Environmental Water Quality
BAE 452/552

Session 12

Atmospheric Deposition

Atmospheric Deposition

Many (severe) diffuse pollution source from atmosphere

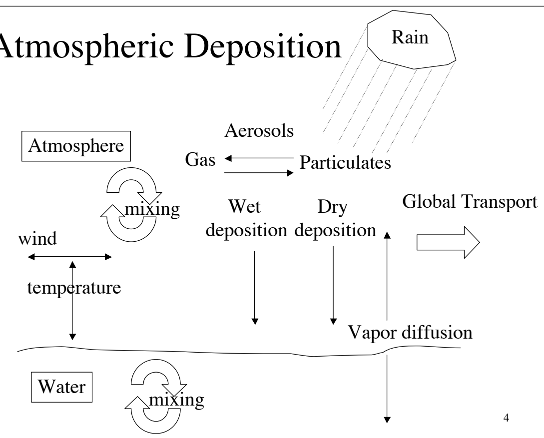
- SO_2 + NO_2 from coal burning + cars: acid rain
- S_2, metals, pesticides, toxic organics, fungi, pollen, soil, ash, nutrients, tar aerosols
- oxides, nitrites, nitrates, chlorides, fluorides, fluorocarbons, ozone, silicates.

Atmospheric Deposition

Atmospheric Pollutants consist of gases and aerosols or atmospheric particulates ($6\text{x}10^{-4}$ to 10^3 μm)

- Dust: particles not water soluble
- Aerosols: also contain water soluble materials
- Aerosols may be formed by precipitation, absorption, and chemical reactions.

Atmospheric Deposition



Sources of Air Pollution

- Industrial and urban: (burning, cars)
- Agricultural and forest: (soil, fires, fertilizers, pesticides, farm wastes)
- Natural (dust, fires, volcanic)

Clean Air Act: control of emissions such as SO_2 and NO_2 (http://www.epa.gov/air/oaq_caa.html)

Global Transport of Pollutants

- Mass balance: $\frac{dM}{dt} = Q - S(M)$

where
M = global mass of the pollutant in the atmosphere
Q = global source strength for the pollutant
S(M) = global sink of the pollutant

Global Transport of Pollutants

- For time-scale on order of years: $Q_{ss} = S(M)$

where
Q_{ss} = steady state source of the pollutant
$S(M)$ = global sink of the pollutant

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Sinks of Atmospheric Pollution

- Deposition (dry + wet) on land and water surfaces
- Adsorption on land and water surfaces
- Decomposition by atm chemical + photochemical processes
- Emissions into stratosphere

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Global Transport of Pollutants

- Removal rate: $S(M) = v_d x C_M$

where
v_d = depositional velocity (m day^{-1})
C_M = average global (background) concentration of the pollutant

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Global Transport of Pollutants

- Residence time: $T = \frac{M}{S(M)} = \frac{C_M V_A}{v_d C_M A_G} = \frac{H}{v_d}$

where
A_G = global surface area
V_A = volume of atmosphere within mixing layer
H = average depth of the surface air boundary (about 1000 m)

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Global Transport of Pollutants

- Most effective natural removal process is attachment of pollutants to atm. aerosols + removal by dry and wet deposition (sea is final sink)
- Aerosols are particles with water soluble components (not dust)

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Global Transport: Example

Background (steady-state) of "inert" pesticide: C_M = 0.1 ng m^{-3} (= 10^{-10} g m^{-3}). World-wide production of the pesticide is ~1000 tonnes yr^{-1} (=10^9 g yr^{-1}) from which 40% is lost to atmosphere during/after application.

Estimate average residence time and deposition velocity of the pesticide. Assume H = 3000 m.

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Global Transport: Example

Solution: $T = \frac{M}{S(M)} = \frac{M}{Q} = \frac{C_M V_A}{Q}$

Atmospheric input: Q =$0.4x10^9$ g yr^{-1}=$4x10^8$ g yr^{-1}

H = 3000 m, C_M=10^{-10} g m^{-3}

Volume of mixing layer (earth radius r = $6.3x10^6$ m):

$V_A = 4\pi r^2 H = 4\pi(6.3x10^6)^2 x3000 = 1.5x10^{18}$ m^3

$$T = \frac{C_M V_A}{Q} = \frac{10^{-10} x1.5x10^{18}}{4x10^8} = 0.375yr = 137days$$

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Global Transport: Example

Solution: $T = \frac{H}{v_d}$

T = 0.375 years

H = 3000 m

$$v_d = \frac{H}{T} = \frac{3000}{0.375} = 8000 m \cdot yr^{-1}$$

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Atmospheric Deposition

Removal of particles (aerosols and dust):

- Dry deposition by sedimentation
- Removal by precipitation
- Dry deposition by impact on vegetation and rough surfaces

Removal of gases:

- During precipitation, absorption at earth surface, and adsorption by aerosols↓

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Dry Deposition

- Important for removal of gases and airborne particles
- Data on dry deposition are sparse
- Force of gravity (diameter > 5 μm)
- Electrostatic attraction, adsorption, chemical interaction
- Greatest in and near urban areas

