2

Physical and Chemical Quality of Water

MWH's Water Treatment: Principles and Design, Third Edition
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Terminology for Physical and Chemical Quality of Water

Term	Definition
Absorbance	Amount of light absorbed by the constituents in a solution.
Aggregate water quality indicators	Measured parameter values caused by a number of individual constituents.
Alkalinity	Measure of the ability of a water to resist changes in pH.
Colloids	Particles smaller than about 1 μm in size; although definitions vary, they are generally distinguished because they will not settle out of solution naturally.
Color	Reduction in clarity of water caused by the absorption of visible light by dissolved substances, including organic compounds (fulvic acid, humic acid) and inorganic compounds (iron, manganese).
Conductivity	Measure of the concentration of dissolved constituents based on their ability to conduct electrical charge.
Hydrogen bonding	Attractive interaction between a hydrogen atom of one water molecule and the unshared electrons of the oxygen atom in another water molecule.
Natural organic matter (NOM)	Complex matrix of organic chemicals present in all water bodies, originating from natural sources such as biological activity, secretions from the metabolic activity, and excretions from fish or other aquatic organisms.
Particles	Constituents in water larger than molecules that exist as a separate phase (i.e., as solids). Water with particles is a suspension, not a solution. Particles include silt, clay, algae, bacteria, and other microorganisms.
pH	Parameter describing the acid–base properties of a solution.

Term	Definition
Radionuclides	Unstable atoms that are transformed through the process of radioactive decay.
Suspended solids	See: particles
Synthetic organic compounds (SOCs)	Man-made (anthropogenic) organic synthetic chemicals. Some SOCs are volatile; others tend to stay dissolved in water instead of evaporating.
Total dissolved solids (TDS)	Total amount of ions in solution, analyzed by filtering out the suspended material, evaporating the filtrate, and weighing the remaining residue.
Total organic halogen	Total mass concentration of organically bound halogen atoms (X = Cl, Br, or I) present in water.
Trace constituents	Constituents (inorganic and organic) of natural waters found in the parts-per-billion to parts-per-trillion range.
Transmittance	Measure of the amount of light, expressed as a percentage, that passes through a solution. The percent transmittance effects the performance of ultraviolet (UV) disinfection processes.
Trihalomethane (THM)	One of a family of organic compounds named as derivative of methane. THMs are generally by-products of chlorination of drinking water that contains organic material.
Trihalomethane (THM) formation potential	Maximum tendency of the organic compounds in a given water supply to form THMs upon disinfection.
Turbidity	Reduction in clarity of water caused by the scattering of visible light by particles.

Naturally occurring water is a solution containing not only water molecules but also chemical matter such as inorganic ions, dissolved gases, and dissolved organics; solid matter such as colloids, silts, and suspended solids; and biological matter such as bacteria and viruses. The structure of water, while inherently simple, has unique physicochemical properties. These properties have practical significance for water supply, water quality, and water treatment engineers. The purpose of this chapter is to present background information on the physical and chemical properties of water, the units used to express the results of physical and chemical analyses, and the constituents found in water and the methods used to quantify them. Topics considered in this chapter include (1) the fundamental and engineering properties of water, (2) units of expression for chemical concentrations, (3) the physical aggregate characteristics of water, (4) the inorganic chemical constituents found in water, (5) the organic chemical constituents found in water, (6) taste and odor, (7) the gases found in water, and (8) the radionuclides found in water. All of the topics introduced in this chapter are expanded upon in the subsequent chapters as applied to the treatment of water.

2-1 Fundamental and Engineering Properties of Water

The fundamental and engineering properties of water are introduced in this section. The fundamental properties relate to the basic composition and structure of water in its various forms. The engineering properties of water are used in day-to-day engineering calculations.

Fundamental Properties of Water

The fundamental properties of water include its composition, dimensions, polarity, hydrogen bonding, and structural forms. Because of their importance in treatment process theory and design, polarity and hydrogen bonding are considered in the following discussion. Details on the other properties may be found in books on water chemistry and on a detailed website dedicated to water science and structure (Chapin, 2010).

POLARITY

The asymmetric water molecule contains an unequal distribution of electrons. Oxygen, which is highly electronegative, exerts a stronger pull on the shared electrons than hydrogen; also, the oxygen contains two unshared electron pairs. The net result is a slight separation of charges or dipole, with the slightly negative charge (δ^-) on the oxygen end and the slightly positive charge (δ^+) on the hydrogen end. Attractive forces exist between one polar molecule and another such that the water molecules tend to orient themselves with the hydrogen end of one directed toward the oxygen end of another.

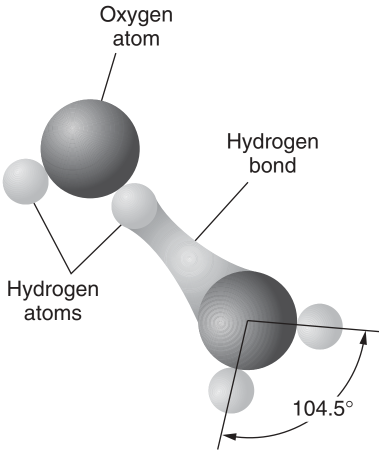


Figure 2-1
Hydrogen bonding between water molecules.

HYDROGEN BONDING

The attractive interaction between a hydrogen atom of one water molecule and the unshared electrons of the oxygen atom in another water molecule is known as a hydrogen bond, represented schematically on Fig. 2-1. Estimates of hydrogen bond energy between molecules range from 10 to 40 kJ/mol, which is approximately 1 to 4 percent of the covalent O–H bond energy within a single molecule (McMurry and Fay, 2003). Hydrogen bonding causes stronger attractive forces between water molecules than the molecules of most other liquids and is responsible for many of the unique properties of water.

Engineering Properties of Water

Compared to other species of similar molecular weight, water has higher melting and boiling points, making it a liquid rather than a gas under ambient conditions. Hydrogen bonding, as described above, can be used to explain the unique properties of water including density, high heat capacity, heat of formation, heat of fusion, surface tension, and viscosity of water. Examples of the unique properties of water include its capacity to dissolve a variety of materials, its effectiveness as a heat exchange fluid, its high density and pumping energy requirements, and its viscosity. In dissolving or suspending materials, water gains characteristics of biological, health-related, and aesthetic importance. The type, magnitude, and interactions of these materials affect the properties of water, such as its potability, corrosivity, taste, and odor. As will be demonstrated in subsequent chapters, technology now exists to remove essentially all of the dissolved and suspended components of water. The principal engineering properties encountered in environmental engineering and used throughout this book are reported in Table 2-1. The typical numerical values given in Table 2-1 are to provide a frame of reference for the values that are reported in the literature.

Table 2-1
Engineering properties of water

		Unit		Value[a]		
Property	**Symbol**	**SI**	**U.S. Customary**	**SI**	**U.S. Customary**	**Definition/Notes**
Boiling point	bp	°C	°F	100	212	Temperature at which vapor pressure equals 1 atm; high value for water keeps it in liquid state at ambient temperature.
Conductivity	κ	μS/m	μS/m	5.5	5.5	Pure water is not a good conductor of electricity; dissolved ions increase conductivity.
Density	ρ	kg/m^3	slug/ft^3	998.2	1.936	
Dielectric constant	ε_r	unitless	unitless	80.2	80.2	Measure of the ability of a solvent to maintain a separation of charges; high value for water indicates it is a very good solvent.
Dipole moment	p	C•m	D (debye)	6.186×10^{-30}	1.855	Measure of the separation of charge within a molecule; high value for water indicates it is very polar.

(*continues*)

Table 2-1 *(Continued)*

		Unit		Value[a]		
Property	**Symbol**	**SI**	**U.S. Customary**	**SI**	**U.S. Customary**	**Definition/Notes**
Enthalpy of formation	ΔH_f	kJ/mol	btu/lb_m	–286.5	–6836	Energy associated with the formation of a substance from the elements.
Enthalpy of fusion[b]	ΔH_{fus}	kJ/mol	btu/lb_m	6.017	143.6	Energy associated with the conversion of a substance between the solid and liquid states (i.e., freezing or melting).
Enthalpy of vaporization[c]	ΔH_v	kJ/mol	btu/lb_m	40.66	970.3	Energy associated with the conversion of a substance between the liquid and gaseous states (i.e., vaporizing or condensing); high value for water makes distillation very energy intensive.
Heat capacity[d]	c_p	J/mol•°C	btu/lb_m•°F	75.34	0.999	Energy associated with raising the temperature of water by one degree; high value for water makes it impractical to heat or cool water for municipal treatment purposes.
Melting point	mp	°C	°F	0	32	
Molecular weight	MW	g/mol[e]	g/mol[e]	18.016	18.016	Also known as molar mass.
Specific weight	γ	kN/m^3	lb_f/ft^3	9.789	62.37	
Surface tension	σ	N/m	lb_f/ft	0.0728	0.00499	
Vapor pressure	p_v	kN/m^2	lb_f/in^2	2.339	0.34	
Viscosity, dynamic	μ	$N \cdot s/m^2$	$lb_f \cdot s/ft^2$	1.002×10^{-3}	2.089×10^{-5}	
Viscosity, kinematic	ν	m^2/s	ft^2/s	1.004×10^{-6}	1.081×10^{5}	

[a] All values for pure water at 20°C (68°F) and 1 atm pressure unless noted otherwise.
[b] At the melting point (0°C).
[c] At the boiling point (100°C).
[d] Often called the molar heat capacity when expressed in units of J/mol • °C and specific heat capacity or specific heat when expressed in units of J/g • °C.
[e] Molecular weight has units of Daltons (Da) or atomic mass units (AMU) when expressed for a single molecule (i.e., one mole of carbon-12 atoms has a mass of 12 g and a single carbon-12 atom has a mass of 12 Da or 12 AMU).

2-2 Units of Expression for Chemical Concentrations

Water quality characteristics are often classified as physical, chemical (organic and inorganic), or biological and then further classified as health related or aesthetic. To characterize water effectively, appropriate sampling and analytical procedures must be established. The purpose of this section is to review briefly the units used for expressing the physical and chemical characteristics of water. The basic relationships presented in this section will be illustrated and expanded upon in subsequent chapters. Additional details on the subject of sampling, sample handling, and analyses may be found in Standard Methods (2005).

Commonly used units for the amount or concentration of constituents in water are as follows:

1. *Mole:*

   6.02214×10^{23} elementary entities (molecules, atoms, etc.) of a substance

   $$1.0 \text{ mole of compound} = \text{molecular weight of compound, g} \tag{2-1}$$

2. *Mole fraction:* The ratio of the amount (in moles) of a given solute to the total amount (in moles) of all components in solution is expressed as

   $$x_B = \frac{n_B}{n_A + n_B + n_C + \cdots + n_N} \tag{2-2}$$

   where x_B = mole fraction of solute B
   n_A = moles of solute A
   n_B = moles of solute B
   n_C = moles of solute C
   $\vdots$
   n_N = moles of solute N

   The application of Eq. 2-2 is illustrated in Example 2-1.

3. *Molarity (M):*

$$M, \text{ mol/L} = \frac{\text{mass of solute, g}}{(\text{molecular weight of solute, g/mol})(\text{volume of solution, L})} \tag{2-3}$$

4. *Molality (m):*

$$m, \text{ mol/kg} = \frac{\text{mass of solute, g}}{(\text{molecular weight of solute, g/mol})(\text{mass of solution, kg})} \tag{2-4}$$

Example 2-1 Determination of molarity and mole fractions

Determine the molarity and the mole fraction of a 1-L solution containing 20 g sodium chloride (NaCl) at 20°C. From the periodic table and reference books, it can be found that the molar mass of NaCl is 58.45 g/mol and the density of a 20 g/L NaCl solution is 1.0125 kg/L.

Solution

1. The molarity of the NaCl solution is computed using Eq. 2-3

$$[\mathrm{NaCl}] = \frac{20\ \mathrm{g}}{(58.45\ \mathrm{g/mol})(1.0\ \mathrm{L})} = 0.342\ \mathrm{mol/L} = 0.342\ \mathrm{M}$$

2. The mole fraction of the NaCl solution is computed using Eq. 2-2
   a. The amount of NaCl (in moles) is

$$n_{\mathrm{NaCl}} = \frac{20\ \mathrm{g}}{58.45\ \mathrm{g/mol}} = 0.342\ \mathrm{mol}$$

   b. From the given solution density, the total mass of the solution is 1012.5 g, so the mass of the water in the solution is 1012.5 g − 20 g = 992.5 g and the amount of water (in moles) is

$$n_{\mathrm{H_2O}} = \frac{992.5\ \mathrm{g}}{18.02\ \mathrm{g/mol}} = 55.08\ \mathrm{mol}$$

   c. The mole fraction of NaCl in the solution is

$$x_{\mathrm{NaCl}} = \frac{n_{\mathrm{NaCl}}}{n_{\mathrm{NaCl}} + n_{\mathrm{H_2O}}} = \frac{0.342\ \mathrm{mol}}{0.342\ \mathrm{mol} + 55.07\ \mathrm{mol}} = 6.17 \times 10^{-3}$$

Comment

The molar concentration of pure water is calculated by dividing the density of water by the MW of water; i.e., 1000 g/L divided by 18 g/mol equals 55.56 mol/L. Because the amount of water is so much larger than the combined values of the other constituents found in most waters, the mole fraction of constituent A is often approximated as $x_A \approx (n_A/55.56)$. If this approximation had been applied in this example, the mole fraction of NaCl in the solution would have been computed as 6.16×10^{-3}.

5. *Mass concentration:*

$$\text{Concentration, g/m}^3 = \frac{\text{mass of solute, g}}{\text{volume of solution, m}^3} \tag{2-5}$$

Note that $1.0\ \mathrm{g/m^3} = 1.0\ \mathrm{mg/L}$.

6. *Normality (N):*

$$N, \text{eq/L} = \frac{\text{mass of solute, g}}{(\text{equivalent weight of solute, g/eq})(\text{volume of solution, L})} \tag{2-6}$$

where

$$\text{Equivalent weight of solute, g/eq} = \frac{\text{molecular weight of solute, g/mol}}{Z, \text{eq/mol}} \tag{2-7}$$

For most compounds, Z is equal to the number of replaceable hydrogen atoms or their equivalent; for oxidation–reduction reactions, Z is equal to the change in valence. Also note that $1.0\ \text{eq/m}^3 = 1.0\ \text{meq/L}$.

7. *Parts per million* (ppm):

$$\text{ppm} = \frac{\text{mass of solute, g}}{10^6\ \text{g of solution}} \tag{2-8}$$

Also,

$$\text{ppm} = \frac{\text{concentration of solute, g/m}^3}{\text{specific gravity of solution (density of solution divided by density of water)}} \tag{2-9}$$

8. *Other units:*

ppm_m = parts per million by mass (for water $\text{ppm}_\text{m} = \text{g/m}^3 = \text{mg/L}$)
ppm_v = parts per million by volume
ppb = parts per billion
ppt = parts per trillion

Also, $1\ \text{g (gram)} = 1 \times 10^3\ \text{mg (milligram)} = 1 \times 10^6\ \mu\text{g (microgram)} = 1 \times 10^9\ \text{ng (nanogram)} = 1 \times 10^{12}\ \text{pg (picogram)}$.

