

Fundamentals of Environmental Engineering

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Chapter 2

Units of Concentration

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In this chapter a reader will become familiar with the different units used to measure pollutant levels in aqueous (i.e., water), soil/sediment, and atmospheric systems. In addition, the last section in the chapter will familiarize the reader with typical magnitudes and units of concentrations that are encountered in various engineered and natural systems.

Chemical concentration is one of the most important determinants in almost all aspects of chemical fate, transport, and treatment in both environmental and engineered systems. This is because concentration is the driving force that controls the movement of chemicals within and between different environmental media, as well as the rate of many chemical reactions. In addition, the severity of adverse effects, such as toxicity and bioconcentration, are often determined by concentration.

Concentrations of chemicals are routinely expressed in a variety of units. The choice of units to use in a given situation depends on the chemical, where it is located (e.g., air, water, or soil/sediments), and often on how the measurement will be used. It is therefore necessary to become familiar with the units used and methods for converting between different sets of units. Representation of concentration usually falls into one of the categories listed in Table 2-1. Important prefixes to know include pico (10^{-12} , abbreviated as p), nano (10^{-9} , abbreviated as n), micro (abbreviated as μ , 10^{-6}), milli (m, 10^{-3}), and kilo (k, 10^{+3}).

2.1 MASS CONCENTRATION UNITS

Concentration units based on chemical mass include mass chemical/total mass and mass chemical/total volume. Examples of these are shown below. In these descriptions, m_i is used to represent the mass of the chemical referred to as chemical i .

Table 2-1. Common Units of Concentration Used in Environmental Measurements

Representation	Example	Typical Units (Defined Below)
Mass chemical/total mass	mg/kg in soil	mg/kg, ppm _m
Mass chemical/total volume	mg/L in water or air	mg/L, µg/m ³
Volume chemical/total volume	volume fraction in air	ppm _v
Moles chemical/total volume	moles/L in water	M

2.1.1 Mass/Mass Units

Mass/mass concentrations are commonly expressed as parts per million, parts per billion, parts per trillion, and so on. For example, 1 mg of a solute placed in 1 kg of solvent equals 1 ppm_m. Parts per million by mass (referred to as ppm or ppm_m) is defined as the number of units of mass of chemical per million units of total mass. That is,

$$\text{ppm}_m = \text{g of } i \text{ in } 10^6 \text{ g total} \quad (2-1)$$

This definition is equivalent to the following general formula, which is used to calculate ppm_m concentration from measurements of chemical mass in a sample of total mass m_{total}:

$$\text{ppm}_m = \frac{m_i}{m_{\text{total}}} \times 10^6 \quad (2-2)$$

Note that the factor 10⁶ in Equation 2-2 is really a conversion factor. It has the implicit units of ppm_m/mass fraction (mass fraction = m_i/m_{total}) as shown in Equation 2-3:

$$\text{ppm}_m = \frac{m_i}{m_{\text{total}}} \times 10^6 \frac{\text{ppm}_m}{\text{mass fraction}} \quad (2-3)$$

In Equation 2-3, m_i/m_{total} is defined as the mass fraction, and the conversion factor of 10⁶ is similar to the conversion factor of 10² that is used to convert fractions to percentages. For example, the expression 0.25 = 25% can be thought of as

$$0.25 = 0.25 \times 100\% = 25\% \quad (2-4)$$

Similar definitions are used for the units ppb_m, ppt_m, and % by mass. That is, 1 ppb_m equals 1 part per billion or 1 g chemical per billion (10⁹) g total, so that the number of ppb_m in a sample is equal to m_i/m_{total} × 10⁹. And 1 ppt_m usually means 1 part per trillion. However, be cautious about interpreting ppt values because

they may refer to either parts per thousand or parts per trillion (10¹²). *Mass/mass concentrations can also be reported with the units explicitly shown (e.g., mg/kg, µg/kg).* In soils and sediments, 1 ppm_m equals 1 mg of pollutant per kg of solid (mg/kg) and 1 ppb_m equals 1 µg/kg. Percent by mass is analogously equal to the number of g pollutant per 100 g total.

EXAMPLE 2.1 CONCENTRATION IN SOIL

A one-kg sample of soil is analyzed for the chemical solvent trichloroethylene (TCE). The analysis indicates that the sample contains 5.0 mg of TCE. What is the TCE concentration in ppm_m and ppb_m?

SOLUTION

$$\begin{aligned} [\text{TCE}] &= \frac{5 \text{ mg TCE}}{1.0 \text{ kg soil}} = \frac{0.005 \text{ g TCE}}{10^3 \text{ g soil}} \\ &= \frac{5 \times 10^{-6} \text{ g TCE}}{\text{g soil}} \times 10^6 = 5 \text{ ppm}_m = 5,000 \text{ ppb}_m \end{aligned}$$

Note that in soil and sediments, mg/kg equals ppm_m and µg/kg equals ppb_m.

2.1.2 Mass/Volume Units: mg/L and µg/m³

In the atmosphere, it is common to use concentration units of mass/volume air such as mg/m³ and µg/m³. In water, mass/volume concentration units of mg/L and µg/L are common. *In most aqueous systems, ppm_m is equivalent to mg/L.* This is because the density of pure water is approximately 1,000 g/L. This is demonstrated in Example 2.2. The density of pure water is actually 1,000 g/L at 5°C. At 20°C the density has decreased slightly to 998.2 g/L. In addition, this equality is strictly true only for “dilute” solutions, in which any dissolved material does not contribute significantly to the mass of the water, and the total density remains approximately 1,000 g/L. Most wastewaters and natural waters can be considered dilute, except perhaps seawaters and brines.

EXAMPLE 2.2 CONCENTRATION IN WATER

One liter of water is analyzed and found to contain 5.0 mg TCE. What is the TCE concentration in mg/L and ppm_m?

