

Lecture 1

Introduction to Environmental Contaminant Fate and Transport: Basic Concepts and Physics Review, Mass Balance and the Control Volume and Advective and Fickian Transport

EOH 2122 TRANSPORT & FATE OF ENVIRONMENTAL AGENTS

MW 5-6:20 A216 Public Health Bldg.

Conrad (Dan) Volz, DrPH, MPH

Bridgeside Point

100 Technology Drive

Suite 564, BRIDG

Pittsburgh, PA 15219-3130

office 412-648-8541 : cell 724-316-5408: Fax 412-624-

3040

cdv5@pitt.edu

Assistant Professor, Environmental and Occupational

Health, University of Pittsburgh, Graduate School of Public Health

<http://www.pitt.edu/~cdv5/> ; Director-Center for Healthy Environments and

Communities <http://www.chec.pitt.edu>;

Director, Environmental Health Risk Assessment Certificate

Program <http://www.publichealth.pitt.edu/interior.php?pageID=82>

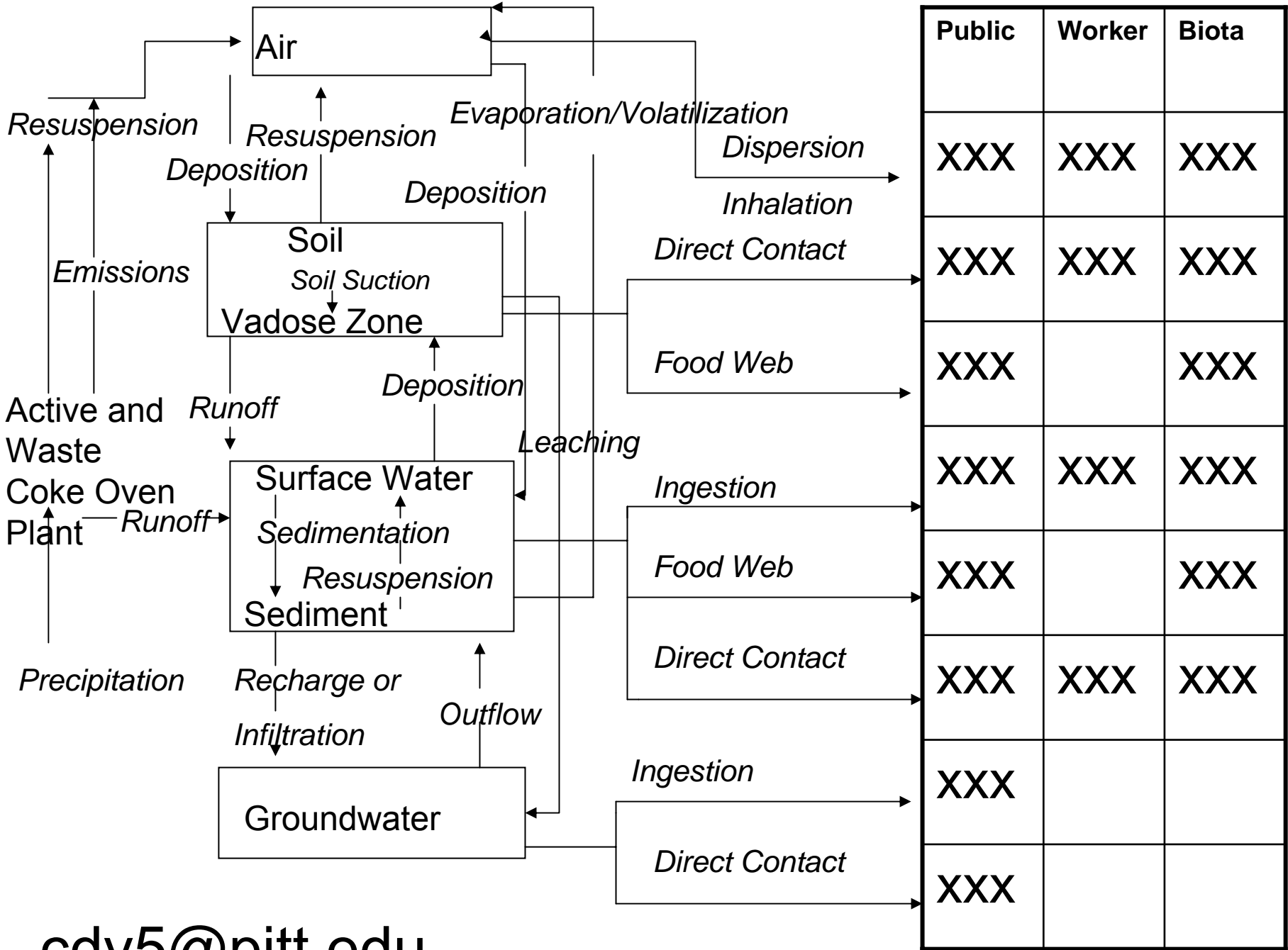
Definitions

- Chemical Transport- Processes that move chemicals through environmental media.
- Chemical Fate- The eventual disposition of a chemical contaminant. This can include destruction or long term storage in a sink and/or exposure-biotransformation in ecological and human receptors.

Definition of Environmental Media -

- Air
- Surface Water
- Sediment
- Groundwater-Saturated Zone
- Soil-Topsoils
- Subsurface area-Vadose Zone-
Unsaturated Zone
- Food Chain

cdv5@pitt.edu



cdv5@pitt.edu

Why study the fate and transport of environmental contaminants?

- Chemicals released into the environment do not respect media boundaries or political boundaries.
- Exchanges continually occur between different environmental media so modeling transport within only one medium will not completely describe the chemicals fate.
- Knowledge of the principals of fate and transport allows predictive capability of the movement of chemicals for both environmental monitoring validation and development of engineering, institutional and/ or administrative controls.

Chemical Concentration

- The chemical concentration is the measure of the mass of a chemical in a specific volume or mass of air, water, soil etc. In our work it will be defined as C .
- $[M/L^3]$ units in text where M is mass and L is length-further T is time.

Units of Concentration

- Water
 - Most common expression of concentration is mass of chemical per unit volume of water or { Mass/Length³}, in the textbook referred to as [M/L³]. Common units are mg, μg per cm^3 or per liter of water.
