NPTEL ONLINE CERTIFICATION COURSES

Course Name: Introduction to Environmental Engineering and Science – Fundamentals and Sustainability Concepts

Faculty Name: Dr. Brajesh Kumar Dubey

Department : Civil engineering

Topic Environmental Measurements from Different Disciplines

Lecture 01: Mass Concentration Units

CONCEPTS COVERED

Concepts to be Covered this week

❑ Mass Concentration Units

❑ Partial Pressure Units

❑ Other Types of Units

Mass Concentration Units

- Physical quantities are always expressed in terms of number associated with unit.

    - Fundamental unit (Mass, Length and Time)
    - Basic unit (Mass, Length, Time, Temperature, electric current, Luminous intensity and the amount of substance)
    - Derived unit (Derived from basic units area, volume etc.,)

Mass Concentration Units

- **Some basic units**

System	Length	Mass	Time
SI (mks)	Meter (m)	Kilogram (kg)	Second (s)
Gaussian (cgs)	Centimeter (cm)	Gram (g)	Second (s)
British (fps)	Foot (ft)	Slug $*_{pound}$	Second (s)

MASS/MASS UNITS

- **Ppm and ppb**

- ppm: 1 mg of solute placed in 1 kg of solvent equals 1 ppm.

ppm = g of i in 10^6 total

$$= \frac{m_i}{m_{total}} \times 10^6$$

Similarly for ppb

ppm = g of i in 10^9 total

$$= \frac{m_i}{m_{total}} \times 10^9$$

MASS/MASS UNITS

Example: 1

A 1 kg sample of soil is analyzed for the chemical solvent trichloroethylene (TCE). The analysis indicates that the sample contains 5.0 mg of TCE. What is the TCE concentration in ppm_m and ppb_m?

MASS/MASS UNITS

Example: 1

A 1 kg sample of soil is analyzed for the chemical solvent trichloroethylene (TCE). The analysis indicates that the sample contains 5.0 mg of TCE. What is the TCE concentration in ppm$_m$ and ppb$_m$?

$$[TCE] = \frac{5.0 mg\ TCE}{1.0\ kg\ soil} = \frac{0.005\ g\ TCE}{10^3 g\ soil}$$

$$= \frac{5 \times 10^{-6} g\ TCE}{g\ soil} \times 10^6 = 5\ ppm_m = 5{,}000\ ppb_m$$

Note that in soil and sediments, mg/kg equals ppm$_m$, and equals ppb$_m$.

MASS/VOLUME UNITS

- mg/L and μg/m^3

mg/L: commonly used in water

μg/m^3: commonly used in air

MASS/VOLUME UNITS

Example: 2

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

MASS/VOLUME UNITS

Example: 2

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

$$[TCE] = \frac{5.0 \; mg \; TCE}{1.0 \; LH_2O} = \frac{5.0 \; mg}{L}$$

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

$$TCE = \frac{5.0\ mg\ TCE}{1.0\ LH_2O} \times \frac{1.0\ LH_2O}{1{,}000\ g\ H_2O}$$

$$= \frac{5.0\ \text{mg TCE}}{1{,}000\ \text{g total}} = \frac{5.0 \times 10^{-6}\ \text{g TCE}}{\text{g total}} \times \frac{10^6\text{ppm}_\text{m}}{\text{mass fraction}}$$

$$= 5.0\ ppm_m$$

In most dilute aqueous systems, mg/L is equivalent to ppm$_\text{m}$.

Example: 3

What is the carbon monoxide (CO) concentration expressed in of a 10 L gas mixture that contains mole of CO?

Example: 3

What is the carbon monoxide (CO) concentration expressed in of a 10 L gas mixture that contains 1.0×10^{-6} mole of CO?

To convert to mass of the chemical per total volume, convert the moles of chemical to mass of the chemical by multiplying moles by CO's molecular weight. The molecular weight of CO (28 g/mole) is equal to 12 (atomic weight of C) plus 16 (atomic weight of O).

$$[CO] = \frac{1.0 \times 10^{-6} \text{ mole CO}}{10 \text{ L total}} \times \frac{28 \text{ g CO}}{\text{mole CO}}$$

$$= \frac{28 \times 10^{-6} \text{ g CO}}{10 \text{ L total}} \times \frac{10^6 \mu g}{g} \times \frac{10^3 \text{ L}}{m^3}$$

$$= \frac{2,800 \ \mu g}{m^3}$$

Using the ideal gas law to convert ppm$_v$ to µg/m³

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

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

Example: 4

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

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

The concentration in ppm_v is determined as:

$$[SO_2] = \frac{V_{SO_2}}{V_{Total}} \times 10^6$$

To solve, convert the number of moles of SO_2 to volume using the ideal gas law and the total number of moles to volume. Then divide the two expressions:

$$V_{SO_2} = 0.001 \text{ moles } SO_2 \times \frac{RT}{P}$$

$$V_{Total} = (0.999 + 0.001)\text{mole total} \times \frac{RT}{P}$$

$$= 1.000 \text{ mole total} \times \frac{RT}{P}$$

Substitute these volume terms for ppm$_v$:

$$PPM_v = \frac{0.001 \text{ mole so}_2 \times \frac{RT}{P}}{1000 \text{ mole total} \times \frac{RT}{P}} \times 10^6$$

$$= 1000 \text{ PPM}_v$$

Example: 5

The concentration of SO_2 is measured in air to be 100 ppb_v. What is this concentration in units of Assume the temperature is 28°C and pressure is 1 atm. Remember that T expressed in K is equal to T expressed in °C plus 273.15.

Example: 5

The concentration of SO_2 is measured in air to be 100 ppb$_v$. What is this concentration in units of Assume the temperature is 28°C and pressure is 1 atm. Remember that T expressed in K is equal to T expressed in °C plus 273.15.

To accomplish this conversion, use the ideal gas law to convert the volume of SO_2 to moles of SO_2, resulting in units of moles/L. This can be converted to using the molecular weight of SO_2 (which equals 64). This method will be used to develop a general formula for converting between ppm$_v$ and.

First, use the definition of ppb$_v$ to obtain a volume ratio for SO_2:

$$100 \text{ ppb}_v = \frac{100 m^3 SO_2}{10^9 m^3 \text{air solution}}$$

Now convert the volume of SO_2 in the numerator to units of mass. This is done in two steps. First, convert the volume to a number of moles, using a rearranged format of the ideal gas law, *n/V = P/RT,* and the given temperature and pressure:

$$\frac{100 \ m^3 \ so_2}{10^9 m^3 \ air \ solution} \times \frac{P}{RT}$$

$$= \frac{100 \ m^3 \ so_2}{10^9 m^3 \ air \ solution} \times \frac{1 \ atm}{8.205 \times 10^{-5} \frac{m^3 - atm}{mole - k} (301 \ k)}$$

$$= \frac{4.05 \times 10^{-6} mole \ so_2}{m^3 \ air}$$

In the second step, convert the moles of SO_2 to mass of SO_2 by using the molecular weight of SO_2:

$$\frac{4.05 \times 10^{-6} \text{mole } SO_2}{\text{m}^3 \text{ air}} \times \frac{64 \text{ g } SO_2}{\text{mole } SO_2} \times \frac{10^6 \mu g}{g} = \frac{260 \ \mu g}{\text{m}^3}$$

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Lecture 02: Partial Pressure Units
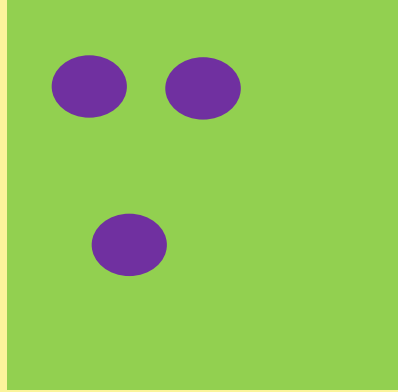
Partial-Pressure Units