2-3 Physical Aggregate Characteristics of Water

Most first impressions of water quality are based on physical rather than chemical or biological characteristics. Water is expected to be clear, colorless, and odorless (Tchobanoglous and Schroeder, 1985). Most natural waters will contain some material in suspension typically comprised of inorganic soil components and a variety of organic materials derived from nature. Natural waters are also colored by exposure to decaying organic material. Water from slow-moving streams or eutrophic water bodies will often contain colors and odors. These physical parameters are known as *aggregate characteristics* because the measured value is caused by a number of individual constituents. Parameters commonly used to quantify the aggregate physical characteristics include (1) absorption/transmittance, (2) turbidity, (3) number and type of particles, (4) color, and (5) temperature. Taste and odor, sometimes identified as physical characteristics, are considered in Sec. 2-6.

Absorbance and Transmittance

The absorbance of a solution is a measure of the amount of light that is absorbed by the constituents in a solution at a specified wavelength. According to the Beer–Lambert law, the amount of light absorbed by water is proportional to the concentration of light-absorbing molecules and the path length the light takes in passing through water, regardless of the intensity of the incident light. Because even pure water will absorb incident light, a sample blank (usually distilled water) is used as a reference. Absorbance is given by the relationship

$$\log\left(\frac{I}{I_0}\right) = -\varepsilon(\lambda)\,Cx = -k_A(\lambda)\,x = -A(\lambda) \tag{2-10}$$

where I = intensity of light after passing through a solution of known depth containing constituents of interest at wavelength λ, mW/cm^2

I_0 = intensity of incident light after passing through a blank solution (i.e., distilled water) of known depth (typically 1.0 cm) at wavelength λ, mW/cm^2

λ = wavelength, nm

$\varepsilon(\lambda)$ = molar absorptivity of light-absorbing solute at a wavelength λ, L/mol · cm

C = concentration of light-absorbing solute, mol/L

x = length of light path, cm

$k_A(\lambda) = \varepsilon(\lambda)\,C$ = absorptivity at wavelength λ, cm^{-1}

$A(\lambda) = \varepsilon(\lambda)\,Cx$ = absorbance at wavelength λ, dimensionless

If the left-hand side of Eq. 2-10 is expressed as a natural logarithm, then the right-hand side of the equation must be multiplied by 2.303 because the absorbance coefficient (also known as the extinction coefficient) is determined in base 10. Absorbance is measured using a spectrophotometer, as illustrated on Fig. 2-2. Typically, a fixed sample path length of 1.0 cm is used. The absorbance $A(\lambda)$ is unitless but is often reported in units of reciprocal centimeters, which corresponds to absorptivity $k_A(\lambda)$. If the

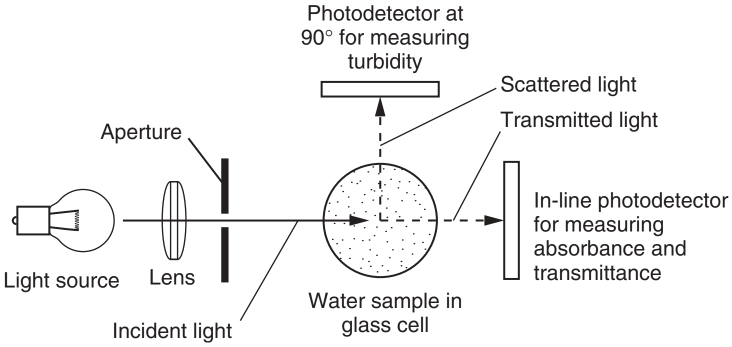


Figure 2-2
Schematic of a spectrophotometer used to measure absorbance and turbidity.

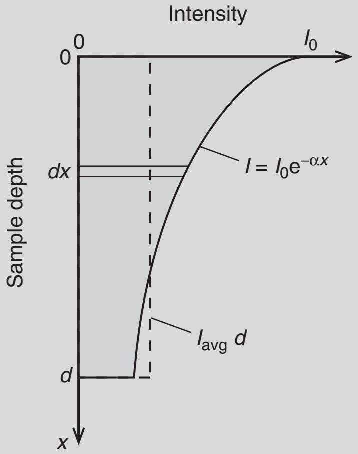
length of the light path is 1 cm, absorptivity is equal to the absorbance. The absorbance of water is typically measured at a wavelength of 254 nm. Typical absorbance values for various waters at $\lambda = 254$ are given in Table 13-10. The application of Eq. 2-10 is illustrated in the following example.

Example 2-2 Determine average UV intensity

If the intensity of the UV radiation measured at the water surface in a Petri dish is 15 mW/cm^2, determine the average UV intensity to which a sample will be exposed if the depth of water in the Petri dish is 12 mm (1.2 cm). Assume the absorptivity $k_A(\lambda) = 0.1/\text{cm}$.

Solution

1. Develop the equation to determine the average intensity.
   a. The definition sketch for this problem is given below.



where

$$\alpha = 2.303 k_A(\lambda)$$

   b. Develop the required equation:

$$I_{avg} = \int_0^d I_0 e^{-\alpha x}\, dx = -\frac{I_0}{\alpha} e^{-\alpha x}\Big|_0^d$$

$$= -\frac{I_0}{d\alpha} e^{\alpha d} + \frac{I_0}{\alpha} = \frac{I_0}{\alpha}(1 - e^{-\alpha d})$$

$$I_{avg} = \frac{I_0}{\alpha d}(1 - e^{-\alpha d})$$

2. Compute the average intensity for a depth of 12 mm (1.2 cm):
   a. Assume $k_A(\lambda) = 0.1/\text{cm}$
   b. $\alpha = 2.303\, k_A(\lambda) = 2.303\ (0.1/\text{cm}) = 0.2303/\text{cm}$
   c. Solve for I_{avg}

$$I_{avg} = \frac{I_0}{\alpha d}(1 - e^{-\alpha d}) = \frac{15\ \text{mW/cm}^2}{(0.2303/\text{cm})(1.2\ \text{cm})}\left[1 - e^{-(0.2303)(1.2)}\right]$$

$$= 13.1\ \text{mW/cm}^2$$

The transmittance of a solution is defined as

$$\text{Transmittance, } T, \% = \left(\frac{I}{I_0}\right) \times 100 \tag{2-11}$$

Thus, the transmittance at a given wavelength can also be derived from absorbance measurements using the relationship

$$T = 10^{-A(\lambda)} \tag{2-12}$$

The term *percent transmittance,* commonly used in the literature, is given as

$$T,\ \% = 10^{-A(\lambda)} \times 100 \tag{2-13}$$

The extreme values of A and T are as follows (Delahay, 1957):

For a perfectly transparent solution $A(\lambda) = 0$, $T = 1$.
For a perfectly opaque solution $A(\lambda) \to \infty$, $T = 0$.

The principal water characteristics that affect the percent transmittance include selected inorganic compounds (e.g., copper and iron), organic compounds (e.g., organic dyes, humic substances, and aromatic compounds such as benzene and toluene), and small colloidal particles ($\leq 0.45\ \mu\text{m}$). If samples contain particles larger that 0.45 μm, the sample should be filtered before transmittance measurements are made. Of the inorganic compounds that affect transmittance, iron is considered to be the most important with respect to UV light absorbance because dissolved iron can absorb UV light directly. Organic compounds containing double bonds and aromatic functional groups can also absorb UV light. Absorbance values for a variety of compounds are given in the on-line resources for this text at the URL listed in App. E. The reduction in transmittance observed in surface waters during storm events is often ascribed to the presence of humic substances and particles from runoff, wave action, and stormwater flows (Tchobanoglous et al., 2003).

Turbidity

Turbidity in water is caused by the presence of suspended particles that reduce the clarity of the water. Turbidity is defined as ‘‘an expression of the optical property that causes light to be scattered and absorbed rather than transmitted with no change in direction or flux level through the sample’’ (Standard Methods, 2005). Turbidity measurements require a light source (incandescent or light-emitting diode) and a sensor to measure the scattered light. As shown on Fig. 2-2, the scattered light sensor is located at 90° to the light source. The measured turbidity increases as the intensity of the scattered light increases. Turbidity is expressed in nephelometric turbidity units (NTU).

It is important to note that the scattering of light caused by suspended particles will vary with the size, shape, refractive index, and composition of the particles. Also, as the number of particles increases beyond a given level, multiple scattering occurs, and the absorption of incident light is increased, causing the measured turbidity to decrease (Hach, 2008). The spatial distribution and intensity of the scattered light, as illustrated on Fig. 2-3, will depend on the size of the particle relative to the wavelength of the light source. For particles less than one-tenth of the wavelength of the incident light, the scattering of light is fairly symmetrical. As the particle size increases relative to the wavelength of the incident light, the light reflected from different parts of the particle creates interference patterns that are additive in the forward direction (Hach, 2008). Also, the intensity of the scattered light will vary with the wavelength of the incident light. For example, blue light will be scattered more than red light. Based on these considerations, turbidity measurements tend to be more sensitive to

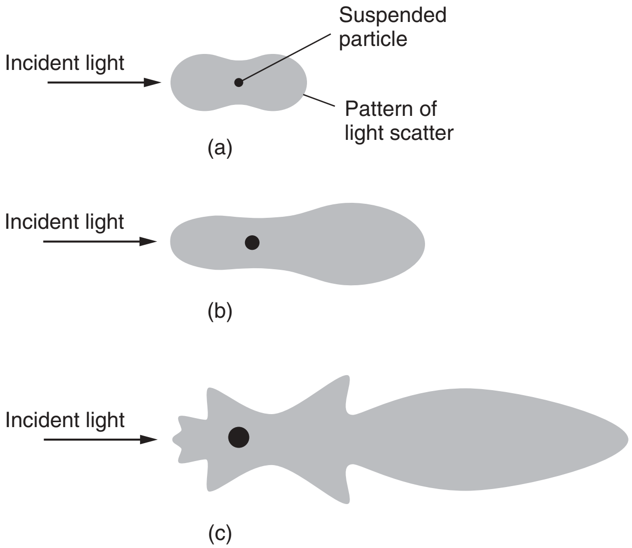


Figure 2-3
Light-scattering patterns for different particle sizes that occur when measuring turbidity. (Adapted from Hach, 2008.)

particles in the size range of the incident-light wavelength (0.3 to 0.7 μm for visible light). A further complication with turbidity measurements is that some particles such as carbon black will essentially absorb most of the light and only scatter a minimal amount of the incident light.

Depending on the water source, turbidity can be the most variable of the water quality parameters of concern in drinking water supplies. Turbidity measurements are useful for comparing different water sources or treatment facilities and are used for process control and regulatory compliance. Increases in turbidity measurements are often used as an indicator for increased concentrations of water constituents, such as bacteria, *Giardia* cysts, and *Cryptosporidium* oocysts.

In lakes or reservoirs, turbidity is frequently stable over time and ranges from about 1 to 20 NTU, excluding storm events. Turbidity in rivers is more variable due to storm events, runoff, and changes in flow rate in the river. Turbidity in rivers can range from under 10 to over 4000 NTU. Streams and rivers where the turbidity can change by several hundred NTU in a matter of hours (see Fig. 2-4) are often described as ''flashing'' because of the rapid change in the turbidity. In such rivers, careful turbidity monitoring is critical for successful process control. The regulatory standard for turbidity in finished water is 0.3 NTU, and many water treatment facilities have a treatment goal of <0.1 NTU, which is near the detection limit for turbidity meters.

Particles

Particles are defined as finely divided solids larger than molecules but generally not distinguishable individually by the unaided eye, although

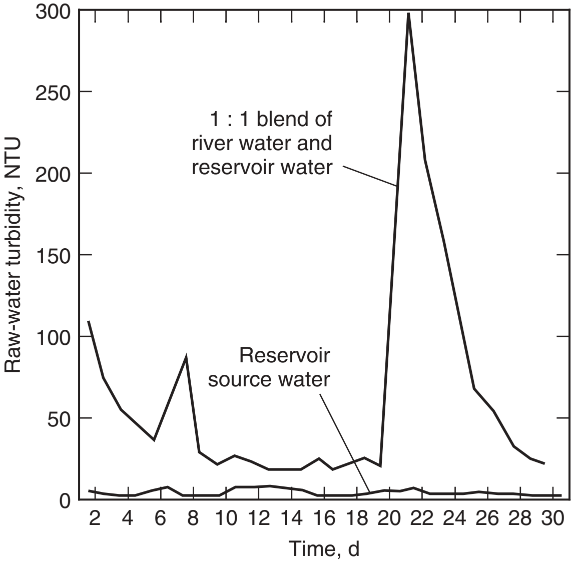


Figure 2-4
Observed variation in raw-water turbidity values. (Adapted from James M. Montgomery, 1981.)

clumps of particles are often encountered. It should be noted that with 20–20 vision it is possible to resolve a particle size of about 37 μm at a distance of 0.3 m. Particles in water are important for a variety of reasons, including their impact on treatment processes and the potential health impacts of pathogen-associated particles. Particles in water may be classified according to their source, size, chemical structure, electrical charge characteristics, and water–solid interface characteristics. The source, size, shape, number and distribution, and quantification of particles is considered in the following discussion. The electrical properties of particles and particle interactions are considered in Chap. 9. The impact of particles in water on key water treatment processes, that is, coagulation, sedimentation, granular filtration, membrane filtration, and disinfection, is considered in Chaps. 9, 10, 11, 12, and 13, respectively.

SOURCE OF PARTICLES IN WATER

The sources of particles in water are summarized in Table 2-2, along with the sources of chemical constituents and gases. As reported in Table 2-2, the principal natural sources of particles in water are soil-weathering processes and biological activity. Clays and silts are produced by weathering. Algae, bacteria, and other higher microorganisms are the predominant types of particles produced biologically. Some particles have both natural and anthropogenic sources, a notable example being asbestos fibers. Industrial and agricultural activities tend to augment these natural sources by increasing areas of runoff through cultural eutrophication, the increase in the rate of natural eutrophication as a result of human activity, or direct pollution with industrial residues. Particles may be transported into water through direct erosion from terrestrial environments, be suspended due to turbulence and mixing in water, or form in the water column during biological activity or chemical precipitation or through atmospheric deposition.

