1,2-dichloroethane	
(11)	75-09-2	200-838-9	Dichloromethane	
(12)	117-81-7	204-211-0	Di(2-ethylhexyl)phthalate (DEHP)	
(13)	330-54-1	206-354-4	Diuron	
(14)	115-29-7	204-079-4	Endosulfan	X
(15)	206-44-0	205-912-4	Fluoranthenevi	
(16)	118-74-1	204-273-9	Hexachlorobenzene	X
(17)	87-68-3	201-765-5	Hexachlorobutadiene	X
(18)	608-73-1	210-158-9	Hexachlorocyclohexane	X
(19)	34123-59-6	251-835-4	Isoproturon	
(20)	7439-92-1	231-100-4	Lead and its compounds	
(21)	7439-97-6	231-106-7	Mercury and its compounds	X
(22)	91-20-3	202-049-5	Naphthalene	
(23)	7440-02-0	231-111-4	Nickel and its compounds	
(24)	25154-52-3	246-672-0	Nonylphenols	X
	104-40-5	203-199-4	(4-nonylphenol)	X
(25)	1806-26-4	217-302-5	Octylphenols	
	140-66-9	Not applicable	(4-(1,1′,3,3′-tetramethylbutyl)-phenol)	
(26)	608-93-5	210-172-5	Pentachlorobenzene	X
(27)	87-86-5	201-778-6	Pentachlorophenol	

(*continued*)

Table 1.13 (Continued)

	CAS number	EU number	Name of priority substance	Identified as priority hazardous substance
(28)	Not applicable	Not applicable	Polyaromatic hydrocarbons	X
	50-32-8	200-028-5	(Benzo(a)pyrene)	X
	205-99-2	205-911-9	(Benzo(b)fluoranthene)	X
	191-24-2	205-883-8	(Benzo(g,h,i)perylene)	X
	207-08-9	205-916-6	(Benzo(k)fluoranthene)	X
	193-39-5	205-893-2	(Indeno(1,2,3-cd)pyrene)	X
(29)	122-34-9	204-535-2	Simazine	
(30)	Not applicable	Not applicable	Tributyltin compounds	X
	36643-28-4	Not applicable	(Tributyltin-cation)	X
(31)	12002-48-1	234-413-4	Trichlorobenzenes	
(32)	67-66-3	200-663-8	Trichloromethane (chloroform)	
(33)	1582-09-8	216-428-8	Trifluralin	

Additional pollutants added by amending directive 88/347/EEC and 90/415/EEC

	CAS number	Name of other pollutant
(6a)	56-23-5	Carbon-tetrachloride[a)]
(9b)	Not applicable	DDT total[a) b)]
	50-29-3	Para-para-DDT[a)]
(9a)		Cyclodiene pesticides
	309-00-2	Aldrin[a)]
	60-57-1	Dieldrin[a)]
	72-20-8	Endrin[a)]
	465-73-6	Isodrin[a)]
(29a)	127-18-4	Tetrachloro-ethylene[a)]
(29b)	79-01-6	Trichloro-ethylene[a)]

a) This is not a priority substance but one of the other pollutants for which the environmental quality standards (EQS) are identical to those laid down in the legislation that applied prior to 13 January 2009.

b) DDT total comprises the sum of the isomers 1,1,1-trichloro-2,2 bis (p-chlorophenyl) ethane (CAS number 50-29-3; EU number 200-024-3); 1,1,1-trichloro-2 (o-chlorophenyl)-2-(p-chlorophenyl) ethane (CAS number 789-02-6; EU number 212-332-5); 1,1-dichloro-2,2 bis (p-chlorophenyl) ethylene (CAS number 72-55-9; EU number 200-784-6); and 1,1-dichloro-2,2 bis (p-chlorophenyl) ethane (CAS number 72-54-8; EU number 200-783-0).

Source: http://ec.europa.eu/environment/water/water-framework/priority_substances.htm.

1.8.13.2 WHO Drinking Water Quality Guidelines

By comparison, the World Health Organization (WHO) has a slightly different list of recommended water quality guidelines. The guidelines are explained in a 564-page document available from the WHO website.[47] The WHO publishes guidelines rather than standards because they generally lack the power to enforce the guidelines in the various countries around the world. Of significance is the fact that the WHO guideline on nitrate is five times the maximum permitted value in the US. Higher nitrate levels may have an association with methemoglobinemia, or the "blue baby syndrome,"[48] and several other diseases.

1.8.13.3 EU Drinking Water Directives

The EU publishes directives that serve as guidelines for the member states. The language is "should comply" rather than "must comply" when compared with the US. One of the principal differences in the EU directives is in the area of nitrate. The *EU Directive on Water Quality* limits the concentration of nitrate to no more than 50 mg l^{-1} NO_3-N.[49] The US requires an upper limit of 10 mg l^{-1} of nitrate, and a different set of bacteriological parameters, and generally comparable but generally slightly higher levels of individual contaminants, such as lead and pesticides.

1.8.13.4 UK Drinking Water Standards

The UK Drinking Water Standards are also generally comparable with the US standards, with some numerical limits higher and some lower than US standards.[50] The UK standards are also comparable with the EU standards, but are a bit more restrictive overall.

1.9 Water Use Data and Some Discharge Characteristics

Industrial water use varies widely with the industry and the technology used. Most if not all industries can be categorized on the basis of water use and product involved. The industrial effluents consist of a base flow (including sanitary flows and some consistent operations) and process-related flows that are often in proportion to the process production. This is true for both quantity of water use and the amount of pollutants produced by a plant or a process. Sometimes, in larger plants, things like boiler blowdown and cooling flows are more constant than the flows and pollutant loadings from individual processes. About the only way to make an accurate determination is to attempt to perform a water balance for the entire plant and account for the flows and water use. (The word "attempt" is used with "water balance" because, more often than not, water use balances do not balance despite one's best efforts!)

