

BAE 820 Physical Principles of Environmental Systems

Fate and transport of pollutants in the air environment

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Units for atmospheric species

- Concentration:
 - The amount (or mass) of a substance in a given volume divided by that volume.
 - Expressed as mole/m³, μg/m³, ...
- Mixing ratio:
 - The ratio of the amount (or mass) of the substance in a given volume to the total amount (or mass) of all constituents in that volume.
 - Expressed as ppm, ppb, ...

Conversion between units

At T(K), P(Pa)	At $T_0=298\text{K}$, $P_0=1.013\times 10^5\text{Pa}$
$C(\text{mole}/\text{m}^3, P, T) = P/(8.314\times T)$	$C(\text{mole}/\text{m}^3) = 40.89$
$C(\text{ppm})=C(q, \text{mole}/\text{m}^3)/ C (\text{mole}/\text{m}^3)\times 10^6$	$C(\text{ppm})=C(q, \text{mole}/\text{m}^3)/40.89\times 10^6$
$C(\mu\text{g}/\text{m}^3)=C(\text{ppm})\times P\times M_q/(8.314\times T)$	$C(\mu\text{g}/\text{m}^3)=C(\text{ppb}) \times M_q/24.45$

At $T_0=298\text{K}$, $P_0=1.013\times 10^5\text{Pa}$

1 ppb $\text{SO}_2=2.61\mu\text{g}/\text{m}^3$,

1 ppb $\text{H}_2\text{SO}_4=4.01\mu\text{g}/\text{m}^3$,

Emissions

- Phase change
 - Gaseous emissions often involve phase change (e.g. volatilization), which will depend on gas properties, solution properties, and environmental conditions.
 - The intermediate products formed may partition between solid and liquid phases.
- Transformation
 - Transformation rates (reaction kinetics) are governed by environmental factors (e.g. temperature), substrate properties, and media properties (e.g. pH).
 - Transformation may result in formation of gaseous pollutants in the liquid phase (dissolved form).
 - Some of the gaseous may convert into other gaseous compounds or secondary PM.

Secondary PM

- Acidic mists
 - Main source of secondary PM is SO_2 some of which converts to H_2SO_4 vapor and mist.
 - Similarly other acidic mists such as HNO_3 and HCl are also formed.
- NH_3 aerosols
 - NH_3 (being a alkaline gas) will react with the acidic mists to form secondary PM, including NH_4NO_3 , NH_4Cl , NH_4HSO_4 , etc.
- Particles produced by gas-to-particle conversion generally are small and fall into the $\text{PM}_{2.5}$ size range.

Ozone and photochemical oxidants

- Photochemical reactions in the atmosphere produce a wide range of powerful oxidants. The most abundant of these photochemical oxidants is ozone (O₃),
- O₃ is not a pollutant directly emitted into the air and can be referred to as a secondary pollutant. O₃ and other photochemical oxidants are formed by photolysis reaction between NO_x and a wide variety of volatile organic compounds (VOCs) in the presence of sunlight.
- Photolysis: transformation of chemical specie due to absorption of a photon of light energy
 - Shorter wavelength (λ) have higher frequency (ν) and energy. $\lambda = c/\nu$.
 - Hitting a molecule with a UV photon (0.005-0.4 μ m) provides the energy to break a chemical bond and start a reaction sequence.

“Good ozone” and “bad ozone”

Ozone can be "good" or "bad" for your health and the environment, depending on its location in the atmosphere.