 - Molarity, M , is the number of moles of a chemical per liter of water, mol/l. Where a mole is 6.02×10^{23} atoms or molecules

Units of Concentration

- Water
- -Normality (n) refers to the number of equivalents of a chemical per liter of water, where an equivalent is the amount of chemical that possesses or transfers one mole of electronic charge. So normality

$N = \#$ of electronic charge units per mole/liter

Example: a mole of sulfate SO_4^{-2} is 2 equivalents and a 1 M solution of Na_2SO_4 is 2 N.

Units of Chemical Concentration

- Water
- - Unitless parts per million by volume { ppm (v) } can also express chemical concentration in water.
- Since 1 g/cm^3 is the density of water than 1 ppm is 1 mg/liter of water.

Units of Chemical Concentration

- Soil
 - Expressed in mass per unit volume of soil $[M/L^3]$, commonly mg/cm^3 or g/m^3 .
 - But this is a problem as soil can be compressed or expanded so the best way to describe concentration is mass chemical/ mass soil.
 - $C = mg_{\text{chemical}} / kg_{\text{soil}}$
 - Unitless ppm (w) is $mg_{\text{chemical}} / kg_{\text{soil}}$ and ppb is $\mu g_{\text{chemical}} / kg_{\text{soil}}$.

Units of Chemical Concentration

- Air
- -chemical concentration is commonly expressed as mass of chemical per unit volume of air $[M/L^3]$, such as mg/m^3 or mg or μg / liter
- But this is a problem again because the volume of a given mass of air changes according to the ideal gas law with temperature and pressure.
- Best to describe concentration in $[M \text{ such as } mg_{\text{chemical}} / M \text{ such as } kg_{\text{air}}]$.

Units of Chemical Concentration

- Air concentration can be expressed in ppm (v).
So 1 ppm of helium in air is 1ml Helium per 1000 liters (1 m³) air.

ppm of chemical in air =

(mg/m³) (24.45)/gram molecular weight of
substance

This conversion is based on a barometric pressure of 760 torr and 25° C temperature. Can use the ideal gas law as we shall see to adjust volumes to changing temperatures and pressures.

Review-Mass

- Mass-determined by measuring the force exerted on an amount of a substance by gravity or by inertia.
- SI units of mass are the gram (g) and kilogram (k).
- The pound (lb) still in use in the English system is really a unit of force-a pound of soil is that amount that gravity exerts one pound of force on.
- In our text mass is referred to as [M].