One of the best sources for information on industrial water use is somewhat outdated, but only because some of the technologies described have changed. In the 1970s through to the early 1980s, the USEPA published Effluent Guidelines for discharges to surface waters. The summary of the documents are reflected in the water pollution control regulations published in the Federal Register 40 CFR Chapter I, Subchapter N – Effluent Guidelines and Standards Parts 400 through 471.[51] The regulations are both broad and deep. The headings of each of the Subparts contain a number of subcategories which deal with individual manufacturing products within a broader industrial category. An example of the organization and breakdown of a typical category can be found in Table 1.14.

Table 1.14 Typical breakout of Federal Register effluent guidelines and standards for the pesticide chemicals subpart.

PART 455 – PESTICIDE CHEMICALS (§§ 455.10–455.67)
§ 455.10 – General definitions.
SUBPART A – Organic Pesticide Chemicals Manufacturing Subcategory (§§ 455.11–455.27)
SUBPART B – Metallo-Organic Pesticide Chemicals Manufacturing Subcategory (§§ 455.30–455.37)
SUBPART C – Pesticide Chemicals Formulating and Packaging Subcategory (§§ 455.40–455.47)
SUBPART D – Test Methods for Pesticide Pollutants (§§ 455.50–455.50)
SUBPART E – Repackaging of Agricultural Pesticides Performed at Refilling Establishments (§§ 455.60–455.67)
Table 1 to Part 455 – List of Organic Pesticide Active Ingredients
Table 2 to Part 455 – Organic Pesticide Active Ingredient Effluent Limitations Best Available Technology Economically Achievable (BAT) and Pretreatment Standards for Existing Sources (PSES)
Table 3 to Part 455 – Organic Pesticide Active Ingredient New Source Performance Standards (NSPS) and Pretreatment Standards for New Sources (PSNS)
Table 4 to Part 455 – BAT and NSPS Effluent Limitations for Priority Pollutants for Direct Discharge Point Sources that use End-of-Pipe Biological Treatment
Table 5 to Part 455 – BAT and NSPS Effluent Limitations for Priority Pollutants for Direct Discharge Point Sources that do not use End-of-Pipe Biological Treatment
Table 6 to Part 455 – PSES and PSNS for Priority Pollutants
Table 7 to Part 455 [Reserved]
Table 8 to Part 455 – List of Pollution Prevention Alternative Practices
Table 9 to Part 455 – Group 2 Mixtures
Table 10 to Part 455 – List of Appropriate Pollution Control Technologies

Note: There are 10 Appendices (Tables 1–10) that address active ingredients, mixtures, priority pollutants, alternative practices, and other similar subjects.
Authority: Secs. 301, 304, 306, 307, and 501, Pub. L. 92-500, 86 Stat. 816, Pub. L. 95-217, 91 Stat. 156, and Pub. L. 100-4 (33 U.S.C. 1311, 1314, 1316, 1317, and 1361).
Source: 43 FR 17776, Apr. 25, 1978, unless otherwise noted.

The regulations were developed by the USEPA through studying the associated industries in detail, and selecting the best technologies available and setting effluent guidelines on those industries. The source documents have useful information, and most if not all can be found with a search for the Effluent Guidelines Development Documents on the USEPA's website. Many of the development documents are available in portable document format (PDF) and are free to download, while others must be ordered from the National Technical Information at a reasonable price. The Development Documents contain recommendations for best available technology, which, in some cases, is still in use, and new source performance standards for any facilities built or rebuilt after the date of issue of the individual regulations. The new source performance standards (NSPS) Regulations are applicable to new industries and processes.

The Development Documents also contain process descriptions and block flow diagrams for many of the regulated processes, but do not contain equipment sizes, flow rates, or technical details, as many of the details are considered proprietary to the companies. The Development Documents also estimate the water usage per unit of production for the various processes. As such, they are extremely helpful for initial investigations and process evaluations.[52]

1.9.1 Water Use by Municipalities

Water use by municipalities is often regulated by both design codes and fire codes. The fire codes specify the amount of water that must be supplied in an emergency, and the minimum pressure in the distribution system. The actual water use depends upon the economic activity and development base of the country. UNESCO cites that municipal water use is expected to grow to between 500 and 1000 liters per person per day (l/d) by the year 2100. In many places in the US, the water consumption rates are already at that figure. In less developed countries, water use is often less than 100–150 l/d.

Figures on how water is used in US households vary widely. A typical family of four living in an older house with 8 l flush toilets, and larger shower heads will use between 480 and 525 liters per capita per day (l/c/d) for interior use, and 280–446 l/c/d for exterior use (lawn watering, etc.).[53] Add to that figure commercial and industrial water use in cities and towns, and system water losses. On average, the domestic water use in the US accounts for 57% of the total water use; commercial water use 15%; industrial water use 13%; thermoelectric power use <1%; and public use losses 14%.[54]

Note that approximately 14% of the treated water used in the United States is lost through leaks, broken piping, cracks, and other sources. The wastewater collection system figures tell quite another story. The wastewater figures in terms of household uses range from 290 l to over 775 l per day, and the projections used for sewer and sewage treatment plant design are generally by code rather than by measurement.[55] Other studies indicate that the wastewater return rate is between 56% and 79% of the water supplied, based on a study of the cities of Lockhart and Luling, Texas, in 2011.[56] The point is that the

wastewater flows coming from residential areas are less than the water supplied to those areas, in dry weather, and may be substantially greater in wet weather. The water use and the wastewater flows have two diurnal peak flows. The first is between 6 and 9 a.m. (weekdays) and the second is between 6 and 8 p.m. weekdays. The peak flow rates are between three and four times the average daily consumption. The night-time low flows are between 20% and 40% of the daily average flow, and during the middle of the day, the residential generation of wastewater generally drops to about 70% of the daily average flow. However, the flow patterns for an individual household vary significantly, and only when one gets above about 20–30 dwelling units does a more uniform pattern exist.