SOLUTION

$$[\text{TCE}] = \frac{5.0 \text{ mg TCE}}{1.0 \text{ L H}_2\text{O}} = \frac{5.0 \text{ mg}}{\text{L}}$$

To convert to ppm_m , which is a mass/mass unit, it is necessary to convert the volume of water to mass of water, by dividing by the density of water, which is approximately 1,000 g/L:

$$\begin{aligned} [\text{TCE}] &= \frac{5.0 \text{ mg TCE}}{1.0 \text{ L H}_2\text{O}} \times \frac{1.0 \text{ L H}_2\text{O}}{1,000 \text{ g H}_2\text{O}} \\ &= \frac{5.0 \text{ mg TCE}}{1,000 \text{ g total}} = \frac{5.0 \times 10^{-6} \text{ g TCE}}{\text{g total}} \times \frac{10^6 \text{ ppm}_m}{\text{mass fraction}} \\ &= 5.0 \text{ ppm}_m \end{aligned}$$

See that in most aqueous systems that are dilute, mg/L is equivalent to ppm_m . Also, in this problem the TCE concentration is well above the allowable U.S. drinking water standard for TCE of 5 $\mu\text{g/L}$ (or 5 ppb), which was set to protect human health. Five ppb is a small value. Think of it: if one assumes the Earth's human population is 5 billion people, this means that 25 individuals sitting in one of your classes constitute a human concentration of 5 ppb!

EXAMPLE 2.3. CONCENTRATION IN AIR

What is the carbon monoxide (CO) concentration expressed in $\mu\text{g/m}^3$ of a 10-L gas mixture that contains 10^{-6} mole of CO?

SOLUTION

In this case, the measured quantities are presented in units of moles chemical/total volume. To convert to mass of chemical/total volume, convert the moles of chemical to mass of chemical by multiplying by CO's molecular weight. Note that the molecular weight of CO (28 g/mole) is equal to 12 (atomic weight of C) plus 16 (atomic weight of O).

$$\begin{aligned} [\text{CO}] &= \frac{1.0 \times 10^{-6} \text{ mole CO}}{10 \text{ L total}} \times \frac{28 \text{ g CO}}{\text{mole CO}} \\ &= \frac{28 \times 10^{-6} \text{ g CO}}{10 \text{ L total}} \times \frac{10^6 \mu\text{g}}{\text{g}} \times \frac{10^3 \text{ L}}{\text{m}^3} = \frac{2,800 \mu\text{g}}{\text{m}^3} \end{aligned}$$

2.2 VOLUME/VOLUME AND MOLE/MOLE UNITS

Units of volume fraction or mole fraction are frequently used for gas concentrations. The most common volume fraction units are ppm_v (parts per million by volume) (referred to as ppm or ppm_v), which is defined as:

$$\text{ppm}_v = \frac{V_i}{V_{\text{total}}} \times 10^6 \quad (2-5)\text{B}$$

In Equation 2-5, V_i/V_{total} is the volume fraction and the factor 10^6 is a conversion factor, with units of $10^6 \text{ ppm}_v/(\text{volume fraction})$.

Other common units for gaseous pollutants are ppb_v (parts per 10^9 by volume). The advantage of volume/volume units is that gaseous concentrations reported in these units do not change as a gas is compressed or expanded. Atmospheric concentrations expressed as mass/volume (e.g., $\mu\text{g/m}^3$) decrease as the gas expands, since the pollutant mass remains constant but the volume increases. Both mass/volume units, such as $\mu\text{g/m}^3$, and ppm_v units are frequently used to express gaseous concentrations (see Equation 2-9 for conversion between $\mu\text{g/m}^3$ and ppm_v).

2.2.1 Using the Ideal Gas Law to Convert ppm_v to $\mu\text{g/m}^3$

The Ideal Gas Law can be used to convert gaseous concentrations between mass/volume and volume/volume. The Ideal Gas Law states that pressure (P) times volume occupied (V) equals the number of moles (n) times the gas constant (R) times the absolute temperature (T) in degrees Kelvin or Rankine. This is written in the familiar form of

$$PV = nRT \quad (2-6)\text{B}$$

Here R , the universal gas constant, may be expressed in many different sets of units. Some of the most common values are displayed below:

$$\begin{aligned} &0.08205 \text{ L-atm/mole-K} \\ &8.205 \times 10^{-5} \text{ m}^3\text{-atm/mole-K} \\ &82.05 \text{ cm}^3\text{-atm/mole-K} \\ &1.99 \times 10^{-3} \text{ kcal/mole-K} \\ &8.314 \text{ J/mole-K} \\ &1.987 \text{ cal/mole-K} \\ &62,358 \text{ cm}^3\text{-torr/mole-K} \\ &62,358 \text{ cm}^3\text{-mmHg/mole-K} \end{aligned}$$

Because the gas constant may be expressed in a number of different units, always be careful of its units and cancel them out to ensure the use of the correct value of R .

The Ideal Gas Law states that the volume occupied by a given number of molecules of any gas is the same, no matter what the molecular weight or composition of the gas, as long as the pressure and temperature are constant. The Ideal Gas Law can be rearranged to show that the volume occupied by n moles of gas is equal to

$$V = n \frac{RT}{P} \quad (2-7)$$

At standard conditions ($P = 1 \text{ atm}$, $T = 273.15 \text{ K}$), one mole of any pure gas will occupy a volume of 22.4 L. This result can be derived by using the corre-

sponding value of R (0.08205 L-atm/mole-K) and the form of the Ideal Gas Law provided in Equation 2-7. At other temperatures and pressures, this volume varies as determined by Equation 2-7.

EXAMPLE 2.4 GAS CONCENTRATION IN VOLUME FRACTION

A gas mixture contains 0.001 mole of sulfur dioxide (SO_2) and 0.999 mole of air. What is the SO_2 concentration, expressed in units of ppm_v ?

SOLUTION

The concentration in ppm_v is determined using Equation 2-5.

$$[\text{SO}_2] = \frac{V_{\text{SO}_2}}{V_{\text{total}}} \times 10^6$$

To solve, convert the number of moles of SO_2 to volume using the Ideal Gas Law (Equation 2-6) and the total number of moles to volume. Then divide the two expressions:

$$\begin{aligned} V_{\text{SO}_2} &= 0.001 \text{ mole SO}_2 \times \frac{RT}{P} \\ V_{\text{total}} &= (0.999 + 0.001) \text{ mole total} \times \frac{RT}{P} \\ &= (1.000) \text{ mole total} \times \frac{RT}{P} \end{aligned}$$

Substitute these volume terms for ppm_v , to obtain

$$\begin{aligned} &= \frac{0.001 \text{ mole SO}_2 \times \frac{RT}{P}}{1.000 \text{ mole total} \times \frac{RT}{P}} \times 10^6 \\ &= \frac{0.001 \text{ L SO}_2}{1.000 \text{ L total}} \times 10^6 = 1,000 \text{ ppm}_v \end{aligned}$$

Note that in Example 2.4, the terms (RT/P) cancel out. This demonstrates an important point that is useful in calculating volume fraction or mole fraction concentrations. *For gases, volume ratios and mole ratios are equivalent.* This is clear from the Ideal Gas Law, because at constant temperature and pressure the

volume occupied by a gas is proportional to the number of moles. Therefore, Equation 2-5 is equivalent to Equation 2-8:

$$\text{ppm}_v = \frac{\text{moles } i}{\text{moles total}} \times 10^6 \quad (2-8)$$

See that the solution to Example 2.4 could have simply been found by using Equation 2-8 and determining the mole ratio. Therefore, in any given problem, either units of volume or units of moles can be used to calculate ppm_v . Being aware of this fact will save unnecessary conversions between moles and volume. The mole ratio (moles i /moles total) is sometimes referred to as the *mole fraction*, X .