SIZE CLASSIFICATION OF PARTICLES

The size of particles in water considered in this text is typically in the range of 0.001 to 100 μm. Suspended particles are generally larger than 1.0 μm. The size of colloidal particles will vary from about 0.001 to 1 μm depending on the method of quantification. It should be noted that some researchers have classified the size range for colloidal particles as varying from 0.0001 or less to 1 μm. In practice, the distinction between colloidal and suspended particles is blurred because the suspended particles that can be removed by gravity settling will depend on the design of the sedimentation facilities. Some standard analytical procedures operationally define dissolved material as that which will pass through a 0.45 μm filter. In practice, however, colloids as small as 0.001 μm can behave as particles and affect water quality and treatment processes as particles rather than dissolved substances. A suspension comprised of particles of one size is

Table 2-2
Summary of important particulate, chemical, and biological constituents found in water according to their source

	Particulate constituents		Ionic and Dissolved Constituents		Gases and Neutral
Source	**Colloidal**	**Suspended**	**Positive ions**	**Negative ions**	**Species**
Contact of water with minerals, rocks, and soil (e.g., weathering)	Clay Silica (SiO_2) Ferric oxide (Fe_2O_3) Aluminum oxide (Al_2O_3) Magnesium dioxide (MnO_2)	Clay, silt, sand, and other inorganic soils	Calcium (Ca^{2+}) Iron (Fe^{2+}) Magnesium (Mg^{2+}) Manganese (Mn^{2+}) Potassium (K^+) Sodium (Na^+) Zinc (Zn^{2+})	Bicarbonate (HCO^-) Borate ($H_2BO_3^-$) Carbonate (CO_3^{2-}) Chloride (Cl^-) Fluoride (F^-) Hydroxide (OH^-) Nitrate (NO_3^-) Phosphate (PO_4^{3-}) Sulfate (SO_4^{2-})	Carbon dioxide (CO_2) Silicate (H_4SiO_4)
Rain in contact with atmosphere			Hydrogen (H^+)	Bicarbonate (HCO^-) Chloride (Cl^-) Sulfate (SO_4^{2-})	Carbon dioxide (CO_2) Nitrogen (N_2) Oxygen (O_2) Sulfur dioxide (SO_2)
Decompostion of organic matter in environment	Various organic polymers	Cell fragments	Ammonium (NH_4^+) Hydrogen (H^+) Sodium (Na^+)	Bicarbonate (HCO^-) Chloride (Cl^-) Hydroxide (OH^-) Nitrate (NO_3^-) Nitrite (NO_2^-) Sulfide (HS^-) Sulfate (SO_4^{2-})	Ammonia (NH_3) Carbon dioxide (CO_2) Hydrogen sulfide (H_2S) Hydrogen (H_2) Methane (CH_4) Nitrogen (N_2) Oxygen (O_2) Silicate (H_4SiO_4)

Living organisms	Bacteria, algae, viruses, etc.	Algae, diatoms, minute animals, fish, etc.	—	—	Ammonia (NH_3) Carbon dioxide (CO_2) Hydrogen sulfide (H_2S) Hydrogen (H_2) Methane (CH_4) Nitrogen (N_2) Oxygen (O_2)
Municipal, industrial, and agricultural sources and other human activity	Inorganic and organic solids, constituents causing color, chlorinated organic compounds, bacteria, worms, viruses, etc.	Clay, silt, grit, and other inorganic solids; organic compounds; oil; corrosion products; etc.	Inorganic ions, including a variety of anthropogenic compounds and heavy metals	Inorganic ions, including a variety of anthropogenic compounds, organic molecules, color, etc.	Chlorine (Cl_2) Sulfur dioxide (SO_2)

Source: Adapted, in part, from Tchobanoglous and Schroeder (1985).

called monodispersed and a suspension with a variety of particle sizes is called heterodispersed (typical of natural waters).

Many water treatment processes are designed to remove particles based on sedimentation and size exclusion. The type and size of various waterborne particles and processes used for measurement and removal are presented on Fig. 2-5. As shown on Fig. 2-5, conventional treatment processes such as sedimentation and depth filtration alone are not sufficient for the removal of all water constituents; however, with the addition of coagulation and flocculation, the effective range of these treatment processes is greatly extended.

PARTICLE SHAPE

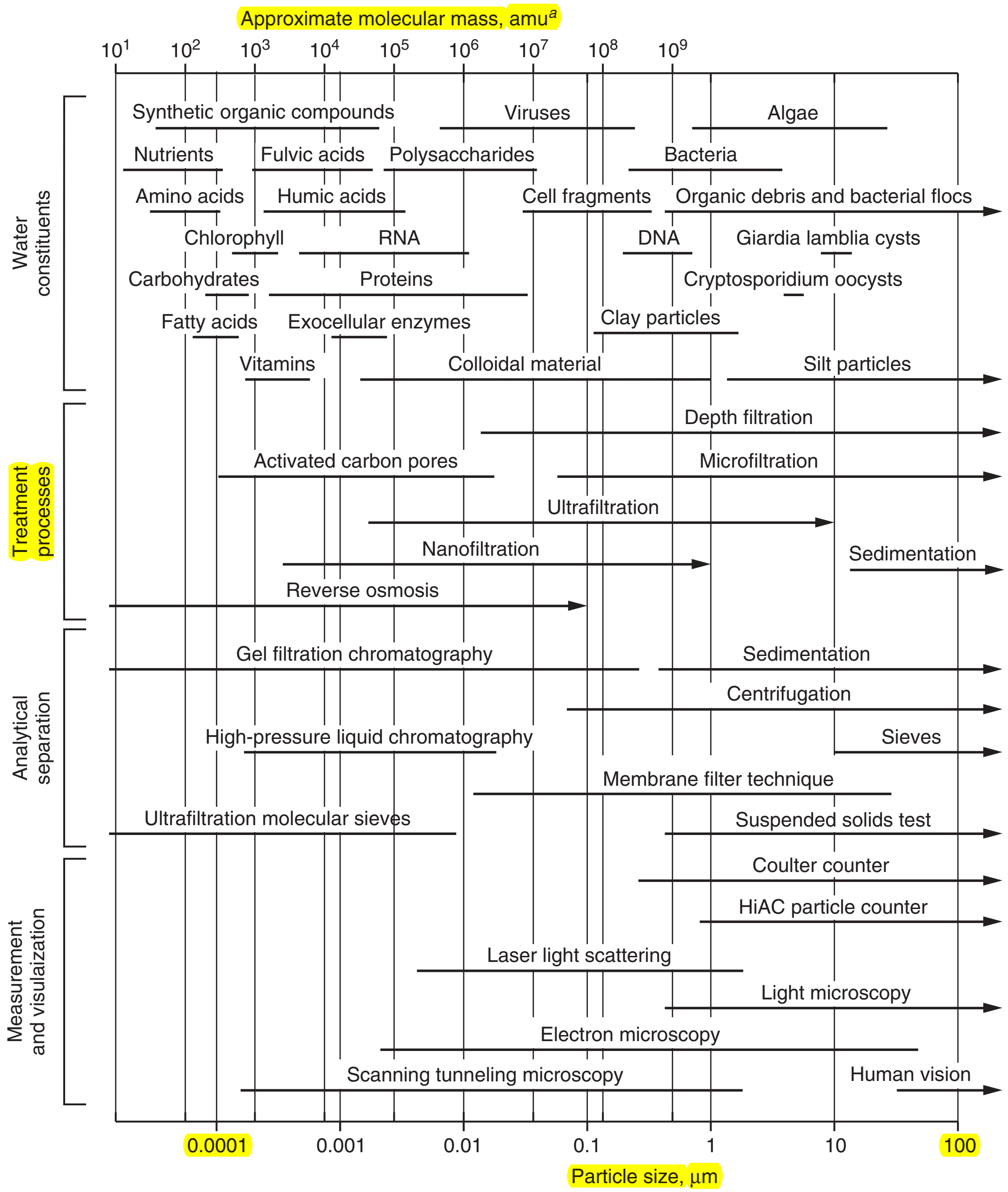
Particle shapes found in water can be described as spherical, semispherical, ellipsoids of various shapes (e.g., prolate and oblate), rods of various length and diameter, disk and disklike, strings of various lengths, and random coils. Inorganic particles are typically defined by the dimensions of their long, intermediate, and short axes and the ratio of the intermediate-to-long and the short-to-intermediate diameters. Because of the many different particle shapes, the nominal or equivalent particle diameter is used (Dallavalle, 1948). Large organic molecules are often found in the form of coils that may be compressed, uncoiled, or almost linear. The shape of some larger particles is often described as fractal. The particle shape will vary depending on the characteristics of the source water.

PARTICLE QUANTIFICATION

Methods used for the quantification and analysis of particulate material include gravimetric techniques, electronic particle size counting, and microscopic observation. Although regulations concerning particle concentrations are typically based on turbidity measurements, monitoring particle counts throughout a treatment process can aid in understanding and controlling the process. Also, as noted above, turbidity measurements cannot be correlated to any quantifiable particle characteristics. While particle quantification may be useful for evaluating a treatment process, except for microscopic observation, these methods cannot be used reliably for determining the source or type of particle (e.g., distinguish between a viable cyst and a colloid). In addition, due to the limitations of particle analysis methods, the use of more than one method is recommended when assessing water quality data.

Gravimetric techniques

The total mass of particles may be estimated by filtering a volume of water through a membrane of known weight and pore size. Filtration of the same water sample through a series of membranes with incrementally decreasing pore sizes is known as serial filtration. Serial filtration may be used to determine an approximate particle size distribution (Levine et al., 1985).



[a] An amu is an atomic mass unit (also known as a dalton, Da) and is equal to 1.66054×10^{-24} g.

Figure 2-5
Characterization of particulate matter in natural water by type and size, appropriate treatment methods, analytical separation methods, and measurement techniques. (Adapted from Tchobanoglous et al., 2003.)

Particle size distribution may also be measured using electronic particle-counting devices, as discussed below.

Electronic particle size counting

Particle concentration measurements provide more specific information about the size and number of particles in a water sample. Electronic particle size counters estimate the particle size concentration by either (1) passing a water sample through a calibrated orifice and measuring the change in conductivity (see Fig. 2-6) or (2) passing the sample through a laser beam and measuring the change in intensity due to light scattering. The change in conductivity or light intensity is correlated to the diameter of an equivalent sphere. Particle counters have sensors available in different size ranges, such as 1.0 to 60 μm or 2.5 to 150 μm, depending on the manufacturer and application. Particle counts are typically measured and recorded in about 10 to 20 subranges of the sensor range. Typical particle size counters are shown on Fig. 2-7. A comparison of analytical techniques used for particle size analysis is presented in Table 2-3. Particle counts may also be used as an indicator of *Giardia* and *Cryptosporidium* cysts from water (LeChevallier and Norton, 1992, 1995).

Microscopic observation

The use of microscopic observation allows for the determination of particle size counts and, in some cases, for more rigorous identification of a particle's

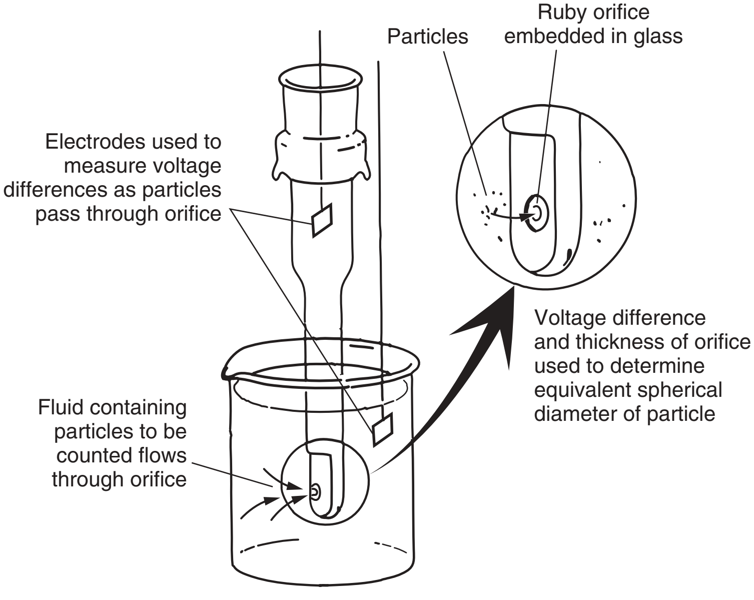


Figure 2-6
Typical particle-counting chamber used to enumerate particles in water using voltage difference to determine the size of an equivalent spherical particle. (Adapted from Tchobanoglous et al., 2003.)

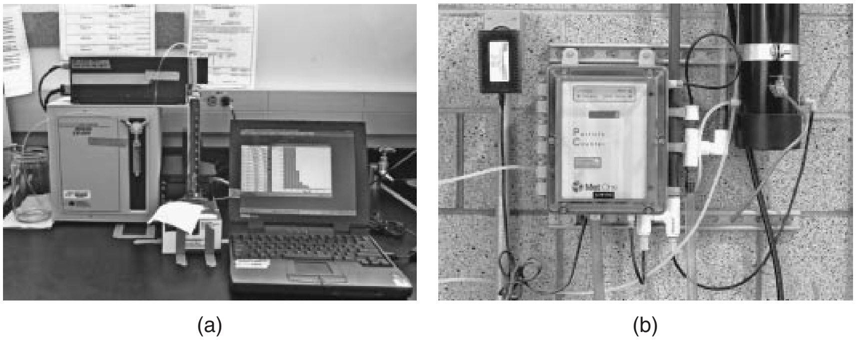

(a) (b)

Figure 2-7
Typical examples of particle size counters are (a) laboratory type connected to a computer (the sample to be analyzed is being withdrawn from the graduated cylinder) and (b) field type used to monitor the particle size distribution from a microfiltration plant.

Table 2-3
Analytical techniques used for analysis of particles in water

Technique	Typical Size Range, μm
Microscopy	
Light	0.2–>100
Transmission electron	0.0002–>0.1
Scanning electron	0.002–50
Image analysis	0.2–>100
Particle counting	
Conductivity difference	0.2–>100
Dynamic light scattering	0.0003–5
Equivalent light scattering	0.005–>100
Light obstruction (blockage)	0.2–>100
Light diffraction	0.3–>100
Separation	
Centrifugation	0.08–>100
Field flow fractionation	0.09–>100
Gel filtration chromatography	<0.0001–>100
Gravitation photosedimentation	0.1–>100
Sedimentation	0.05–>100
Membrane filtration	0.0001–1

Source: Adapted from Levine et al. (1985).

origin than is possible with other analysis techniques. A measured volume of sample is placed in a particle-counting cell and the individual particles may be counted, often with the use of a stain to enhance the particle contrast. Optical imaging software may also be used to obtain a more quantitative assessment of particle characteristics. Images of water particles are obtained with a digital camera attached to a microscope and sent to a computer for imaging analysis. The imaging software typically allows for the determination of minimum, mean, and maximum size, shape, surface area, aspect ratio, circumference, and centroid location.

