**Beltsville PBL Air Quality Modeling – Atmospheric Chemistry
3-D Air Quality Models –processes: emissions, transport,
deposition, cloud / aerosol physics – chemistry**

**William R. Stockwell, Belay Demoz, Rosa Fitzgerald**

**Objective:** Students will learn about many of the required components of an air quality modeling system. This unit includes supplemental material on topics that are the focus of other units in this workshop too.

3-D air quality models require a number of components to simulate air quality, Figure 1. Meteorological observations are required inputs to a meteorological model that provides wind fields, temperature, water vapor and others that are required by an air quality model.
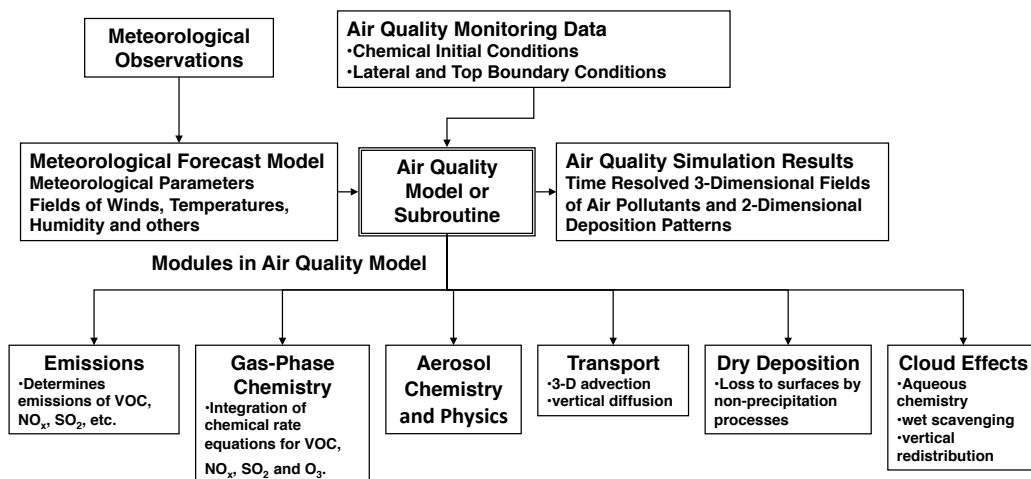


**Figure 1.** Typical components of a 3-D air quality model

The air quality model may use observations or another model to prepare chemical initial and boundary conditions. The air quality model is composed of modules for emissions. gas-phase chemistry, cloud and aerosol chemistry and physics, pollutant transport/diffusion and dry deposition. Evaluation of model results is mentioned at the end of this unit and discussed more fully in the unit Evaluation of Meteorological and Air Quality Simulations with Observations.

Selected aspects of air quality model modules are discussed below. Two models are of particular importance here, the Community Multiscale Air Quality Model (CMAQ) and the Weather Research and Forecasting (WRF) model coupled with Chemistry (WRF-Chem).

Please remember that a complete presentation would require several books of material. At the end of the unit references to more information are provided.

**Meteorological Forecast Modeling Component**

In this section an overview of the equations that a 3_D air quality model must solve are presented. A discussion of the Weather Research and Forecasting Model (WRF) is presented because of its dominate role in weather and air quality simulation. Finally, a discussion of atmospheric stability is provided because of its strong effects on air quality

An air quality modeling system needs to solve the following differential equation. Typically, the different elements of the equation are solved using decoupled (time-splitting) methods. The emissions, chemistry and deposition terms are solved within an air quality system. In the following equation the first line refers to terms involving meteorology and transport. The necessary meteorological fields of winds, temperature, water vapor, etc. are supplied by a meteorological model. The meteorological model may be run as a separate model or as a module in-line with a coupled meteorological-air quality model.

$$\frac{\partial [X]_i}{\eth t} = -\nabla_H \bullet V_H [X]_i + \left\{ \frac{\partial ([X]_i \eta)}{\partial z} - [X]_i \frac{\partial}{\partial z}\left(\frac{\partial h}{\partial z}\right) \right\} - \nabla \bullet \rho K \nabla \left(\frac{[X]_i}{\rho}\right)$$

$$+ \frac{\eth [X]_i}{\partial t}\Big|_{Emissions} + \frac{\eth [X]_i}{\partial t}\Big|_{Chemistry} + \frac{\eth [X]_i}{\partial t}\Big|_{Deposition}$$

where

| Variable | Quantity |
|---|---|
| $t$ | time |
| $[X]_i$ | concentration of $i^{th}$ species |
| $V_H$ | horizontal wind vector |
| $\eta$ | net vertical entrainment rate |
| $z$ | terrain following vertical coordinate |
| $h$ | layer interface height |
| $\rho$ | atmospheric density |
| $K$ | turbulent diffusion coefficient |
| $\frac{\eth [X]_i}{\partial t}\Big|_{Emissions}$ | change in concentration of $i^{th}$ species due to emissions |
| $\frac{\eth [X]_i}{\partial t}\Big|_{Chemistry}$ | change in concentration of $i^{th}$ species due to chemistry |
| $\frac{\eth [X]_i}{\partial t}\Big|_{Deposition}$ | change in concentration of $i^{th}$ species due to deposition |

*Weather Research and Forecasting Model*
One of the most widely used models for providing meteorological fields for air quality modeling is the Weather Research and Forecasting Model (WRF). It is a model usually used to simulate regional domains and it is applied operational weather forecasting, air quality modeling and other research applications. The National Centers for Environmental Prediction (NCEP) and many other meteorological forecasting centers use WRF for operational forecasts and real-time applications (WRF Model – General Information).

The WRF system code and programming standards support extensive parallelization. The user can select between two dynamical cores, one is the Advanced Research WRF core, ARW, and the other is the Nonhydrostatic Mesoscale Model core, NMM (WRF Model – General Information; WRF Users Page). The ARW includes a dynamic solver with one-way, two-way nesting and moving nests. ARW supports grid and observation nudging as well. The NMM core is used in a version of WRF used for hurricane forecasting (HWRF) and the core was developed by the National Centers for Environmental Prediction (NCEP). There is a WRF Data Assimilation system (WRFDA; WRF Data Assimilation System Users Page).

