Structure of Environmental Media

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ESM 222



Atmospheric Composition

| Gas | Concentration (µL L-1) | |
|---|---|--|
| Nitrogen (N ₂) | 780,840 | |
| Oxygen (O ₂) | 209,460 | |
| Argon (Ar) | 9,340 | |
| Neon + helium + krypton (Ne + He + Kr) | 24 | |
| . Variable gas concentra | ions in the atmosphere. | |
| Gas | Concentration (µL L-1) | |
| Water vapor (H ₂ O) | Saturation-10,000 | |
| | 355 | |
| Carbon dioxide (CO ₂) | 333 | |
| Carbon dioxide (CO ₂) Methane (CH ₄) | 1.5 | |
| Carbon dioxide (CO ₂) Methane (CH ₄) Hydrogen (H ₂) | 1.5 0.50 | |
| Carbon dioxide (CO ₂) Methane (CH ₄) Hydrogen (H ₂) Nitrous oxide (N ₂ O) | 1.5 0.50 0.27 | |
| Carbon dioxide (CO ₂) Methane (CH ₄) Hydrogen (H ₂) Nitrous oxide (N ₂ O) Ozone (O ₃) | 1.5 0.50 0.27 0.02 | |
| Carbon dioxide (CO ₂) Methane (CH ₄) Hydrogen (H ₂) Nitrous oxide (N ₂ O) Ozone (O ₃) Carbon monoxide (CO) | 1.5 0.50 0.27 0.02 <0.05 | |
| Carbon dioxide (CO ₂) Methane (CH ₄) Hydrogen (H ₂) Nitrous oxide (N ₂ O) Ozone (O ₃) Carbon monoxide (CO) Ammonia (NH ₃) | 1.5 0.50 0.27 0.02 <0.05 0.004 | |
| Carbon dioxide (CO ₂) Methane (CH ₄) Hydrogen (H ₂) Nitrous oxide (N ₂ O) Ozone (O ₃) Carbon monoxide (CO) Ammonia (NH ₃) Nitrogen dioxide (NO ₂) | 1.5 0.50 0.27 0.02 <0.05 0.004 0.001 | |
| Carbon dioxide (CO ₂) Methane (CH ₄) Hydrogen (H ₂) Nitrous oxide (N ₂ O) Ozone (O ₃) Carbon monoxide (CO) Ammonia (NH ₃) Nitrogen dioxide (NO ₂) Sulfur dioxide (SO ₂) | 1.5 0.50 0.27 0.02 <0.05 0.004 0.001 0.001 | |
| Carbon dioxide (CO ₂) Methane (CH ₄) Hydrogen (H ₂) Nitrous oxide (N ₂ O) Ozone (O ₃) Carbon monoxide (CO) Ammonia (NH ₃) Nitrogen dioxide (NO ₂) Sulfur dioxide (SO ₂) Nitric oxide (NO) | 1.5 0.50 0.27 0.02 <0.05 0.004 0.001 0.001 0.0005 | |

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Atmosphere □ Pollutants of concern in the atmosphere are: Urban air pollutants: $\Box O_3$ via NO_x and VOCs, CO, NO_x, SO₂, particulates, HAPs, ... □Acid rain gases: ■NO_x, SO₂, ... Greenhouse gases: $\Box CO_2$, CH_4 , N_2O , CFCs, ... □Ozone destroyers in stratosphere: **CFCs**, ... ESM 222 © ARTURO KELLER







Atmosphere

- □ Atmospheric boundary layer
 - Height of boundary layer varies throughout day, with maximum thickness by midafternoon
 - Boundary layer shrinks to about 100 to 200 m at night
 - Thermal "inversion" may cause trapping of pollutants in boundary layer, reducing the mixing depth