Sewers leak into the groundwater, and they can serve as a good collection source for groundwater. When the local water table is above the sewer line, one can count on infiltration. In fact, there are American Society for Testing Materials (ASTM) standards and American Society of Civil Engineers (ASCE) standards for acceptance of new sewers based upon infiltration. The infiltration allowance is quite wide and varies from 100 to 100 000 gal/d-inch of diameter-mile (90–95 l cm^{-1} diameter/km of pipe to 90 000–95 000 l cm^{-1}/km) or 30–3000 gal/in. of circumference-mile (27–30 l cm^{-1} circumference/km to 2700–3000 l cm^{-1}/km).

Another way of checking the water infiltration rates is by comparison of the BOD_5 loading and the strength of the wastewater. The standard figure for generation of BOD_5 per person per day for the US is 0.17 lb or 77 g. At a flow rate of 100 gal per person/per day, the wastewater would have a strength of around 203 mg l^{-1}. Industrial and commercial wastes have a much greater strength and can influence the estimate of the waste strength. In other countries, the figures do not necessarily apply: in Zambia and Kenya, the per capita waste loadings contributed by each individual are 36 and 23 g respectively, according to a Water Research Commission report dated 1993.[57]

In times of wet weather, such as snow-melt or rainfall, the quantity of storm-water can increase by three to five times because of increased infiltration, and connections of household downspouts and surface drains to the sanitary sewer. In older parts of the world, combined sewers are used. The dry weather flow may represent between 1% and 10% of the capacity of the sewer system. Surface drainage during wet weather can cause immense increases in flows, and the sewer systems have been connected to bypasses, so that they can discharge directly to a river. In recent times, there has been a movement to capture and contain the "first flush," that portion of the storm flow that contains the majority of the surface dust and contamination from surface drainage that occurs with the onset of precipitation. A number of US cities have large underground structures designed to capture the first flush, and then, after the storm subsides, pump it to the treatment works.

1.9.2 Agricultural Water[58]

Water used for agricultural purposes must be relatively free from salts, especially boron, sediments, and herbicides. Water used for certain vegetable and fruit crops where the product is generally eaten raw, should also be free from pathogens and parasites. All water used in canning or cooking operations should be drinking water quality, and free from metals, various carbonate salts, and especially free from bacterial contamination. In certain areas of southeast Asia, where crops are fertilized and irrigated with human wastes, the cultural practice is only to eat cooked vegetables. The WHO limits on bacterial quality for irrigation water are more related to clogging of drip systems.[59]

Irrigation water uses a combination of measures, including some restrictions on contents such as boron 0.75 mg l^{-1}; iron 5 mg l^{-1}; selenium 0.02 mg l^{-1}; and a balance of different types of salts such as the sodium absorption ratio, which is a proportioning of the sodium, calcium, and magnesium salts dissolved in the water. Calcium and magnesium tend to counter the adverse effects of sodium on the structure of the soil, to maintain its porosity and other characteristics. For many agricultural uses, the users plot the sodium absorption ratio (SAR) against the conductivity to determine the potential for salt damage to the crops. The classical reference on the subject of SAR is listed Handbook 60 from the US Agricultural Research Service.[60]

The principal concern for agricultural crops is the *adjusted* sodium absorption ratio or SAR. The SAR is given by the formula:

$$\mathrm{SAR} = \frac{\mathrm{Na}}{\sqrt{(\mathrm{Ca} + \mathrm{Mg})/2}}$$

where Na, Ca, and Mg are the concentrations of sodium, calcium, and magnesium ions expressed in milliequivalents per liter. Various authors have suggested modifications to the equation to help account for carbonate and bicarbonate alkalinity.[61] Among the principal concerns are the buildup of sodium and potassium in the soils, and the reduction of soil permeability and reduction in crop yields up to about 50% for high SAR values of around 30.

1.9.3 Cooling Water

Cooling water is a heat receiver from hot process equipment. As such it needs to be relatively clean (low in suspended solids), a near-neutral pH, and relatively free of chemicals that will cause deposition on hot and warm surfaces, such as silicates and calcium bicarbonate, and free of chemicals that will corrode the equipment it is cooling. The cooling water is used and re-used between an average of three times and a maximum of eight times before it is too concentrated to

use and must be removed from the system to reduce the corrosion and fouling potentials of the water. The principal factors that cause the tower to lose water include evaporation, drift, and splashing. Tower losses from drift and splashing represent about 0.01% of the tower throughput. The principal loss is from evaporation, where 1000 BTU (British Thermal Units) of heat loss represents the evaporation of 1 pt of water, or 2260 kJ per kg of liquid evaporated.