_Atmospheric Stability_

A stable atmosphere occurs when there is little vertical mixing to disperse the emissions of particulate matter, its precursors and ozone forming precursors. High atmospheric stability when combined with a low mixing height traps emissions, promoting the production of air pollution in the PBL. Atmospheric stability has a strong effect on air quality, therefore meteorological measurements and modeling focusing on synoptic conditions and the planetary boundary layer (PBL). Synoptic meteorology is discussed further in the unit on Air Pollution Meteorology while factors influencing the mixing height are discussed in the unit on Atmospheric Chemistry / Air Quality 1-D models.

A rising air parcel in an ideal atmosphere without energy input would cool with increasing altitude (Finlayson-Pitts and Pitts, 2000). These conditions are known as adiabatic. The rate at which the atmosphere cools is known as the lapse rate, $\Gamma$ and by convention it is taken as the negative of the change in temperature, T, with altitude, z.

$$\Gamma = -\frac{dT}{dz}$$

The dry adiabatic lapse rate in the troposphere is -9.8 °K km$^{-1}$. Humidity affects the lapse rate and the water vapor saturated lapse rate is -6 °K km$^{-1}$. In the discussion below we assume the dry adiabatic lapse rate.

Unstable conditions occur when the environmental lapse rate is greater than the adiabatic lapse rate, Figure 2. This condition is known also as superadiabatic.

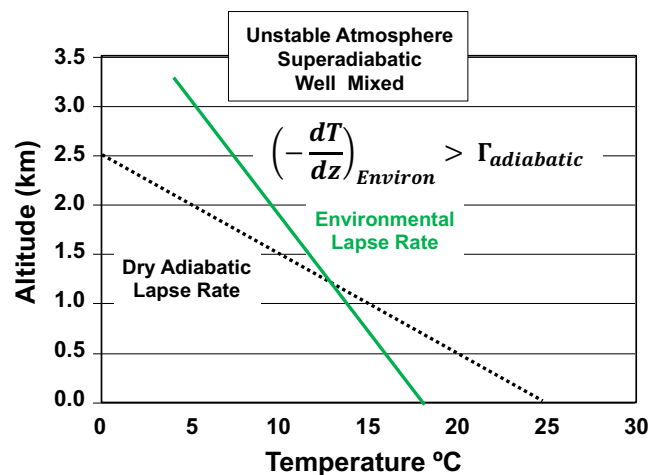$$\left(-\frac{dT}{dz}\right)_{Environ} > \Gamma_{adiabatic}$$



**Figure 2.**   An example of the atmospheric lapse rate for an unstable atmosphere.

A stable atmosphere occurs when the environmental lapse rate is less than the adiabatic lapse rate, Figure 3. This condition is known also as subadiabatic. Consider a warm parcel of air containing emissions. If the air parcel has a density that is less than the ambient air it will rise until its density becomes equal to the ambient air density. Under unstable conditions, with a lower environmental lapse rate, the atmosphere cools at a rate that is greater than adiabatic. The warm air parcel will rise, and this causes the air parcel to cool at a rate that is near the adiabatic lapse rate. However, the ambient air cools at the environmental lapse rate. This means that the air parcel remains less dense and will continue under unstable atmospheric conditions.

$$\left(-\frac{dT}{dz}\right)_{Environ} < \Gamma_{adiabatic}$$
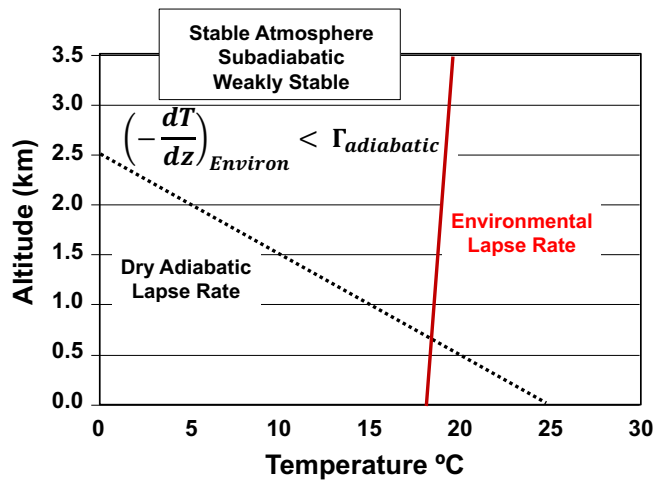


**Figure 3.** An example of the atmospheric lapse rate for a stable atmosphere.

Now reconsider the warm parcel of air containing emissions under stable conditions. Under warmer stable conditions the air parcel may have a greater density than the ambient air and due to its buoyancy it will sink. Even if the air parcel rises initially, it will cool at the adiabatic lapse rate while the ambient air cools at the environmental lapse rate that is less than adiabatic. The air parcel will not continue to rise very far until it reaches a density equal to ambient air and therefore the atmosphere is stable.

A temperature inversion occurs if atmospheric temperature increases strongly with altitude, Figure 4. In this case the environmental lapse rate is much less than the adiabatic lapse rate and the atmosphere is very stable with little mixing. Under these conditions the air may become very polluted.

$$\left(-\frac{dT}{dz}\right)_{Environ} << \Gamma_{adiabatic}$$

**Stable Atmosphere Temperature Inversion Reduced Mixing**

$$\left(-\frac{dT}{dz}\right)_{Environ} << \Gamma_{adiabatic}$$

Dry Adiabatic Lapse Rate
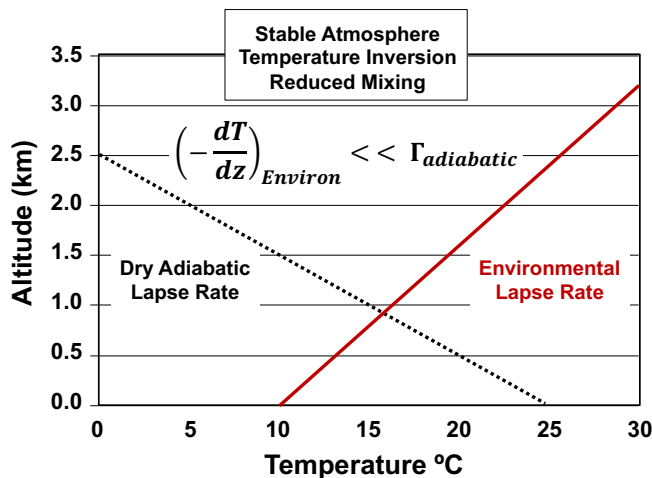
Environmental Lapse Rate

**Figure 4.** An example of a temperature inversion. The environmental lapse rate is much less than the adiabatic lapse rate and the atmosphere is very stable and there is very little mixing.