Example 2.5 and Equation 2-9 show how to use the Ideal Gas Law to convert concentrations between $\mu\text{g}/\text{m}^3$ and ppm_v .

EXAMPLE 2.5 CONVERT GAS CONCENTRATION BETWEEN ppb_v AND $\mu\text{g}/\text{m}^3$

The concentration of SO_2 is measured in air to be 100 ppb_v . What is this concentration in units of $\mu\text{g}/\text{m}^3$? Assume the temperature is 28°C and pressure is 1 atm. Remember that $T(\text{K})$ is equal to $T(^{\circ}\text{C})$ plus 273.15.

SOLUTION

To accomplish this conversion, use the Ideal Gas Law to convert the volume of SO_2 to moles of SO_2 , resulting in units of moles/L. This can be converted to $\mu\text{g}/\text{m}^3$ using the molecular weight of SO_2 ($\text{MW} = 64$). This method will be used to develop a general formula for converting between ppm_v and $\mu\text{g}/\text{m}^3$.

First, use the definition of ppb_v to obtain a volume ratio for SO_2 :

$$100 \text{ ppb}_v = \frac{100 \text{ m}^3 \text{ SO}_2}{10^9 \text{ m}^3 \text{ air solution}}$$

Now convert the volume of SO_2 in the numerator to units of mass. This is done in two steps. First, convert the volume to a number of moles, using a rearranged format of the Ideal Gas Law ($n/V = P/RT$) and the given temperature and pressure:

$$\begin{aligned} &= \frac{100 \text{ m}^3 \text{ SO}_2}{10^9 \text{ m}^3 \text{ air solution}} \times \frac{P}{RT} \\ &= \frac{100 \text{ m}^3 \text{ SO}_2}{10^9 \text{ m}^3 \text{ air solution}} \times \frac{1 \text{ atm}}{8.205 \times 10^{-5} \left(\frac{\text{m}^3 \text{ atm}}{\text{mole K}} \right) (301 \text{ K})} \\ &= \frac{4.05 \times 10^{-6} \text{ mole SO}_2}{\text{m}^3 \text{ air}} \end{aligned}$$

In the second step, convert the moles of SO₂ to mass of SO₂ using the molecular weight of SO₂.

$$\frac{4.05 \times 10^{-6} \text{ mole SO}_2}{\text{m}^3 \text{ air}} \times \frac{64 \text{ g SO}_2}{\text{mole SO}_2} \times \frac{10^6 \mu\text{g}}{\text{g}} = \frac{260 \mu\text{g}}{\text{m}^3}$$

Example 2.5 demonstrates that a useful conversion for converting air concentrations between units of $\mu\text{g}/\text{m}^3$ and ppm_v can be written as

$$\frac{\mu\text{g}}{\text{m}^3} = \text{ppm}_v \times \text{MW} \times \frac{1,000 P}{RT} \quad (2-9) \text{B}$$

where MW is the chemical species molecular weight; R equals 0.08205 L-atm/mole-K; T is the temperature in degrees K; and the 1,000 is a conversion factor (1,000 L = m^3). Note that for 0°C, RT has a value of 22.4 L-atm/mole, while at 20°C RT has a value of 24.2 L-atm/mole.

2.3 PARTIAL-PRESSURE UNITS

In the atmosphere, concentrations of chemicals in the gas and particulate phases may be determined separately. A substance will exist in the gas phase if the atmospheric temperature is above the substance's boiling (or sublimation) point or if its concentration is below the saturated vapor pressure of the chemical at a specified temperature (vapor pressure is defined in Section 3.4.1). The major and minor gaseous constituents of the atmosphere all have boiling points well below atmospheric temperatures. Concentrations of these species typically are expressed either as volume fractions (e.g., %, ppm_v , or ppb_v) or as partial pressures (units of atmospheres, atm). Table 2-2 summarizes the concentrations of the most abundant atmospheric gaseous constituents.

The total pressure exerted by a gas mixture may be considered as the sum of the partial pressures exerted by each component of the mixture. The partial pressure of each component is equal to the pressure that would be exerted if all of the other components of the mixture were suddenly removed. Partial pressure is commonly written as P_i , where i refers to the particular gas being considered. For example, the partial pressure of oxygen in the atmosphere P_{O_2} is 0.21 atm.

Remember that the Ideal Gas Law states that, at a given temperature and volume, pressure is directly proportional to the number of moles of gas present; therefore, pressure fractions are identical to mole fractions (and volume fractions). For this reason, *partial pressure can be calculated as the product of the mole or volume fraction and the total pressure.* For example,

$$\begin{aligned} P_i &= [\text{volume fraction, or mole fraction}] \times P_{\text{total}} \\ &= [(\text{ppm}_v)_i \times 10^{-6} \times P_{\text{total}}] \end{aligned} \quad (2-10) \text{B}$$

Table 2-2. Composition of the Atmosphere*

Compound	Concentration (% volume or moles)	Concentration (ppm_v)
Nitrogen (N ₂)	78.1	781,000
Oxygen (O ₂)	20.9	209,000
Argon (Ar)	0.93	9,300
Carbon dioxide (CO ₂)	0.035	350
Neon (Ne)	0.0018	18
Helium (He)	0.0005	5
Methane (CH ₄)	0.00017	1.7
Krypton (Kr)	0.00011	1.1
Hydrogen (H ₂)	0.00005	0.500
Nitrous oxide (N ₂ O)	0.000032	0.316
Ozone (O ₃)	0.000002	0.020

Data from Graedel and Crutzen, 1993.

*Values represent concentrations in dry air at remote locations.