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1/









| The following is a list of U user is referred to the Gui | J.S. EPA approved Appendix A | Constants |
|---|--|--|
| user's guide (see the follow | deline on Air Quality Models ving references) to select and ap | A guideline models and their intended application. The (U.S. EPA 1978; 1986; 1987; 1993) and the appropria pply the appropriate model. |
| Mode | Model | Reference |
| | | |
| Both | SCREEN3 | U.S. EPA 1988; 1992a |
| Both | ISC3 | Bowers, Bjorklund, and Cheney |
| D - sh | TECHTEN | 1979; U.S. EPA 1987; 19920; 1995 |
| Dotti | RAM | U.S. EFA 17700 Turner and Novak 1978- |
| Orban | No LON | Catalano, Turner, and Novak 1987 |
| Rural | COMPLEXI | Chico and Catalano 1986; Source code. |
| Urban | SHORTZ | Bjorklund and Bowers 1982 |
| Rural | RTDM3.2 | Paine and Egan 1987 |
| Rural | VALLEY | Burt 1977 |
| Both | CTSCREEN | U.S. EPA 1989; Perry, Burns, and Cinnorelli 1990 |
| Both | BLP | Schulman and Scire 1980 |
| | | |
| Urban | RAM | Turner and Novak 1978; Catalano, Turner, and Novak 1987 |
| Both | ISC3 | Bowers, Bjorklund, and Cheney 1979; U.S. EPA 1987; 1992b; 1995 |
| | EDMS | Segal 1991; Segal and Hamilton 1988; Segal 1988 |
| Urban | CDM2.0 | Irwin, Chico, and Catalano 1985 |
| Both | CTDMPLUS | Paine et al. 1987; Perry et al. 1989; U.S. EPA 199 |
| Both | BLP | Schulman and Scire 1980 |
| Both | CALINE3 | Benson 19/9 |
| (irban | UAM-V | U.S. EPA 1990a |
| | Mode Both Both Urban Rural Urban Rural Both Both Urban Both Urban Both Both | Mode Model Both SCREEN3 Both ISC3 Both TSCREEN Urban RAM Rural COMPLEXI Urban SHORTZ Rural VALLEY Both CTSCREEN Both CTSCREEN Both BLP Urban RAM Both ISC3 Urban CDM2.0 Both CDM2.0 Both BLP Both BLP Both BLP |

Atmospheric Structure

 Aerosols & Particulate Matter
 dust particles from soil
 dust from combustion
 water (fog to rain drops)
 aggregated particles from conversion of gas species to aqueous species (e.g. SO₂ to HSO⁻₄)
 Concern with particles from ~1

to 10 microns

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Concentrations

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- **Ω** Rural area typically 5 µg/m³
- Urban area may have more than 100 μg/m³
- Density of particles: 1000 -2600 kg/m³
- Aerosols may be hydrophilic, hydrophobic (if mostly organic) or mixed
- Contribute significantly to dry or wet deposition of pollutants to ground surface, as well as reaction sites















| - | Soi | I structure | |
|----|----------|---|--|
| | USI | DA definition | |
| | Particle | Size range (diameter) | |
| | Gravel | > 2 mm | |
| | Sand | 0.05 to 2 mm | |
| | Silt | 0.002 to 0.05 mm | |
| | Clay | $< 0.002 \text{ mm} (= 2 \ \mu \text{m})$ | |
| | | | |
| | | | |
| | | | |
| | | | |
| 33 | | ECN 3/3 © YBJIRO VE | |













Soil Organic Matter (SOM)

 soil biomass (live bugs)
 organic residues (decaying plant and microbial biomass)
 humic substances (high molecular weight organic macromolecules, very slow decay ~ 2%/yr)
 amino acids, organic acids, carbohydrates, fats



- Soil Organic Matter
 In humid areas, SOM up to 5% on a dry-weight basis
 In arid areas, with low inputs of plant residues
 - inputs of plant residues, SOM typically < 1%
 - Significant natural recycling of nutrients via formation of SOM and its decomposition

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Soil Structure - Biotic Activity

- Factors Affecting Growth of Microbes
 - Biotic stress competition (e.g. pathogens)
 - Soil moisture
 - Temperature and its fluctuations
 important in bioremediation at higher latitudes
 - Soil pH

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- Soil carbon, nitrogen and nutrients
- Soil redox potential (i.e. aerobic or anaerobic conditions)

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Structure of Water Bodies

- □ Rivers and streams
 - Hydraulic properties: flow, velocity, dispersion
 - Geometric properties: depth, width, slope
 - Properties change frequently over the course of river
 - Temporal distribution of water flow: annual hydrograph
 - Perennial vs. ephemeral flow; baseflow

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| Structure of Water |
|--------------------|
| Bodies |

TABLE 14.1

Hydrogeometric parameters for a range of rivers ordered by flow (Fischer et al. 1979)











Structure of Water Bodies

Reach estimates

Assumption that width is less variable than depth

Easier to measure width along river

Determine flow at a point along river

Measure travel time, t, using a tracer (dye)

 $\Box Mean velocity is U = x/t$

Average cross-sectional area from velocity and flow rate, $A_c = Q/U$

 \Box Mean depth, H = A_c/B



Structure of Water Bodies

EXAMPLE 14.2. REACH ESTIMATION OF VELOCITY AND MEAN DEPTH. Suppose that the point estimate calculated in Example 14.1 is at the downstream end of a 2-km reach with a mean width of 22 m. Recall that the point estimate of flow was 2.3105 m³ s⁻¹. You perform a dye study and determine that it takes 3.2 hr for the dye to traverse the 2 km. Use the reach approach to determine the velocity, cross-sectional area, and mean depth for the reach.