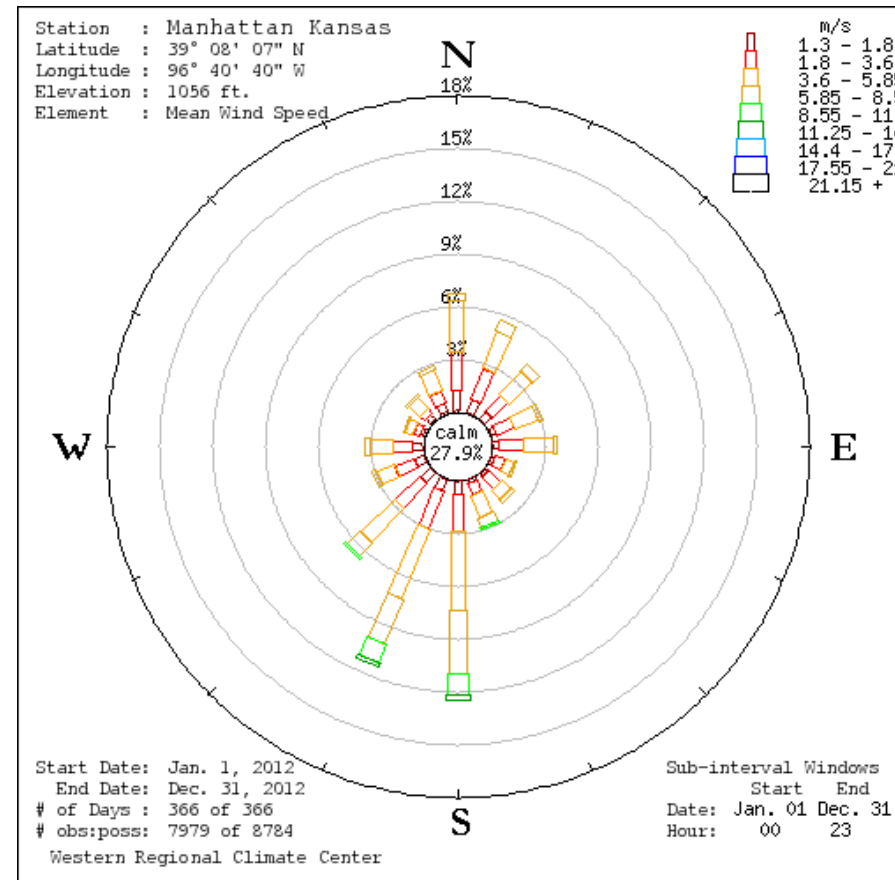
- “Good ozone”
 - The stratospheric or "good" ozone (extends upward from about 6 to 30 miles) protects life on Earth from the sun's harmful ultraviolet (UV) rays. But this "good" ozone is gradually being destroyed by man-made chemicals referred to as ozone-depleting substances (ODS), including chlorofluorocarbons (CFCs),
- “Bad ozone”
 - At ground level, ozone is a harmful pollutant, and is a main ingredient of urban smog. Ground level ozone can trigger a variety of health problems, and can also damage vegetation and ecosystems.

Transport of gaseous pollutants

- Horizontal dispersion of pollutants
- Vertical dispersion of pollutants
- Deposition: The gaseous pollutants may travel some distance and be deposited on the ground and the surface water.
 - Dry deposition
 - Wet deposition