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Dry Deposition

- Rate of deposition of aerosol particles:
- $D_d = v_d C(x,y,z)$

where

D_d = amount of aerosols removed per unit area per unit time (g $m^{-2}day^{-1}$)

C(x,y,z) = average concentration of aerosols at x,y,z locations from the source (g m^{-3})

v_d = deposition velocity of particles (m day^{-1})

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Dry Deposition

- For gravitational settling: use Stoke's Law:

$$v_d = \frac{g(ad)^2(\rho - \rho_a)}{18\mu}$$

v_d = settling velocity (cm sec^{-1})

a = conversion factor (10^{-4})

g = acceleration of gravity (981 cm s^{-2})

ρ_s = density of particle (~2 g cm^{-3})

ρ_a = density of air (0.001243 g cm^{-3})

μ = dynamic viscosity ($1.77x10^{-4}$ g cm^{-1} s^{-1} @10°C)

d = an effective particle diameter (μm)

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Dry Deposition

- For particles < 5 μm, v_d of 0.1 to 0.5 cm sec^{-1} have been suggested for trace organics
- Pollutant Loading (g sec^{-1}): $L = v_d C\ A\ f$

where

C = concentration of atm. particulates (g m^{-3})

A = projected receptor area (m^2)

f = fraction (by mass) of the pollutant adsorbed to the particulates

Dry Deposition

- Gas phase pollutant loading (g sec^{-1}): $L = v_d C\ A$

where

C = ambient concentration of gas phase pollutant (g m^{-3})

A = projected receptor area (m^2)

v_d = gas deposition velocity (m sec^{-1})

Wet Deposition

- by rain and snow: "P scavenging"
- pollutants: acidity, toxic metals, org. chem., phosphates + nitrogen compounds
- acifidication of lakes, fish kill, cation leaching from soils (Al), and from urban infrastructure
- contamination within clouds: rainout/snow out

  below clouds: wash out

Wet Deposition

- Gaseous chemicals in the atmosphere can be removed by dissolving into rain droplets, if sufficient time is available:
- $C_{liquid} = C_{air}/H$

where H is dimensionless Henry's Law constant

- Particulate chemicals are included during nucleation

Wet Deposition

Washout function:

- Scavenging of pollutants by raindrops during washout (or rain out) $\frac{dC_w}{dt} = -\lambda C_w \longrightarrow C_w = C_{w,o} e^{-\lambda t}$
- where
- C_w = pollutant concentration after rain (g m^{-3})
- $C_{w,o}$ = pollutant concentration before rain (g m^{-3})
- T = duration of rain (sec)
- λ = the washout coefficient (~10^{-4} sec^{-1}): $\lambda = 10^{-4} i^{0.53}$ (i=rainfall intensity in mm/hr)

Wet Deposition

Wet fallout per unit area:

$$D_w = (C_{w,o} - C_w)H = C_{w,o}(1 - e^{-\lambda t})H$$

where H is atmospheric mixing depth (m)

Pollutant concentration in rain water (mg L^{-1}):

$$C_{rain} = \frac{D_w}{V_R}$$

where V_R is rain volume (m^3 m^{-2} x 1000 L m^{-3})

Wet Deposition

Mass Load (g sec^{-1}):

$$L = 10 C_{rain} I\ A$$

where

I = cm sec^{-1}

A = projected area (m^2)

Wet Deposition: Example

Atmospheric concentration of phosphate before rain $C_{w,0}$ = 1 μg m^{-3}

Depth of mixed atm layer = 1000 meters

Estimate amount of wet fallout during a storm with a volume of 10 mm lasting 2 hours, on a 5 ha area.

Wet Deposition: Example

Solution:

$$\lambda = 10^{-4} i^{0.53} = 2.35 \cdot 10^{-4} (1/\sec) = 0.846 (1/\mathrm{hr})$$

$$i = \frac{10\mathrm{mm}}{2\mathrm{hr}} = 5\mathrm{mm/hr}$$

Wet Deposition: Example

Mass of fallout (“wash out”) per unit area is :

$C_{w,0}$ = 1 μg m^{-3}

$$D_w = C_{w,o}(1 - e^{-\lambda t}) \cdot H$$

$$= 1(1 - e^{-0.846 \cdot 2}) \cdot 1000 = 816 \mu g \cdot m^{-2}$$

$$= 0.816 mg \cdot m^{-2}$$

Wet Deposition: Example

phosphate concentration in rainwater :

$$C_{rain} = \frac{D_w}{V_R} = \frac{0.816 mg \cdot m^{-2}}{0.010 m^3 \cdot m^{-2} x 1000 L \cdot m^{-3}} = 0.082 mg \cdot L^{-1}$$

Rain volume = 10 mm = 0.01 $m^3 m^{-2}$

Mass Load:

$$L = 10 C_{Rain} I \cdot A$$

$$= 10 \cdot 0.082 \cdot 1.39 \cdot 10^{-4} \cdot 50.000 = 5.67 mg \cdot sec^{-1}$$