In addition, rearranging Equation 2-10 shows that ppm_v values can be calculated from partial pressures as follows:

$$\text{ppm}_v = \frac{P_i}{P_{\text{total}}} \times 10^6 \quad (2-11) \text{B}$$

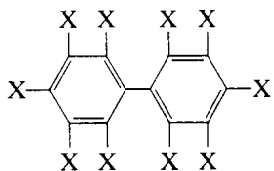
Thus, partial pressure can be added to the list of unit types that can be used to calculate ppm_v . That is, either volume (Equation 2-5), moles (Equation 2-8), or partial pressures (Equation 2-11) can be used in ppm_v calculations.

EXAMPLE 2.6. CONCENTRATION AND PARTIAL PRESSURE

The concentration of gas-phase polychlorinated biphenyls (PCBs) in the air above Lake Superior was measured to be 450 picograms per cubic meter (pg/m^3). What is the partial pressure (in atm) of PCBs? Assume the temperature is 0°C, the atmospheric pressure is 1 atm, and the average molecular weight of PCBs is 325.

SOLUTION

The chemical structure of PCBs along with some general information is provided in Figure 2-1. The partial pressure is defined as the mole or volume fraction times the total gas pressure. First, find the number of moles of PCBs in a liter of air. Then use the Ideal Gas Law (Equation 2-7) to calculate that one mole of gas at



X = chlorine or hydrogen

Figure 2-1. Chemical Structure of Polychlorinated Biphenyls (PCBs). PCBs are a family of compounds produced commercially by chlorinating biphenyl. Chlorine atoms can be placed at any or all of ten available sites, with 209 possible PCB congeners. The great stability of PCBs caused them to have a wide range of uses, including serving as coolants in transformers and as hydraulic fluids and solvents. However, the chemical properties that resulted in this stability also resulted in a chemical that did not degrade easily, bioaccumulated in the food chain, and was also hazardous to humans and wildlife. Accordingly, in 1976 Congress passed the Toxic Substances Control Act (TSCA) that banned the manufacture of PCBs and PCB-containing products. TSCA also established strict regulations regarding the future use and sale of PCBs. PCBs were typically sold as mixtures that are commonly referred to as Aroclors. For example, the Arochlor 1260 mixture consists of 60% chlorine by weight, which meant the individual PCBs in the mixture are primarily substituted with 6–9 chlorines per biphenyl molecule. In contrast, Arochlor 1242 consists of 42% chlorine by weight; thus, it primarily consists of PCBs with 1–6 substituted chlorines per biphenyl molecule.

0°C and 1 atm occupies 22.4 L and substitute this value into the first expression to determine the mole fraction of PCBs:

$$450 \frac{\text{pg}}{\text{m}^3 \text{ air}} \times \frac{\text{mole}}{325 \text{ g}} \times 10^{-12} \frac{\text{g}}{\text{pg}} \times 10^{-3} \frac{\text{m}^3}{\text{L}} = 1.38 \times 10^{-15} \frac{\text{mole PCB}}{\text{L air}}$$

$$1.38 \times 10^{-15} \frac{\text{mole PCB}}{\text{L}} \times \frac{22.4 \text{ L}}{\text{mole air}} = 3.1 \times 10^{-14} \frac{\text{mole PCB}}{\text{mole air}}$$

Multiplying the mole fraction by the total pressure (1 atm) (see Equation 2-10) yields the PCB partial pressure of 3.1×10^{-14} atm.

EXAMPLE 2.7. CONCENTRATION AS PARTIAL PRESSURE CORRECTED FOR MOISTURE

What would be the partial pressure (atm) of carbon dioxide (CO_2) when the barometer reads 29.0 inches of Hg, the relative humidity is 80%, and the temperature is 70°F? Use Table 2-2 to obtain the concentration of CO_2 in dry air.

SOLUTION

The partial-pressure concentration units in Table 2-2 are for dry air, so the partial pressure must first be corrected for the moisture present in the air. In dry air, the

CO_2 concentration is 350 ppm_v. The partial pressure will be this volume fraction times the total pressure of dry air. The total pressure of dry air is the total atmospheric pressure (29.0 in Hg) minus the contribution of water vapor. The vapor pressure of water can be looked up at 70°F to be 0.36 lb/in². Thus the total pressure of dry air is

$$P_{\text{total}} - P_{\text{water}} = 29.0 \text{ inHg} - \left[0.36 \frac{\text{lb}}{\text{in}^2} \times \frac{29.9 \text{ inHg}}{14.7 \frac{\text{lb}}{\text{in}^2}} \times 0.8 \right] = 28.4 \text{ inHg}$$

The partial pressure of CO_2 would be

$$\text{Vol fraction} \times P_{\text{total}} = 350 \text{ ppm}_v \times \frac{10^{-6} \text{ volfrac}}{\text{ppm}_v} \times \left[28.4 \text{ inHg} \times \frac{1 \text{ atm}}{29.9 \text{ inHg}} \right]$$

$$= 3.3 \times 10^{-4} \text{ atm}$$

2.4 MOLE/VOLUME UNITS

Units of moles per liter (molarity, M) are often used to report concentrations of compounds dissolved in water. Molarity is defined as the number of moles of compound per liter of solution. Thus a 10^{-4} M solution of copper contains 10^{-4} moles of copper per liter of solution. Concentrations expressed in these units are read as *molar*. Thus, the copper solution would be described as being 10^{-4} molar.

Molarity, M, should not be confused with molality, m. Molarity is usually used in equilibrium calculations and throughout the remainder of this book. Molality is the number of moles of a solute added to exactly one liter of solvent. Thus, the actual volume of a molal solution is slightly larger than one liter. Molality is more likely to be used when properties of the solvent, such as boiling and freezing point, are a concern. Therefore, it is rarely used in environmental situations.

EXAMPLE 2.8. CONCENTRATION AS MOLALITY

Convert the concentration of trichloroethene (TCE) (5 ppm) to units of molarity. The molecular weight of TCE is 131.5 g/mole.

SOLUTION

Remember, in water, ppm_m is equivalent to mg/L, so the concentration of TCE is 5.0 mg/L. Conversion to molarity units requires only the molecular weight:

$$5.0 \frac{\text{mg TCE}}{\text{L}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} \times \frac{1 \text{ mole}}{131.5 \text{ g}} = \frac{3.8 \times 10^{-5} \text{ moles}}{\text{L}} \text{ or M}$$

Often, concentrations below 1 M are expressed in units of millimoles per liter, or millimolar (1 mM = 10^{-3} moles/L) or micromoles per liter or micromolar (1 μ M = 10^{-6} moles/L). Thus, the concentration of TCE could be expressed as 0.038 mM or 38 μ M.