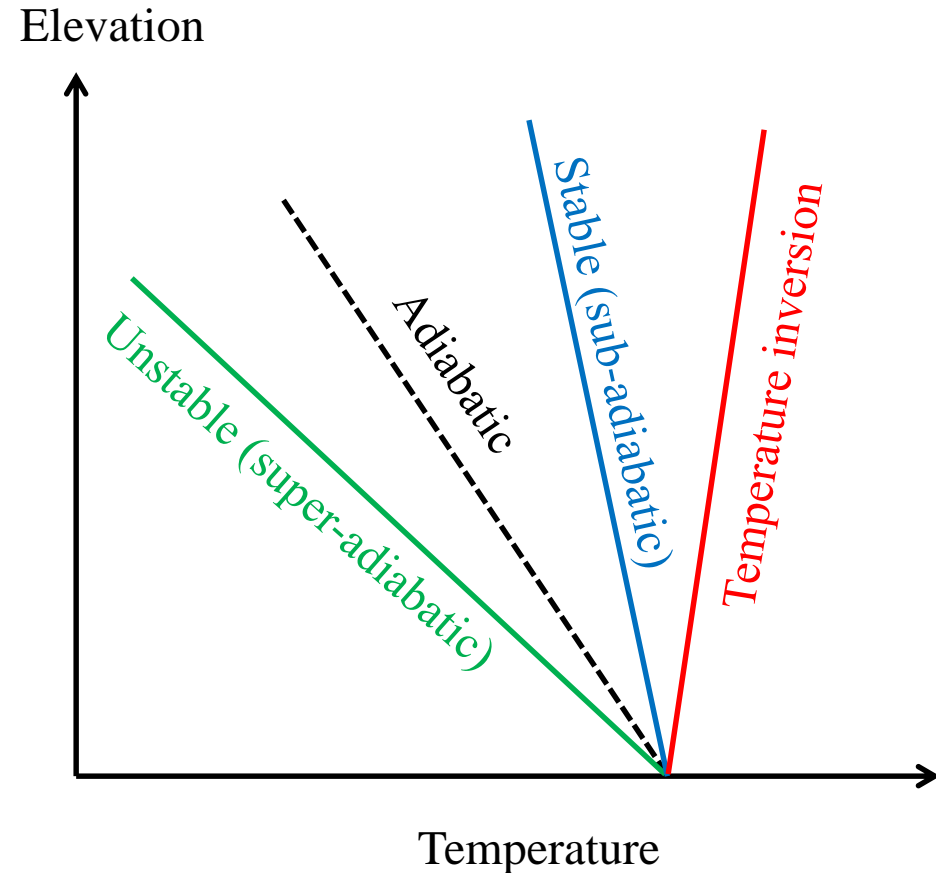
Horizontal dispersion of pollutants and wind rose

- Wind is probably the most important factor in the horizontal dispersion of pollutants. Pollutants move predominantly downwind. Wind rose is a graphic picture of wind velocities and wind directions.
 - The orientation of each segment shows the directions from which the wind came.
 - The length of each segment is proportional to the percent of time that wind at that particular speed was coming from that particular direction.
 - The width of each segment is proportional to the wind speed.



Vertical dispersion of pollutants and air stability

- As a parcel of air rises, it experiences decreasing pressure and thus expands and cools as it rises. The rate at which dry air cools as it rises is called the dry adiabatic lapse rate ($\sim -9.8^{\circ}\text{C}/\text{km}$).
- The relationship between the prevailing lapse rate and the dry adiabatic lapse rate essentially determine the stability of the air and the vertical dispersion of pollutants.



Wet deposition

- Gas or aerosols deposited on ground or water surfaces by any form of precipitation. Wet deposition flux (F_{wet}) can be expressed as

$$F_{\text{wet}} = IC_w$$

Where I is the precipitation rate as liquid and C_w is the pollutant concentration in precipitation water. Washout ratio $= C_w / C_{\text{air}}$.

- For aerosol scavenging, there are two mechanisms involved
 - Rainout: removal of aerosol during cloud formation and their subsequent deposition during precipitation.
 - Washout: during rainfall, raindrops collect aerosols and deposit back on earth.
- For gas scavenging, it can be reversible with the absorbed gas released back into the atmosphere. Washout ratios are large for soluble and polar compounds such as NH_3 and low for VOCs.

Dry deposition for gas

- Dry gas deposition (F_{dry}) can be expressed using dry deposition velocity (V_d) and gas concentration in air (C_g).

$$F_{\text{dry}} = V_d C_g$$

Where V_d can be expressed using the analog of three resistances (aerodynamic resistance r_a , laminar sub-layer resistance r_b , and surface resistance r_s).

$$V_d = \frac{1}{r_a + r_b + r_s}$$

- r_a depends on factors such as friction velocity and atmosphere stability. It may be zero in very turbulent air and 400 s/m in very still air.
 - r_b depends on diffusivity of gas and viscosity of air.
 - r_s is function of stomatal, canopy, plant internal organs, and soil resistances.
- Under same conditions, when the V_d for one gas is measured, V_d for another gas can be estimated as

$$V_{dB} = V_{dA} (D_B/D_A)^{2/3}$$

Where D_A and D_B are molecular diffusivity of gases A and B, respectively.