PARTICLE NUMBER AND DISTRIBUTION

The number of particles in raw surface water can vary from 100 to over 10,000/mL depending on the time of year and location where the sample is taken (e.g., a river or storage reservoir). The number of particles, as will be discussed later, is of importance with respect to the method to be used for their removal. The size distribution of particles in natural waters may be defined on the basis of particle number, particle mass, particle diameter, particle surface area, or particle volume. In water treatment design and operation, particle size distributions are most often determined using a particle size counter, as discussed above. In most particle size counters, the detected particles of a given size are counted and grouped with other particles within specified size ranges (e.g., 1 to 2 μm, 5 to 10 μm). When the counting is completed, the number of particles in each bin is totaled.

The particle number frequency distribution $F(d)$ can be expressed as the number concentration of particles, dN, with respect to the incremental change in particle size, $d(d_p)$, represented by the bin size:

$$F(d_p) = \frac{dN}{d(d_p)} \tag{2-14}$$

where $F(d_p)$ = function defining frequency distribution of particles d_1, d_2, d_3

dN = particle number concentration with respect to incremental change in particle diameter $d(d_p)$

$d(d_p)$ = incremental change in particle diameter (bin size)

Because of the wide particle size ranges encountered in natural waters, it is common practice to plot the frequency function $dF(d)$ against the logarithm of size, log d_p:

$$2.303(d_p)F(d) = \frac{dN}{d(\log\ d_p)} \tag{2-15}$$

Similar relationships can be derived based on particle surface area and volume (Dallavalle, 1948; O'Melia, 1978).

It has also been observed that in natural waters the number of particles increases with decreasing particle diameter and that the frequency distribution typically follows a power law distribution of the form

$$\frac{dN}{d(d_p)} = A\left(d_p\right)^{-\beta} \simeq \frac{\Delta N}{\Delta(d_p)} \tag{2-16}$$

where A = power law density coefficient
d_p = particle diameter, µm
β = power law slope coefficient

Taking the log of both sides of Eq. 2-16 results in the following expression, which can be plotted to determine the unknown coefficients A and β:

$$\log\left[\Delta N/\Delta(d_p)\right] = \log A - \beta \log(d_p) \tag{2-17}$$

The value of A is determined when $d_p = 1$ µm. As the value of A increases, the total number of particles in each size range increases. The slope β is a measure of the relative number of particles in each size range. Thus, if $\beta < 1$, the particle size distribution is dominated by large particles; if $\beta = 1$, all particle sizes are represented equally; and if $\beta > 1$, the particle size distribution is dominated by small particles (Trussell and Tate, 1979). The value of the coefficient for most natural waters varies between 2 and 5 (O'Melia, 1978; Trussell and Tate, 1979). Typical plots of particle size data determined using a particle size counter for various waters are given on Fig. 2-8. On Fig. 2-8a, the effect of flocculation in producing large particles is evident by comparing the β values for the unflocculated versus the flocculated influent (4.1 versus 2.1). As shown on Fig. 2-8b, the removal of all particle sizes by filtration is very similar, because the slopes of the two plots are nearly identical. The analysis of data obtained from a particle size counter is shown in Example 2-3.

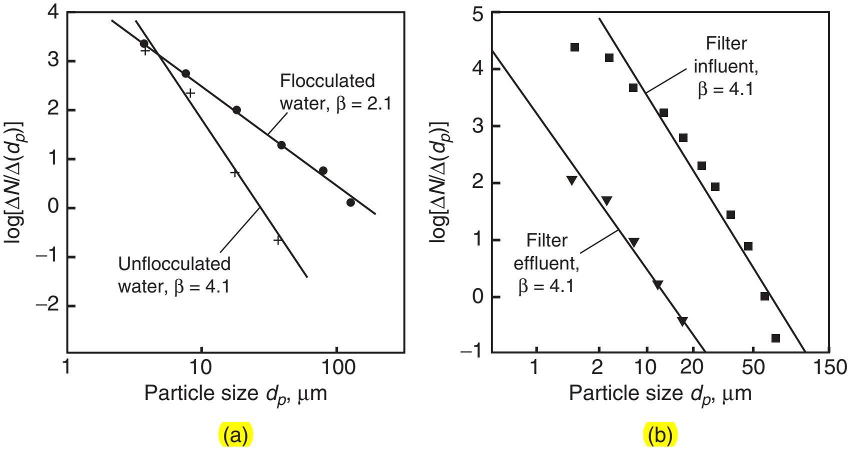


Figure 2-8
Typical examples of particle size distributions: (a) unflocculated and flocculated and (b) filter influent and effluent. (Adapted from Trussell and Tate, 1979.)

Example 2-3 Analysis of particle size information

Determine the slope and density coefficients A and β in Eq. 2-17 for the following particle size data obtained from settled water during a pilot study.

Channel (Bin)	Particle size range, μm	Number of Particles, #/mL
1	1–3	1785
2	3–5	243
3	5–7	145
4	7–12	186
5	12–32	132
6	32–120	2.9
	Total	2493.9

Solution

1. Calculate the necessary values for the first data channel.
   a. Mean particle diameter:

$$d_p = \frac{1}{2}(1\,\mu\text{m} + 3\,\mu\text{m}) = 2\,\mu\text{m}$$

   b. Log of the mean particle diameter:

$$\log(d_p) = \log(2\,\mu\text{m}) = 0.301$$

   c. Particle diameter range:

$$\Delta(d_p) = 3\,\mu\text{m} - 1\,\mu\text{m} = 2\,\mu\text{m}$$

   d. Number of particles:

$$\Delta N = 1785/\text{mL}$$

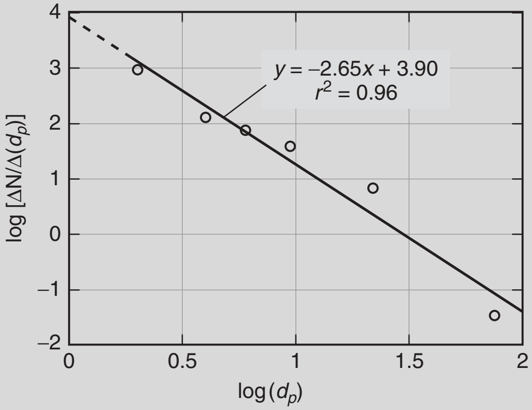
   e. Log of the particle size distribution function:

$$\log\left[\frac{\Delta N}{\Delta(d_p)}\right] = \log\left(\frac{1785/\text{mL}}{2\,\mu\text{m}}\right) = 2.95$$

2. Calculate the necessary values for the remaining data channels. The results are tabulated below.

Channel	(A) d_p	(B) $\log(d_p)$	(C) $\Delta(d_p)$	(D) ΔN	(E) $\log[\Delta N/\Delta(d_p)]$
1	2	0.301	2	1785	2.95
2	4	0.602	2	243	2.08
3	6	0.778	2	145	1.86
4	9	0.978	5	186	1.57
5	22	1.342	20	132	0.82
6	76	1.881	88	2.9	−1.48

3. Prepare a plot of $\log[\Delta N/\Delta(d_p)]$ versus $\log(d_p)$ draw a linear trendline and display the treadline equation and r^2 value on the chart. The resulting chart is shown below.



4. Determine A and β in Eq. 2-17 from the line of best fit in the above plot.
   a. When $\log(d_p) = 0$, the intercept value is equal to $\log(A)$. Thus, $A = 7{,}940$.
   b. The slope of the line of best fit is equal to $-\beta$. Thus, $\beta = 2.65$.

Color

The color of a water is an indication of the organic content, including humic and fulvic acids, the presence of natural metallic ions such as iron and manganese, and turbidity. Apparent color is measured on unfiltered samples and true color is measured in filtered samples (0.45-μm filter). Turbidity increases the apparent color of water, while the true color is caused by dissolved species and is used to define the aesthetic quality of water. The color of potable waters is typically assessed by visually comparing a water sample to known color solutions made from serial dilutions or concentrations of a standard platinum–cobalt solution. The platinum–cobalt standard is related to the color-producing substance in the water only by hue.

The presence of color is reported in color units (c.u.) at the pH of the solution. In water treatment, one of the difficulties with the comparison method is that at low levels of color it is difficult to differentiate between low values (e.g., 2 versus 5 c.u.). If the water sample contains constituents (e.g., industrial wastes) that produce unusual colors or hues that do not match the platinum–cobalt standards, then instrumental methods must be

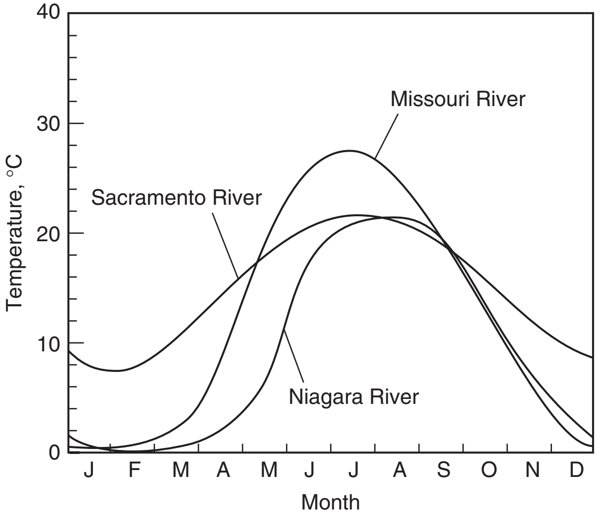


Figure 2-9
Generalized monthly variations in temperature in the Missouri River near Blair, Nebraska; in the Niagara River at Buffalo, New York; and in the Sacramento River near Sacramento, California. (Adapted from Tchobanoglous and Schroeder, 1985.)

used. Instrumental methods are used to determine (1) the hue (red, green, yellow, etc.), (2) the luminance (brightness), and (3) the saturation (pale, deep, etc.) of a solution. In turn, these three parameters can be related to the *chromaticity*. It should be noted that the results obtained with the two methods are not comparable.

Temperature

Water temperature is of importance because it affects many parameters that impact engineering designs. These parameters include density, viscosity, vapor pressure, surface tension, solubility, the saturation value of gases dissolved in water, and the rates of chemical, biochemical, and biological activity. As the heat capacity of water is much greater than that of air, water temperature changes much more slowly than air temperature. Depending on the geographic location, the mean annual temperature of river water in the United States varies from about 0.5 to 3°C in the winter to 23 to 27°C in the summer (see Fig. 2-9). In small slow-moving streams, summer temperatures may exceed 30°C. Lakes, reservoirs, ponds, and other impoundments are also subject to temperature changes. Extremely wide temperature variations can occur in shallow impoundments. Typical groundwater temperatures are as shown on Fig. 2-10. In general, groundwater temperatures are not as variable as surface water temperatures.

2-4 Inorganic Chemical Constituents

Water in the environment can contain a variety of colloidal and suspended solids inorganic and organic ionic and dissolved constituents and

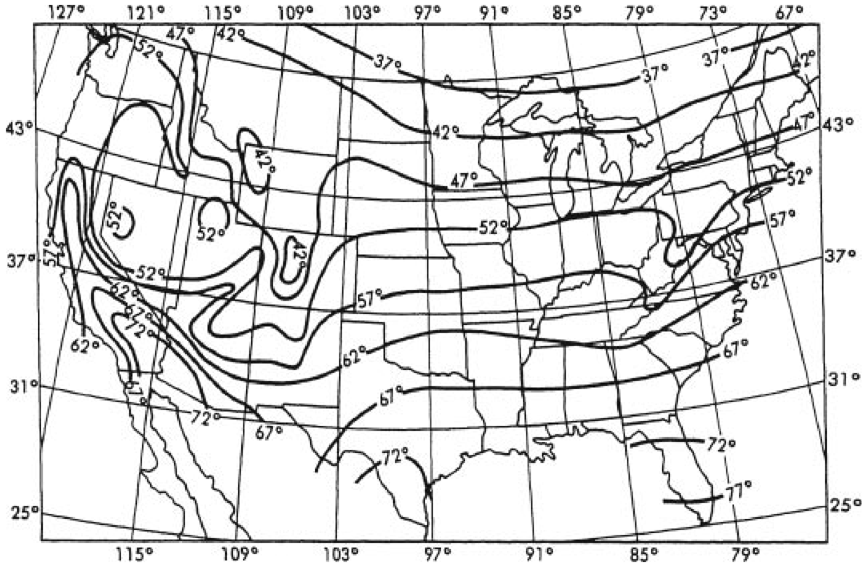


Figure 2-10 Approximate temperature of groundwater from nonthermal wells at depths varying from 10 to 20 m. Note temperatures are given in degrees Fahrenheit.

compounds, and gases (see Table 2-2). The sources of particulate (both colloidal and suspended) constituents in water were discussed previously in Sec. 2-3. The focus of this section is on the ionic and dissolved inorganic constituents found in most natural waters as identified in Table 2-2. Specific topics include (1) the major inorganic chemical constituents in natural water, (2) the minor inorganic constituents found in natural waters, and (3) the principal inorganic water quality indicators. Organic constituents are considered in Sec. 2-5.

Major Inorganic Constituents

Inorganic chemical constituents commonly found in water in significant quantities (1.0 to 1000 mg/L) include calcium, magnesium, sodium, potassium, bicarbonate, chloride, sulfate, and nitrate. Inorganic constituents that are generally present in lesser amounts (0.01 to 10 mg/L) include iron, lead, copper, arsenic, and manganese. The range of concentrations found for individual inorganic constituents in a survey of natural waters is shown on Fig. 2-11. The plotted lines for each constituent represent the percent of the samples in which each constituent was found to be equal to or less than a specified concentration. For example, potassium occurred over a range of 0.4 to 15 mg/L, and samples from 80 percent of the natural waters in this survey had potassium concentrations below 5 mg/L. Additional details on the major inorganic constituents found in natural waters are presented in Table 2-4.

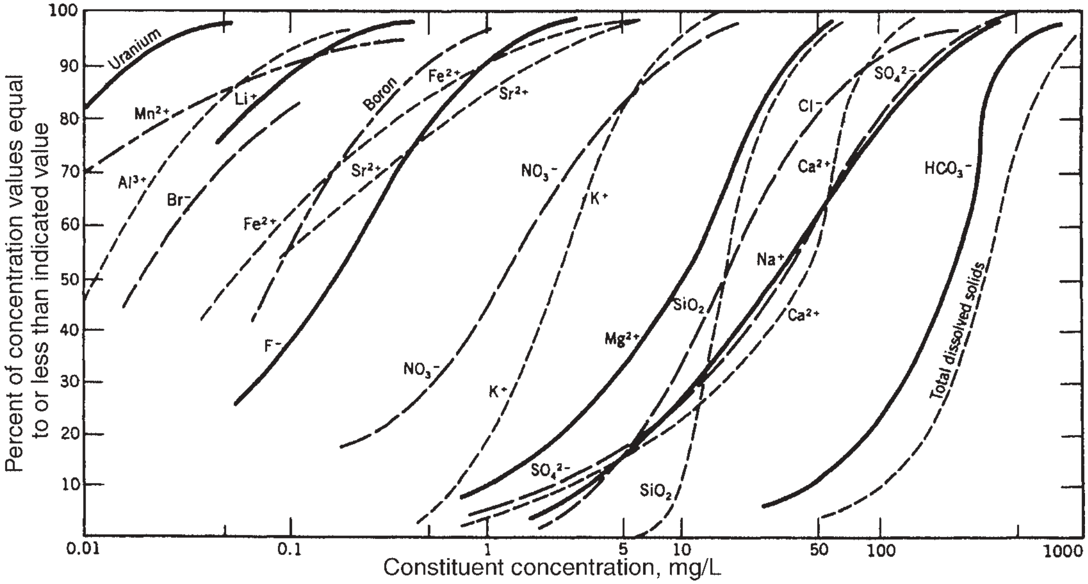


Figure 2-11
Cumulative curves showing frequency distribution of various constituents in terrestrial water. Data are mostly from the United States from various sources. (Adapted from Davies and DeWiest, 1966.)