EXAMPLE 2.9. CONCENTRATION AS MOLARITY

The concentration of alachlor, a common herbicide, in the Mississippi River was found to range from 0.04 to 0.1 μ g/L. What is the concentration range in nmole/L? The molecular formula for alachlor is $C_{14}H_{20}O_2NCl$ (MW = 270).

SOLUTION

The lowest concentration range in nmole/L can be found as follows:

$$\frac{0.04 \mu\text{g}}{\text{L}} \times \frac{\text{mole}}{270 \text{ g}} \times \frac{10^{-6} \text{ g}}{\mu\text{g}} \times \frac{10^9 \text{ nmole}}{\text{mole}} = \frac{0.15 \text{ nmol}}{\text{L}}$$

Similarly, the upper limit (0.1 μ g/L) can be calculated to be 0.37 nmol/L. Hence the concentration range of alachlor is 0.15–0.37 nmol/L.

2.5 OTHER TYPES OF UNITS

Sometimes concentrations are expressed as “normality,” as a “common constituent,” or represented by “effect.” The following three sections describe these methods to express concentration in further detail.

2.5.1 Normality

Normality (equivalents/L) is typically used in defining the chemistry of water, especially in instances where acid/base and oxidation/reduction reactions are taking place. It is also used in determining the accuracy of a water analysis, as demonstrated in Example 2.12, and in calculating dosages of chemicals during some water treatment processes (e.g., softening hard water). Normality is also used frequently in the laboratory during the analytical measurement of water constituents. For example, “Standard Methods for the Examination of Water and Wastewater” (American Public Health Association (APHA), 1992) has many examples where concentrations of chemical reagents are prepared and reported in units of normality and not molarity.

Reporting concentration on an equivalent basis is useful because if two chemical species react and the two species reacting have the same strength on an equiv-

alent basis, a 1-mL volume of reactant number 1 will react with a 1-mL volume of reactant number 2. In acid/base chemistry the number of equivalents per mole of acid equals the number of moles of H^+ the acid can potentially donate. For example, HCl has 1 equivalent/mole, H_2SO_4 has 2 equivalents/mole, and H_3PO_4 has 3 equivalents/mole. Likewise, the number of equivalents per mole of a base equals the number of moles of H^+ that will react with one mole of the base. Thus, NaOH has 1 equivalent/mole, $CaCO_3$ has 2 equivalents/mole, and PO_4^{3-} has 3 equivalents/mole.

In oxidation/reduction reactions the number of equivalents is related to how many electrons a species donates or accepts. For example, the number of equivalents of Na^+ is 1 (where e^- equals an electron) because: $Na \rightarrow Na^+ + e^-$. Likewise, the number of equivalents for Ca^{2+} is 2 because: $Ca \rightarrow Ca^{2+} + 2e^-$. The equivalent weight (units = g/eqv) of a species is defined as the molecular weight of the species divided by the number of equivalents in the species (g/mole/eqv/mole = g/eqv).

EXAMPLE 2.10. CALCULATION OF EQUIVALENT WEIGHT

What is the equivalent weight of HCl, H_2SO_4 , NaOH, $CaCO_3$, and aqueous CO_2 ?

SOLUTION

The equivalent weight is found by dividing the molecular weight by the number of equivalents.

$$\text{eqv wt of HCl} = \frac{1 + 35.5 \text{ g}}{\text{mole}} \div \frac{1 \text{ eqv}}{\text{mole}} = \frac{36.5 \text{ g}}{\text{eqv}}$$

$$\text{eqv wt of } H_2SO_4 = \frac{(2 \times 1) + 32 + (4 \times 16) \text{ g}}{\text{mole}} \div \frac{2 \text{ eqv}}{\text{mole}} = \frac{49 \text{ g}}{\text{eqv}}$$

$$\text{eqv wt of NaOH} = \frac{23 + 16 + 1 \text{ g}}{\text{mole}} \div \frac{1 \text{ eqv}}{\text{mole}} = \frac{40 \text{ g}}{\text{eqv}}$$

$$\text{eqv wt of } CaCO_3 = \frac{40 + 12 + (3 \times 16) \text{ g}}{\text{mole}} \div \frac{2 \text{ eqv}}{\text{mole}} = \frac{50 \text{ g}}{\text{eqv}}$$

Determining the equivalent weight of aqueous CO_2 requires a bit of thinking and some new information. Aqueous carbon dioxide is not an acid until it hydrates in water and forms carbonic acid ($CO_2 + H_2O \rightarrow H_2CO_3$). So aqueous CO_2 really has 2 eqv/mole. Thus one can see that the equivalent weight of aqueous carbon dioxide is

$$\frac{12 + (2 \times 16) \text{ g}}{\text{mole}} \div \frac{2 \text{ eqv}}{\text{mole}} = \frac{22 \text{ g}}{\text{eqv}}$$

EXAMPLE 2.11: CALCULATION OF NORMALITY

What is the normality of 1 M solutions of HCl and H₂SO₄?

SOLUTION

$$1 \text{ M HCl} = \frac{1 \text{ mole HCl}}{\text{L}} \times \frac{1 \text{ eqv}}{\text{mole}} = \frac{1 \text{ eqv}}{\text{L}} = 1 \text{ N}$$

$$1 \text{ M H}_2\text{SO}_4 = \frac{1 \text{ mole H}_2\text{SO}_4}{\text{L}} \times \frac{2 \text{ eqv}}{\text{mole}} = \frac{2 \text{ eqv}}{\text{L}} = 2 \text{ N}$$

Note that on an equivalent basis, a 1-M solution of sulfuric acid is twice as strong as a 1-M solution of HCl.

An example of how normality is used in analytical measurements can be seen when determining the chemical oxygen demand (COD) of a water sample. After performing a titration to determine the concentration of oxidized chromium (Cr⁶⁺) remaining in solution, a conversion factor of 8,000 is employed in the expression to determine the COD based upon the amount of titrant used. This conversion factor results because an oxidation/reduction reaction occurs during the titration, the equivalent weight of oxygen is 8, and there are 1,000 mL per liter of water. Oxygen's equivalent weight can be found from dividing the molecular weight of O₂ (32 g/mole) by 4 eqv/mole.