The partial pressure of one of the gases in a mixture is the pressure which it would exert if it alone occupied the whole container. The partial pressure of gas A is often given the symbol P_A. The partial pressure of gas B would be P_B - and so on. There are two important relationships involving partial pressures. The first is again fairly obvious. The total pressure of a mixture of gases is equal to the sum of the partial pressures.
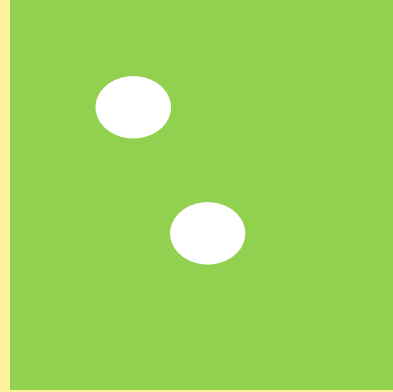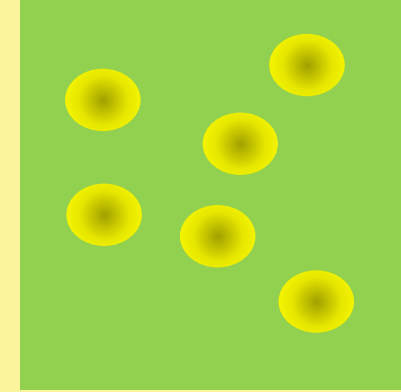
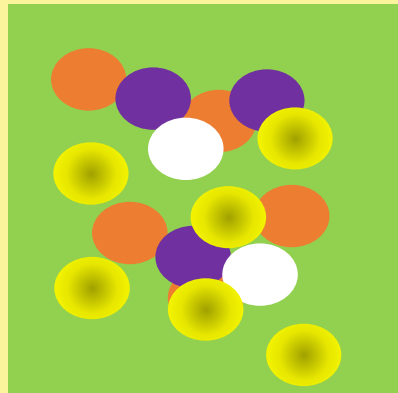# Partial-Pressure Units

Gas A, P_A

Gas B, P_B

Gas C, P_C

Gas D, P_D

$P_{total} = P_A + P_B + P_C + P_D$

Gas mixture

Partial-Pressure Units

The ideal gas law states that, at a given temperature and volume pressure is directly Proportional to the number of moles of gas present; therefore, pressure fractions are identical to mole fractions. For this reason, partial pressure can be calculated as the product of the mole Or volume fraction and the total pressure. For example

$$P_i = [\text{volume fraction}_i \text{ or mole fraction}_i \times P_{total}]$$
$$= [(ppm_v \times 10^{-6} \times P_{total}]$$

$$ppm_v = \frac{P_i}{P_{total}} \times 10^6$$

Partial-Pressure Units

Example: 6

The concentration of gas-phase PCBs in the air above Lake Superior was measured to be 450 picograms per cubic meter (pg/m³). What is the partial pressure (in atm) of PCBs? Assume the temperature is 0°C, the atmosphere pressure is 1 atm, and the average molecular weight of PCBs is 325.

Partial-Pressure Units

The partial pressure is defined as the mole or volume fraction time the total gas pressure. First, find the number of moles of PCB$_s$ in a liter of air. Then use the ideal gas law to calculate that 1 mole of gas at 0°C and 1 atm occupies 22.4 L. Substitute this value into the first expression to determine the mole fraction of PCB$_s$:

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

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

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

Partial-Pressure Units

Table 1: Composition of the atmosphere

Gas Name	Formula	Volume in ppmv	in %
Nitrogen	N_2	780,840	78.084
Oxygen	O_2	209,460	20.946
Argon	Ar	9,340	0.9340
Carbon dioxide	CO_2	400	0.04
Neon	Ne	18.18	0.001818
Helium	He	5.24	0.000524
Methane	CH_4	1.79	0.000179

Source: Intergovernmental Panel on Climate Change (IPCC)

Partial-Pressure Units

Example: 7

What would be the partial pressure (in atm) of carbon dioxide (CO_2) when the barometer reads 29.0 inches of Hg, the relative humidity is 80 percent, and the temperature is 70°F? Use Table 1 to obtain the concentration of CO_2 in dry air.

Partial-Pressure Units

The partial-pressure concentration units in Table 1 are for dry air, so the partial pressure must first be corrected for the moisture present in the air. In dry air, the CO_2 concentration is 391 ppm_v. The partial pressure will be this volume fraction times the total pressure of dry air. The total pressure of dry air is the total atmospheric pressure (29.0 in. Hg) minus the contribution of water vapor. The vapor pressure of water at 70°F is 0.36 lb/in². Thus, the total pressure of dry air is

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

Partial-Pressure Units

The partial pressure of CO_2 would be:

$$\text{vol. fraction} \times P_{total} = 391 \text{ppm}_v \times \frac{10^{-6} \text{vol. fraction}}{\text{ppm}_v} \times \left[28.4 \text{ in. Hg} \times \frac{1 \text{ atm}}{29.9 \text{ in. Hg}} \right]$$
$$= 3.7 \times 10^{-4} \text{atm}$$

Mole/Volume Units

Molarity

Moles of solute per <u>liter of solution.</u>
Denoted as: M

Molality

Moles of solute per <u>mass of solvent</u>.
Denoted as: m

Mole/Volume Units

Example: 8

The concentration of TCE is 5 ppm. Convert this to units of molarity. The molecular weight of TCE is 131.5 g/mole.

Mole/Volume Units

Example: 8

The concentration of TCE is 5 ppm. Convert this to units of molarity. The molecular weight of TCE is 131.5 g/mole.

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

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

Mole/Volume Units

Often, concentrations below 1 M are expressed in units of mill moles per liter, or mill molar (1mM = 10^{-3} moles/L), or in micromoles per liter, or micro molar $(1 \mu M = 10^{-6} \, moles/L)$. Thus, the concentration of TCE could be expressed as 0.038 mM or $38 \mu M$.

Mole/Volume Units

Example: 9

The concentration of alachlor, a common herbicide, in the Mississippi River was found to range from 0.04 to 0.1 μg/L. What is the concentration range in nmoles/L? The molecular formula for alachlor is $C_{14}H_{20}O_2 NCl$, and its molecular weight is 270.

Mole/Volume Units

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

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

Similarly, the upper limit ($0.1 \ \mu g/L$) can be calculated as 0.37 nmoles/L.

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Lecture 03: Other Types of Units

Other Types of Units

NORMALITY

The strength of a solution measured in terms of gram equivalent per litre is called normality.

Denoted by: N

A solution having 1 g equivalent of the dissolved solute in 1 litre of its solution is called normal solution.

The solution in which $1/10^{th}$ g equivalent of solute is dissolved per litre of its solution,

is called decinormal solution i.e., the solution will have N/10 strength.

Normality depends on two factors

a) Dilution
b) Temperature

Other Types of Units

NORMALITY

Mathematically,

$$N = \frac{\text{weight in g} \times 1000}{\textbf{equivalent weight} \text{ expressed in g} \times \text{volume of solution}}$$

$$N = \frac{\text{strength in g/l}}{\text{gm.eq.wt of the compound}}$$

Other Types of Units

Equivalent weight

Equivalent weight (also known as gram equivalent) is a term which has been used in several contexts in chemistry. In its most general usage, it is the mass of one equivalent, that is the mass of a given substance which will:

supply or react with one mole of hydrogen ions(H^+) in an acid–base reaction; or

supply or react with one mole of electrons in a redox reaction.

NORMALITY

Example: 10

What are the equivalent weights of HCl, H2SO4, NaOH, CaCO3 and aqueous CO2?

To find the equivalent weight of each compound, divide the molecular weight by the number of equivalents:

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

$$\text{eqv wt of H}_2\text{SO}_4 = \frac{(2 \times 1) + 32 + (4 \times 16) \text{ g/mole}}{2 \text{ eqv/mole}} = \frac{49 \text{ g}}{\text{eqv}}$$

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

$$\text{eqv wt of CaCO}_3 = \frac{40 + 12 + (3 \times 16) \text{ g/mole}}{2 \text{ eqv/mole}} = \frac{50 \text{ g}}{\text{eqv}}$$

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

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

NORMALITY

Example: 11

What is the normality (N) of 1 M Solutions of HCl and H_2SO_4?

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

$$1 \text{ M } H_2SO_4 = \frac{1 \text{ mole } H_2SO_4}{L} \times \frac{2 eqv}{mole} = \frac{2 \text{ eqv}}{L} = 2 \text{ N}$$

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

Example: 12

Chemical analysis of the mineral water resulted in the following cations and anions being identified with corresponding concentrations (in mg/L):

$$[Ca^{2+}] = 2.9 \quad [Mg^{2+}] = 2.0 \quad [Na^+] = 11.5 \quad [K^+] = 3.3$$
$$[SO_4^{2-}] = 4.7 \quad [Fl^-] = 0.09 \quad [Cl^-] = 7.7$$
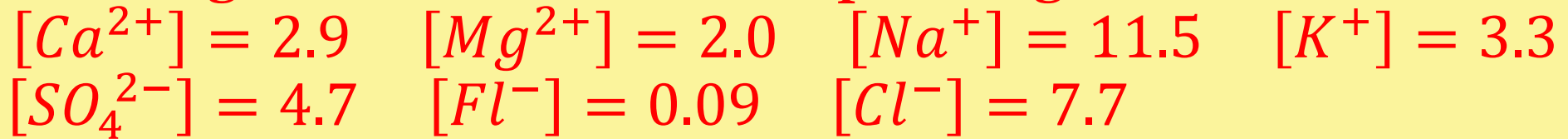
Is the analysis correct?