Review- Length and Time

- SI units of meter (m) and centimeter (cm).
- English unit is the foot (ft)
- Table A-2, page 416, gives units of length and interconversion factors and page 417, Table A-3 gives multiplier prefixes for SI unit use.
- Time-SI unit is the second (sec) but useful to use hours, days, years and 70 year lifetime.

Review, Area and Volume

- Area is defined in text as $[L^2]$ and is commonly expressed as square meters (m^2).
- Table A-4, page 418 presents other area units and interconversion factors { ft^2 , acre, mi^2 , are commonly used}.
- Volume in text is defined as $[L^3]$. Common SI unit is cubic meter (m^3) but in environmental chemistry the liter is often used. 10^{-3} liters = $1 m^3$, interconversion volume factors are on page 418, table A-5.

Force

- Force $F = \text{mass [M]} * \text{acceleration [L/T}^2\text{]}$.
- F in dynes (*dyn*) is in units $[\text{ML/T}^2]$. 1 dyn is the amount of force that gives a gram of mass an acceleration of 1 cm/sec².
- Newton (*N*) is the force required to accelerate 1 kg of mass at a rate of 1 m/sec².
- A kg- force is 9.8 N, the weight of a mass of 1 kg at the earths surface. Table A-6, page 419 has force interconversion factors.

Pressure

- *Pressure is force per unit area and SI unit is Pascal which is N/m².*
- *Since 1N= 1kg-m/sec². than:*

$$\text{Pascal} = 1\text{kg}\cdot\text{m}/\text{sec}^2 / \text{m}^2 = 1\text{kg}/(\text{m}\cdot\text{sec}^2)$$

$P = F / (L^2)$ or $[ML/T^2] / [L^2] = [M/LT^2]$, pressure is often expressed in $\text{kg}/(\text{m}\cdot\text{sec}^2)$.

-Other pressure units are mm Hg, atm=760 mm Hg, barr and psi. Interconversion units are given in Table A-7, page 419.

Energy

- Energy is the capability to perform work can be potential or kinetic.
- SI unit is the joule (J).
- 1J = energy conveyed by a force of 1N exerted over a distance of 1 m- units commonly in $\text{kg} \cdot \text{m}^2/\text{sec}^2$).
- Book notation $[\text{ML}^2/\text{T}^2]$

Power

- Power is the rate at which energy is transferred so has dimensions of $[ML^2/T^3]$.
- 1 Watt (W) = 1 J/sec, Table A-9 has power interconversion factors, page 420.

Atomic and Molecular Weight

- The atomic weight of an element is equal to the mass in grams of a mole (6.02×10^{23} atoms) of the element.
- The molecular weight (MW) of a molecule is the sum of the atomic weights of all its elements

Gas Constant

- Important constant in the Ideal Gas Law
- $PV = nRT$

Where P is pressure, V is volume, n is the number of moles of a chemical, R is the gas constant and T is absolute temperature (By international agreement, absolute zero is defined as precisely 0 K on the Kelvin scale, which is a thermodynamic (absolute) temperature scale, and -273.15 °C on the Celsius scale and -459.67 °F on the Fahrenheit scale).

8.31 J/(mol* K) is the SI Gas Constant

Mass Balance and Units

- Mass balance or mass conservation is an application of conservation of mass (matter cannot disappear or be created spontaneously) to the analysis of physical systems.
- By accounting for material entering and leaving a system, mass flows can be identified which might have been unknown, or difficult to measure without this technique.
- For a particular chemical present at a specific location at a certain time there are three possible outcomes
 - the chemical can remain in that location and/or
 - the chemical can be transported elsewhere and/or
 - the chemical can be transformed into another chemical.

Mass Balance and Units

- Control volume- any closed volume, across whose boundaries we propose to account for all transport of a chemical, and within whose boundaries we can account for all chemical initially present (stored) as well as all processes that produce (sources) or consume (sinks) the chemical.
- Common control volumes are lakes as shown in figure 1-2.

Mass Balance Expression

- Δ storage mass in control volume = mass transported_{in} - mass transported_{out} + mass produced by sources - mass consumed by sinks
- Also Rate of Δ in storage mass = $[M/T]_{in} - [M/T]_{out} + [M/T]_{sources} - [M/T]_{sinks}$.
- If all but one of the terms are known, or can be estimated, then the mass balance expression can be rearranged to determine an otherwise unmeasurable transport, source, or sink term.
- Steady state situations result in a net storage of 0.