If the environmental lapse rate is equal (or nearly equal) to the adiabatic lapse rate the stability is considered to be neutral, Figure 5.

$$\left(-\frac{dT}{dz}\right)_{Environ} = \Gamma_{adiabatic}$$

**Neutral Atmosphere Adiabatic Neutral to Mixing**

$$\left(-\frac{dT}{dz}\right)_{Environ} = \Gamma_{adiabatic}$$

Environmental Lapse Rate

Dry Adiabatic Lapse Rate
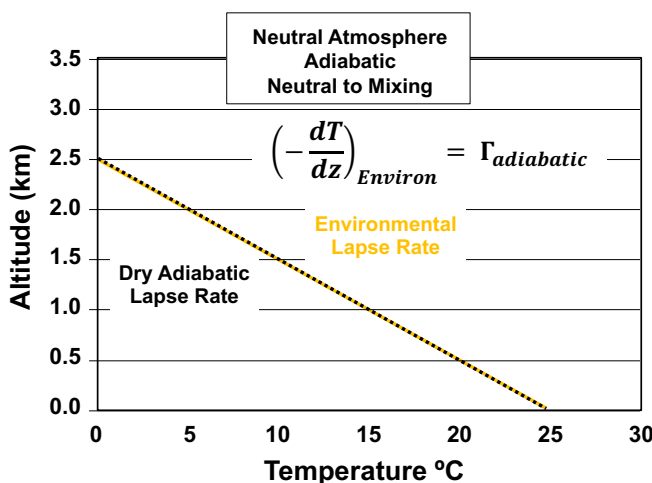
**Figure 5.** An example of an atmosphere with neutral stability.

Heat deficit $H_h$, (J m$^{-2}$), is another measure of the atmospheric stability. The heat deficit is the heat required to warm an air column with a 1 m$^2$ cross-section that extends from the Earth's surface, s, to height, h, (altitude in meters above sea level, m) to the dry adiabatic lapse rate.

Heat deficit $H_h$, (J m$^{-2}$) is defined by the following equation where $c_p$ is the specific heat capacity of air at constant pressure, 1005 J kg$^{-1}$ K$^{-1}$; z is altitude; $\rho(z)$ is the air density as a function of altitude; $\theta_h$ is the potential temperature at altitude h; and $\theta(z)$ is the potential temperature as a function of altitude.

$$H_h = c_p \int_S^h \rho(z)[\theta_h - \theta(z)]dz$$

One advantage of the heat deficit concept is that it can be used to define stability of the atmosphere at any altitude. Karle et al. (2020) applied heat deficit to analyze observations made by ozonesondes and radiosondes launched from El Paso during an ozone campaign during 2017. The heat deficit calculations of atmospheric stability were used to distinguish the meteorology associated with the high and low ozone episodes. They found that on days with a high-pressure ridge and higher stability, as defined by heat deficit, were  associated with high ozone in El Paso. On days with lower stability the ozone concentrations were lower.

**Gas-Phase Chemistry**
Gas-phase chemistry is discussed in unit "Atmospheric Chemistry Air Quality Box Models" but here is a survival guide to important chemical compounds found in the atmosphere. The large number of organic compounds is one reason that preparing emissions inventories is difficult.

Alkanes – Have no double bonds or aromatic rings.

Methane ($CH_4$) is the simplest.

Ethane ($CH_3CH_3$) is the next.
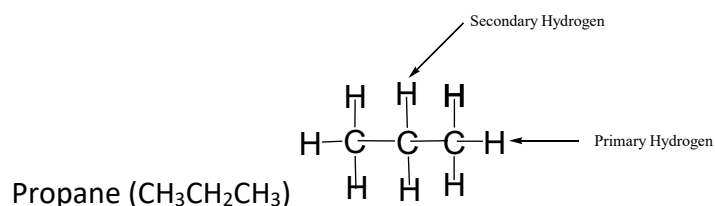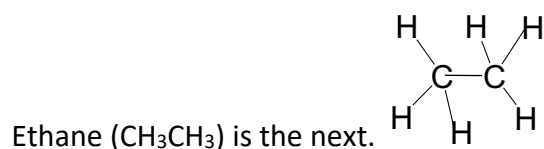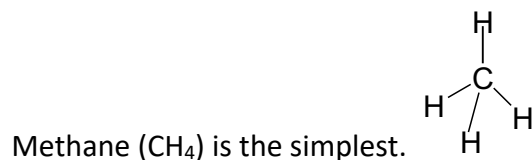
Propane ($CH_3CH_2CH_3$)

Butanes have four carbon atoms and can have two different arrangements called isomers.

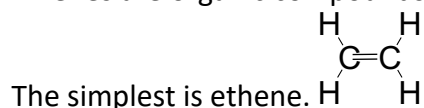n-butane ($CH_3CH_2CH_2CH_3$)  I will omit the stick diagram here because it follows the trends given above.
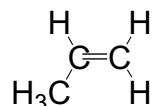
iso-butane
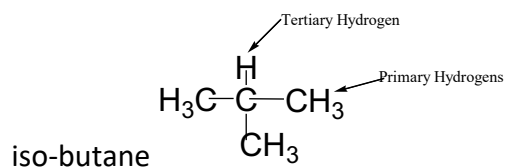
Pentanes and alkanes with more carbon atoms can have many arrangements and some carbons are not attached to any hydrogen atoms.
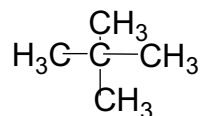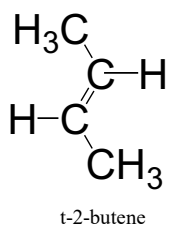
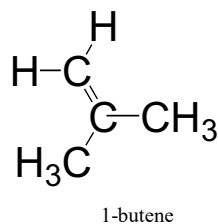Alkenes are organic compounds with at least one double bond.

The simplest is ethene.

$$\underset{H}{\overset{H}{\diagdown}}C=C\underset{H}{\overset{H}{\diagup}}$$

Propene is next. $\underset{H_3C}{\overset{H}{\diagdown}}C=C\underset{H}{\overset{H}{\diagup}}$ Note that all of the carbons in this structure are in the same plane because there is no rotation around the double bond.

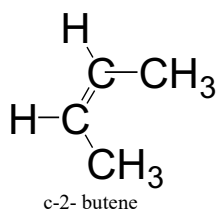Because there is no rotation around the double bond there are three possible butenes.