First, convert all concentrations of major ions to an equivalent basis, to do this, multiply the concentration in mg/L by a unit conversion (g/1,000 mg) and then divide by the equivalent weight of each substance (g/eqv). Then sum the concentrations of all cations and anions on equivalent basis. A solution with less than 5 percent error generally is considered acceptable.

Cations	Anions
$[Ca^{2+}] = \dfrac{1.45 \times 10^{-4} \text{ eqv}}{L}$	$[SO_4^{2-}] = \dfrac{9.75 \times 10^{-5} \text{ eqv}}{L}$
$[Mg^{2+}] = \dfrac{1.67 \times 10^{-4} \text{eqv}}{L}$	$[Fl^{-}] = \dfrac{4.73 \times 10^{-6} \text{eqv}}{L}$
$[Na^{+}] = \dfrac{5 \times 10^{-4} \text{eqv}}{L}$	$[Cl^{-}] = \dfrac{2.17 \times 10^{-4} \text{eqv}}{L}$
$[K^{+}] = \dfrac{8.5 \times 10^{-5} \text{ eqv}}{L}$	

The Total amount of cations equal $9.87 \times 10^{-4} \; eqv/L$, and the total amount of anions equals $3.2 \times 10^{-4} \; eqv/L$.

The analysis is not within 5 percent. The analysis resulted in more than three times more cations than anions on an equivalent basis.

Therefore, either of two conclusions is possible:

(1) One or more of the reported concentrations are incorrect, assuming all major cations and anions are accounted for.

(2) One or more important anions were not accounted for by the chemical analysis. (Bicarbonate, HCO_3^-, would be a good guess for the missing anion, as it is a common anion in most natural waters.)

Other Types of Units

Concentration as a Common constituent

Concentrations can be reported as a common constituent include contribution from different chemical compounds

- Green house gases (GHGs)

- Nitrogen

- phosphorus

Other Types of Units

- Green house gases (GHGs) in atmosphere

    Water vapor (H_2O)

    Carbon dioxide (CO_2)

    Methane (CH_4)

    Nitrous oxide (N_2O)

    Ozone (O_3)

    Chlorofluorocarbons (CFCs)

    Hydrofluorocarbons (incl. HCFCs and HFCs)

Example: 13

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

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

$$\frac{30 \text{ mg NH}_3}{\text{L}} \times \frac{\text{mole NH}_3}{17 \text{ g}} \times \frac{\text{mole N}}{\text{mole NH}_3} \times \frac{14 \text{ g}}{\text{mole N}} = \frac{24.7 \text{ mg NH}_3 - \text{N}}{\text{L}}$$

$$\frac{5 \text{ mg NO}_3^-}{\text{L}} \times \frac{\text{mole NO}_3^-}{62 \text{ g}} \times \frac{\text{mole N}}{\text{mole NO}_3} \times \frac{14 \text{ g}}{\text{mole N}} = \frac{1.1 \text{ mg NO}_3^- - \text{N}}{\text{L}}$$

Total nitrogen concentration = $24.7 + 1.1 = \frac{25.8 \text{ mg N}}{\text{L}}$

Other Types of Units

- Phosphorus

Orthophosphates $(H_3PO_4, H_2PO_4^-, PO_4^{3-}, HPO_4^{2-})$

Polyphosphates $(H_4P_2O_7 \text{ and } H_3P_3O_{10}^{2-})$

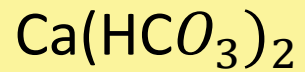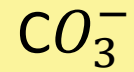Metaphosphates $(HP_3O_9^{2-})$

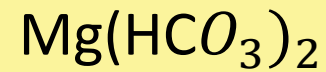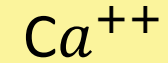Organic phosphate

Other Types of Units

Alkalinity

Hardness

Bicarbonate
HCO_3^-

Carbonate
CO_3^-

Calcium
Ca^{++}

Magnesium
Mg^{++}

$Ca(HCO_3)_2$

$CaCO_3$

$Mg(HCO_3)_2$

$MgCO_3$
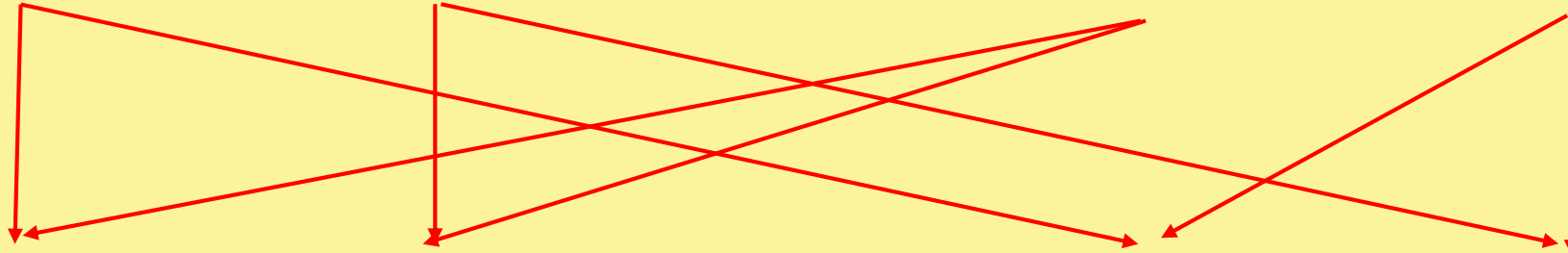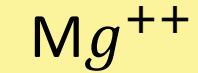
Other Types of Units

Hardness

To convert the concentration of specific cations (from mg/L) to hardness (as mg/L $CacO_3$), use the following expression, where M^{2+} represents a divalent cation:

$$\frac{M^{2+} \text{ in } mg}{L} \times \frac{50}{\text{eqv wt of } M^{2+} \text{ in } g/eqv} = mg/L \text{ as } CaCO_3$$

Where 50 is the equivalent weight of $CaCO_3$

Equivalent weight of divalent metallic cation ions are Mg, 24/2; Ca, 40/2; Mn, 55/2
Fe, 56/2; Sr, 88/2.

Example: 14

Water has the following chemical composting: $[Ca^+]$ 15 mg/L; $[Mg^{2+}] =$ 10 mg/L; $[SO_4^{2-}] = 30\ mg/L$.

What is the total hardness in units of mg/L as $CaCO_3$?

Example: 14

Water has the following chemical composition: $[Ca^+]$ $15\,mg/L$; $[Mg^{2+}] = 10\,mg/L$; $[SO_4^{2-}] = 30\,mg/L$.

What is the total hardness in units of mg/L as CaCO$_3$?

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

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

$$\frac{10 \text{ mg Mg}^{2+}}{\text{L}} \times \left(\frac{\frac{50 \text{ g CaCO}_3}{\text{eqv}}}{\frac{24 \text{ g Mg}^{2+}}{2 \text{ eqv}}} \right) = \frac{42 \text{ mg}}{\text{L}} \text{ as CaCO}_3$$
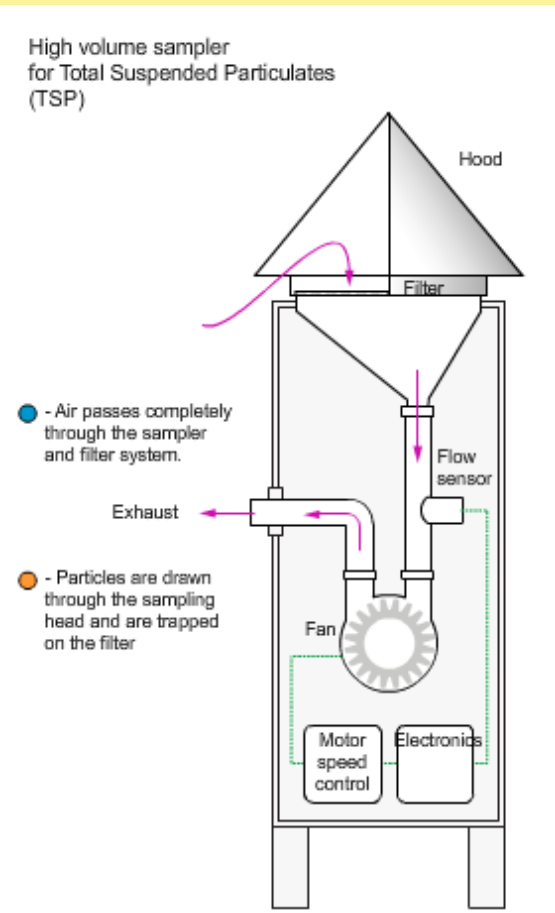
Therefore, the total hardness is 38 + 42 = 80 mg/L as $CaCO_3$. This water is moderately hard.