Example 1-1, page 8

- Discharge pipe input rate= 20 kg/day butanol
- Stream input rate = 0
- Stream output rate = (storage in control volume) (streamflow @ outlet) = $(10^{-4} \text{ kg/m}^3) (3 \cdot 10^4 \text{ m}^3/\text{day}) = 3 \text{ kg/day}$
- Assume no internal sources of butanol=0
- Lake is at steady state at 10^{-4} kg/m^3 so rate of change of storage is 0.

$$0 = 20 \text{ kg/day} + 0 - 3 \text{ kg/day} + 0 - [\text{M/T}] \text{ sinks} \Rightarrow$$

$$[\text{M/T}] \text{ sinks} = 20 \text{ kg/day} - 3 \text{ kg/day} = 17 \text{ kg/day}$$

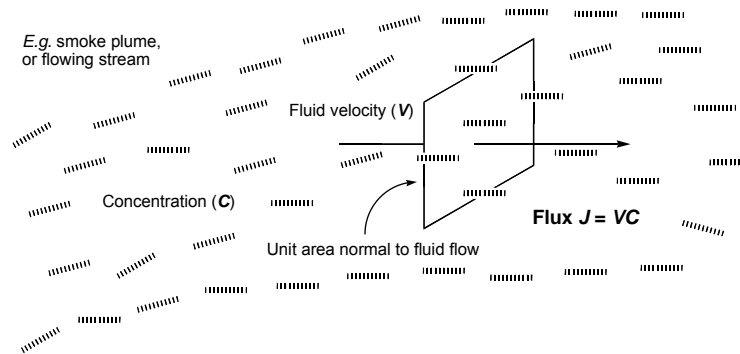
Internal sink process unknown-could be biodegradation, fish consumption or sequestration in sediments.

Physical Transport Mechanisms

- **Advection**- The bulk movement of fluids (air-water) from one place to another moves the chemical.
- Bulk movement of fluid in some particular direction is called advection; with prevailing winds and flowing streams being good examples. (direction-vector and velocity-magnitude)
- The term convection, stemming from density variation in different regions of a fluid, is sometimes used to describe vertical advection, as encountered in weather patterns and ocean currents.

Advection Continued

- In the context of advection, it is convenient to define flux density (J) as the mass of some chemical flowing across an imaginary surface of unit area per unit time.



Where V is velocity, and C is concentration. J is thus in units of $[M/L^2T]$

[you have to choose the particular consistent (!) system of units]; e.g. Ex. 1-2:

$$C = 20 \text{ mg/L} = 0.02 \text{ mg/mL} = 0.02 \text{ mg/cm}^3$$

$$J = (0.02 \text{ mg/cm}^3) \cdot (100 \text{ cm/s}) = 2.0 \text{ mg/cm}^2 \cdot \text{s}$$

Peterson, 2006

Fickian Processes

- **Fickian Transport**

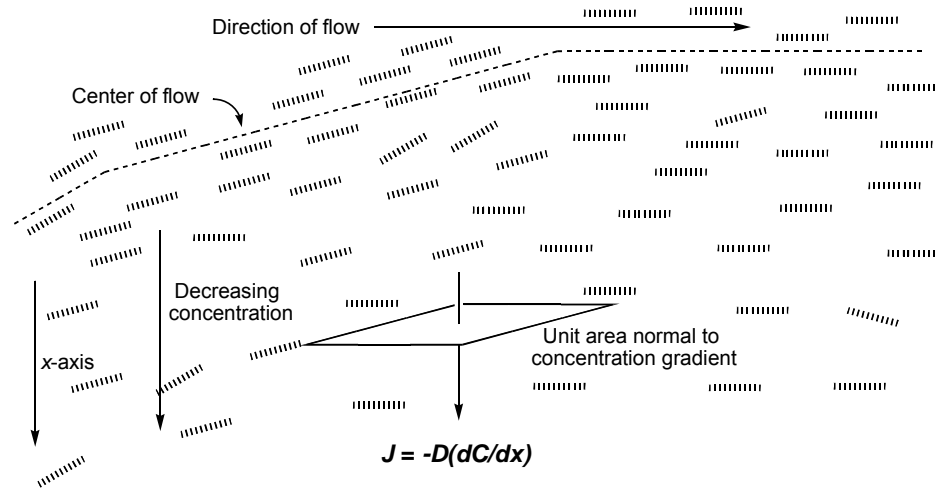
- Molecular diffusion- chemical moves, due to random molecular motion, from a location where its C is high to one where it is relatively lower. Usually practically less important than turbulent diffusion or dispersion below.
- Turbulent diffusion- random motion of the fluid (air – water) that carries the chemical. Eddy currents etc.
- Diffusive transport -Combination of molecular and turbulent diffusion.
- Dispersion- model transport as Fickian if movement is complex such as movement of water through soil.