Solution: The mean velocity can be calculated as (Eq. 14.10)

$$U = \frac{2 \text{ km}}{3.2 \text{ hr}} \left(\frac{1 \text{ hr}}{3600 \text{ s}} \frac{1000 \text{ m}}{\text{ km}} \right) = 0.1736 \text{ m s}^{-1}$$

The velocity and flow rate can then be used to determine the average cross-sectional area according to Eq. 14.11,

$$A_c = \frac{2.3105}{0.1736} = 13.3 \text{ m}^2$$

which can then be used to determine the mean depth (Eq. 14.12),

$$H = \frac{13.3}{22} = 0.605 \,\mathrm{m}$$

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Source: Surface Water Quality Modeling, Chapra, 1997



Structure of Water Bodies

- Very different mixing behavior than in rivers
- Typically long residence times (years)
- Light only penetrates 1-2 m, so photosynthetic activity limited to thin surface layer
- Seasonal variation in temperatures has a significant effect on mixing













Structure of Water Bodies

- Stratification may last several months with little mixing among layers
- Bottom conditions may become anaerobic
- □ If organic matter, nitrogen and/or phosphorus loading is large, even epilimnion may become anaerobic resulting in eutrophication
- In autumn, turnover of lake may result in the remobilization of pollutants

Structure of Water Bodies

- MTBE study findings
- ■Watercraft release up to 25% unburned gasoline with MTBE
- High concentrations only in surface layer (40-50 ppb)
- Bottom is below 5 ppb
- Can draw water from below but have problems with dissolved gases (H₂S) from anaerobic degradation

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- Large regional to global circulation patterns result in significant transport and mixing horizontally in short time
- Vertical currents may also result in significant mixing among layers but on very long time frames
- Topography and structure of ocean floor is a significant factor in mixing

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Oceans

- Salinity and Temperature gradients serve to stratify the ocean so that vertical mixing is slow
- Biota can contribute significantly to the "dispersion" of some pollutants due to uptake, accumulation and bioconcentration (e.g. DDT, PCBs)

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Sediments

- Bottom of lakes and oceans has a very active (fluffy) layer, the benthic region, typically 95% water and 5% particles, with high organic content
- ❑At greater depths, water content decreases to ~50%
- The benthic region may be aerobic or anaerobic (anoxic), which has an impact on inorganic substances (metals, arsenic); organic material is decomposed by either microbial community, at different rates

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Structure of Water Bodies

Sediments

- Most active area is top 5 cm, but deeper sediments also participate in degradation and/or storage of organic and inorganic pollutants (e.g. PCBs, metals)
- Deposition is a cyclic process, with frequent resuspension.
 Typical net rates are 1 mm/yr.
 For a sediment depth of 5 cm, this requires 50 years to bury an average particle.
- Toxic chemicals may desorb from the particles before burial



Particulate Matter

- Chemicals may sorb into the particles
- May consist of mineral matter (silica, clay, carbonates)
- Usually contains decaying organic matter, which is usually lipophilic but may also contain some acidic portion (e.g. humic acids)
- Sometimes arbitrarily distinguish between particulate and "dissolved" using a mesh or filter of around 0.45 μm



□ Particulate Matter

- Typically have about 7.5 g/m³ of particulate matter, with 33% organic matter (density ~ 1000 kg/m³) and 67% mineral (density ~ 2000 kg/m³)
- Deposition velocities vary significantly depending on water body and mixing conditions but typically range from 0.5 to 2 m/day
- Biota (from plankton to fish and mammals) represent about 1 ppmv, with an average lipid (fat) content of ~ 5%

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Patterns of deposition of fine sediments in natural waters. (a) Top view of river; (b) side

view of estuary; (c) top view of lake; and (d) side view of impoundment.