Trans Structure

$$H_3C$$
$$\diagdown$$
$$C-H$$
$$\diagup\diagup$$
$$H-C$$
$$\diagdown$$
$$CH_3$$

t-2-butene

A Primary Alkene

$$H-C\overset{H}{\diagdown}$$
$$\diagup\diagup$$
$$C-CH_3$$
$$H_3C$$

1-butene

Cis Structure

$$H$$
$$\diagdown$$
$$C-CH_3$$
$$\diagup\diagup$$
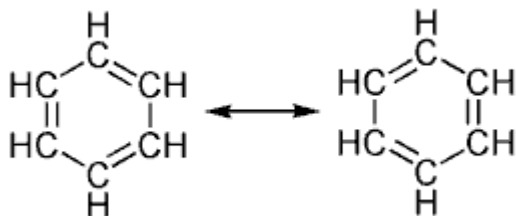$$H-C$$
$$\diagdown$$
$$CH_3$$

c-2- butene

Aromatic Compounds

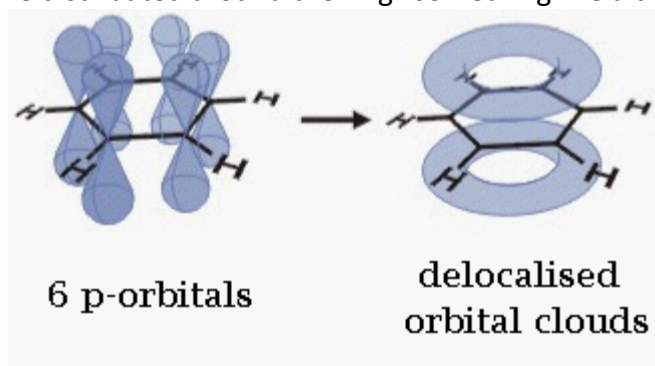These have an aromatic ring and benzene ($C_6H_6$) is the simplest.

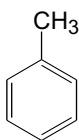There should be two possible rings but in reality there are not.

(Image from Wikipedia)

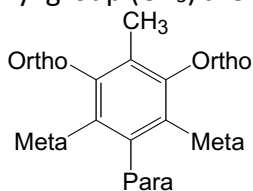Electrons are distributed around the ring "something like a dinner plate."



6 p-orbitals          delocalised
                      orbital clouds

(Image from Wikipedia)

The next highest is toluene ($C_7H_8$).


CH$_3$

Relative to the methyl group ($CH_3$) there are three different kinds of positions for attaching



CH$_3$
Ortho          Ortho
Meta          Meta
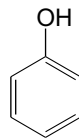groups to the ring.          Para

This is important for the xylenes.



CH$_3$
  CH$_3$
ortho-xylene
o-xylene

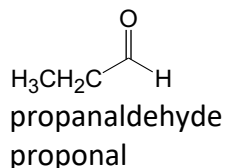CH$_3$
  CH$_3$
meta-xylene
m-xylene

CH$_3$
  CH$_3$
para-xylene
p-xylene
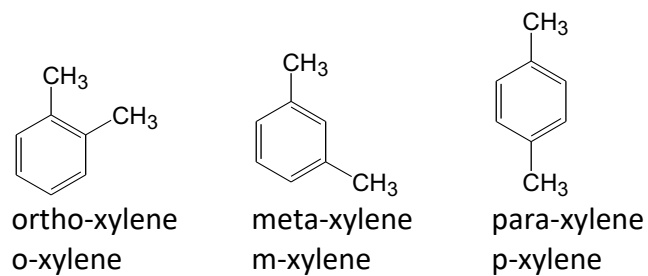
Another important aromatic in the atmosphere is phenol.


OH

Atmospheric oxidation adds oxygen to hydrocarbons to make aldehydes, ketones and alcohols (although many of all these compounds are directly emitted too).

Aldehydes have a [structure] H group.

formaldehyde    acetaldehyde    propanaldehyde
methanal        ethanal         proponal
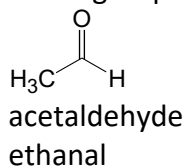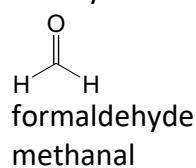
Ketones have a [structure] group without a hydrogen atom attached to the C=O group.

acetone         methyl ethyl ketone
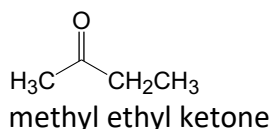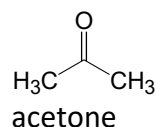
Alcohols have an OH group attached.

(CH₃OH)         CH₃CH₂OH
Methanol        Ethanol

CH₃CH₂CH₂OH n-propanol     iso-propyl alcohol

Organic Nitrates

methyl nitrate          ethyl nitrate          propyl nitrate
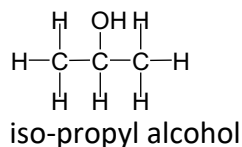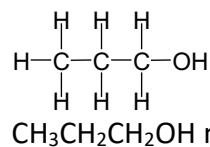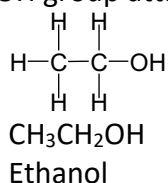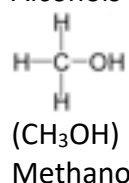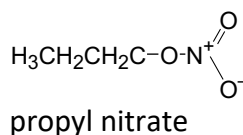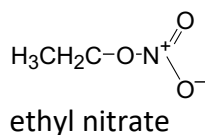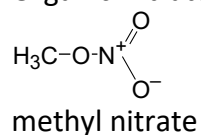
An important compound is peroxyacetylnitrate or PAN.
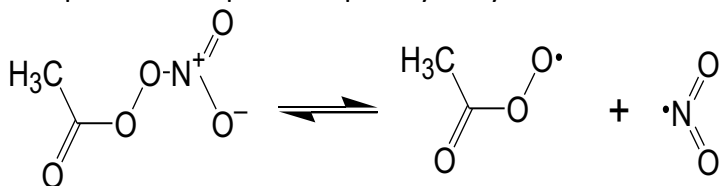
Peroxy Acetyl Nitrate (PAN)  Acetyl Peroxy Radical  Nitrogen Dioxide

Note that radicals are molecular species with an unpaired electron.