The tower water is chemically treated to reduce the tendency of the dissolved materials to deposit on the inside of pipes and heat exchangers, and it also has to be passivated so that it does not attack metal used in the tower internals, or form "white rust" (zinc oxides) on galvanized metals. Control of algae and bacteria in the tower is also necessary, as algal buildup can also lead to corrosion. Depending upon the location of the facility and the water quality, silicate buildup often tends to be a limiting factor which controls the amount of blowdown to maintain the tower water quality. At one time in the US, hexavalent chromium (Cr^{6+}) was used to prevent corrosion and bacterial fouling. This practice was banned in 1994 under the provisions of the Toxic Substances Control Act for all systems used in "comfort cooling" (air conditioning), but is still permitted in certain other industrial applications.[62] Other chemical treatment systems use a variety of organic compounds to prevent bacterial growth, and zinc, antimony, molybdenum, and phosphorus compounds, to prevent corrosion and passivate the metals in the cooling water system.[63]

Baltimore Air Coil[64] provides the following guidance: pH 6.5–9; hardness as $CaCO_3$ 30–750 mg l^{-1}; silica (maximum) 150 mg l^{-1}. The numbers are higher because the cooling tower loses up to 3% due to drift (droplets of water being blown out of the tower by wind), and much greater quantities due to evaporation. Another handy reference is the San Diego, CA, County Water Authority,[65] and more detailed guides are available from EPRI, the Electric Power Research Institute,[66] the Water District for San Jose, California,[67] and a Best Management Practices Guide prepared by Jacksonville Environmental Authority.[68] The water in the towers is always balanced with makeup and blowdown waters to maintain the water chemistry at certain ranges. In areas where water is in short supply, it is not uncommon for power and other companies to use treated municipal effluent and other wastewater sources for tower makeup water.[69]

1.9.4 Boiler Water

The two types of boilers in use are fire tube and water tube. The fire tube boilers are also called Scotch Marine Boilers. For safety and heat transfer reasons, the fire tube boilers do not usually operate at pressures in excess of 16 bar.[70] Some specially designed water tube boilers operate at pressures well above 100 bar.

The two types have slightly different water quality requirements. A boiler has been described as a firebox with a metal oxide housing, and it is important to provide and condition the water so that it does not cause unwanted deposits

Table 1.15 ASME boiler water quality guidelines.

Pressure (PSI)/bar	Hardness (mg l^{-1} as $CaCO_3$)	Iron (mg l^{-1})	Copper (mg l^{-1})	Silica (SiO_2) (mg l^{-1})	Total alkalinity (mg l^{-1} $CaCO_3$)	Specific conductance – un-neutralized ($\mu\Omega$ cm^{-1})
(0–300) 0–20.5	0.3	0.1	0.05	150	700	7000
(301–450) 20.5–30.6	0.3	0.05	0.025	90	600	6000
(451–600) 30.6–41	0.2	0.03	0.02	40	500	5000
(601–750) 41–51	0.2	0.025	0.02	30	400	4000
(751–900) 51–61	0.1	0.20	0.015	20	300	3000
(901–1000) 61–67	0.05	0.02	0.015	8	200	2000
(1001–1500) 67–102	0.0	0.10	0.01	2	0	150
(1501–2000) 102–136	0.0	0.10	0.01	1	0	150

in turbines or pipes, and it is not corrosive to the iron oxide coating. Solids in the water will accumulate in the boiler water, and there is the added requirement that the water has little or no measurable dissolved oxygen and carbon dioxide because the presence of either will attack the boiler and the steam distribution system. Boilers also use oxygen scavengers to control corrosion. An excellent guide to boiler water treatment is available as a free download from EPRI Publication NP-6377-SLV2.[71]

A high-pressure boiler will have much more restrictive water quality requirements than low-pressure systems. The recommendations from the American Society of Mechanical Engineers (ASME) give water quality limits for the different types of boilers, based on their operating pressures (Table 1.15). The dissolved oxygen water quality requirement for the feed water is shown before the oxygen scavenger chemicals are added to reduce the oxygen concentrations in the boiler system to zero.

Cooling tower water quality and heat exchanger water quality are often linked or interchangeable. In one unusual instance, a combination of phosphate, ammonia, and calcium in groundwater which was used for cooling heat exchangers was found to cause hard scale-forming deposits in a refinery in southern Ohio. The source of the scale was attributed to struvite, a phosphorus-magnesium-ammonia compound which has the general formula of $NH_4MgPO_4{\cdot}6H_2O$, which can form when the principal components are present in approximately 1 : 1 : 1 M ratios. It can be removed by acid dissolution.

1.9.5 Other Industrial Water Quality Requirements

We covered the water requirements for boilers, agriculture, drinking, and cooling towers above. There are a few more we need to examine: the petrochemical, petroleum, and steel and paper industries, and fracking.

1.9.5.1 Steel Industry

Water quality is generally for cooling and quenching. The water should have low bacterial content, and generally be free from excessive carbonate hardness or other chemicals that could cause deposits in the piping or on steel slabs during quenching. Similarly, the water should not have a pH less than 5, and should be free from suspended solids. Steel production in North America and Europe has declined about 20% between 1980 and 2013, but still represents two of the largest two components of manufacturing, producing a total of almost 374 000 000 tons, with the Asian subcontinent excluding China producing 827 313 000 tons annually. Integrated steel plants consume about 93 000–109 500 l of water per MT of steel produced. Cooling water use is between 1000 and 2200 l per ton of steel produced, depending upon the process.[72]

1.9.5.2 Paper Industry

According to a study by the University of Minnesota, the "US Benchmark for water use within pulp and paper mills is approximately 17 000 gal/ton of paper (58 336 l/MT) with one of the most efficient Kraft pulp and paper mills using 4500 gal/ton (15 441 l/MT)."[73] The entire paper industry has been attempting to reduce water use since the 1970s, and their efforts to recover black liquor, implement new changes in non-chlorine bleaching, using counter-current washing techniques, water recycling in the press section, and generally implementing water conservation and recycling practices has reduced the water use in some plants by up to 40%, at an annual saving of over $700 000.