Minor and Trace Inorganic Constituents

Constituents of natural waters found in the parts-per-billion to parts-per-trillion range may still be of significant health or water quality concern. Constituents of concern include a number of inorganics and numerous trace organics, as discussed in the following section. Information on the water quality significance of several inorganic trace constituents is presented in Table 2-5. As shown, the trace constituents have been grouped under four categories: (1) alkali metals, (2) alkaline metals, (3) other metallic elements depending on their properties, and (4) nonmetals.

Inorganic Water Quality Indicators

Several chemically related quality measures are utilized to characterize the properties of a water supply including (1) the hydrogen ion concentration (pH), (2) polyvalent cation content (hardness), (3) total dissolved solids (TDS), and (4) electrical conductivity.

pH (HYDROGEN ION CONCENTRATION)

pH is a measurement of the acid–base properties of a solution. pH is an important parameter in water treatment as it directly influences the dosages of chemicals added to reduce hardness and coagulate particles. pH is measured as the negative logarithm of the concentration of hydrogen ions:

$$\mathrm{pH} = -\log_{10}[\mathrm{H}^+] \qquad (2\text{-}18)$$

Table 2-4
Summary of the major cations and anions in natural water[a]

Ion	Description
	Cations
Calcium (Ca^{2+})	Calcium is generally among the most prevalent three or four ions in groundwaters. Common mineral forms of calcium are calcite, also known as aragonite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), and fluorite (CaF_2). Calcium is generally present as the free ion, Ca^{2+}, in natural waters and adsorbed onto soil particles. Along with magnesium and other multivalent ions Ca^{2+} is responsible for the hardness of a water as discussed later in this section.
Iron ($Fe^{2+,\ 3+}$)	Iron is found in rocks, soils, and waters in a variety of forms and oxidation states. Common mineral sources (deposits) of iron include ferric oxides and hydroxides such as hematite (Fe_2O_3) and ferric hydroxide [$Fe(OH)_3$], which gives rocks and soils their red and yellow color. In oxygenated surface waters (pH 5–8), typical concentrations of total iron are around 0.05–0.2 mg/L. In groundwater, the occurrence of iron at concentrations of 1.0–10 mg/L is common, and higher concentrations (up to 50 mg/L) are possible in low-bicarbonate and low-oxygen waters.
Magnesium (Mg^{2+})	Magnesium salts are more soluble than calcium, but they are less abundant in rocks and therefore less available for weathering reactions. Concentrations of magnesium are typically below 10–20 mg/L in surface waters and below 30–40 mg/L in groundwaters. Taken together, calcium and magnesium comprise most natural water hardness.
Manganese (Mn^{2+})	Manganese is abundant in rocks and soils, typically in the form of manganese oxides and hydroxides in association with other metallic cations. At low and neutral pH values, the predominant dissolved form of manganese is the divalent cation Mn^{2+}. Concentrations on the order of 0.1–1 mg/L are common, although in low-pH waters higher concentrations can occur. Manganese often is present with iron in groundwaters and, like iron, may cause aesthetic problems such as laundry and fixture staining.
Potassium (K^+)	Although a common element of the earth's crust, the concentration of potassium in natural waters is much lower than sodium. Potassium occurs in nature only in ionic or molecular form and has many properties that are similar to sodium, so it occasionally replaces sodium in industrial applications.
Sodium (Na^+)	Sodium compounds comprise almost 3% of the earth's crust, and a significant amount is found in rock and soil. Sodium is transported into water from rocks through weathering and soil through ion exchange reactions. In natural waters, sodium is generally present as the free ion Na^+. Several complexes and ion pairs may occur in natural waters, including sodium carbonate ($NaCO_3^-$), sodium bicarbonate ($NaHCO_3$), sodium sulfate ($NaSO_4^-$), and sodium chloride (NaCl).

(*continues*)

Table 2-4 *(Continued)*

Ion	Description
	Anions and neutral species
Bicarbonate (HCO_3^-)	The carbonate–bicarbonate system in natural water performs important functions in acid–base chemistry, buffer capacity, metal complexation, solids formation, and biological metabolism. Species comprising the carbonate system include CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}. The dominant role of the carbonate system in acid–base chemistry of natural waters is well documented, although exceptions occur in waters with very high concentrations of dissolved organics or in high-sulfate groundwaters.
Chloride (Cl^-)	Chloride is present in water supplies almost exclusively as the chloride ion (Cl^-), although hydrolysis products of chlorine (HOCl and OCl^-) exist temporarily where chlorine has been added as a disinfectant. In typical surface waters the concentration of chloride ion is less than 10 mg/L; however, in areas subject to seawater intrusion or hot-spring inflows or where evaporation greatly exceeds precipitation, the chloride concentrations can approach seawater levels.
Flouride (F^-)	Although the amount of fluoride in crustal rocks is much greater than chloride, fluoride remains bound in minerals to a much greater degree. Fluorite (CaF_2) is a common fluoride mineral and fluorapatite [$Ca_5F(PO_4)_3$] also commonly contains fluoride. In natural waters, fluoride is present primarily as the F^- ion or as a complex with aluminum, beryllium, or ferric iron. In waters with TDS < 1000 mg/L, fluoride is typically <1 mg/L, although ground waters affected by volcanic activity are found with levels higher than 10 mg/L.
Nitrogen (N)	The most common and important forms of nitrogen in water and their corresponding oxidation state in the water/soil environment are ammonia gas (NH_3, $-$III), ammonium (NH_4^+, $-$III), nitrogen gas (N_2, 0), nitrite ion (NO_2^-, $+$ III), and nitrate ion (NO_3^-, $+$ V). The oxidation state of nitrogen in most organic compounds is –III. The oxidation states of nitrogen range from -3 to $+5$ and are summarized below (Sawyer et al., 2003): $$\overset{-\text{III}}{NH_3} — \overset{0}{N_2} — \overset{\text{I}}{N_2O} — \overset{\text{II}}{NO} — \overset{\text{III}}{N_2O_3} — \overset{\text{IV}}{NO_2} — \overset{\text{V}}{N_2O_5}$$ Other forms of nitrogen in water include organic compounds such as urea (NH_2CONH_2), amino acids and their breakdown products, ammonia (NH_3), ammonium ion (NH_4^+), hydroxylamine (NH_2OH), nitrogen gas (N_2), and nitrite (NO_2^-). Ammonia, ammonium ion, and protein by-products are all reduced species, N_2 gas is in the zero oxidation state, nitrite is at $+3$, and nitrate is at $+5$. Transformation from one state to another is closely tied to biological activity, the influx of domestic wastes, and the local use of nitrogen fertilizers.
Silica (SiO_2)	Silica is present in almost all rocks, soils, and natural waters. In water, silica is hydrated as H_4SiO_4 or $Si(OH)_4$, although water analyses commonly represent dissolved silica as SiO_2. The concentration of silica most commonly found in natural waters is between 1 and 30 mg/L. The solubility of silica is complex, but temperature is a critical factor. Sodium silicates have been used as coagulants in water treatment and as corrosion inhibitors on iron pipes.

Table 2-4 *(Continued)*

Ion	Description
Anions and neutral species	
Sulfur (S)	Sulfur occurs in natural waters as sulfate (e.g., SO_4^{2-}) and sulfides (e.g., H_2S, HS^-, $Na_2S_2O_3$). The primary sources of sulfates are evaporite rocks, which are formed by water evaporation and mineral precipitation, such as gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$), sedimentary rock such as pyrite (FeS_2), rainfall, and bacterial metabolism. The concentration of sulfate in oxidized waters typically range from 5 to 30 mg/L.

[a]Cations and anions are arranged alphabetically

Table 2-5
Minor and trace elements found in natural waters[a]

Constituent	Concentration in Natural Waters, μg/L	Significance in Water Supplies
		Alkali Metals
Cesium	0.05–0.02[b]	
Lithium	0.001–0.3	Potentially toxic to plants, but not at concentrations likely to be encountered in irrigation waters
Rubidium	0.0015	
		Alkaline Earth Metals
Barium	0.043 (median public water)	Ingestion of soluble barium salts can be fatal. Normal water concentrations have no effect.
Beryllium	0.001–1	Highly toxic, but occurs at very low concentration.
Strontium	0.6 (median river water), 0.11 (median public water)	Concentration in natural water is less than solubility.
		Other Metallic Elements
Cadmium	ND–10	Toxic. Presence may indicate industrial contamination.
Chromium	5.8 (median river water), 0.43 (median public water)	Industrial pollutant.
Cobalt	ND–1.0	Essential in nutrition in small quantities.
Copper	10	Utilized in water treatment and metal fabrication; used to inhibit algae growth in reservoirs; essential for nutrition of flora and fauna.
Gold	ND–trace	—
Lead	1–10	Older plumbing systems contain lead, which may dissolve at low pH.

(continues)

Table 2-5 *(Continued)*

Constituent	Concentration in Natural Waters, μg/L	Significance in Water Supplies
Mercury	ND–<10	Highly toxic. Presence indicates pollution from mining, industry, or metallurgical works.
Molybdenum	0.35 (median river water); 1.4 (median public water)	Accumulated by vegetation. Forage crops may become toxic.
Nickel	10	—
Silver	0.1–0.3	Has been used as disinfectant.
Titanium	8.6 (median river water); <1.5 (median public waters)	—
Vanadium	<70	May concentrate in vegetation.
Zinc	10	Widely found in industry wastes; found in wastes dissolved from galvanized pipes, cooling-water treatment, etc.
Arsenic	0–1000	Used in industry in some herbicides and pesticides; lethal in animals above 44 mg/kg. Long-term ingestion of 0.21 mg/L reported to be poisonous.
Bromine	20	May react with disinfectants and form brominated species, which are suspected carcinogens.
Iodine	0.2–2	Essential nutrient in higher animals; has been used to seed clouds.
Selenium	0.2	Taken up by vegetation.

[a] Values presented are approximate and represent one or more author's best estimate. ND = nondetected. Public water refers to drinking water.
[b] Values observed in six analyses of rivers in Japan.
Sources: NAS (1977), Livingstone (1963), Turekian (1971), and Hem (1971).

The hydrogen ion concentration in water is connected closely with the extent to which water molecules dissociate. Water will dissociate into hydrogen and hydroxide ions as follows:

$$H_2O \rightleftarrows H^+ + OH^- \tag{2-19}$$

Applying the law of mass action (see discussion in Chap. 5) to Eq. 2-19 yields

$$\frac{[H^+][OH^-]}{[H_2O]} = K \tag{2-20}$$

where the brackets indicate concentration of the constituents in moles per liter. Because the concentration of water in a dilute aqueous system is essentially constant, this concentration can be incorporated into the equilibrium constant K to give

$$[\mathrm{H}^+][\mathrm{OH}^-] = K_w \tag{2-21}$$

where K_w is known as the ionization constant or ion product of water and is approximately equal to 1×10^{-14} at a temperature of 25°C. Equation 2-21 can be used to calculate the hydroxide ion concentration when the hydrogen ion concentration is known, and vice versa.

With pOH, which is defined as the negative logarithm of the hydroxyl ion concentration, for water at 25°C, the following relation is used:

$$\mathrm{pH} + \mathrm{pOH} = 14 \tag{2-22}$$

The pH of aqueous systems typically is measured with a pH-sensing electrode. Various pH papers and indicator solutions that change color at definite pH values are also used. When using pH paper or indicator solution, pH is determined by comparing the color of the paper or solution to a series of color standards.

HARDNESS

Multivalent cations, particularly magnesium and calcium, are often present at significant concentrations in natural waters. These ions are easily precipitated and in particular react with soap to form a difficult-to-remove scum. Hardness is an important parameter to industry as an indicator of potential (interfering) precipitation, such as with carbonates in cooling towers or boilers, with soaps and dyes in cleaning and textile industries, and with emulsifiers in photographic development. For most practical purposes, hardness of water can be represented as the sum of the calcium and magnesium concentrations, given in milliequivalents per liter:

$$\text{Hardness, eq/L} = 2\left[\mathrm{Ca}^{2+}\right] + 2\left[\mathrm{Mg}^{2+}\right] \tag{2-23}$$

In Eq. 2-23, the concentrations of Ca and Mg are given in mol/L, and the coefficient 2 reflects the divalent nature of both ions, i.e., both have 2 equivalents per mole. Two general types of hardness are of interest: carbonate hardness, associated with $\mathrm{HCO_3}^-$ and $\mathrm{CO_3}^{2-}$, and noncarbonate hardness, associated with other anions, particularly Cl^- and $\mathrm{SO_4}^{2-}$. The balance between carbonate and noncarbonate hardness is important in water softening (hardness removal) and in scale formation. Because $\mathrm{HCO_3}^-$ dissociates at high temperatures, the result of heating hard water is scale formation due to $\mathrm{CaCO_3}$ precipitation:

$$\mathrm{Ca}^{2+} + 2\mathrm{HCO_3}^- \rightleftarrows \mathrm{CaCO_3} + \mathrm{CO_2} + \mathrm{H_2O} \tag{2-24}$$

Scale formation plugs pipes, decreases heat transfer coefficients, and changes the frictional resistance to flow in pipes. Hardness is also of concern to consumers due to the occurrence of scaling on fixtures and water-related appliances. With respect to hardness, waters are typically classified as follows:

Soft	0 to <50 mg/L as $CaCO_3$
Moderately hard	50 to <100 mg/L as $CaCO_3$
Hard	100 to <150 mg/L as $CaCO_3$
Very hard	>150 mg/L as $CaCO_3$

Another range of values that may be encountered in the literature for the same classifications are 0 to <60, 60 to <120, 120 to <180, and >180 as $CaCO_3$.