Dry deposition for aerosol/particles

- General equation for V_d of particles can be expressed as

$$V_d = \frac{1}{r_a + r_b + r_a r_b V_t} + V_t$$

Where V_t is the sedimentation velocity

- Recall when Stokes law is obeyed, $V_t = \frac{2r^2(\rho_s - \rho_l)g}{9\eta}$.
 - For particles $\geq 10\mu\text{m}$, V_t is much more important than the resistance terms in the above equation.
 - For smaller particles, Brownian motion is more important than sedimentation.

Typical dry deposition velocity for gases and aerosols

Species	Range of V_d (cm/s)
SO ₂	0.3-1.6
NO _x	0.01-0.5
O ₃	0.01-1.5
NH ₃	0.2-4
NH ₄ ⁺	0.05-2.0
HNO ₃	1-3
Fine particles (1μm)	0.1-1.2

Potential importance of emissions at different spatial scales

Emissions	Global & Regional	Local & Property Line	Primary Effects of Concern
Odor	Insignificant	Major	Nuisance, quality of life
VOCs	Significant	Minor	Odorous, ozone formation
NH ₃	Major	Minor	Atmospheric deposition
H ₂ S	Insignificant	Significant	Odorous, health
PM	Insignificant	Significant	Health, haze
GHGs	Significant	Insignificant	Global climate change

Rank order from high to low importance is major, significant, minor, and insignificant.
Adapted from NRC, 2003.

Temporal dynamics

- An atmospheric substance can be characterized by its lifetime (also called its residence time) in the atmosphere—defined as the time required (in the absence of sources) to decrease its concentration to $1/e$ (where e is the base of the system of natural logarithms; $1/e$ is approximately 0.37) of the initial concentration.
- Soluble species (i.e., NH_3 , some VOCs) have lifetimes equivalent to those of water in the atmosphere, about 1 to 10 days, depending on precipitation. Reactive species such as NO and H_2S have lifetimes on the order of days or less before they are oxidized to other more water-soluble species such as nitric and sulfuric acids. The lifetimes of VOCs are controlled by the rates of hydroxyl radical attack and water solubility, and range from hours to months. CH_4 has a much longer lifetime of about 8.4 years. N_2O has a lifetime of about 100 years and is essentially inert in the troposphere.

Typical lifetimes in the Planetary Boundary Layer for some air pollutants

Species	Lifetime	Notes
NH ₃	~1-10 days	Very active, NH ₃ gas will not travel very far and will be mostly dry-deposited. NH ₄ ⁺ aerosols will travel far and be primarily wet-deposited.
H ₂ S	~1 days	Heavier than air, most H ₂ S will be oxidized to SO ₂
CH ₄	8.4 years	Eventually oxidized to CO ₂
N ₂ O	100 years	Diffuses from the troposphere to the stratosphere, where it is lost to photolysis and other processes.
PM	~1-10 days, depending on size.	Coarse particles are rapidly removed from the air by sedimentation; particles in the nucleation mode are rapidly transformed into coarser particles by coagulation processes. Particles in accumulation mode (0.1-1μm) have the highest residence time and can be easily transported by the wind up to thousands of km.
VOCs	hours to months, depending on the compound	Many VOCs are highly reactive and may undergo photolysis.

Problem solving #9-1

- NH_3 concentration is 10 mg/m^3 at $T=273\text{K}$, $P=1.013 \times 10^5 \text{Pa}$. What is the mixing ratio in ppm?

Problem Solution #9-1

- NH_3 concentration is 10 mg/m^3 at $T=273\text{K}$,
 $P=1.013 \times 10^5 \text{Pa}$. What is the mixing ratio in ppm?
- $$\begin{aligned} C(\text{ppm}) &= C(\text{mg/m}^3) \times 1000 \times 8.314 \times T / P / M \\ &= 10 \times 1000 \times 8.314 \times 273 / 1.013 \times 10^5 / 17 \\ &= 13 \text{ ppm} \end{aligned}$$