1.9.5.3 Petrochemical Industry

The petrochemical industry is a major user of water. The world-wide production of oil is estimated at 90.5 million barrels per day. The US is a major producer of oil, estimated at 12.4 million barrels per day.[74] Of that, approximately 17.7 million barrels per day are refined. (The difference between refinery capacity and production is the approximate quantity of oil imports).

The World Bank, in a 1999 study, estimated the water use for production at 0.7–0.83 m^3 of water per barrel of oil produced on an industry average. The estimated total water use figure for the US is then in the range of 12.4–14.7 million m^3/day (3.275–3880 Mgal/day).

Most of the wastewater generated is from cooling, but some of the water is also from desalting operations and includes moderate chlorides in the effluent (see Table 1.16).

Other waste streams may have greater quantities of oil, but most have some levels of heavy metals including lead, chromium, cadmium, nickel, and vanadium.

Table 1.16 Wastewater characteristics from petroleum refining.

Pollutant	Strength (mg l^{-1})
BOD_5	150–250
COD	300–600
Phenol	20–200
Oil in the desalter	100–300
Benzene	1–100

1.9.5.4 Petroleum Exploration and Production Operations

The petroleum industry uses a lot of water for production operations. The Texas Railroad Commission (who regulates the production of oil in Texas) has indicated that the act of fracking in Texas uses significant quantities of water. There is a difference between fracking of vertical and horizontal wells, principally due to the difference between the length of the horizontal well in the formation versus the vertical thickness of the formation. Vertical well fracking uses about 1.2 million gallons of water (4540 m^3) per well, while horizontal well fracking uses about three times as much water.[75] The effluent characteristics for fracking water are difficult to determine because of what is added by the geologists drilling the wells. Table 1.17 from the Penn State University study of fracking in the Marellus Shale (principally in Pennsylvania and West Virginia) indicates some of the chemicals added to the water by the geologists who drill the wells.

There are well over 150 different additives used in fracking. The principal compounds include propants (sand and other compounds to hold the frack

Table 1.17 Principal chemicals added to enhance one fracked well in Pennsylvania.

3.81 million gallons of water
4.57 million pounds of sand
1333 gal of hydrochloric acid
1695 gal of a friction reducer
2211 gal of an antimicrobial agent
386 gal of a scale inhibitor (which includes ethylene glycol, a component of antifreeze).

Source: http://extension.psu.edu/natural-resources/water/marcellus-shale/waste-water/current-and-emerging-treatment-and-disposal-technologies.

open), antimicrobial compounds, hydrochloric (muriatic) acid, gel compounds such as guar gum, friction-reducing compounds, petroleum derivatives, and just about anything else the geologist in charge of the well drilling believes will increase the production. All of these compounds will come out of the well in varying concentrations as the well is producing. The acids added to the well will tend to dissolve the fracked rock and open the cracks, but will dissolve the metals and other compounds in the rock, so heavy metals are also expected in the effluent. The quantity of formation water produced will initially be high, depending upon the tightness of the formation and other factors. The quantity of the formation water will drop off over time, on a power curve until it stabilizes between 90 and 120 days.

If left untreated, the fracking water will comprise hazardous waste and must be treated or sent to a chemical disposal facility. Disposal of the water into a publicly owned treatment works (POTW) is possible, but some pretreatment may be required, and the sludges from the treatment will also be hazardous wastes in need of proper labeling, packaging, transportation, and disposal at an approved disposal facility. In some instances, fracking wastewaters can be disposed of in underground wells specially designed for the purpose, but these wells are in different formations and deep underground so as to contain the pumped wastes.

Notes

1 Distilled water has no dissolved solids. The human intestines are membranes. Low dissolved solids in the intestine can cause the membrane to pass dissolved solids, extracting them from the blood in an attempt to equalize the concentrations and reduce trans-membrane pressures.
2 Some typical ranges for various types of water are: deionized water ~0.1 $\mu S\ cm^{-1}$; distilled water ~0.5 $\mu S\ cm^{-1}$; tap water ~500–800 $\mu S\ cm^{-1}$; seawater ~56 000 $\mu S\ cm^{-1}$, and brackish water~100 000 $\mu S\ cm^{-1}$. (*Source*: MBH Engineering Systems: http://www.mbhes.com/conductivity_measurement.htm).
3 See http://www.analyticexpert.com/2012/08/measuring-total-dissolved-solids-tds-with-a-tds-meter for more information.
4 For example, G.W.C. Kaye and T.H. Laby (1986) *Tables of Physical and Chemical Constants*, 15, New York, Longman; *The Handbook of Physics and Chemistry*, CRC Press.
5 *Solubility of Selected Gases in Water*, by L.E. Geventman. Found in http://sites.chem.colostate.edu/diverdi/all_courses/CRC%20reference%20data/solubility%20of%20gases%20in%20water.pdf.
6 American Public Health Association, American Water Works Association, and the Water Environment Federation (2017). Oxygen Dissolved Method

4500/Azide Modification. In: *Standard Methods for the Examination of Water and Wastewater*, 23e. Or see www.standardmethods.org.