ALKALINITY

Alkalinity is a measure of the ability of a water to resist changes in pH. Alkalinity in water is due to the presence of weak acid systems that consume hydrogen ions produced by other reactions or produce hydrogen ions when they are needed by other reactions, allowing chemical or biological activities to take place within a water without changing the pH. The primary source of alkalinity is the carbonate system, although phosphates, silicates, borates, carboxylates, and other weak acid systems can also contribute. Alkalinity is determined by titrating with acid, and the results are expressed in concentrations of meq/L or as concentration of calcium carbonate (mg/L as $CaCO_3$). When the individual species are expressed as molar concentrations, alkalinity is calculated as

$$\text{Alkalinity, eq/L} = [HCO_3^-] + 2\left[CO_3^{2-}\right] + [OH^-] - [H^+] \qquad (2\text{-}25)$$

where the coefficient on carbonate (CO_3^{2-}) is necessary because carbonate is divalent (2 eq/mol) and the other species are monovalent (1 eq/mol). When the individual species are expressed in concentrations of meq/L, alkalinity is calculated as

$$\text{Alkalinity, meq/L} = (HCO_3^-) + (CO_3^{2-}) + (OH^-) - (H^+) \qquad (2\text{-}26)$$

In practice, alkalinity is expressed in terms of mass concentration as calcium carbonate. To convert from meq/L to mg/L as $CaCO_3$, it is helpful to remember that

$$\begin{aligned}\text{Millequivalent mass of } CaCO_3 &= \frac{100 \text{ mg/mmol}}{2 \text{ meq/mmol}}\\ &= 50 \text{ mg/meq}\end{aligned}$$

Thus 3 meq/L of alkalinity would be expressed as 150 mg/L as $CaCO_3$:

$$\begin{aligned}\text{Alkalinity as } CaCO_3 &= (3.0 \text{ meq/L})(50 \text{ mg/meg } CaCO_3)\\ &= 150 \text{ mg/L as } CaCO_3\end{aligned}$$

TOTAL DISSOLVED SOLIDS

Total dissolved solids (TDS) is a measure of the total ions in solution, analyzed by filtering out the suspended material, evaporating the filtrate, and weighing the remaining residue. Local TDS concentrations in arid regions or in waters subjected to pollution runoff can be high. For example, Colorado River water, after reaching southern California, has a TDS content in the range of 700 to 800 mg/L. The TDS of seawater is about 35,000 mg/L.

CONDUCTIVITY

A parameter related to TDS is electrical conductivity (EC) or specific conductance. Electrical conductivity is actually a measure [in microsiemens per centimeter (μS/cm) or micromhos per centimeter (μ℧/cm)] of the ionic activity of a solution in terms of its capacity to transmit current. In dilute solutions, the two measures are reasonably comparable; that is, TDS = 0.5 × EC. However, as the solution becomes more concentrated (TDS > 1000 mg/L, EC > 2000 μS/cm), the proximity of the solution ions to each other depresses their activity and consequently their ability to transmit current, although the physical amount of dissolved solids is not affected. At high TDS values, the ratio of TDS to EC increases and the relationship tends toward TDS = 0.9 (slope of line) × EC. Thus, the slope for any one sample can fall between 0.5 and 0.9, but for several samples having the same TDS the slope will also vary; therefore, each water sample should be characterized separately.

2-5 Organic Chemical Constituents

A variety of organic compounds that can affect water quality are found in drinking water supplies. Several types of organic chemicals cause disagreeable tastes and odors in drinking water, and other types are known to be toxic. Many organic contaminants are known to be carcinogenic or are classified as cancer-suspect agents. Organic compounds in water are derived from natural and anthropogenic sources. Anthropogenic contaminants are generally present at extremely low concentrations and might not pose an immediate health hazard. However, a number of long-term research studies have been focused on the question ‘‘at what level do trace organic contaminants exert an impact on human health?’’ Based on the results to date it seems likely that the answers to this question will continue to be pursued.

Topics discussed in this section are (1) a brief review of organic compounds and their properties, (2) the potential sources of organic compounds and their introduction to drinking water and drinking water supplies, (3) the characteristics of the natural organic matter found in water, (4) organic compounds originating from human activity, (5) organic compounds formed during disinfection, (6) organic compounds added during treatment, (7) surrogate measures for organic water quality indicators, and (8) the analysis of trace organics.

Definition and Classification

The term *organics* refers to the general class of chemicals composed of carbon (C) and one or more of the following elements: hydrogen (H), nitrogen (N), and oxygen (O). The term organic dates to early studies of chemistry when substances were categorized as inorganic when they were obtained from mineral sources and as organic when they were derived from living organisms. Today, many organic compounds are derived from sources other than biological activity. A wide variety of materials are synthesized by the chemicals industry. The molecular structure of these synthesized compounds may also contain atoms of sulfur (S), phosphorus (P), and/or one or more of the halogens, that is, fluorine (F), chlorine (Cl), bromine (Br), and iodine (I), as well as a variety of other elements. Many naturally occurring compounds may also contain these atoms as well, but they are found to a lesser degree. There are many chemical species that are commonly considered to be inorganic in spite of having C, H, O, and N within their structure. Examples of such compounds include carbon monoxide (CO), carbon dioxide (CO_2), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and cyanide (CN^-). The principal structural feature that distinguishes organic compounds from inorganic substances is the existence of strong carbon–carbon bonds.

CLASSIFICATION ACCORDING TO SIZE AND MOLECULAR WEIGHT

From an environmental standpoint, it is especially convenient to classify organic substances into groups according to their chemical or physical properties. Knowledge of these properties facilitates the selection of appropriate methods for the analysis and treatment of these materials in water. One important property of organic compounds is molecular weight. The molecular weight of organic compounds ranges from 16 g/mol for methane (CH_4) to values approaching one million (10^6) grams per mole for polymeric materials. The dimension of organic molecules varies from less than 1 nm for simple compounds such as chloroform ($CHCl_3$) to approximately 0.1 μm for complex organic polymers. The relative size of some organic molecules as compared to microorganisms and other material commonly found in aquatic systems was illustrated previously on Fig. 2-5.

OTHER METHODS OF CLASSIFICATION

The polarity of an organic substance can also be used to define the degree to which one segment of a molecule is either positively or negatively charged with respect to another part of the molecular structure (McMurry and Fay, 2003). A frequently used measure of the polarity of a compound is given by the dipole moment. The dipole moment of organic substances can vary from a value of 0 D (debye) for molecules such as carbon tetrachloride (CCl_4), which have a highly symmetric spatial distribution of electron density about their bonding structures, to approximately 1.87 D for chloromethane (CH_3Cl) (McMurry and Fay, 2003). The volatility of an organic substance is generally reflected by its boiling point or vapor pressure. At ambient atmospheric pressure (1 atm, 760 mm Hg), the boiling points of organic contaminants may vary from as low as −13.4°C for highly volatile compounds such as vinyl chloride to temperatures in excess of 400°C for nonvolatile polycyclic aromatic hydrocarbons.

Sources of Organic Compounds in Drinking Water

There are four major sources from which organics may be introduced to drinking water:

1. Natural organic material
2. Compounds originating from human activities
3. Compounds formed through chemical reactions that occur during disinfection
4. Compounds added or formed during the treatment and transmission of water

Each of these sources is considered in the following discussion.

Natural Organic Matter

Natural organic matter (NOM) is the term used to describe the complex matrix of organic chemicals originating from natural sources that are present in all water bodies. Natural organic matter originates from a water body due to biological activity, including secretions from the metabolic activity of algae, protozoa, microorganisms, and higher life-forms; decay of organic matter by bacteria; and excretions from fish or other aquatic organisms. The bodies and cellular material of aquatic plants and animals contribute to NOM. Natural organic matter can also be washed into a watercourse from land, originating from many of the same biological activities but undergoing different reactions due to the presence of soil and different organisms.

Historically, the significance of NOM in drinking water was related to its impact on aesthetic quality, as NOM imparts a yellowish tinge to water that many people find unpalatable. More recently, concern about NOM has focused on its ability to react with chlorine and form disinfection by-products, which are often carcinogenic. The presence of NOM affects many water quality parameters and processes. A summary of some important impacts of NOM is provided in Table 2-6.

In drinking water supplies, NOM is measured most commonly using total organic carbon (TOC) as a surrogate measure. Typical TOC concentrations for a variety of waters are reported on Fig. 2-12. The TOC concentrations of ground and surface waters often fall in the ranges of 0.1 to 2 and 1 to 20 mg/L, respectively. By contrast, the TOC levels of highly colored waters found in swamps can be in the range of 100 to 200 mg/L.

Table 2-6
Effect of NOM on water quality parameters and processes

Parameter	Effect of NOM
	Water Quality Parameters
Color	NOM can impart an unpalatable yellowish tinge to water at high concentrations.
Disinfection by-products	NOM reacts with chemical disinfectants, forming disinfection by-products. Many of these by-products have been demonstrated to be carcinogenic or have other adverse public health effects.
Metals/synthetic organics	NOM can complex with metals and hydrophobic organic chemicals (such as pesticides), making them more soluble. Once these chemicals are soluble, they can be transported more easily in the aquatic environment and are more difficult to remove during treatment.
	Water Treatment Processes
Disinfection	NOM reacts with and consumes disinfectants, so that the required dose to achieve effective disinfection is much higher than it would be in the absence of NOM.
Coagulation	NOM reacts with and consumes coagulants, so that the required dose to achieve effective turbidity removal is much higher than it would be in the absence of NOM.
Adsorption	NOM adsorbs to activated carbon, rapidly depleting the adsorption capacity of the carbon. Adsorption isotherms are much harder to predict in the presence of NOM.
Membranes	NOM adsorbs to membranes, clogging membrane pores and fouling surfaces, leading to a rapid decline in flux through the membrane.
Distribution	NOM can be biodegradable, leading to corrosion and slime growth in distribution systems (especially when oxidants are used during treatment).

CHEMISTRY OF NOM

Biological matter is composed primarily of four basic classes of organic compounds: carbohydrates, lipids, amino acids, and nucleic acids. Natural organic matter is composed of these chemicals and the products of biotic and abiotic chemical reactions between NOM molecules or between NOM and inorganic constituents of water. The wide array of biological activity in the environment leads to the production of thousands of different chemicals, so NOM is a complex mixture of different compounds with varying chemical properties, which may vary significantly from one water body to another as a result of local soil, climate, and hydrologic conditions. This complexity makes the characterization of the basic chemistry of NOM (such as functional groups or physical and chemical properties) difficult

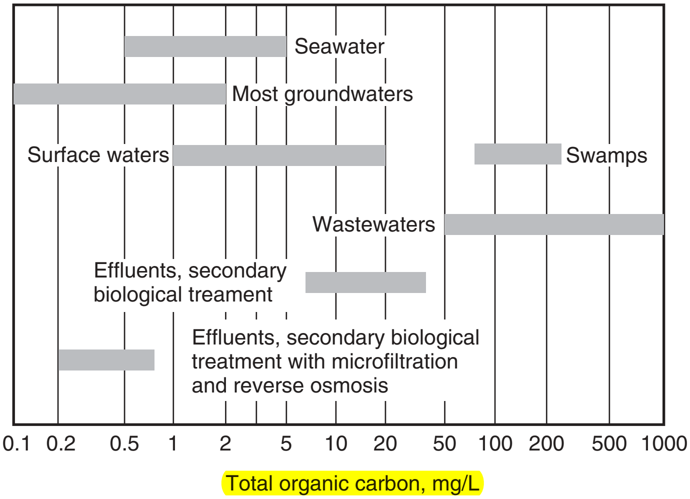


Figure 2-12
Ranges of TOC reported in a variety of waters. (Adapted from Rainwater and White, 1958.)

and causes NOM from different water bodies to have different effects when subjected to water treatment processes.

Natural organic matter is not volatile. It is fairly soluble and can be concentrated to greater than 1000 mg/L without precipitating. Most NOM molecules are negatively charged and many have multiple anionic functional groups, making them polyelectrolytic. The NOM molecules have a distribution of molecular weights, with about 90 percent of NOM between about 500 and 3000 Da. The elemental composition of NOM is about 45 to 60 percent carbon, 4 to 5 percent hydrogen, 35 to 40 percent oxygen, and 1 percent nitrogen (Thurman, 1985).

Based on their solubility in acid and alkali, aquatic humates are usually divided into two principal components: humic acid (HA), which is soluble in dilute alkaline solutions but is precipitated upon acidification, and fulvic acid (FA), which remains in solution at low pH. The structural features of HA and FA are similar, but the two fractions differ considerably in molecular weight and functional group composition. The molecular weight of fulvic acid varies from 200 to 1000 g/mol, whereas the molecular weight of HA ranges up to 200,000 g/mol. The FA fraction also possesses a higher content of oxygen-containing constituents per unit weight than humic acid. However, due to the arbitrary nature of this classification scheme, the term humic material is frequently used in reference to an aggregate of FA and HA.

MEASUREMENT AND CLASSIFICATION OF NOM

The complexity of NOM makes it impractical to routinely measure individual compounds. Instead, NOM is typically quantified using bulk parameters. The most common parameters in water treatment are TOC, dissolved organic carbon (DOC), biodegradable dissolved organic carbon (BDOC), assimilable organic carbon (AOC), UV_{254} absorbance, and specific UV absorbance (SUVA). SUVA is calculated as

$$\text{SUVA} = \frac{\text{UV}_{254}}{\text{DOC}} \times 100 \tag{2-27}$$

where SUVA = specific UV absorbance, L/mg·m
UV_{254} = UV absorbance at 254 nm, cm^{-1}
DOC = dissolved organic carbon concentration, mg/L

Methods that have been used to quantify and characterize NOM are described in Table 2-7. For more detailed research, NOM can be characterized by separation into discrete fractions based on properties such as hydrophobicity, polarity, or molecular weight (Croue et al., 2000; Owen et al., 1993, 1995).

Organic Compounds from Human Activities

Organic chemicals from industry, agriculture, and municipal effluents are routinely found in water supply sources and in trace amounts in many water supplies. Surface waters are especially vulnerable to these types of contaminants, but groundwater systems can also become contaminated. Contaminants that originate from a specific site are defined as *point source pollutants*, whereas substances that enter the aquatic environment over a broad area are referred to as *non–point source pollutants*. Groundwaters are most commonly subjected to point source contamination. By contrast, large-scale surface water basins may contain organic chemicals such as trichloroethene that cannot be traced to a single site.

USE OF SYNTHETIC ORGANIC COMPOUNDS

Industries that utilize large quantities of chemicals in manufacturing processes are major sources of organic pollutants. The vast majority of organic compounds used in industry are synthesized. Synthetic organic compounds (SOCs) comprise an extremely diverse group of compounds. A general classification according to polarity and volatility is illustrated on Fig. 2-13a. Typical compounds in each of the categories identified on Fig. 2-13a are presented on Fig. 2-13b. While generally found at very low concentrations in water, many SOCs are of significant health concern. Among the sources of these compounds are the industrial and commercial facilities located in close proximity to major bodies of surface water. For example, the Mississippi and Ohio Rivers provide a plentiful supply of process and cooling water for a large fraction of the industries in the United States. Consequently, effluents from these activities can introduce a broad range of chemical contaminants to these river systems, depending on the nature of the materials being processed at each facility.