·$CH_3$ is the methyl radical

·$CH_3O$ is the methoxy radical

·$CH_3O_2$ is the methylperoxy radical

$RO_2$· (where the R is any organic group) represents any organic peroxy radical

Carbon containing sulfur compounds

| $S{=}C{=}S$ | $O{=}C{=}S$ | $H_3C\overset{S}{\diagdown}CH_3$ | $H_3C\overset{\overset{O}{\uparrow}{\underset{S}{}}}{\diagdown}CH_3$ |
|---|---|---|---|
| carbon disulfide | carbonyl sulfide (COS) | methyl sulfide | dimethyl sulfide |
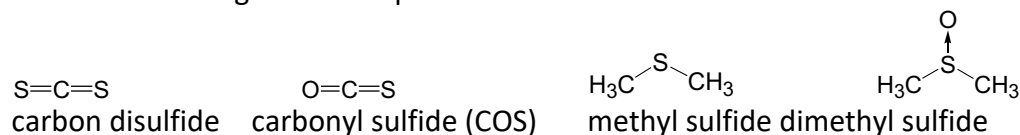
Finally, Some Important Inorganics

| | | | |
|---|---|---|---|
| H | hydrogen atom | HO· | hydroxyl radical |
| $O(^3P)$ | ground state oxygen atom | $HO_2$· | hydroperoxy radical |
| $O(^1D)$ | energetically excited oxygen atom | $NO_3$· | nitrate radical |
| $H_2O$ | water | $HNO_3$ | nitric acid  (note that $NO_3^-$ is nitrate as in sodium nitrate: $Na^+NO_3^-$ ) |
| NO | nitric oxide | $NH_4^+NO_3^-$ | ammonium nitrate |
| $NO_2$ | nitrogen dioxide | HONO | nitrous acid |
| $N_2O$ | nitrous oxide (chemistry occurs in stratosphere) | $H_2SO_4$ | sulfuric acid |
| $O_3$ | ozone | NaCl | sodium chloride |

*Some Specific Mechanisms Used by Air Quality Models*

The carbon bond series of mechanisms have a long history with the US EPA. These mechanisms take their name from the approach used to simplify organic chemistry. The SAPRC mechanisms take their name from what was the Statewide Air Pollution Research Center at the University of California Riverside. The SAPRC mechanisms are widely used for air quality modeling in California. The Regional Atmospheric Chemistry Mechanism, version 2 (RACM2) was developed from a series of mechanisms for modeling regional atmospheric chemistry. The Marine Halogen Chemistry and ClNO2 Chemistry are specialized chemical modules.

Table 1. Gas-phase Chemical Mechanisms Implemented in CMAQ

| Versions of Carbon Bond | Versions of SAPRC | Others |
|---|---|---|
| CBO6 | SAPRC07T | RACM2 |
| CBO5 | SAPRC07tic | Marine Halogen Chemistry |
| CB05TU | | ClNO2 Chemistry |
| CB05TUCl | | |
| CB05e51 | | |

**Emissions**

An emission inventory is required for air quality models to calculate air pollutant concentrations such as ozone, particulate matter, atmospheric acids and toxic pollutants. There are several classes of emissions that are commonly used for air quality modeling. These include stationary point source emissions, line-source, distributed area sources, natural/biogenic, mobile source emissions (both on-road and off-road), and point source emissions.

| Source Category | Examples |
|---|---|
| Stationary Point Source | The smokestack of an electric power plant. $SO_2$, $NO_x$ |
| Line Source | A crowded freeway, $NO_x$ |
| Area Source | A residential area, volatile organic compounds (VOC), $NO_x$ |
| Biogenic | Parks, agricultural areas, cattle feed lots, $NH_3$, VOC such as isoprene |
| Natural | Volcanic emissions, $SO_2$ |
| Mobile On-road | Cars, trucks, busses, $NO_x$, VOC |
| Mobile Off-road | Construction agricultural and machinery, $NO_x$, VOC |

Note that most $NO_x$ is emitted as nitric oxide (NO).

For 3-D air quality models the emission inventory of pollutants needs to be provided on a 3-dimensional grid with temporal resolution of at least 1-hr (Stockwell et al., 2002**).** Simulation of ozone requires the emissions of its precursors, $NO_x$, VOC and CO. To simulate atmospheric particulate matter such as $PM_{2.5}$ and $PM_{10}$ emissions of $SO_2$, $NH_3$, and primary PM (size-distributed and chemically speciated) are required along with $O_3$ precursor emissions. Emissions, E, if not directly measured are often calculated from emissions factors, F, and the level of an activity, A, over some time period. Emission factors are specific to specified activities.

$$E = F \times A$$

Production of an emissions inventory involves the processing of a massive amount of data that is performed by an emissions model. One widely used system is the Sparse Matrix Operator Kerner Emissions modeling system (SMOKE; SMOKE-website). SMOKE reads emissions data that includes national emissions inventory data at the state and county level with their timing and chemical files, meteorological, land-use and other files such as population, housing, and industry to produce emission inventory data files required by widely used models such as CMAQ. The format of the chemically speciated VOC depends upon the specific chemical mechanism used by the air quality model. An emissions processing system must take meteorology into account because it affects emissions from mobile sources, the evaporation rates of VOC and biogenic emissions (Stockwell et al., 2002).

The name, SMOKE, is derived from a numerical sparse matrix approach that is used by the system which reduces the required processing time. SMOKE has an advantage in that changes in emissions, say to evaluate possible control strategies, does not require repeating all processing steps (SMOKE-website). SMOKE interfaces with other specialized emission processing programs

such as the Biogenic Emission Inventory System (BEIS2) and on-road emissions models such as MOBILE6 (MOBILE-website) and MOVES (MOVES-website).

Figure 6 shows an emissions map for $NO_x$ emissions across the continental United States. Notice that the highest $NO_x$ emissions follow the population centers especially on the East and West Coast, the Midwest and the Gulf Coast. Figure 7 shows that the anthropogenically emitted VOC follow a similar pattern. Figure 8 shows that for biogenically emitted volatile organic compounds these have their greatest emissions in the Southern US and in the Northwest.
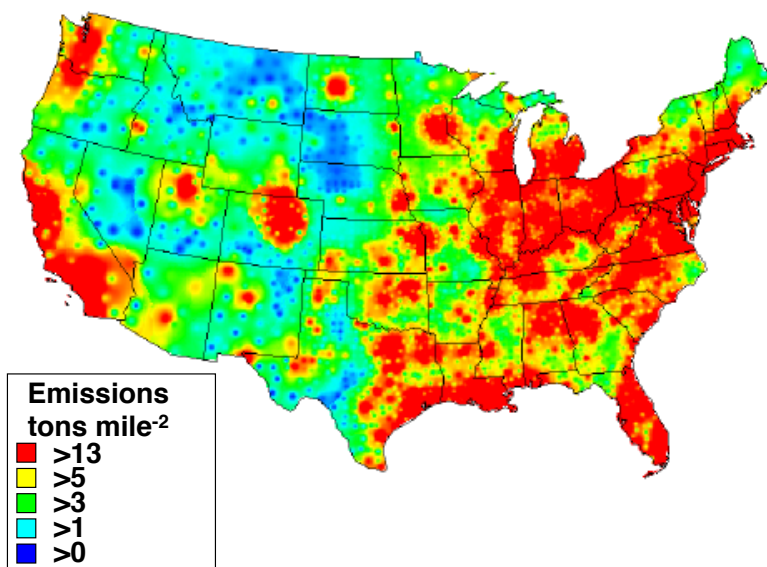