EXAMPLE 2.12: USING EQUIVALENTS IN DETERMINING THE ACCURACY OF A WATER ANALYSIS

All aqueous solutions must maintain charge neutrality. Another way to state this is that the sum of all cations on an equivalent basis must equal the sum of all anions on an equivalent basis. Thus, water samples can be checked to determine if something is either incorrect in the analyses or a constituent(s) is missing. The following example shows how this is done. The label on a bottle of New Zealand mineral water purchased in the city of Dunedin stated that a chemical analysis of the mineral water resulted in the following cations and anions being identified with corresponding concentrations (in mg/L):

$$\begin{aligned} [\text{Ca}^{2+}] &= 2.9; & [\text{Mg}^{2+}] &= 2.0; & [\text{Na}^+] &= 11.5; & [\text{K}^+] &= 3.3; \\ [\text{SO}_4^{2-}] &= 4.7; & [\text{F}^-] &= 0.09; & [\text{Cl}^-] &= 7.7 \end{aligned}$$

Is the analysis correct?

SOLUTION

First convert all concentrations of major ions to an equivalent basis. This is done by first multiplying the concentration in mg/L by a unit conversion (g/1,000 mg) and then dividing by the equivalent weight of each substance (#g/eqv). The concentrations of all cations and anions are then summed up on an equivalent basis. A solution with less than 5% error is generally considered acceptable.

Cations	Anions
$[\text{Ca}^{2+}] = \frac{1.45 \times 10^{-4} \text{ eqv}}{\text{L}}$	$[\text{SO}_4^{2-}] = \frac{9.75 \times 10^{-5} \text{ eqv}}{\text{L}}$
$[\text{Mg}^{2+}] = \frac{1.67 \times 10^{-4} \text{ eqv}}{\text{L}}$	$[\text{F}^-] = \frac{4.73 \times 10^{-6} \text{ eqv}}{\text{L}}$
$[\text{Na}^+] = \frac{5 \times 10^{-4} \text{ eqv}}{\text{L}}$	$[\text{Cl}^-] = \frac{2.17 \times 10^{-4} \text{ eqv}}{\text{L}}$
$[\text{K}^+] = \frac{8.5 \times 10^{-5} \text{ eqv}}{\text{L}}$	

The total amount of cations equals 9.87×10^{-4} eqv/L, and the total amount of anions equals 3.2×10^{-4} eqv/L.

The analysis is not within 5%. The analysis resulted in over 3 times more cations than anions on an equivalent basis. Therefore, it can be concluded that either (a) one or more of the reported concentrations are incorrect (assuming all major cations and anions are accounted for), or (b) one or more important anions were not accounted for by the chemical analysis (e.g., bicarbonate, HCO₃⁻, would be a good guess for the missing anion, as it is a common anion in most natural waters).

2.5.2 Concentration as a Common Constituent

Concentrations can be reported as a common constituent, and can therefore include contributions from a number of different chemical compounds. Nitrogen and phosphorus are chemicals that have their concentration typically reported as a common constituent. For example, the phosphorus in a lake or wastewater may be present in inorganic forms called orthophosphates (i.e., H₃PO₄, H₂PO₄⁻, HPO₄²⁻, PO₄³⁻ and PO₄³⁻ and HPO₄²⁻ complexes), polyphosphates (e.g., H₄P₂O₇, H₃P₃O₁₀⁻), metaphosphates (e.g., HP₃O₆⁻), and/or organic phosphates. Because phosphorus can be chemically converted between these forms and can thus be found in several of these forms, it makes sense at some times to report the total P concentration, without specifying which form(s) are present. Thus each concentration for every individual form of phosphorus is converted to mg P/L using

the MW of the individual species, the MW of P (32), and simple stoichiometry. These converted concentrations of each individual species can then be added to determine the total phosphorus concentration. The concentration is then reported in units of mg/L as phosphorus (written as mg P/L, mg/L as P, or mg/L P).

Nitrogen can also exist in many different chemical forms in aqueous systems. These forms include ammonia (NH_3 and NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), and organic nitrogen (e.g., amino acids like alanine ($\text{CH}_3\text{CHNH}_2\text{COOH}$) or glycine ($\text{H}_2\text{NCH}_2\text{COOH}$), amines, etc.). To express the concentration of total nitrogen (all forms of nitrogen combined), the concentration of each individual species of nitrogen is converted to mg N/L (MW = 14), as is done in Example 2.13. Thus the concentration could be reported as mg NO_3^- /L or mg NO_3^- -N/L (mg of NO_3^- as nitrogen/L).

EXAMPLE 2.13. CONCENTRATIONS AS A COMMON CONSTITUENT

A water contains two nitrogen species. The concentration of NH_3 is 30 mg/L NH_3 and the concentration of NO_3^- is 5 mg/L NO_3^- . What is the total nitrogen concentration in units of mg N/L?

SOLUTION

Use the appropriate molecular weight and stoichiometry to convert each individual species to the requested units of mg N/L, then add the contribution of each species.

$$\begin{aligned} \frac{30 \text{ mg } \text{NH}_3}{\text{L}} \times \frac{\text{mole } \text{NH}_3}{17 \text{ g}} \times \frac{\text{mole N}}{\text{mole } \text{NH}_3} \times \frac{14 \text{ g}}{\text{mole N}} &= \frac{24.7 \text{ mg } \text{NH}_3\text{-N}}{\text{L}} \\ \frac{5 \text{ mg } \text{NO}_3^-}{\text{L}} \times \frac{\text{mole } \text{NO}_3^-}{62 \text{ g}} \times \frac{\text{mole N}}{\text{mole } \text{NO}_3^-} \times \frac{14 \text{ g}}{\text{mole N}} &= \frac{1.1 \text{ mg } \text{NO}_3^-\text{-N}}{\text{L}} \\ \text{Total nitrogen concentration} &= 24.7 + 1.1 = \frac{25.8 \text{ mg N}}{\text{L}} \end{aligned}$$

The “alkalinity” and “hardness” of a water are typically reported by determining all of the individual species that contribute to either alkalinity or hardness, then converting each of these species to units of mg CaCO_3 /L, and finally summing up the contribution of each species. Thus, hardness is normally expressed as mg/L as CaCO_3 .

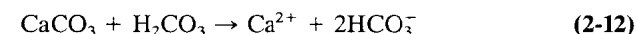
The hardness of a water is caused by the presence of divalent cations in water. Ca^{2+} and Mg^{2+} are by far the most abundant divalent cations in natural waters, though Fe^{2+} , Mn^{2+} , and Sr^{2+} may contribute as well. These cations are released

Table 2-3. Scale to Quantify the Hardness of Water

Hardness (as mg/L CaCO_3)	Hardness Evaluation
<50	Soft
50–150	Moderately hard
151–300	Hard
>300	Very hard

From Hammer and Hammer, 1996.

from the dissolution of minerals. For example, calcium carbonate can react with the natural acidity found in rain water to release hardness (shown as Ca^{2+}) and alkalinity (here in the form of HCO_3^-) according to the following reaction:



There is no adverse health effect from drinking hard waters; however, they can hinder soap formation and produce scale in boilers and piping. This increases the cost to society because of increased soap usage and plugging up of boilers and pipes with scale. Furthermore, hard waters can leave a “slimy” feeling on your body after bathing, so they are not aesthetically pleasing to some consumers.