Note that if reduced iron (Fe^{2+}) or manganese (Mn^{2+}) were present, they would be included in the Hardness calculation.
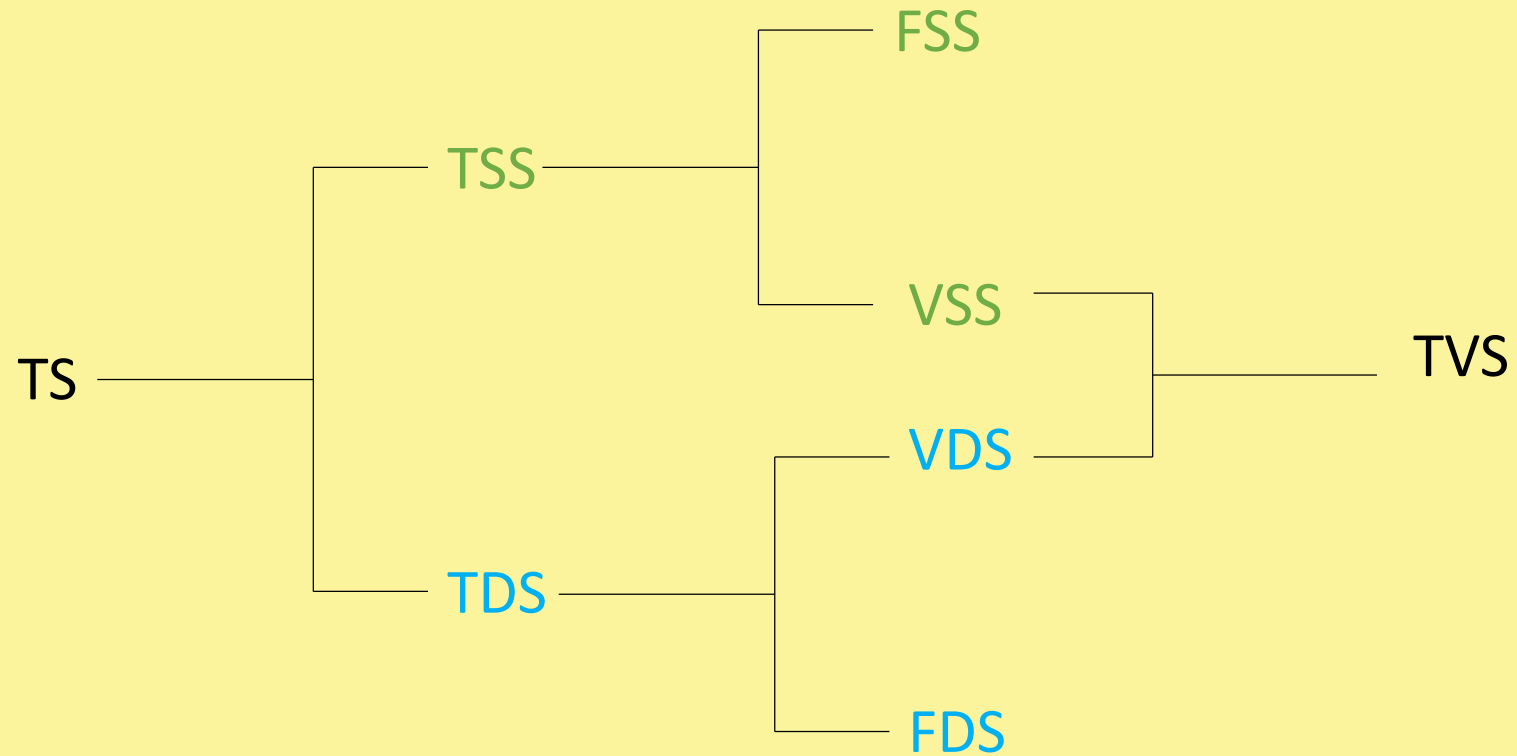
Reporting particle concentrations in air

High volume sampler
for Total Suspended Particulates
(TSP)

Hood

Filter

- Air passes completely
  through the sampler
  and filter system.

Flow
sensor

Exhaust

- Particles are drawn
  through the sampling
  head and are trapped
  on the filter

Fan

Motor
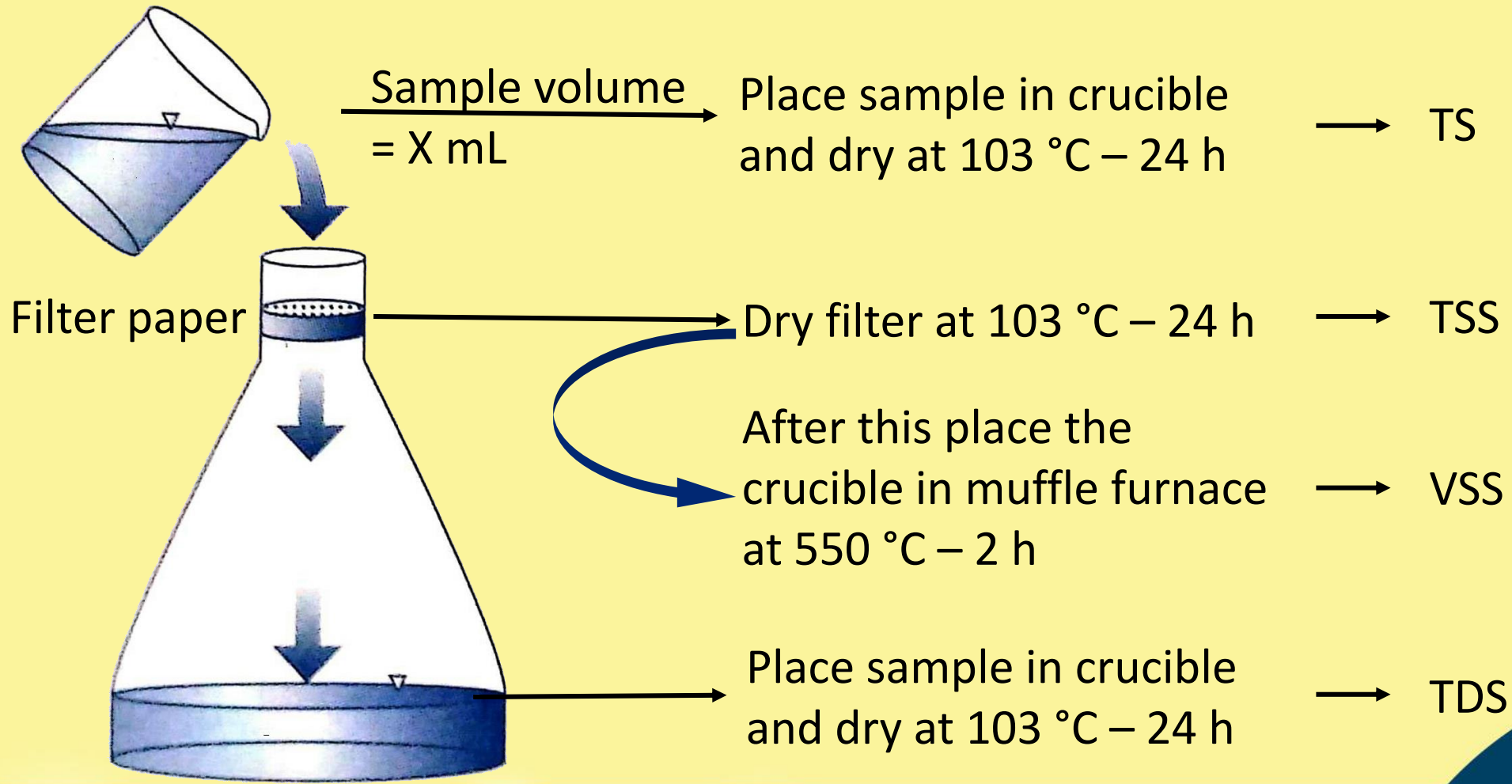speed
control

Electronics

Particle concentration

$$= \frac{\text{Final weight of filter paper} - \text{Initial weight of filter paper}}{\text{amount of air sampled}}$$

Reporting particle concentrations in water

Reporting particle concentrations in water

Sample volume = X mL

Place sample in crucible and dry at 103 °C – 24 h → TS

Filter paper →

Dry filter at 103 °C – 24 h → TSS

After this place the crucible in muffle furnace at 550 °C – 2 h → VSS

Place sample in crucible and dry at 103 °C – 24 h → TDS

Example: 15

A laboratory provides the following analysis obtained from a 50 mL sample of wastewater: total solids = 200 mg/L, total suspended solids = 160 mg/L, fixed suspended solids = 40 mg/L, and volatile solids = 120 mg/L. What is the concentration of total dissolved solids of this sample? Suppose this sample was filtered through a glass-fiber filter, and the filter was then placed in a muffle furnace at 550°C overnight. What would be the weight of the solids (in mg) remaining on the filter after the night in the furnace? Is this sample turbid? Estimate the percent of solids that are organic matter.