**Figure 6.** A nitrogen oxide ($NO_x$) emissions inventory for the continental United States.
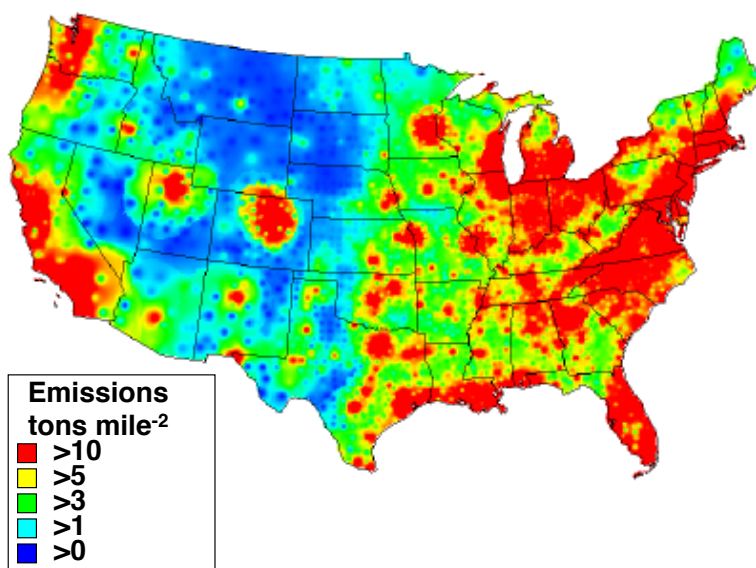


**Figure 7.** An anthropogenically emitted volatile organic compound (VOC) emissions inventory for the continental United States.
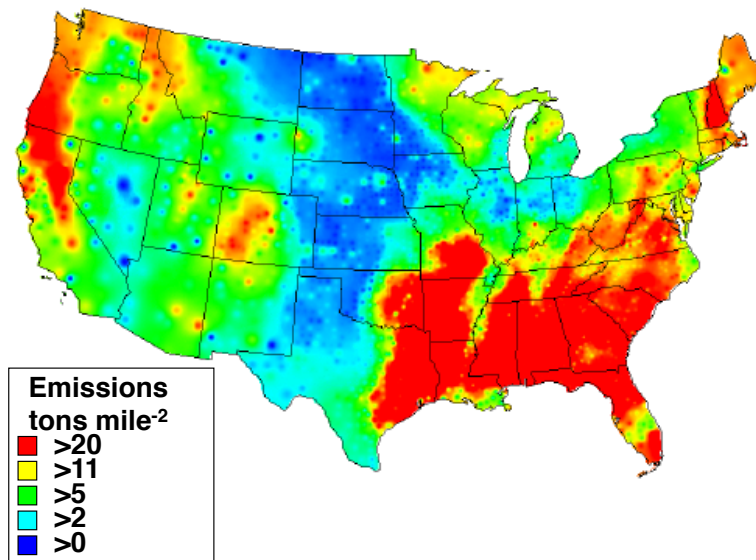
**Figure 8.**  An biogenically emitted volatile organic compound (BVOC) emissions inventory for the continental United States.

## Deposition

Chemical species may be removed from the atmosphere by dry and wet deposition (Finlayson-Pitts and Pitts, 2000). Dry deposition is transfer of gases from the atmosphere to surfaces that include soils, buildings, trees, lakes, etc. The surfaces may be dry or wet with water but in either case this is dry deposition. Wet deposition occurs when gases become dissolved in water droplets such as fog, cloud droplets and precipitation (rain or snow). Particulate matter may be deposited by dry and wet deposition too.

Deposition is usually characterized as a flux which is the flow of material through a unit area that is parallel to the surface per unit time, Figure 9 and follows the following equation where $\phi$ is the flux, $V_d$ is the deposition velocity and $[X]$ is the concentration of species X in the layer being considered such as the PBL in this workshop. While the deposition velocity is considered to be positive the sign is negative because deposition is a loss of species X from the atmosphere (Finlayson-Pitts and Pitts, 2000).

$$\phi = -V_d[X]$$
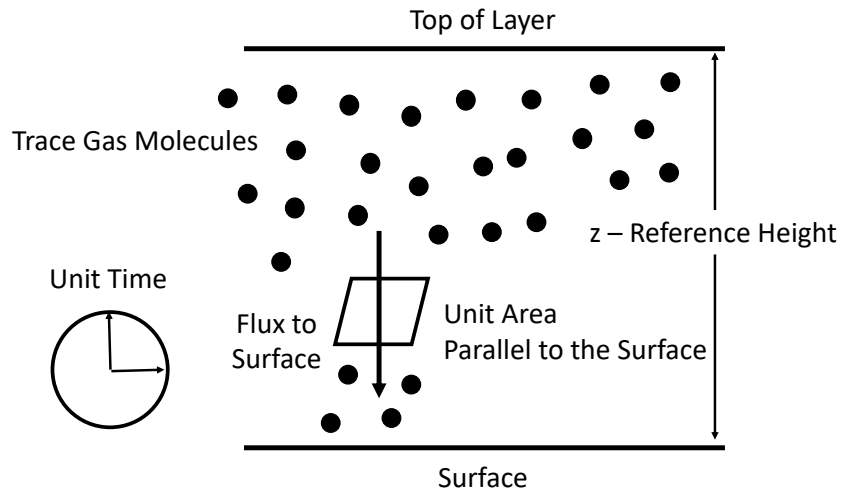
**Figure 9.** Shows the definition of deposition flux to a surface. Trace gas or dry particulates flow to a surface. The flux is the flow of molecules per unit area per unit time. Note that the surface does not need to be horizontal. It could be vertical as in the case of the side of a building.