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FIGURE 17.1

Source: Surface Water Quality Modeling, Chapra, 1997

Sediments

TABLE 17.1

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Suspended solids concentrations encountered in natural waters and sewage (from Di Toro et al. 1971, O'Connor 1988c, Lung 1994, Thomann and Mueller 1987)

| Syste | m | Suspended solids (mg L ⁻¹) |
|---------|--|---|
| Great | Lakes: | |
| Sup | erior/Huron | 0.5 |
| Sag | inaw Bay | 8.0 |
| We | stern Lake Erie | 20.0 |
| Flint I | River, Michigan | 8-12 |
| Rapid | Creek, South Dakota | 158 |
| Clinto | n River, Michigan | 10-120 |
| Hudso | on River, NY | 10-60 |
| Potom | ac Estuary | 5-30 |
| James | Estuary, Virginia | 10-50 |
| Sacran | mento-San Joaquin Delta, | 50-175 |
| - Cai | 11.571 11144 | |
| Raw s | TABLE 17.2 Densities of water | 300 |
| Raw s | ewage TABLE 17.2 Densities of water particulate matter | and |
| Raw s | TABLE 17.2 Densities of water particulate matter Substance | and Density (g cm ⁻³) |
| Raw s | TABLE 17.2 Densities of water particulate matter Substance Water | 300 and Density (g cm ⁻³) |
| | TABLE 17.2 Densities of water particulate matter Substance Water Organic matter | 300 and Density (g cm ⁻³) 1 |
| | TABLE 17.2 Densities of water particulate matter Substance Water Organic matter Wet-weight basis | 300 and Density (g cm ⁻³) 1 1.02-1.1 |
| | TABLE 17.2 Densities of water particulate matter Substance Water Organic matter Wet-weight basis Dry-weight basis | 300 and Density (g cm ⁻³) 1 1.02–1.1 1.27 |
| | TABLE 17.2 Densities of water particulate matter Substance Water Organic matter Wet-weight basis Dry-weight basis Siliceous minerals | 300 and Density (g cm ⁻³) 1 1.02–1.1 1.27 2.65 |

Sediments $v_s = \alpha \frac{g}{18} \left(\frac{\rho_s - \rho_w}{\mu} \right) d^2$ (17.1) where $v_s =$ settling velocity (cm s⁻¹) α = a dimensionless form factor reflecting the effect of the particle's shape on settling velocity (for a sphere it is 1.0) $g = \text{acceleration due to gravity } (= 981 \text{ cm s}^{-2})$ ρ_s and $\rho_w = \text{densities of the particle and water, respectively } (g \text{ cm}^{-3})$ μ = dynamic viscosity (g cm⁻¹ s⁻¹) d = an effective particle diameter (cm) Thomann and Mueller (1987) have reexpressed Stokes' law in a convenient form, $v_s = 0.033634\alpha(\rho_s - \rho_w)d^2$ (17.2) 100 ρ = 2.65 Velocity (m d⁻¹) ⁶⁹ ⁰⁹ 2 1.5 1.25 1.027 0 100 20 40 60 80 0 Diameter (mm) FIGURE 17.3 Plot of setting velocity versus diameter for various levels of particle density. This figure assumes that the particles are perfect spheres ($\alpha = 1.0$ and d = diameter). 74 Source: Surface Water Quality Modeling, Chapra, 1997



Sediments

TABLE 17.3

Settling velocities of particles found in natural waters (Wetzel 1975, Burns and Rosa 1980)

| Particle type | Diameter (µm) | Settling velocity (m d ⁻¹) | |
|----------------------------|------------------|---|--|
| Phytoplankton: | | | |
| Cyclotella meneghiniana | 2 | 0.08(0.24) [†] | |
| Thalassiosira nana | 4.3-5.2 | 0.1-0.28 | |
| Scenedesmus quadricauda | 8.4 | 0.27(0.89) | |
| Asterionella formosa | 25 | 0.2(1.48) | |
| Thalassiosira rotula | 19-34 | 0.39-2.1 | |
| Coscinodiscus lineatus | 50 | 1.9(6.8) | |
| Melosira agassizii | 54.8 | 0.67(1.87) | |
| Rhizosolenia robusta | 84 | 1.1(4.7) | |
| Particulate organic carbon | 1-10 | 0.2 | |
| - | 10-64 | 1.5 | |
| | > 64 | 2.3 | |
| Clay | 2–4 | 0.3-1 | |
| Silt | 10-20 | 3-30 | |

[†]Parenthetical numbers are for the stationary phase (see Lec. 32 for an explanation of the different phases of microbial growth).

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Source: Surface Water Quality Modeling, Chapra, 1997