Refer to previous figure to see the relationship between the various forms of solids. TDS equals TS minus TSS; thus,

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

The solids remaining on the filter are suspended solids. (Dissolved solids would pass through the filter) Because the filter was subjected to a temperature of 550°C, the measurement was made for the volatile and fixed fraction of the suspended solids, i.e., the VSS and FSS. However, during the ignition fraction of the suspended solids. Thus, this problem is requesting the fixed fraction of the suspended solids. Accordingly, the 50 mL sample had FSS of 40 mg/L. Therefore,

$$FSS = \frac{40 \text{ mg}}{L}$$

$$= \frac{\text{wt of suspended solids remaining on filter after ignition}}{\text{mL sample}}$$

$$= \frac{x}{50 \text{ mL}}$$

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

The sample is turbid because of the suspended particles, measured as TSS. If the sample was allowed to sit for some time period, the suspended solids would settle, and the overlaying water might not appear turbid. The solids found in this sample contain at least 60-percent organic matter. The total solids concentration is 200 mg/L, and of this, 120 mg/L are volatile suspended solids. Because volatile solids consist primarily of organic matter, we can conclude that approximately 60 percent (120/200) of the solids are organic.

NPTEL ONLINE CERTIFICATION COURSES

Course Name: Introduction to Environmental Engineering and Science – Fundamentals and Sustainability Concepts

Faculty Name: Dr. Brajesh Kumar Dubey

Department : Civil engineering

Topic Environmental Measurements from Different Disciplines

Lecture 03: Importance of quantitative measurements

Importance of quantitative measurements

- Helps in defining the problem

- Reliable results from various lab/hands

- Once the extent of problem is quantified, fix can be designed

- Basis of research studies

- Used in finding answers to new problems and better answers to the old one

Character of environmental problems

- Relationships between living organisms and their environment

- Analytical procedures used are a strange mix of chemical and biochemical methods

- Interpretation of data is related to effect on microorganisms and/or human being

- Many of the determinants fall in realm of microanalysis

Standard methods of analysis

- Initial days: different methods proposed for the same determinations, leading to difficulty in comparing the data coming out from various methods

- Hence, need of a comprehensive manual of standard methods which everybody can refer to

- Leading to the development of "Standard Methods of Water Analysis" by APHA, AWWA, and WEF

- Standard Methods is normally accepted in courts

Expression of results

- Parts per Million

- mg/L

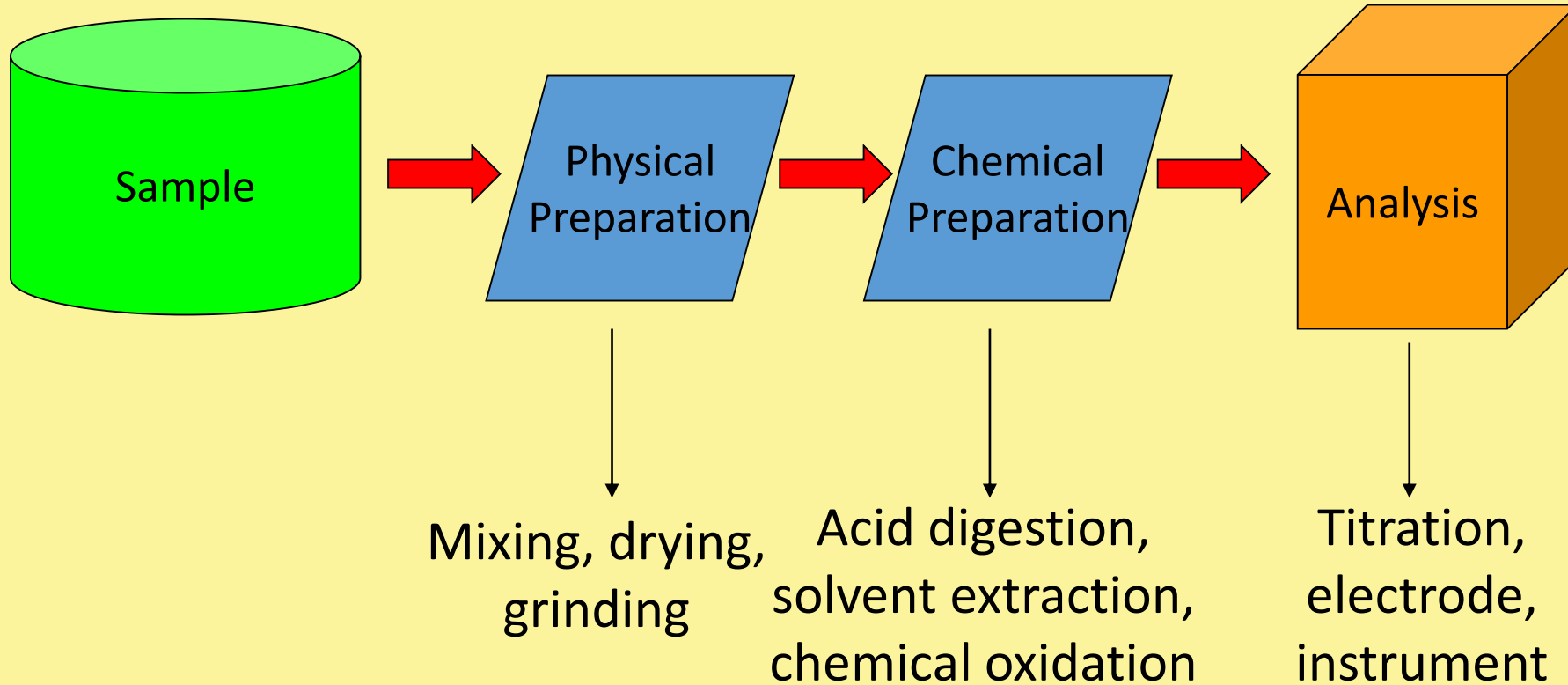- Milli-equivalents

- Fractions

Chemical Analysis Procedures

- Direct chemical measurement

- Titration of sample for alkalinity or hardness

- Use of a sensor or an instrument

- pH meter, chromatograph

- In many, some form of sample "preparation" will be necessary

Sample Preparation & analysis

Instrumental Analysis

- Many different instruments have been developed to measure the concentration of pollutants in environmental samples