The total hardness of a water can be found by summing the contributions of all divalent cations after converting their concentrations to a common constituent. Then the resulting value can be compared to the scale shown in Table 2-3 to evaluate the hardness of the water. In Michigan, Wisconsin, and Minnesota untreated waters usually have a hardness of 121–180 mg/L as CaCO_3 . In Illinois and Iowa water is harder with many values greater than 180 mg/L as CaCO_3 .

The conversion of concentration of specific cations (from mg/L) to hardness (as mg/L CaCO_3) can be accomplished by the following expression, where M^{2+} represents a divalent cation.

$$\frac{\text{M}^{2+} \text{ in mg}}{\text{L}} \times \frac{50}{\text{eqv wt of } \text{M}^{2+} \text{ in g/eqv}} = \frac{\text{mg}}{\text{L}} \text{ as } \text{CaCO}_3 \quad (2-13)$$

The origin of the 50 in Equation 2-13 comes from the fact that the equivalent weight of calcium carbonate is 50 (100 grams CaCO_3 /2 equivalents). The equivalent weights (in units of g/eqv) of the following divalent cations are Mg = 24/2; Ca, 40/2; Mn, 55/2; Fe, 56/2; Sr, 88/2.

EXAMPLE 2.14. DETERMINATION OF A WATER'S HARDNESS

Water has the following chemical composition. $[\text{Ca}^{2+}] = 15 \text{ mg/L}$; $[\text{Mg}^{2+}] = 10 \text{ mg/L}$; $[\text{SO}_4^{2-}] = 30 \text{ mg/L}$. What is the total hardness in units of mg/L as CaCO_3 ?

SOLUTION

Find the contribution of hardness from each divalent cation. Anions and all non-divalent cations are not included in the calculation.

$$\frac{15 \text{ mg Ca}^{2+}}{\text{L}} \times \left(\frac{50 \text{ g CaCO}_3}{\frac{40 \text{ g Ca}^{2+}}{2 \text{ eqv}}} \right) = \frac{38 \text{ mg}}{\text{L}} \text{ as CaCO}_3$$

$$\frac{10 \text{ mg Mg}^{2+}}{\text{L}} \times \left(\frac{50 \text{ g CaCO}_3}{\frac{24 \text{ g Mg}^{2+}}{2 \text{ eqv}}} \right) = \frac{42 \text{ mg}}{\text{L}} \text{ as CaCO}_3$$

Therefore, the total hardness is $38 + 42 = 80 \text{ mg/L}$ as CaCO_3 . Note this water is moderately hard. Also, note that if reduced iron (Fe^{2+}) or manganese (Mn^{2+}) were present, they would be included in the hardness calculation.

2.5.3 Reporting Particle Concentrations in Air and Water

Particles present in the air may reduce visibility (even in some of our remote National Parks!), blacken, corrode, or erode buildings and historical monuments, and adversely affect the health of humans and animals. The concentration of particles in an air sample is determined by pulling a known volume (e.g., several thousand m^3) of air through a filter. The increase in weight of the filter due to collection of particles on the filter can be determined and if this value is divided by the volume of air passed through the filter, the total suspended-particulate (TSP) concentration can be determined in units of g/m^3 or $\mu\text{g}/\text{m}^3$. In the United States, TSP concentrations average $20 \mu\text{g}/\text{m}^3$ in clean areas and 60 to $200 \mu\text{g}/\text{m}^3$ in urban areas. In order to penetrate deep into a human lung, particles must have a diameter between 0.1 and about $2.5 \mu\text{m}$. Particulate concentrations determined after removing all particles larger than $2.5 \mu\text{m}$ are termed $\text{PM}_{2.5}$. Thus, $\text{PM}_{2.5}$ refers to particles less than $2.5 \mu\text{m}$ in size.

In aquatic systems and in the analytical determination of metals, the solid phase is distinguished by filtration using a filter opening of $0.45 \mu\text{m}$. This size typically determines the cutoff between the “dissolved” and “particulate” phases. Therefore, in analytical chemistry, the $0.45\text{-}\mu\text{m}$ cutoff can be used to separate metals into a “dissolved” and “particulate” phase.

In the areas of drinking water, wastewater, and landfill leachate, solids are first divided into a “dissolved” or “suspended” fraction. This is done by a combination of filtration and evaporation procedures. Each of these two types of solids can be further broken down into a “fixed” and “volatile” fraction. Figure 2-2 shows the analytical difference between total solids, total suspended solids, total dissolved solids, and volatile suspended solids.

Total solids (TS) are determined by placing a well-mixed water sample of known volume in a drying dish and evaporating the water at $103\text{--}105^\circ\text{C}$. The

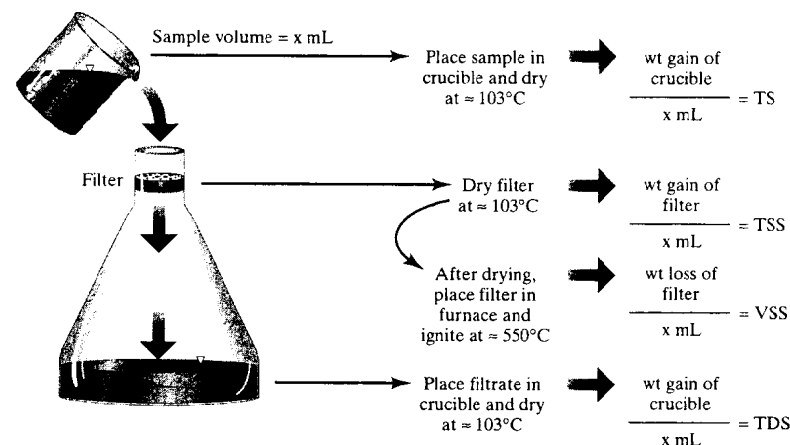


Figure 2-2. The analytical difference between total solids (TS), total suspended solids (TSS), volatile suspended solids (VSS), and total dissolved solids (TDS).

increase in the weight of the drying dish is due to the total solids. Total solids can thus be determined by dividing the increase in weight gain of the drying dish by the sample volume. Concentrations are typically reported in mg/L .