7 A table of aqueous solubility and Henry's law constants for almost 600 organic compounds can be found at: http://chemistry.mdma.ch/hiveboard/rhodium/pdf/chemical-data/solubility_organic.pdf.

8 The solubility of nitrogen in water at ambient temperature is approximately 20 mg l^{-1}, which we have ignored in the calculations. Similarly the solubility of oxygen in water is about 16 mg l^{-1} at the same temperature.

9 http://www.epa.gov/superfund/health/conmedia/soil/pdfs/part_5.pdf.

10 http://cece.ucf.edu/people/taylor/teaching/pdf/Coagulation-Softening.pdf.

11 pH will vary somewhat with temperature. The value of pH = 7.0 is only valid for 25 °C. At 100 °C the value of pH for pure water is approximately pH ≈ 6.75, and at 10 °C, pH ≈ 7.24. See the following articles: http://reagecon.com/pdf/technicalpapers/Effects_of_Temperature_on_pH_v4-_TSP-01-2.pdf, and: http://chemwiki.ucdavis.edu/Physical_Chemistry/Acids_and_Bases/Aqueous_Solutions/The_pH_Scale/Temperature_Dependent_of_the_pH_of_pure_Water.

12 See http://www.atsdr.cdc.gov/csem/csem.asp?csem=10&po=10 for human toxicity, and according to the USGS, trivalent chromium is between one third and one tenth as toxic as the hexavalent form of chromium. See https://www.pwrc.usgs.gov/eisler/CHR_6_Chromium.pdf.

13 Sources for these figures are personal laboratory experience in treating chromium wastewaters from a cooling tower, and http://www.hofflandenv.com/hydroxide-precipitation.

14 The US Geological Survey and the USEPA monitor the concentrations of certain contaminants in US waters. Their website http://water.usgs.gov/nawqa/trace/arsenic lists areas where arsenic is a potential contaminant. Radium contamination is tracked at http://water.usgs.gov/nawqa/trace/radium. It should also be noted that radium and radon are potential exposure problems in areas where the geology contains granite. Uranium is a natural contaminant of granite rock, and the daughter product is radium. In other parts of the world, arsenic is a natural contaminant found in waters from coal mining, and commonly in India. The issue was first identified in 1983, and since that time, West Bengal, Jharkhand, Bihar, Uttar Pradesh, Assam, and Minipur in the flood plain of the Brahamaputra and Imphal rivers have had groundwater concentrations of arsenic in excess of 50 μg l^{-1}. These concentrations are well above the recommended drinking water concentrations. See www.cgwb.gov.in/documents/papers/incidpapers/Paper%208%20-%20Ghosh.pdf for additional information.

15 http://www.epa.gov/region02/ust.

16 The Atlanta Toxic Substances and Disease Registry (ATSDR) has a paper on the health effects of BTEX. See: http://www.atsdr.cdc.gov/interactionprofiles/IP-btex/ip05.pdf. The individual constituents each have a TOX profile:

http://www.atsdr.cdc.gov/ToxProfiles/tp.asp?id=468&tid=83, as do many of the other individual components in petroleum.

17 See the following for more information: https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=2&cad=rja&uact=8&ved=0CDUQFjAB&url=http%3A%2F%2Fwater.epa.gov%2Fscitech%2Fmethods%2Fcwa%2Fbioindicators%2Fupload%2F2007_07_10_methods_method_200_7.pdf&ei=5BfIVICnL4m4ggTei4SQDA&usg=AFQjCNHGXd8BmBbcQ93nFICfVbw00WoDjw&sig2=9YRKvuVxdYpy2qkcMvETOA&bvm=bv.84349003,d.eXY

18 http://eecelabs.seas.wustl.edu/files/Flame%20AA%20Operating%20Manual.pdf.

19 For example: See http://www.epa.gov/watersecurity/pubs/guide_watersecurity_samplingforunknown.pdf.

20 For example, see http://chemistry.about.com/od/chemistrylabexperiments/a/cleanglassware.htm and the fact that there are several companies that supply specially cleaned glassware and plastic for collecting environmental samples including www.uline.com, www.coleparmer.com, www.fishersci.com, etc. Another reference for sampling water, and other media can be found at the following site: www.cdpr.ca.gov/docs/emon/pubs/ehapreps/eh9404.pdf.

21 Not all countries have the same detection capabilities; in the example, we had to settle for one with a higher detection limit than that available in the US.

22 Non-detects (ND) and values below the practical quantification limits (PQL) often occur, indicating the machine detection limits. There is a debate in the regulatory community about how to handle the reporting and interpretation of something that the laboratory either did not find, or had an indication that the compound was present even if was below the quantification limits. One school of thought requires reporting a PQL or ND at half of the detection limit for the compound. (There is some logic in the reporting of the former, but not the latter.) Another school of thought requires that a ND or PQL value be reported at the detection limit. Still a third school of thought reports a non-detect or a PQL value as a zero. This is often important when the regulatory agency wants to sum up the total for all the detects and non-detects, and have them considered as part of a permit scheme.

23 The references are specific to the US only, but many other countries use the USEPA definitions and analytical provisions for their regulatory work. If in doubt, check with the country environmental agency laboratory.

24 There is a good guide to EU analytical protocols and procedures, with an excellent guide to the analytical protocols in the Appendices to the documents. See: http://www.european-accreditation.org/publication/citac-eurachem-ta. The standards biogroup also has a guide to statistical protocols in the EU: http://www.standardsproposals.bsigroup.com/Home/getPDF/830.

25 http://www.who.int/water_sanitation_health/hygiene/emergencies/fs2_33.pdf.