- These instruments give a "response" that correlates the amount of sample present
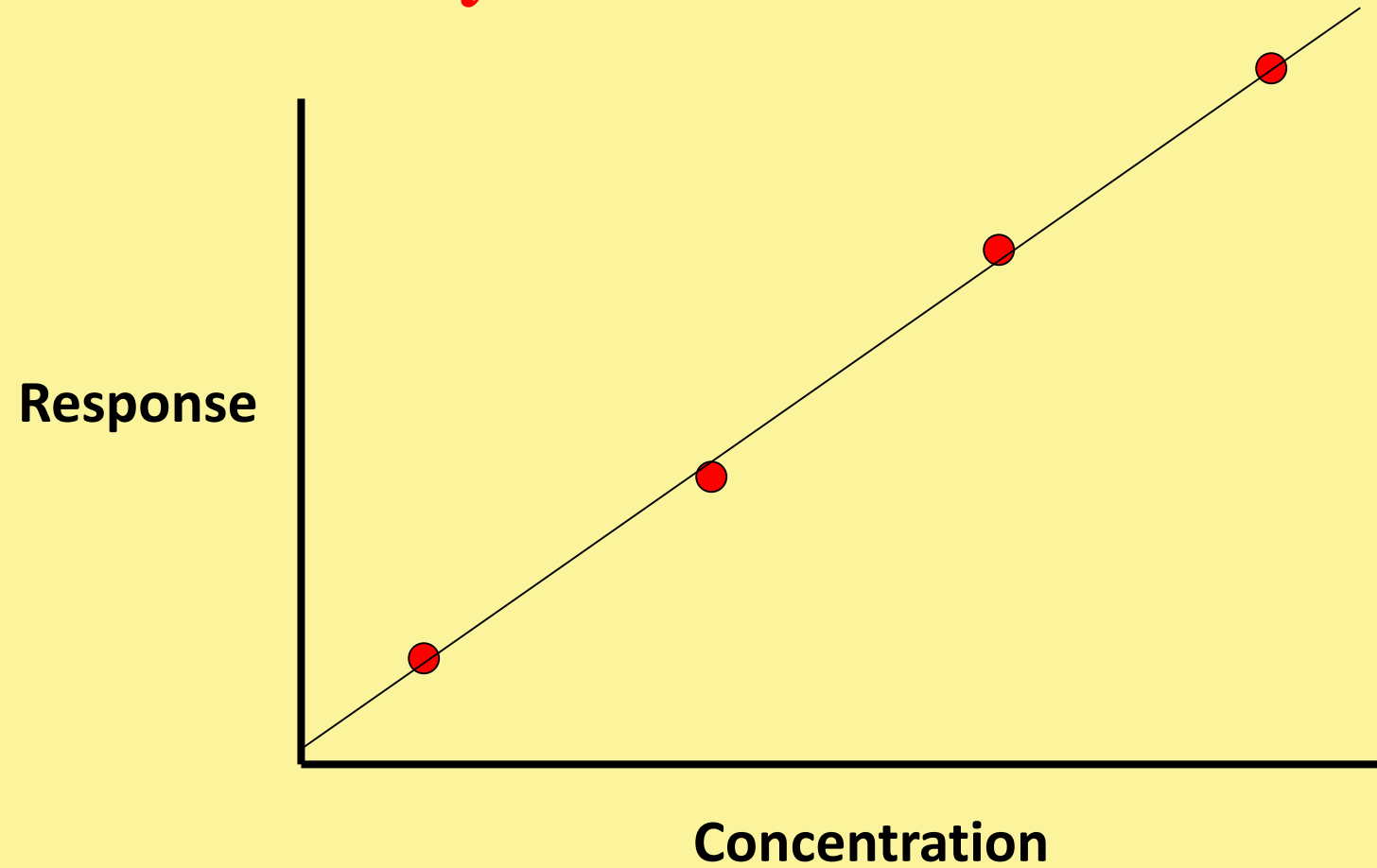
- Responses:

Increase in conductivity
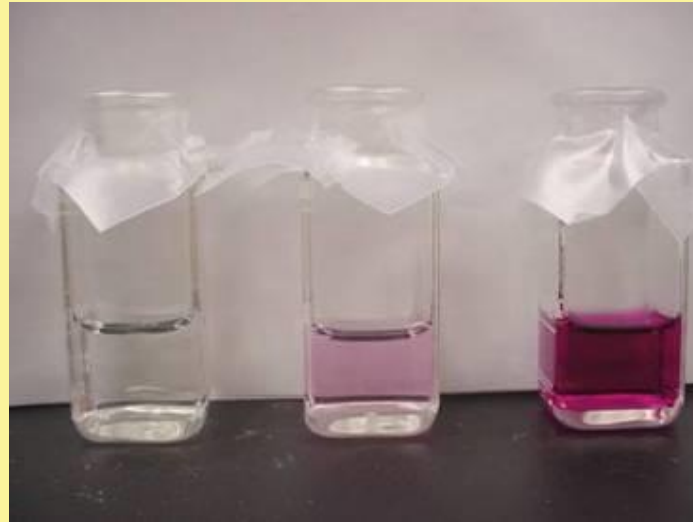
Absorbance of light

Emission of light

Instrumental Analysis

Instrumental Analysis

- Spectrophotometers – Measure absorption of light at specific wavelengths

- Some chemicals are directly proportional to absorbance

- Many methods that were developed based on color changes in titrations can be measured using absorbance

Quality Control/Quality Assurance

QA/QC

Designed to make sure that the data you gather are sufficiently accurate, precise, and rpeatable

Mechanisms

Blanks

Spikes

Replicates

Quality Control/Quality Assurance

QA/QC

QA project plans are list of detailed activities performed at each stage of the dredged material evaluation and outline project-specific data quality objectives that should be archived for field observations and measurements, physical analyses, laboratory chemical analyses, and biological tests.

Quality Control/Quality Assurance

- Standard Operating Procedures

- Sampling strategy and procedures

- Sample custody

- Calibration procedure and frequency

- Analytical procedures

- Data validation, reduction and reporting

- Internal QC checks

- Performance and system audits

- Preventive maintenance

- Calculation of data quality indicators

- Corrective actions

Method Detection Limit (MDL)

"The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte" (EPA, 1992)

Method Detection Limit (MDL)

MDL = t (n-1, a=0.99)(S)

where,

      t (n-1, a=0.99) = one-sided critical t-value at 99% level

      n = number of sample

      S = standard deviation

MDL can be calculated by multiplying standard deviation by one sided critical t-value at 99% level. Different t-value should be applied by number of sample. EPA recommends that number of sample would be greater than 7 to make MDL confident.

Example-16

Sample No.	Analysis results (mg/L)
1	12.11
2	12.02
3	12.21
4	12.06
5	12.57
6	12.42
7	12.09
8	12.32

- N = 8
- Standard deviation = 0.19
- t (7, a=0.99) = 3.00

MDL = 0.19 X 3.00 = 0.57 mg/L

MDL at given results is 0.57 mg/L. It indicates that 0.57 mg/L would be minimum concentration you can trust with 99% confidence level.

Ion Exchange Chromatograph

Ion exchange chromatograph is used to analyze liquid samples for dissolved ionic or polar materials by charge properties

Gas Chromatograph

Gas chromatograph is an instrument to separate complex gas or liquid samples to single components. Injected samples are separated in gas phase (mobile phase) through the column. Separated components are detected by various types of detector such as flame-ionized detector (FID) and thermal conductivity detector (TCD).

Gas Chromatograph / Mass Spectrometry

GC/MS is a GC equipped with mass spectrometry as a detector. After complex chemicals are separated through a GC column, separated components are fragmented by high energy source in a mass spectrometry. With size and patterns of fragments, components can be identified.

High-Performance Liquid Chromatograph (HPLC)

Like other chromatograph, an HPLC is also used to separate complex chemicals to single components. Unlike a GC, HPLC uses liquid as a mobile phase. Separated components can be detected by UV-Vis absorbance detector. Since an HPLC can handle only liquid sample, more complex and greater molecular-weight chemicals can be analyzed.

Liquid Chromatograph /Mass Spectrometry

Like GC-MS, LC-MS is a LC equipped with mass spectrometry as a detector. An LC-MS can be used to analyze large molecules such as pharmaceutical products and protein.

Inductively Coupled Plasma (ICP)

ICP-AES is used to analyze elements such as heavy metals and cations using an inductively coupled plasma (ICP).

Each element can be recognized by electromagnetic radiation produced by excited atoms at a wavelength of a particular element.

Atomic Absorption Spectrometer

Working with Concentrations

- Must be able to convert from chemical concentration based on dry weight and chemical concentration based on wet (or total) weight.

Example

- Sludge has a total arsenic concentration of 0.6 mg/kg based on total weight.

- Moisture content of sludge is 80%

- Dry weight arsenic concentration is:

$$\frac{0.6 \; mg \; arsenic}{1 \; kg \; wet \; sludge} \times \frac{1 \; kg \; wet \; sludge}{0.2 \; kg \; dry \; sludge} = 3.0 \; \frac{mg \; As}{kg \; dry \; sludge}$$

Working with Concentrations

- You should be able to find the average concentration of mixed waste streams

Example

- You have two waste components:

    Sludge, 100 mg/kg (wet) Pb

    Solids Content = 10%

    Wood Chips, 300 mg/kg (wet) Pb

    Moisture Content = 20%

Example (continued)

- If you mix the components in a 50/50 mix by total weight, what is the Pb concentration in the dry sludge?

Example (continued)

$$\frac{\dfrac{100 \; mg \; Pb}{1 \; kg \; wet \; sludge} \; x \; 50 \; kg \; \cancel{wet \; sludge} \; + \; \dfrac{300 \; mg \; Pb}{1 \; kg \; \cancel{wet} \; wood} \; x \; 50 \; kg \; \cancel{wet \; wood}}{50 \; kg \; \cancel{wet \; sludge} \; x \; \dfrac{0.1 \; kg \; dry \; sludge}{1 \; kg \; \cancel{wet \; sludge}} \; + \; 50 \; kg \; \cancel{wet \; wood} \; x \; \dfrac{0.8 \; kg \; dry \; wood}{1 \; kg \; \cancel{wet \; wood}}}$$

$$X = \; 444 \; \frac{mg \; Pb}{kg \; dry \; waste}$$

Working with Concentrations

- Must be able to go back and forth between "total" and "leachable" concentrations.