Table 2-7
Methods for quantifying and characterizing NOM

Parameter	**Description**
	Aggregate Properties
Total organic carbon (TOC)	NOM is oxidized completely to CO_2, which is stripped from the sample and measured in the gas phase. TOC is not equal to the NOM concentration but is a surrogate that gives an indication of the NOM concentration as long as the elemental composition does not change. The NOM concentration is typically 2 times the TOC concentration (based on the elemental composition).
Dissolved organic carbon (DOC)	The sample is analyzed identically to TOC after filtration through a 0.45-μm filter. The DOC concentration is typically 80–90% of the TOC concentration.
Biodegradable dissolved organic carbon (BDOC)	Dissolved organic carbon that can be assimilated biologically. Final value depends on the specific test procedure employed. Important in assessing the potential for regrowth of microorganisms after disinfection in the distribution system.
Assimilable organic carbon (AOC)	The fraction of the BDOC that can be readily assimilated biologically as opposed to the total, which can be biodegraded over a longer period of time. In general, the methods used to determine the BDOC and AOC will yield different results.
UV_{254} absorbance	The sample is filtered and the absorbance of UV light at a wavelength λ of 254 nm is measured with a spectrophotometer. Like TOC and DOC, UV_{254} absorbance is a surrogate for the NOM concentration. Specific molecular structures (chromophores) within NOM molecules absorb UV light, so the relationship between UV_{254} absorbance and NOM concentration can vary between water bodies or seasonally because of differences in NOM composition. In addition, UV_{254} absorbance may not be representative of NOM removal in a treatment process if the process removes molecules with chromophores differently than molecules without chromophores.
Specific UV absorbance (SUVA)	SUVA is calculated as the ratio of UV_{254} absorbance to the DOC (TOC has also been used). SUVA has been correlated to the hydrophobic fraction of NOM and has been used as a guide for the treatability of NOM by some processes. For instance, water with a low SUVA value may not be amenable to enhanced coagulation.
	Specific Compound Classes and Individual Constituents
Molecular weight distribution	The molecular weight distribution of NOM can be determined by serial ultrafiltration or chromatographic methods. The most advanced method is high-performance size exclusion chromatography.
Hydrophobic and ionic fractions	NOM is separated into hydrophobic, hydrophilic, cationic, neutral, and anionic fractions by retention or passage through resin columns. The effect of these specific properties is then evaluated with respect to treatment processes.
Fluorescence	Fluorescence is strongly correlated with the molecular weight of NOM.

(*continues*)

Table 2-7 *(Continued)*

Parameter	Description
Relative polarity	Compounds can be separated based on polarity by reverse-phase high-pressure liquid chromatography (RP-HPLC) or other chromatographic methods and compared to the polarity of a standard compound. Polarity affects the reactivity and fate of NOM in many environmental processes.
Compound class identification	Assays can be performed to measure the total protein or carbohydrate concentration in samples of water containing NOM.
Spectrometry	Spectrometric methods, such as nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR) spectrometry, solid-state cross-polarization magic-angle spinning (CPMAS), ^{13}C nuclear magnetic resonance spectrometry, electrospray ionization/mass spectrometry, and pyrolysis gas chromatography mass spectrometry (pyr-GC-MS) can be used to identify the primary functional groups or compound classes present in NOM.

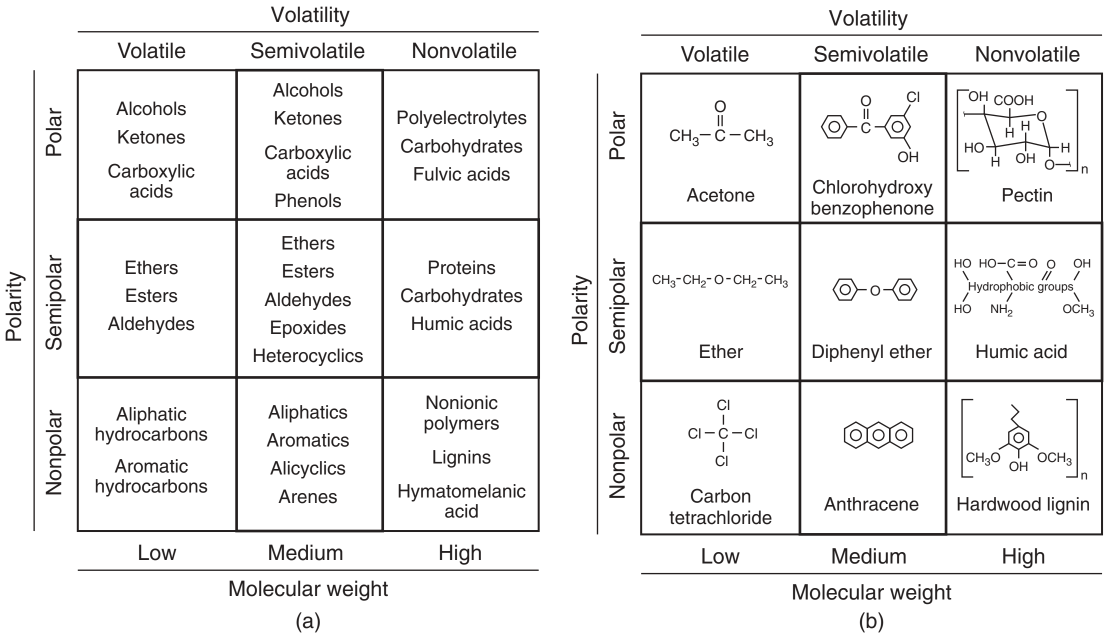


Figure 2-13
Organic compounds found in water: (a) classification based on molecular weight, polarity, and volatility and (b) representative examples of compounds in each classification. (Adapted from Trussell and Umphres, 1978.)

AGRICULTURAL PESTICIDES AND HERBICIDES

The quantity of agricultural pesticides used annually in the United States is extremely large. In California alone, over 4000 tonnes of chemicals is applied each year. The vast majority of these substances are organic chemicals. In general, pesticide treatments are distributed evenly over a large acreage. Modern agricultural practice has been directed toward the use of nonrefractory pesticides, such as organophosphates, that degrade rapidly in the environment following application. Use of nonrefractory pesticides has helped to minimize the risk of water contamination. Nevertheless, the use of such large quantities of agricultural chemicals requires that programs be developed to monitor water supplies subject to agricultural runoff.

MUNICIPAL WASTEWATER DISCHARGES

Municipal wastewater treatment plants are also a major point source of organic contamination. Even with effective secondary treatment, an ever-increasing number of organic compounds is being found in the effluent from treatment plants. The U.S. Geological Survey (USGS) has identified a number of compounds termed *emerging organic compounds* that are now being found in stream waters (USGS, 2000). Many of the emerging compounds are derived from veterinary and human antibiotics, human prescription and nonprescription drugs, and industrial and household wastewater products.

Organic Compounds Formed During Water Disinfection

The processing of water for commercial applications and human consumption introduces a variety of organic compounds. More specifically, a variety of organic compounds can be formed through chemical transformations of NOM during water disinfection. For example, chlorine can efficiently convert humic substances (NOM) to trihalomethanes (THMs) and other organohalogen oxidation products under the reaction conditions encountered in water treatment systems. The formation and treatment of compounds formed during disinfection are considered in detail in Chaps. 13 and 19.

Surrogate Measures for Aggregate Organic Water Quality Indicators

A variety of measures have been developed or adapted for the quantification of the array of synthetic and naturally occurring aquatic organic material. Two types of measures are in common use: (1) those measures that are used to quantify organic matter that is composed of an aggregate (nonspecific) of constituents with similar characteristics and (2) those measures that are used to quantify individual organic constituents (specific) from within the total organic compounds present. Aggregate measures are intended to quantify part or all of the organic content of a water. They include UV absorbance, TOC, total organic halogen (TOX), and trihalomethane formation potential (THMFP). The use of some of these measures for NOM was reported previously in Table 2-7.

ULTRAVIOLET ABSORBANCE

Organic substances absorb UV light, which is light that is beyond the visible spectrum at the violet end, generally defined as having a wavelength between 100 and 400 nm. Specific organic materials show definitive UV absorbance bands reflecting their particular unsaturation pattern and/or aromatic components. Such configurations desorb the short-wavelength/high-energy excitation of UV radiation, corresponding to excitation of electrons; increasingly shorter wavelengths are required to excite more stable molecules. Thus, simple aliphatic molecules will not tend to absorb UV light, whereas the complex multiaromatic, multiconjugated humic substances would be expected to absorb UV light very strongly. Ultraviolet absorbance at a wavelength λ of 254 nm is used as a surrogate measurement for the concentration of NOM, as described in Table 2-7. In some cases, UV absorbance at a wavelength λ of 285 nm has also been measured. In reporting the absorbance of a solution, the pH must be noted. The SUVA (see Table 2-7) is another measure that has been used to quantify the NOM in water.

TOTAL ORGANIC CARBON AND DISSOLVED ORGANIC CARBON

The TOC analysis is used to quantify the total amount of organic carbon contained in a sample by converting the dissolved organic compounds to a single chemical form while excluding inorganic carbon compounds from the analysis (see Fig. 2-14). Total organic carbon is a useful measurement because it provides an assessment of organic contamination and may be correlated to the amount of disinfection by-products (DBPs) that are produced during chlorination on a case-by-case basis. Dissolved organic carbon is the fraction of the TOC that passes through a 0.45-μm filter, and

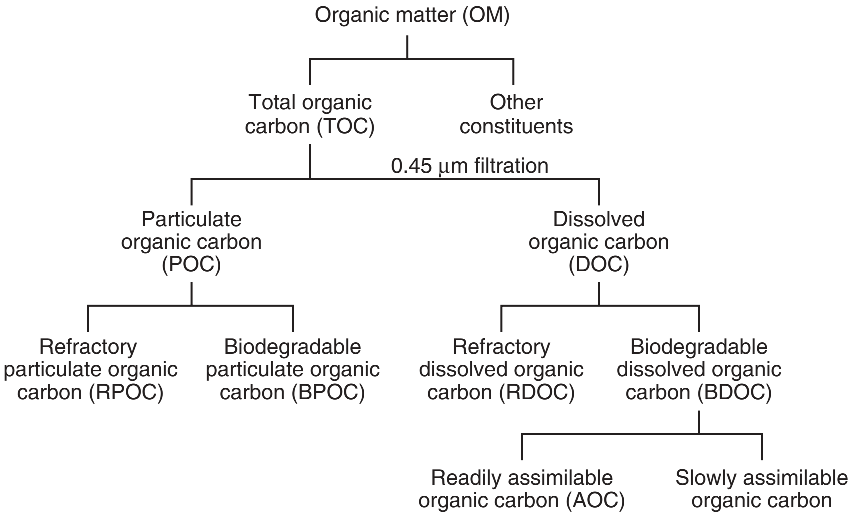


Figure 2-14
Classification of organic matter based on TOC method of analysis for total, particulate, and dissolved organic carbon. When different analytical methods of analysis are used, the term DOM is used in place of DOC. Refer to Table 2-7 for descriptions of these quantification methods.

the TOC of the material retained on the filter is defined as particulate TOC. As noted previously, the definition of DOC is operational, as a considerable amount of colloidal nondissolved material can pass through a 0.45-μm filter.

TOTAL ORGANIC HALOGEN

Total organic halogen refers to the total mass concentration of organically bound halogen atoms (X = Cl, Br, or I) present in water. From the standpoint of water quality, TOX is especially significant because it accounts not only for volatile halogen-containing compounds such as the THMs, trichloroethene, and tetrachloroethene but also includes the contribution of halogenated organic substances of high molecular weight that are also suspected health hazards. One commonly used method for TOX analysis involves the adsorption of organohalide solutes onto activated carbon (Dressman and Stevens, 1983). The particles of carbon are then washed to displace inorganic halides (predominantly Cl^-). After treatment with nitrate, the carbon adsorbent is subjected to pyrohydrolysis, which converts the organically bound halogen to hydrogen halides (HX) and hypohalous acids (HOX). The aqueous effluent from the pyrohydrolysis step (pyrohydrozylate) can be analyzed for halide ion using a specific ion probe or by direct injection of the sample into a microcoulometric titration cell.

TRIHALOMETHANE FORMATION POTENTIAL

The THMFP is employed to assess the maximum tendency of the organic compounds in a given water supply to form THMs upon disinfection. Water supply sources with low THMFP values are considered to be superior when it becomes necessary to choose between alternative sources of water. The subject of THMFP is considered further in Chap. 19.

2-6 Taste and Odor

The human senses of taste and odor (smell) are stimulated by a myriad of chemical compounds, both inorganic and organic. Certain ones of these compounds are found occasionally in domestic water supplies and, more than any other factor, influence the palatability of the product. Many water treatment plants include facilities for the feeding of taste and odor control chemicals, adsorbents, or both. Additionally, some agencies employ preventative and control measures in raw-water reservoirs, lakes, and rivers. It is impossible to estimate accurately the annual expenditure, nationally, on taste and odor control measures. Recommended limits on odors are set by the U.S. EPA in the National Secondary Drinking Water Regulations. The purpose of this section is to (1) identify the sources of tastes and odors in water supplies and (2) outline means to control their development or to remove them once they have appeared.

Sources of Tastes and Odors in Water Supplies

Tastes and odors in water supplies can generally be attributed to two different causative elements: natural forces within the environment and the actions of human beings upon the aquatic environment. These sources of tastes and odors are not unrelated. For example, odors due to biological degradation of algae and their waste products may sometimes be traced to an upstream nutrient input of human origin. Sources directly responsible for taste and odor production in groundwater and surface water supplies are considered in the following discussions. The examination of these sources is essential when attempting to identify particular tastes or odors.

TASTES AND ODORS IN SURFACE WATERS

Taste and odor problems are proportionally more common in surface waters than in groundwaters largely because of the presence of algae. In addition, direct organic inputs such as autumnal leaf fall, stormwater runoff, and agricultural drainage provide ample nutrients for microorganisms that can often generate taste- and odor-producing compounds. Decaying vegetation from leaf fall and other sources may result in brown-colored, sweet-smelling water. These effects are due to suspended and dissolved glucosides, such as tannin, that originate in vegetative matter. Other suspended particulates, such as colloidal silts and clays, may render a water unpalatable if not removed in treatment.

TASTES AND ODORS IN GROUNDWATER

Most tastes and odors in groundwater supplies are natural in origin. For example, tastes and odors are caused by bacterial actions within the groundwater aquifers or the dissolution of salts and minerals as groundwater percolates and flows through geologic deposits. Intrusion of salt or mineral-bearing waters (such as seawater) may also result in taste or odor problems. Recently, tastes and odors in some groundwaters have been attributed to human sources, such as landfill leachate.