A deposition velocity can be considered to be the reciprocal of atmospheric resistance, $r$.

$$V_d = \frac{1}{r}$$

Figure 10 shows that the total resistance is the sum of a gas resistance, a boundary layer resistance and a surface resistance.

$$r = r_{gas} + r_{boundary} + r_{surface}$$
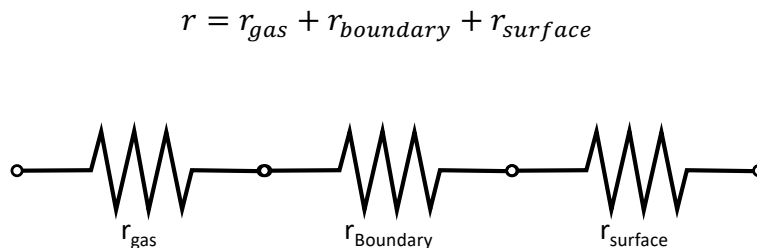


**Figure 10.** The total resistance for a depositing species can be expressed by analogy to a resistor circuit. The total resistance is often expressed as the sum of a gas resistance, a boundary layer resistance and a surface resistance.

The gas resistance depends on height of the atmospheric layer, z, and the micrometeorology of the transport processes. Factors such as wind velocity components and atmospheric stability can be important for gas resistance too. Boundary layer in this case refers to a very thin stagnant layer of air above the surface so this resistance is related to the molecular diffusivity of the gas. Surface resistance is related to the stickiness or affinity of a gas or particles to a surface. For example, ammonia ($NH_3$) has a high affinity for wet surfaces while ozone does not.

Note that much more complex resistance models can be created for gases and additional considerations may be necessary for describing particulate matter. Resistance models for vegetation covered surfaces would include stomatal resistances, canopy resistances and other resistances arrayed a circuit with both series and parallel elements.

**Multi-phase: Aerosol, Cloud, Chemistry and Physics**
Seinfeld and Pandis, 2016, provide an excellent summary of aerosol chemistry and physics. Here the terms atmospheric aerosols and particulate matter (PM) are synonymous. Aerosols are either directly emitted (known as primary aerosols) or formed through atmospheric chemical processes (secondary aerosols). Primary aerosols include wind-blown mineral dust, soot and brown carbon. Secondary inorganic aerosols include ammonium nitrate and ammonium sulfate that are produced from the precursors, nitric acid, sulfate and ammonia. These secondary inorganic aerosols may represent a large fraction of aerosol mass in polluted urban regions. Secondary aerosols also include aerosols that are produced by organic chemistry, known as secondary organic aerosol (SOA; Calvert et al. 2015). Large organic compounds consisting of five or more carbon atoms, that are often biogenically emitted alkenes such as isoprene may react to produce high molecular weight oxygenated products with low vapor pressures that condense to form SOA (Stockwell et al., 2020).

Emissions of mineral dust are very significant in desert regions dust that these emissions are largely determined by prevailing wind speeds and surface vegetation [Kim et al., 2017]. Mineral dust affects climate because of its radiation scattering effects and recent evidence suggests that mineral dust causes cardiopulmonary disease and lung cancer.

Soot is a product of high temperature combustion, but it is not a single substance, it is composed of elemental carbon and other carbonaceous material that incorporates trace amounts of hydrogen, nitrogen, oxygen and other elements (Seinfeld and Pandis, 2016). Soot has a strong effect on climate because it strongly absorbs atmospheric radiation across the spectrum from the ultraviolet through the infrared (Jacobson 2001; Seinfeld and Pandis, 2016). The absorption of radiation by soot may reduce the production of $O_3$ by reducing the rate of $NO_2$ photolysis. Soot may play a direct role in atmospheric chemistry by being a heterogeneous sink for ozone and promoting the production of nitrous acid (HONO) by catalyzing the conversion of $NO_2$ to HONO.

Another direct aerosol emission source is the low-temperature combustion of organic material. This source emits brown carbon that is seen as smoke. Brown carbon is not a single substance. It is composed of organic compounds that include alcohols, aromatics, organic acids, hydroxyacids, ketoacids and sugars [Seinfeld and Pandis, 2016; Chow et al., 2018].

Characterizing the size of aerosol particles is not a simple task because many particles have very irregular shapes. Effective or equivalent diameters that are based on a physical property rather than geometry are often used. The aerodynamic diameter is one example often used because it is related to the residence time of aerosol particles in the atmosphere and to where particles may deposit in the human respiratory system (Finlayson-Pitts and Pitts, 2000). Aerodynamic diameter,

$D_a$, is defined by the following equation where $D_g$ is the geometric diameter, $k$ is a shape factor, $\rho_p$ is the density of the aerosol particles and $\rho_o$ is a reference density defined to be 1 g cm$^{-3}$.

$$D_a = D_g k \sqrt{\frac{\rho_p}{\rho_o}}$$

The shape factor is equal to 1.0 for spherical particles. The density of the aerosol particles is defined to be absent of air buoyancy effects. For most particles, $\rho_p < 10$ so the aerodynamic diameter is greater than the geometric diameter by no more than a factor of three. Another effective diameter is the Stokes diameter that is defined as the diameter of a spherical particle with the same density and settling velocity as the measured aerosol particles.

The atmosphere contains mixtures of aerosols with distributions of number ($N$), mass ($m$), surface area ($A$), volume ($V$) or other properties. There are many ways to characterize aerosol distributions (Finlayson-Pitts and Pitts, 2000). For example, histograms of the number of particles, $\Delta N$, binned by aerodynamic diameter, D, are possible. However, typically the number of small diameter particles is much greater than those with greater diameters so a distorted picture results. Normalization such as plotting $\Delta N/\Delta logD$ (y-axis) vs $\Delta logD$ (x-axis) is one way to reduce the distortion. Figure 11 provides an example of aerosol distribution plots for a mixture.
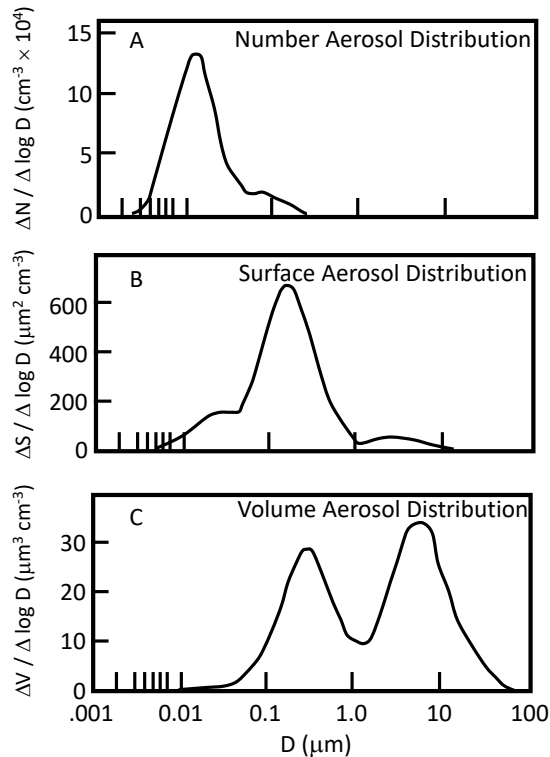