Total dissolved solids (TDS) and total suspended solids (TSS) are determined by first filtering a well-mixed sample of known volume through a glass-fiber filter ($2\text{-}\mu\text{m}$ size opening). The suspended solids are the particles caught on the filter. The concentration of TSS can be determined by drying the filter at $103\text{--}105^\circ\text{C}$, determining the weight increase in the filter, and then dividing this weight gain by the sample volume (results in mg/L). Suspended solids (collected on the filter) may adversely impact aquatic ecosystems by impairing light penetration or act as a source of nutrients or oxygen-depleting organic matter. Also, a water high in suspended solids may be unsuited for human consumption or swimming. The TDS are determined by collecting the sample that passes through the filter, drying this filtrate at 180°C , and then determining the weight gain of the drying dish. This weight gain divided by the sample volume is the concentration of TDS (results in mg/L). Dissolved solids may adversely affect the taste of a water and can also lead to scale formation. This is because dissolved solids tend to be less organic in composition and consist of dissolved cations and anions. For example, one would expect that hard waters would also be high in dissolved solids.

TS, TDS, and TSS can be further broken down into a “fixed” and “volatile” fraction. For example, the volatile portion of the TSS is termed the volatile suspended solids (VSS) and the fixed portion is termed the fixed suspended solids (FSS). Determining the volatile fraction of a sample is done by taking each sample just discussed and igniting it in a furnace at 500°C ($\pm 50^\circ\text{C}$). The weight loss due to this high-temperature ignition provides the volatile fraction, and the fixed fraction is what sample remains after ignition. Figure 2-3 shows how to relate the various solid determinations used in water treatment, wastewater, and leachate situations. In wastewater treatment plants, the volatile fraction is a good approx-

TS	=	TDS	+	TSS
		=		=
TVS	=	VDS	+	VSS
		+		+
TFS	=	FDS	+	FSS

Figure 2-3. Matrix showing how the various measurements of solids in aqueous samples can be related. For example, if the TSS and VSS are measured, the FSS can be determined by difference.

imation of the organic matter content of the solids. Thus, determination of volatile solids in a biological aeration tank (e.g., 3,000 mg VSS/L) can be related to the number of microorganisms in the tank.

EXAMPLE 2.15. DETERMINING TSP AND $PM_{2.5}$ CONCENTRATIONS IN AN AIR SAMPLE

An air-sampling program sampled 100,000 L of air for particles. The following mass of particles were collected for particular size fractions: 12 mg retained with particle size $> 2.5 \mu\text{m}$ and 6 mg retained with particle size $< 2.5 \mu\text{m}$. What are the $PM_{2.5}$ and total suspended particulate (TSP) concentrations of this air sample?

SOLUTION

By definition, $PM_{2.5}$ is the concentration of particles between 0.1 and $2.5 \mu\text{m}$, or in this case the mass of particles retained with size $< 2.5 \mu\text{m}$. Therefore,

$$PM_{2.5} = \frac{6 \text{ mg}}{100,000 \text{ L}} \times \frac{10^3 \text{ L}}{\text{m}^3} \times \frac{10^3 \mu\text{g}}{\text{mg}} = \frac{60 \mu\text{g}}{\text{m}^3}$$

$$TSP = \frac{12 \text{ mg} + 6 \text{ mg}}{100,000 \text{ L}} \times \frac{10^3 \text{ L}}{\text{m}^3} \times \frac{10^3 \mu\text{g}}{\text{mg}} = \frac{180 \mu\text{g}}{\text{m}^3}$$

Note that these particulate concentrations are relatively high. The sample was most likely collected from an urban area where TSP concentrations range from $60 \mu\text{g}/\text{m}^3$ to $200 \mu\text{g}/\text{m}^3$.

EXAMPLE 2.16. DETERMINING CONCENTRATIONS OF SOLIDS IN A WATER SAMPLE

A laboratory provides the following analysis obtained from a 50-mL sample of wastewater. Total solids = 200 mg/L, total suspended solids = 160 mg/L, fixed suspended solids = 40 mg/L, and volatile suspended solids = 120 mg/L. (a) What

is the concentration of total dissolved solids of this sample? (b) If this sample was filtered through a glass-fiber filter, then the filter was placed in a muffle furnace at 550°C overnight, what would be the weight of the solids (in mg) remaining on the filter after the night in the furnace? (c) Is this water sample turbid, and approximately what percent of the solids are composed of organic matter?

SOLUTION

- (a) Refer to Figure 2-3 to see the relationship between the various forms of solids. TDS equals $TS - TSS$; thus,

$$TDS = \frac{200 \text{ mg}}{\text{L}} - \frac{160 \text{ mg}}{\text{L}} = \frac{40 \text{ mg}}{\text{L}}$$

- (b) The solids remaining on the filter are suspended solids (dissolved solids would pass through the filter). Because the filter was subjected to a temperature of 550°C , the measurement was being made for the volatile and fixed fraction of the suspended solids, that is, the VSS and FSS. However, during the ignition phase, the volatile fraction is burned off, while what remains on the filter is the inert or fixed fraction of the suspended solids. Thus, this problem is requesting the fixed fraction of the suspended solids. Accordingly, the 50-mL sample had $FSS = 40 \text{ mg/L}$. Therefore,

$$FSS = \frac{40 \text{ mg}}{\text{L}} = \frac{\text{wt of SS remaining on filter after ignition}}{\text{mL sample}} = \frac{x}{50 \text{ mL}}$$

The unknown, x , can be solved for and equals 2 mg.

- (c) The sample is turbid. This is because the suspended matter, which is measured as TSS, causes the sample to appear turbid. Of course, if one allows the sample to sit for some time period, the suspended solids would settle and the sample might appear to be nonturbid. The solids found in this sample contain at least 60% organic matter. The total solids concentration is 200 mg/L and of this, 120 mg/L are volatile suspended solids. Therefore, because volatile solids consist primarily of organic matter (e.g., organic carbon, nitrogen, phosphorus, etc.), it can be concluded that approximately 60% (120/200) of the solids are organic.

2.5.4 Representation by Effect

In some cases, the actual concentration of a specific substance is not used at all, especially in instances where mixtures of ill-defined chemicals are present (e.g., raw sewage). Instead, the strength of the solution or mixture is defined by some common factor on which all the chemicals within the mixture depend (e.g., oxygen depletion from biological and chemical decomposition of the chemicals that make up the raw sewage). Thus, the strength of a wastewater is determined, not