One of the most common odor problems in groundwater supplies is hydrogen sulfide (H_2S). Hydrogen sulfide is frequently characterized as a rotten-egg odor, but at low concentrations it may also impart a swampy, musty odor. The odor threshold concentration of H_2S in water is less than 100 ng/L (0.0001 mg/L), and odors from waters containing 0.1 to 0.5 mg/L or greater are offensive (Lochrane, 1979; Pomeroy and Cruze, 1969). Sulfides in groundwater result from anaerobic bacterial action on organic sulfur, elemental sulfur, sulfates, and sulfites.

Reduced iron and manganese may also pose taste problems in groundwater. Although tastes due to dissolved iron or manganese are not particularly noxious, they can render a water unpalatable and cause problems in pipelines, water services, and laundry facilities.

High salt content, as characterized by TDS or conductivity, can result in taste problems but does not usually result in objectionable odors. In general, consumers prefer waters with lower TDS content. The current widespread use of bottled mineral-bearing waters, however, may indicate that other psychophysical effects may affect taste preference.

Human-induced tastes and odors in groundwater occur as a result of chemical dumping, landfill disposal, mining and agricultural activities, or industrial waste disposal. A variety of synthetic organic chemicals have been identified in groundwater supplies. Examples include trichloroethylene (TCE), which has been found at objectionable concentrations in wells throughout the country.

Prevention and Control of Tastes and Odors at the Source

Taste and odor prevention and control may be accomplished at the source, in the treatment plant, and to a certain extent in the distribution system. Ideally, the most satisfactory site for control in surface supplies is at the source. Source control generally involves controlling the growth of algae and related organisms. For groundwater supplies, source control must be accomplished through watershed management—a difficult task. For surface reservoirs, algaecides, destratification/aeration, and watershed management are used as control methods. Purveyors using continuous draft intakes with negligible raw-water storage or detention most often address taste and odor problems in-plant rather than at the source. Taste and odor can be treated by oxidation (Chap. 8) or adsorption (Chap. 15).

2-7 Gases in Water

Gases commonly found in water, as reported in Table 2-2, include nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), hydrogen sulfide (H_2S), ammonia (NH_3), and methane (CH_4). The first three are common gases of the atmosphere and are found in all waters exposed to the atmosphere. The latter three are derived from the bacterial decomposition of the organic matter present in water. Although not found in untreated water, other gases with which the environmental engineer must be familiar include chlorine (Cl_2) and ozone (O_3), which are used for oxidation, disinfection, and odor control.

Gases in water can form bubbles, which may interfere with sedimentation processes, as the bubbles carry particles up through the water column and filtration, as gases accumulate and disrupt flow through the filter. Gas bubbles in water can also interfere with water quality measurements such as dissolved oxygen, ions measured with electrodes, and turbidity. The quantity of a gas present in solution is governed by (1) solubility of the gas, (2) partial pressure of the gas in the atmosphere, (3) temperature, and (4) concentration of the impurities in the water (e.g., salinity, suspended solids). A discussion of the ideal gas law is presented below. The solubility of gases in water and Henry's law as applied to the gases of interest may be found in Chap. 14.

Ideal Gas Law

The ideal gas law, derived from a consideration of Boyle's law (volume of a gas is inversely proportional to pressure at constant temperature) and Charles' law (volume of a gas is directly proportional to temperature at constant pressure) is

$$PV = nRT \tag{2-28}$$

where P = absolute pressure, atm
V = volume occupied by gas, L, m^3
n = amount of gas, mol
R = universal gas law constant, 0.082056 atm/(mol/L) · K
T = temperature, K (273.15 + °C)

Using the universal gas law, it can be shown that the volume of gas occupied by 1 mole of a gas at standard temperature (0°C, 32°F) and pressure (1.0 atm) is equal to 22.414 L:

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{(1\text{ mole})[0.082056\text{ atm}/(\text{mol}/\text{L})\cdot\text{K}][(273+0)\text{K}]}{1\text{ atm}} = 22.414\text{ L} \end{aligned}$$

The following relationship, based on the ideal gas law, is used to convert between gas concentrations expressed in ppm_v and $\mu\text{g/m}^3$:

$$\mu\text{g/m}^3 = \frac{(\text{concentration, ppm}_\text{v})(\text{MW, g/mol of gas})(10^6\ \mu\text{g/g})}{22.414 \times 10^{-3}\ \text{m}^3/\text{mol of gas}} \tag{2-29}$$

The application of the Eq. 2-29 is illustrated in the following example.

Naturally Occurring Gases

Gases that are commonly found in untreated water include nitrogen, oxygen, carbon dioxide, ammonia, hydrogen sulfide, and methane. Ammonia, hydrogen sulfide, and methane are typically formed during the anaerobic decomposition of organic matter (see Table 2-2). Dissolved nitrogen, oxygen, and carbon dioxide are generally present in natural waters from equilibration with the atmosphere; however, these gases also have biological origins, from processes such as atmospheric nitrogen fixation, photosynthesis, and respiration, respectively.

Example 2-4 Conversion of gas concentration units

The gas released from a natural seep was found to contain 20 ppm_v (by volume) of hydrogen sulfide (H_2S). Determine the concentration in mg/m^3 and in mg/L at standard conditions (0°C, 101.325 kPa).

Solution

1. Compute the concentration in mg/L using Eq. 2-29.
   The molecular weight of $H_2S = 34.08\ \text{g/mol}\ [2(1.01) + 32.06]$.

$$20\ \text{ppm}_v = \left(\frac{20\ \text{m}^3}{10^6\ \text{m}^3}\right)\left(\frac{34.08\ \text{g/mol H}_2\text{S}}{22.4 \times 10^{-3}\ \text{m}^3/\text{mol of H}_2\text{S}}\right)\left(\frac{10^6\ \mu\text{g}}{\text{g}}\right)$$

$$= 30{,}429\ \mu\text{g/m}^3$$

2. The concentration in mg/L is

$$30{,}429\ \mu\text{g/m}^3 = \left(\frac{30{,}429\ \mu\text{g}}{\text{m}^3}\right)\left(\frac{\text{mg}}{10^3\ \mu\text{g}}\right)\left(\frac{\text{m}^3}{10^3\ \text{L}}\right)$$

$$= 0.0304\ \text{mg/L}$$

Comment

If gas measurements, expressed in mg/L, are made at other than standard conditions, the concentration must be corrected to standard conditions, using the ideal gas law, before converting to ppm.

2-8 Radionuclides in Water

Radionuclides are unstable atoms that are transformed through the process of radioactive decay. Radioactive decay results in the release of radioactive particles (radiation). Radionuclides are of interest because of the health effects resulting from exposure to radioactive particles and their occurrence in natural waters. A brief review of the fundamental properties of atoms, types of radiation, and units of expression is presented in this section.

Fundamental Properties of Atoms

An atom is composed of three basic subatomic constituents: protons (positive charge, located in the nucleus), neutrons (no charge, located in the nucleus), and electrons (negative charge, located in the outer shell or orbitals surrounding the nucleus). An element is defined by its atomic number, which is equal to the number of protons in its nucleus. Elements with the same number of protons and variable number of neutrons are known as isotopes. Radium, for example, has six isotopes, ^{223}Ra, ^{224}Ra, ^{225}Ra, ^{226}Ra, ^{227}Ra, and ^{228}Ra, all of which have an atomic number of 88 (88 protons) and atomic mass of 223 to 228 (88 protons, 135 to 141 neutrons). The isotope that decays is known as the parent, and the resulting element is known as the progeny or daughter. Radioactive decay is the spontaneous disintegration of an element, resulting in greater atomic stability through change of electron orbits or release of radioactive particles or radiation.

Types of Radiation

The primary forms of radioactive decay are (1) alpha (particle) radiation, (2) beta (particle) radiation, and (3) gamma (ray) radiation. The release of alpha and beta particles transforms an isotope into a different element, while the release of gamma radiation reduces the energy of the element. Alpha, beta, and gamma radiations are known as ionizing radiation because of their ability to free electrons from their orbit in adjacent atoms.

Alpha particles are large, positively charged helium nuclei (two protons and two neutrons) released by certain isotopes during radioactive decay. Alpha particles are relatively slow and massive and are the least penetrating (may be stopped by the skin); however, when ingested, these particles can be very damaging to internal tissue and may cause cell mutation and possibly cancer. When an element emits an alpha particle, the element's atomic mass is reduced by 4 and its atomic number is reduced by 2. Beta particles are high-energy negatively charged particles released by certain elements during radioactive decay. Beta particles have smaller mass than alpha particles, which allows greater speed and penetration but creates less damage. The release of beta particles is characterized by the transformation of a neutron to a proton in the nucleus of an element and results in an increase of the atomic number. Gamma-ray emission, consisting of high-energy short-wave electromagnetic radiation (similar to x-rays) emitted from a nucleus, has tremendous penetrating power but has limited effect at low levels.

Units of Expression

The units used to quantify radionuclides in water include expressions for activity, exposure/dose, and rate of decay. Activity refers to the amount of radiation being emitted from a radioactive agent. Exposure is a function of the activity, type of radiation, and pathway of human contact, while the dose is used to express the bodily uptake of radioactivity from a given exposure scenario. The life span of a radionuclide is estimated by its rate of decay, or half-life. Activity, adsorbed dose, and dose equivalent are described below.

ACTIVITY

Radionuclides have unique properties that require units other than milligrams or moles per liter. Because the emission of radioactivity is not dependent on the mass of the element, units that quantify the activity of the element must be used. In the International System (SI) of units, the becquerel (Bq), equivalent to one disintegration or nuclear transformation (radioactive emission) per second, is the unit of radioactivity. In U.S. customary units, radiation is expressed in curies (Ci), 1 Ci is equivalent to 3.7×10^{10} disintegrations per second (37×10^9 Bq).

ADSORBED DOSE AND DOSE EQUIVALENT

Exposure to radionuclides through ingestion results in damage to internal organs as the element disintegrates. The amount of radiation that is imparted to the tissue is dependent on the number of particles emitted and is known as the absorbed dose. The SI unit for absorbed dose is the gray (Gy), where one gray equals one joule of radiation energy per kilogram of absorbing material. The corresponding U.S. customary unit is the radiation adsorbed dose (rad); 1 Gy is equal to 100 rad. Exposure to alpha, beta, and gamma radiation has different biological effects, so an exposure term known as the ‘‘dose equivalent’’ is used to quantify radiation that produces the same biological effect regardless of the type of radiation involved. The dose equivalent is determined by multiplying the adsorbed dose (in Gy or rad) by a quality factor. The quality factor is 1 for x-rays, gamma rays, and beta particles, and 20 for alpha particles. The units for dose equivalent is the sievert (Sv) in SI units and the Röntgen equivalent man (rem) in U.S. customary units ; 1 Sv is equivalent to 100 rem.

Problems and Discussion Topics

2-1 Given the following test results, determine the mole fraction of calcium (Ca^{2+}).

Cation	Concentration, mg/L	Anion	Concentration, mg/L
Ca^{2+}	40.0	HCO_3^-	91.5
Mg^{2+}	12.2	SO_4^{2-}	72
Na^+	15.1	Cl^-	22.9
K^+	5.1	NO_3^-	5.0

2-2 Determine the mole fraction of magnesium (Mg^{2+}) for the water given in Problem 2-1.

2-3 Determine the mole fraction of sulfate (SO_4^{2-}) for the water given in Problem 2-1.

2-4 Commercial-grade sulfuric acid is about 95 percent H_2SO_4 by mass. If the specific gravity is 1.85, determine the molarity, mole fraction, and normality of the sulfuric acid.

2-5 If the UV intensity measured at the surface of a water sample is 180 mW/cm^2, estimate the average intensity in a Petri dish with an average depth of 15 mm (used to study the inactivation of microorganisms after exposure to UV light, as discussed in Chap. 13). Assume the absorptivity of the water, $k_A(\lambda)$ at $\lambda = 254$ nm, is 0.10 cm^{-1} and that the following form of the Beer–Lambert law applies:

$$\ln\left(\frac{I}{I_0}\right) = -2.303 k_A(\lambda) x$$

2-6 If the average UV intensity in a Petri dish containing water at a depth of 10 mm is 120 mW/cm^2, what is the UV intensity at the surface of the water sample? Assume the absorptivity of the water, $k_A(\lambda)$ at $\lambda = 254$ nm, is 0.125 cm^{-1} and that the equation given in Problem 2-5 applies.

2-7 If the transmittance is 92 percent and a photo cell with a 12-mm path length was used, what is the absorptivity?

2-8 Given the following data obtained on two water supply sources, determine the constants in Eq. 2-16 (power law density and slope coefficients) and estimate the number of particles in the size range between 2.1 and 5. Also, comment on the nature of the particle size distributions.

	Particle Count	
Bin Size, μm	**Water A**	**Water B**
5.1–10	2500	110
10.1–15	850	80
15.1–20	500	55
20.1–30	250	36
30.1–40	80	25
40.1–50	60	20
50.1–75	28	15
75.1–100	10	10

2-9 The following particle size data were obtained for the influent and effluent from a granular medium filter. Determine the constants in Eq. 2-16 (power law density and slope coefficients) and assess the effect of the filter in removing particles.

	Particle Count	
Bin Size, μm	**Influent**	**Effluent**
2.51–5	20000	101
5.1–10	8000	32
10.1–20	2000	6
20.1–40	800	3.2
40.1–80	400	1.2
80.1–160	85	0.34
160.1–320	40	0.12

2-10 Determine the alkalinity and hardness in milligrams per liter as $CaCO_3$ for the water sample in Problem 2-1.

2-11 Given the following incomplete water analysis, determine the unknown values if the alkalinity and noncarbonate hardness are 50 and 150 mg/L as $CaCO_3$, respectively:

Ion	Concentration, mg/L
Ca^{2+}	42.0
Mg^{2+}	?
Na^{+}	?
K^{+}	29.5
HCO_3^{-}	?
SO_4^{2-}	96.0
Cl^{-}	35.5
NO_3^{-}	4.0

2-12 Given the following incomplete water analysis measured at 25°C, determine the unknown values if the alkalinity and noncarbonate hardness are 40 and 180 mg/L as $CaCO_3$:

Ion	Concentration, mg/L
Ca^{2+}	55.0
Mg^{2+}	?
Na^{+}	23.0
K^{+}	?
HCO_3^{-}	?
SO_4^{2-}	48.0
Cl^{-}	?
CO_2	4.0

2-13 Review the current literature and cite three articles in which the SUVA (specific UV absorbance) measurements were made. Prepare a summary table of the reported values. Can any conclusions be drawn from the data in the summary table you have prepared?

2-14 Review the current literature and prepare a brief synopsis of two articles in which the DOM (dissolved organic matter) was measured. What if any conclusions can be drawn from these articles about the utility of DOM measurements.

2-15 Determine the concentration in $\mu g/m^3$ of 10 ppm_v (by volume) of trichloroethylene (TCE) (C_2HCl_3) at standard conditions (0°C and 1 atm).

2-16 If the concentration of TCE at standard conditions (0°C and 1 atm) is 15 $\mu g/m^3$, what is the corresponding concentration in ppm_v (by volume)?

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