Example

- You have a soil contaminated with lead based paint debris.
- Below what total concentration (mg/kg) would you know that the soil is not a toxicity characteristic hazardous waste for lead?

Example (continued)

- Toxicity Characteristic Concentration for lead = 5 mg/l

- TCLP uses 100 g of waste and 2,000 g (2 L) of leaching fluid (20:1 liquid to solid ratio)

Example (continued)

$$\frac{X \; mg \; Pb}{1 \; kg \; soil} \; x \; \frac{0.1 \; kg \; soil}{2 \; L \; Leachate} = 5.0 \; \frac{mg \; Pb}{L}$$

$$X = 100 \; \frac{mg \; Pb}{kg \; soil}$$

Note

- ou could do the same thing for SPLP and compare to groundwater standards
- You could also assume that only a fraction leached
- You could calculate the opposite direction

Statistical Calculations are Often Needed when Working with Concentrations

- Since concentration results are often directly used as part of regulatory decision-making (i.e. is it a hazardous waste, is it a safe to be land applied), it is necessary to perform a statistical analysis.

What is the Chemical Concentration of a Waste?

- Very rarely are wastes or contaminated soils completely homogenous with respect to chemical concentration.

- You must collect and analysis multiple samples to determine what some "representative" concentration is.

- The more heterogeneous the matrix, the more samples may be needed to accurately describe the "representative" concentration.
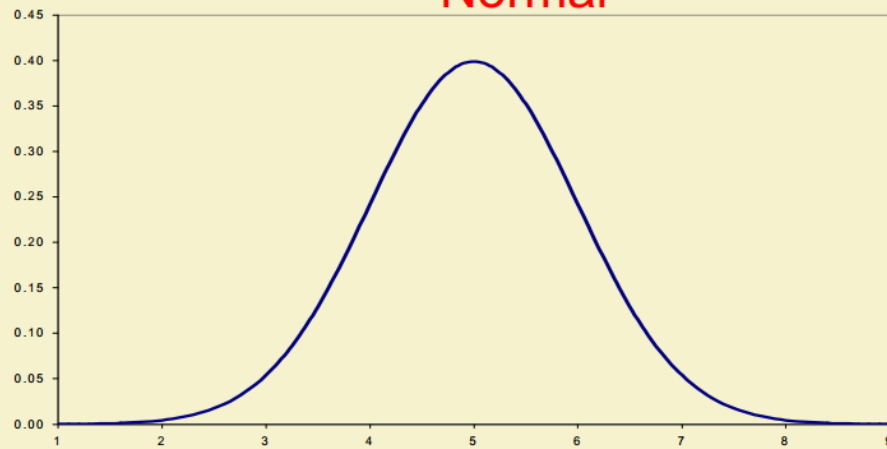
What is the Representative Concentration?

- Some estimate of the central tendency
    - The mean (the average)
    - The median (the middle number)
    - The mode (the most common number)
    - Some upper or lower confidence limit
- Must consider
    - The sample distribution
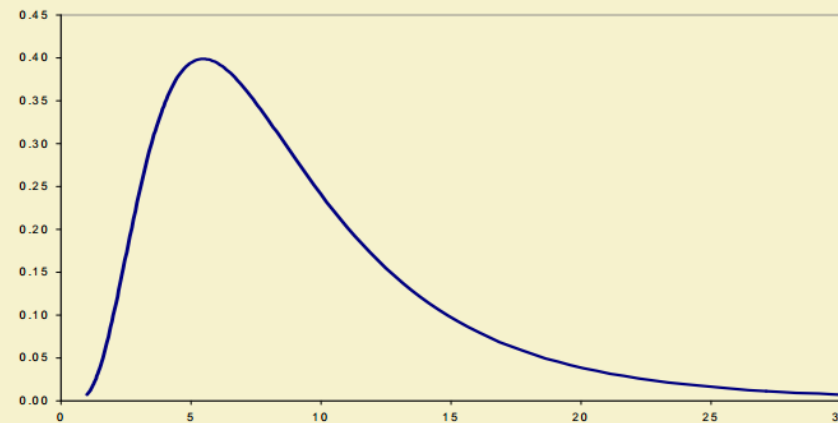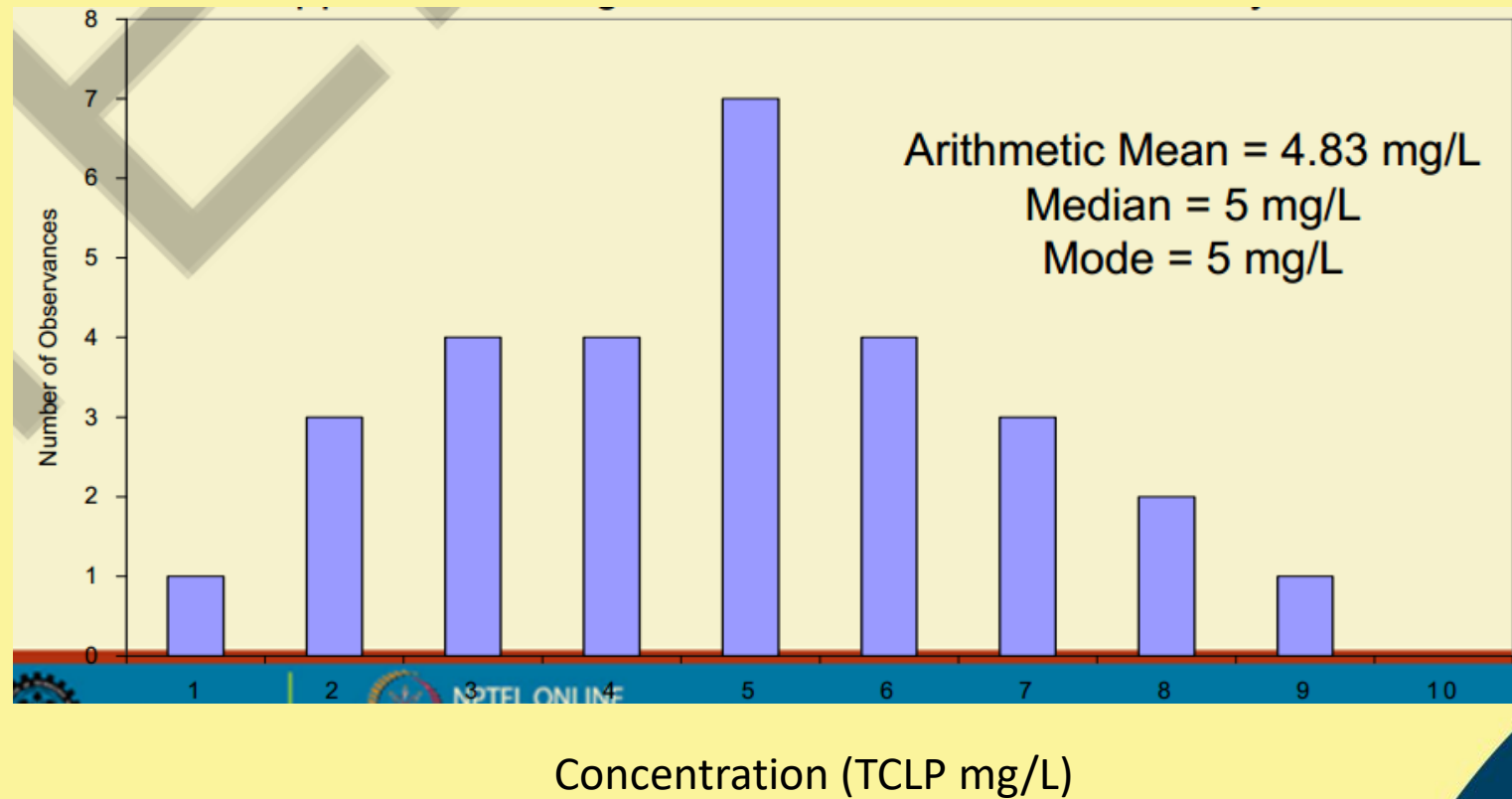   - What the data will be used for

Sample Distributions

The Type of Distribution Dictates How You Calculate the Central Tendency

- Consider the following data set for some TCLP results (in mg/L)
  - ➤ 3, 2, 3, 5, 4, 4, 5, 7, 8, 1, 6, 2, 5, 9, 6, 5, 7, 7, 3, 4, 2, 8, 5, 4, 5, 6, 6, 3, 5
  - ➤ N = 29

The resulting histogram has a similar shape as a normal distribution.