26 See: http://or.water.usgs.gov/grapher/fnu.html and http://www.optek.com/Turbidity_Measurement_Units.asp.

27 A suspension of 100 ppm of silica (principally as diatomaceous earth) had a JTU of 21.5 units, and it is considered the "standard" for that measurement. Also see: http://www.optek.com/Real_World_Turbidity.asp.

28 The definition of the navigable waters of the United States is actually quite complex. The definition used to be "any body of water in which one could float a log." Since the passage of the CWA in 1972, and subsequent to legal challenges the new definition of "navigable waters" has been modified. The clearest summary of the extent of these waters can be found in the Federal Register, Vol. 79, No.76, Monday April 21, 2014, Proposed Rules, pp. 22192–22194. The currently proposed changes will be found in the 40 CFR 203.3 when fully adopted. In general "navigable waters" includes the following:

- All waters that are currently used, were used in the past, or may be susceptible to use in interstate or foreign commerce, including all waters that are subject to the ebb and flow of the tide;
- All interstate waters, including interstate wetlands;
- The territorial seas;
- All impoundments of a traditional navigable water, interstate water, the territorial seas or a tributary;
- All tributaries of a traditional navigable water, interstate water, the territorial seas or impoundment;
- All waters, including wetlands, adjacent to a traditional navigable water, interstate water, the territorial seas, impoundment or tributary; and
- On a case-specific basis, other waters, including wetlands, provided that those waters alone, or in combination with other similarly situated waters, including wetlands, located in the same region, have a significant nexus to a traditional navigable water, interstate water or the territorial seas.

Note that in certain specific cases defined in the regulations, some ditches, culverts, and other activities may be exempt from regulation.

29 Here the definition of a navigable waterway can be critical. Generally, it is taken to mean anything that has links to interstate commerce and in which one can float a log. That definition has been expanded slightly to include an area of drainage basin, but as a practical matter there are several industrial sites in the State of Florida which discharge to sink holes in a Floridian aquifer that were exempt from Federal but not State regulation, principally because the discharge could not be tracked in the aquifer because it was greatly diluted to the point that it could not be identified in the aquifer, without a very intensive and expensive groundwater investigation.

30 http://water.epa.gov/learn/training/standardsacademy/upload/module_mixingzone.pdf.

31 http://www.mixzon.com/sales/uspricing.php.

32 For example, see the EPA's guidance on mixing zones: http://water.epa.gov/scitech/swguidance/standards/upload/2007_01_31_standards_mixingzone_compendium.pdf.

33 See the following: http://www.law360.com/articles/486315/epa-raises-fines-for-air-water-pollution-violations, and http://www.epa.gov/region7/public_notices/CWA/309.htm, and starting on page (349) 13 of 36, look at the penalty provisions http://www.emlf.org/clientuploads/directory/whitepaper/McLusky_Vining_07.pdf.

34 American humor sometimes is used to highlight the adversarial relations between government and industry, as in this joke. *There are 3 great lies told in the US. The first is, "The check is in the mail." The second occurs when the boyfriend says to his girlfriend, "If you let me make love to you tonight, I promise that we will get married in the morning." The third great lie is when the local regulatory person shows up at the industry gate and says to the plant manager, "Hi, I'm from the EPA and I'm here to help you*!"

35 From Section 101(a)(2) and Section 303(c)(2) of the Clean Water Act.

36 http://www.gpo.gov/fdsys/pkg/CFR-2011-title40-vol29/pdf/CFR-2011-title40-vol29-sec401-15.pdf.

37 Personal communications from Jeremy Dudley (WRc.Plc), and Youri Amerlinck (University of Ghent).

38 In some cases, the removal standard based upon influent values is approximately 50% for TSS but only 20% for BOD (see https://www.google.com/url?q=www.sepa.org.uk/about_us/idoc.ashx%3Fdocid%3Dcf86e6d5-6e0f-4f7e-8c5a-f1aac520b5df%26version%3D-1&sa=U&ei=fFXRVIfmHMmBywPV2YLgCw&ved=0CAUQFjAA&client=internal-uds-cse&usg=AFQjCNFUzabYAwS0UATD_quHxHqnRuqcqA. The foregoing was supplied by personal communication with Dr Jeremy Dudley of WRc Plc.

39 http://archive.defra.gov.uk/environment/policy/enforcement/pdf/envleg-enforce-wrcreport.pdf

40 http://www.fwr.org/WQreg/Appendices/uwwtreport2.pdf. These maps may be slightly out of date but illustrate the manner in which the standards are established.

41 www.legislation.gov.uk/uksi/2010/675/pdfs/uksi_20100675_en.pdf.

42 By comparison, the US does not have exceptional circumstances, partially because its infrastructure is younger and has a design philosophy that requires separation of sanitary and storm sewers, treatment of stormwater first flush, and regulation of groundwater infiltration and inflows into the stormwater sewer system to keep the sanitary flows as small as practicable, even in wet weather. It is not uncommon for wet weather flows in municipal sewer systems to increase by a factor of between 3x and 6x the dry weather flows.

43 http://ec.europa.eu/environment/water/water-urbanwaste/index_en.html.

44 Personal communication: Dr. Youri Amerlinck.

45 There are a host of waterborne diseases which can be transmitted by contaminated water. A good list of those diseases can be found on the Arizona Public Health site: http://www.azdhs.gov/phs/oids/epi/waterborne/list.htm. Of most recent concern has been the issue of *Giardia lamblia*, and certain types of spore-forming bacteria that tend to be more resistant to certain types of disinfection.