Notes on Dispersive Transport

- Dispersion involves net movement of an agent down a concentration gradient by several mechanisms which all exhibit approximately “Fickian” behavior.
 - We are usually concerned with dispersion normal (perpendicular) to the prevailing direction of fluid flow; *i.e.* dispersion in conjunction with advection.
 - Turbulent diffusion by means of circulating eddy currents tangential to the flow is the dominant process.
 - Where it exists, mechanical dispersion (e.g. fluid flowing through a particle bed) is the next largest effect.
 - The true Fickian process of molecular diffusion is usually a minor contributor and any animal activity is insignificant most of the time.
- Peterson, 2006

Ficks First Law

- Fick's first law (in one dimension) is $J = -D(dC/dx)$ where J is now the dispersive flux density [M/L^2T], D is the Fickian mass transport coefficient- “diffusion” coefficient [L^2T], C is the concentration of the agent [M/L^3], x is the distance [L] and the minus sign shows the concentration gradient to be negative.
- D is called the a turbulent (or eddy) diffusion coefficient when it is because of fluid turbulence.



Peterson, 2006

- So if flux density has the units mass/(length²•time) and the concentration per distance must be mass/(length³•length), then the diffusion coefficient has to have units of length²/time.
- In the absence of more specific information, assume that most compounds exhibit a molecular diffusion coefficient of ~0.2 cm²/s in air and ~10⁻⁵ cm²/s in water.
- Using vector notation, Fick's first law can be expressed in three dimensions [$\mathbf{J} = -D\nabla C$, where $\nabla = (\partial/\partial x + \partial/\partial y + \partial/\partial z)$] but the one-dimensional version turns out to be pretty robust and applicable in a large number of instances; e.g. Ex. 1-3:
 25 ppm = (25 g/10⁶ g)•(1.2 g/1,000 cm³) = 3.0 x 10⁻⁸ g/cm³
 $dC/dz = (3.0 \times 10^{-8} \text{ g/cm}^3)/200 \text{ cm} = 1.5 \times 10^{-10} \text{ g/cm}^4$
 $J = (10^{-2} \text{ cm}^2/\text{s}) \cdot (1.5 \times 10^{-10} \text{ g/cm}^4) = 1.5 \times 10^{-12} \text{ g}/(\text{cm}^2\text{s})$
 $[1.5 \times 10^{-12} \text{ g}/(\text{cm}^2\text{s})] \cdot (10^6 \text{ cm}^2) \cdot (3,600 \text{ s/hr}) \cdot (24 \text{ hr/day}) = 0.13 \text{ g/day}$

Advection-Dispersion-Reaction Equation

- Considers the “control volume” to be a single point, where the rate of change of storage of some chemical agent, dC/dt , is the sum of the input and out put by physical means (advection and dispersion) and the rate of net internal production (sources minus sinks).
- In one dimension: $dC/dt = -[V \cdot (dC/dx)] + (d/dx)[D \cdot (dC/dx)] + r$, where r is the net input or output of the agent associated with internal sources or sinks – such as a biological process or chemical reaction.
- Again, in three dimensions the equation must be expressed using vector notation and becomes: $dC/dt = -\mathbf{V} \cdot \nabla C + \nabla \cdot D(\nabla C) + r$.
- Implicitly, we have so far assumed that D is isotropic, but this need not be the case; in particular, there are many circumstances when the value of this coefficient in the direction of flow is distinct from its value normal to the flow.

Homework

- This lecture includes 1.1 to 1.5.
- For next class read 1.6-1.65 and do problems p. 58 #3,4 and 59, #6.