The mean appears to be a good estimate of central tendency.

Arithmetic Mean = 4.83 mg/L
Median = 5 mg/L
Mode = 5 mg/L

Concentration (TCLP mg/L)

The Type of Distribution Dictates How You Calculate the Central Tendency

- Consider a different data set, again for some TCLP results (in mg/L)
- ➢ 3, 5, 2, 5, 3, 3, 4, 3, 7, 1, 7, 2, 4, 9, 5, 5, 11, 6, 2, 6, 2, 8, 4, 2, 4, 6, 16, 4, 20, 3, 3
- ➢ N = 31

- The resulting histogram gives the appearance that it might be a log-normal distribution. The mean appears to be somewhat less reliable as an estimate of central tendency.

Arithmetic Mean = 5.32 mg/L
Median = 4 mg/L
Mode = 3 mg/L

Concentration (TCLP mg/L)
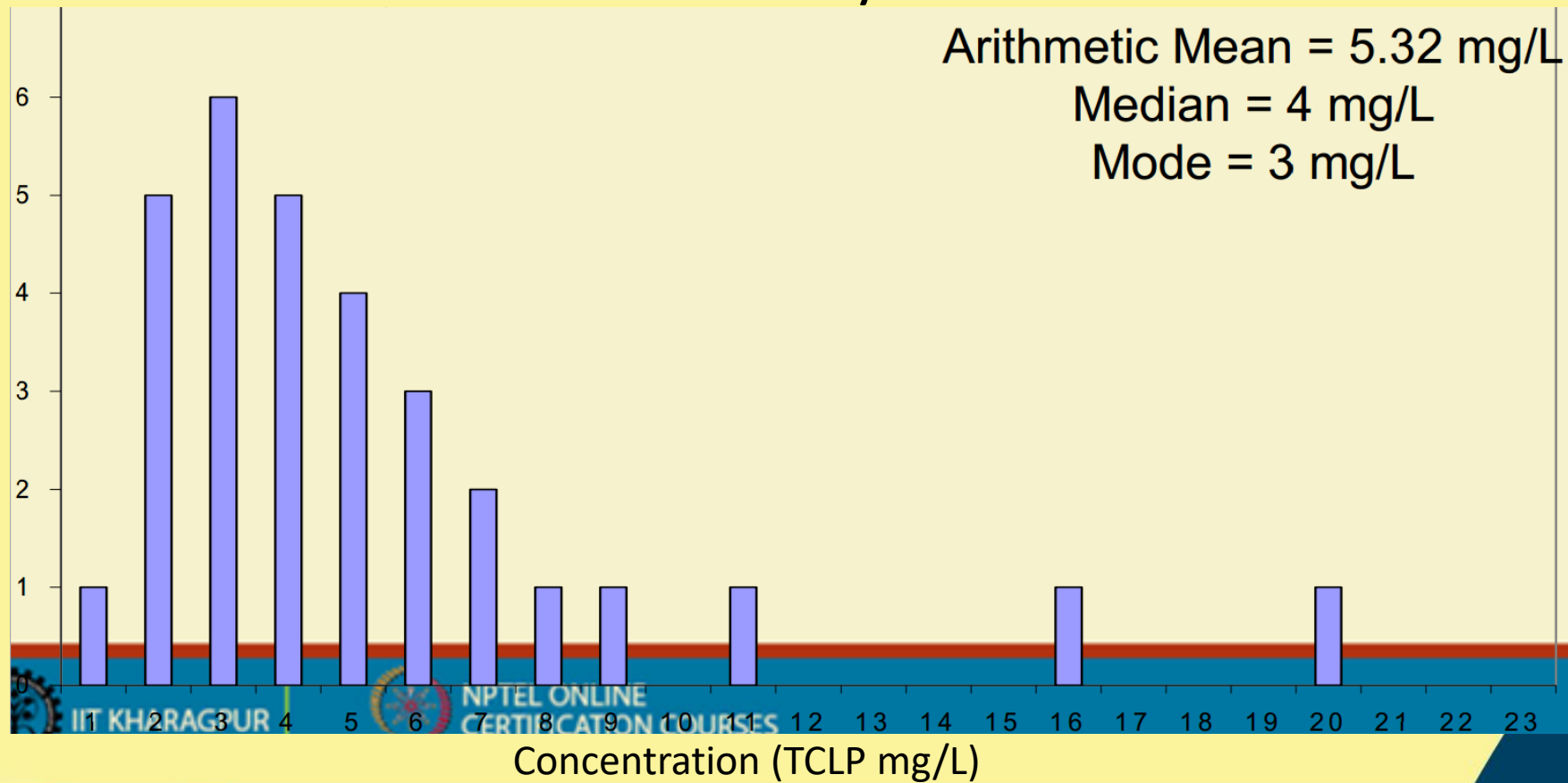
It is Important to Check for Normalcy

- A quick test may be used to assess whether the data are normally distributed:

- Is the mean greater than the standard deviation and the variance?

- If the mean is not greater than both, the data set is probably not normally distributed.

Previous Data Sets

- Data set I
  - Arithmetic mean = 4.83 mg/L
  - Standard deviation = 2.0
  - Variance = 4.0
- It is likely that the data are normally distributed

Previous Data Sets

- Data set II
    - Arithmetic mean = 5.32 mg/L
    - Standard deviation = 4.10
    - Variance = 16.8
- It is likely that the data are not normally distributed

How Do You Handle Data that are Not Normal?

- First step, check to see whether the data are log-normally distributed
- Environmental data are often log-normally distributed
- Perform a log transform on the data and check for normality again.

Transformed Data

- Transformed Data Set #2

  – Arithmetic mean = 1.46

  – Standard deviation = 0.65

  – Variance = 0.42

- The mean of the transformed data is greater than the standard deviation and variation of the transformed data. It is thus reasonable to treat the original data as log-normally distributed.

Geometric Mean

- When the mean of the transformed data is transformed back, this is known as the geometric mean.

  –Geometric mean of data set II: 4.28 mg/L

What if the Data are Neither Normally or Log-Normally Distributed?

- Find another distribution
- Use a more advanced statistical method (e.g. a nonparametric method)

Incorporating Uncertainty

- Assume that the TCLP results presented for data sets 1 and 2 were for lead. The TC limit is 5 mg/L.

- The arithmetic mean for data set I (4.83 mg/L) and the geometric mean for data set II (4.28 mg/L) were less than 5 mg/L.

- These were based on a limited number of samples, and thus may be somewhat different than the true mean.

Incorporating Uncertainty

- We need to factor in this uncertainty.

- Calculate the upper confidence limit (UCL).

- The UCL is a conservative estimate of the mean that takes into account uncertainties in the data set.

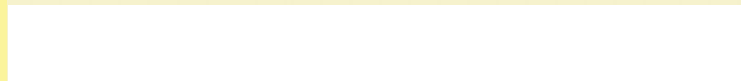- It is associated with some degree of statistical significance, e.g., 95% UCL.

$$UCL_{|1-\alpha} = Mean + t_{\alpha,\, n-1} \frac{Standard\ \ Deviation}{\sqrt{number} \ \ of\ \ samples}$$

Student t statistic

Example

- For data set I, find UCL at 95%.

Note: Higher than TC Limit

$$UCL_{1-0.05} = 4.83 + 1.70\left|1\right.\frac{2.0}{\sqrt{29}} = 5.46$$

T statistic at 0.05 level and 28 degrees of freedom

Example

- For data set II, find UCL at 95%.

$$UCL_{1-0.05} = 1.46 + 1.697 \frac{0.65}{\sqrt{31}} = 1.65$$

$$e^{1.65} = 5.19$$

T statistic at 0.05 level and 30 degrees of freedom

Data Below the Detection Limit

- In many cases, sample results will be below the analytical instrument's detection limit.

- If you have BDLs in your sample set, you must handle them appropriately with statistics. You can not just neglect them; they say something valuable about the data.

Options for Handling Samples Below the Detection Limit

- Assume to be zero
- Assume to be the detection limit
- Assume to be ½ the detection limit
- Other more rigorous statistical approaches

Conclusion:

In this chapter, goal was to make the students familiar with the different units used to measure pollutant levels in water, soil, atmosphere and global systems.

Conclusion

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Thank you