46 Source for Drinking Water Standards: http://water.epa.gov/drink/contaminants/#List. Note that these standards are considered to be health protective over many years, and the levels of toxicity or acute hazard or damage to an individual would be many times higher. For many contaminants, the active levels of those materials are found on the CDC website: http://www.astdr.cdc.gov/toxfaqs/Index.asp.

47 http://www.who.int/water_sanitation_health/publications/2011/dwq_guidelines/en/.

48 http://www.newscientist.com/article/mg18925380.200-blue-baby-links.html.

49 https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31991L0676:EN:HTML. See Annex 1 (several pages into the text), and see page 2 of http://ec.europa.eu/environment/pubs/pdf/factsheets/nitrates.pdf. The majority of cases have occurred in the UK when nitrate levels have been over 100 mg l^{-1}. However, in many cases bacterial contamination of the water causing gut infections was present or suspected. There have been no cases in the UK since 1972.

50 http://dwi.defra.gov.uk/consumers/advice-leaflets/standards.pdf.

51 See http://water.epa.gov/scitech/wastetech/guide/industry.cfm, and look at industry studies for the regulations: http://water.epa.gov/scitech/wastetech/guide/industry.cfm#studies.

52 One important caution is to be noted when using the Development Documents: there is no substitute for recent analyses of the wastestream to be investigated. Some of the documents are over 40 years old, and describe technologies that are no longer in use, and the regulations regarding what can be discharged have changed dramatically. For example, some of the documents relating to discharge from cooling towers contain information that one could expect up to 250 mg l^{-1} of hexavalent chromium in the blowdown from a tower. The use of hexavalent chromium was banned in 1994 under the provisions of the Clean Air Act, as Cr^{6+} is a human carcinogen and can cause lung cancers. See http://www.epa.gov/ttnatw01/cool/fscoolt.pdf for the citation.

53 Source: Desert Water Agency public data and http://www.csgnetwork.com/waterusagecalc.html calculator.

54 Source: "How we use water in the United States," USEPA: http://esa21.kennesaw.edu/activities/water-use/water-use-overview-epa.pdf.

55 See Appendix A: http://www.doh.wa.gov/Portals/1/Documents/Pubs/337-103.pdf.

56 See Table 9.3: http://www.gbra.org/documents/studies/caldwell/09-WastewaterFlows.pdf.

57 http://www.unep.or.jp/Ietc/Publications/TechPublications/TechPub-15/3-1Africa/1-1.asp.

58 Source for Irrigation Water Quality Standards: Texas A&M Agrilife Extension Service. Values listed are for long-term use – see page 6 for a comparison: http://soiltesting.tamu.edu/publications/B-1667.pdf.

59 http://www.fao.org/docrep/t0551e/t0551e07.htm. See comments at Table 27.

60 See the following articles: http://www.iaees.org/publications/journals/piaees/articles/2011-1%283-4%29/assessment-of-groundwater-quality-for-drinking-and-irrigation.pdf, and a second article that instructs the method of creating a salinity diagram: http://aces.nmsu.edu/pubs/_a/A116/welcome.html. A third article from the US Agricultural Research Service, Handbook 60, discusses the repair of alkaline and salty soils: http://www.ars.usda.gov/SP2UserFiles/Place/20360500/hb60_pdf/hb60complete.pdf.

61 Two different formulations for the modified SAR are found in the following publications: Water Quality for Agriculture, a 1977 publication by the Food and Agriculture Division of the UN, found at www.calwater.ca.gov/Admin_Record/C-110101.pdf, and Sodium Adsorption Ratio-Exchangeable Sodium Percentage Relationships in a High Potassium Saline-Sodic Soil by Charles published in 1983 by Springer-Verlag, in Irrig Sci (1984) 5: 173–179 found at http://eprints.nwisrl.ars.usda.gov/422/1/532.pdf.

62 See the US Code of Federal Regulations: 40 CFR 749.68 – Hexavalent chromium-based water treatment chemicals in cooling systems.

63 For greater detail see: www.emsd.gov.hk/emsd/e_download/pee/wcacsCoP_Part_3.pdf.

64 Source: Baltimore Air Coil http://www.baltimoreaircoil.com/english/resource-library/file/579.

65 http://www.sdcwa.org/sites/default/files/files/water-management/recycled/techinfo-cooling-towers.pdf.

66 http://mydocs.epri.com/docs/PublicMeetingMaterials/0712/watertreatment_RFI_Final.pdf.

67 https://www.sanjoseca.gov/Archive/ViewFile/Item/1443.

68 https://www.jea.com/.../JEA_Cooling_Tower_BMP_pdf.aspx.

69 http://www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=CS-5373%20%20%20%20%20%20%20%20%20%20%20&Mode=download.

70 In a water tube boiler the pressure is in the individual tubes inside the boiler. In a Scotch Marine or fire tube boiler, the boiler shell is under pressure. Failures of the shell, with its larger volume of pressurized water, could be much more catastrophic than failures of an individual pressurized water tube in a boiler.

71 http://www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=NP-6377-SLV2%20%20%20%20%20%20%20&Mode=download.

72 *Water Requirement of the Iron and Steel Industry*, US Geological Survey Water Supply Paper 1330-H (1967).

73 http://www.mntap.umn.edu/paper/water.html, and also see: http://www.eco-tec.com/techpapers/TP%20133%20CPPA%20REV3.pdf.

74 Source: http://www.eia.gov/countries/country-data.cfm?fips=US.

75 http://www.rrc.state.tx.us/about-us/resource-center/faqs/oil-gas-faqs/faq-hydraulic-fracturing/.