**Figure 11.** Comparison of (A) number, (B) surface and (C) volume aerosol distributions for the same aerosol mixture (Finlayson-Pitts and Pitts, 2000).

Particulate matter may be grouped by their aerodynamic diameters: particles with diameters less than 0.01 µm are ultrafine particles; particles with diameters between 0.01 µm and 0.08 µm are Atkin nuclei, particles with diameters between 0.08 µm and 2.5 µm are considered to be in the accumulation range and particles with diameters greater than 2.5 µm are known as coarse particles. Gas-phase chemistry produces low volatile substances that may condense to produce ultrafine particles. Coagulation of ultrafine particles and the condensation of vapors (from hot emissions sources) produce Aiken particles. Aiken particles may further coagulate to produce particles in the accumulation range. Particles in the accumulation range may be removed by wet deposition (rainout and washout). Course particles result from combustion, windblown dust (mineral dust), bursting bubbles in the oceans and particles derived from plants and animals. It should be noted that aerosol-phase chemistry may interact with gas-phase chemistry because particles may be sources and sinks of gas-phase species.

The size distributions and the associated physical and chemical processes are all important in the modeling of particulate matter concentrations in the PBL. See EPA-CMAQ-Processes for an overview of the treatment of aerosols and multi-phase chemistry in CMAQ, CMAQ has a number different models to simulate aerosol physics and chemistry

**Transport and Dispersion**

A Gaussian distribution function, f(x) is given below where $\mu$ is a real number and $\sigma$ is a real number greater than zero.

$$f(x) = \frac{1}{\sigma\sqrt{(2\pi)}} exp\left[\frac{-(x-\mu)^2}{2\sigma^2}\right]$$

In statistics $\mu$ corresponds to the mean value while corresponds to the standard deviation. In a Gaussian plume model $\mu$ corresponds to the maximum concentration value while $\sigma$ corresponds to the spread of the plume, Figure 12.
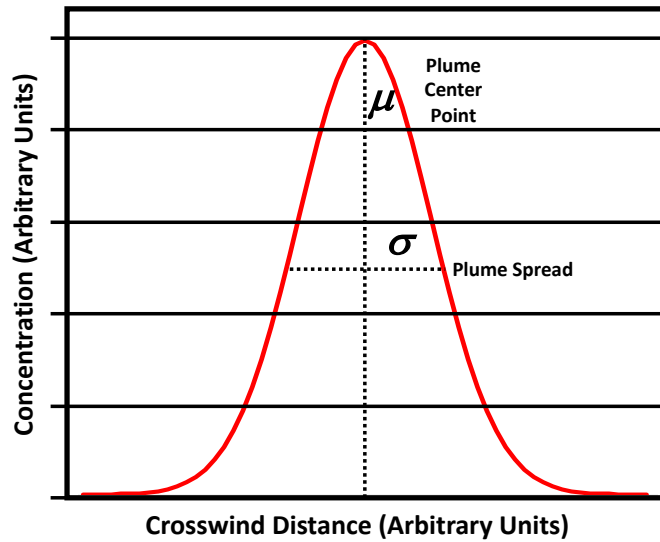
**Figure 12.** A Gaussian function used to represent a plume of emissions.

Suppose that there is a point emissions source such as an elevated smokestack with wind blowing from the x-direction. The emissions will move away from the source in the x direction while spreading in the y and z-directions, Figure 13. In this idealized case the concentrations, [X], are given by the following equation where $K$ is a constant dependent on the specific atmospheric conditions, $D_y$ and $D_z$ are mass diffusivity constants in the y and z direction, respectively, and u is the wind speed in the x direction.

$$[X] = \frac{K}{x} exp\left[-\left(\frac{y^2}{D_y} + \frac{z^2}{D_z}\right)\frac{u}{4x}\right]$$
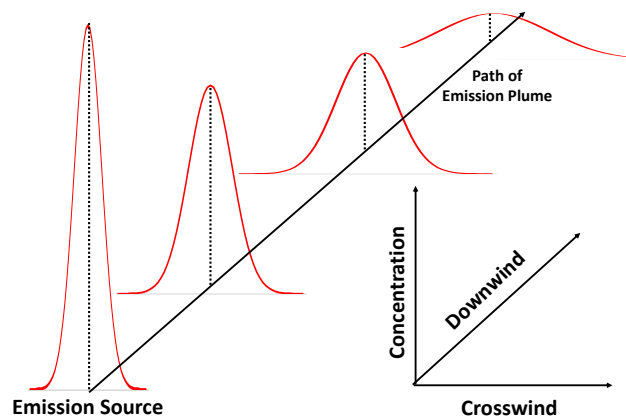


**Figure 13.** The spread of a Gaussian emission plume as it is transported downwind.

Here it is assumed that the emissions have about the same density as the ambient air and therefore the emissions and air have approximately the same buoyancy. Wind and atmospheric turbulence are the forces that determine the movement of emissions from the source. Wind blows the emissions through the air away from the source while "turbulent mixing" causes the emissions to spread out in the y-crosswind and z-upward directions. Figure 13 shows that as the emissions are transported away from the source, the concentrations become lower but cover a greater area in the crosswind direction.

*Gradient Diffusion Approximation for Transport*
On a statistical basis gases will diffuse from a volume with greater concentrations to the surrounding air with lower concentrations. In other words, if there is a concentration gradient a gas will flow from high toward lower concentrations. Molecular diffusion is far too slow to be a major factor in the transport atmospheric gases; however, the mathematical form of diffusion is a good first approximation to describe mixing due to convection and turbulence.

Consider two grid boxes from an air quality model, Figure 14.
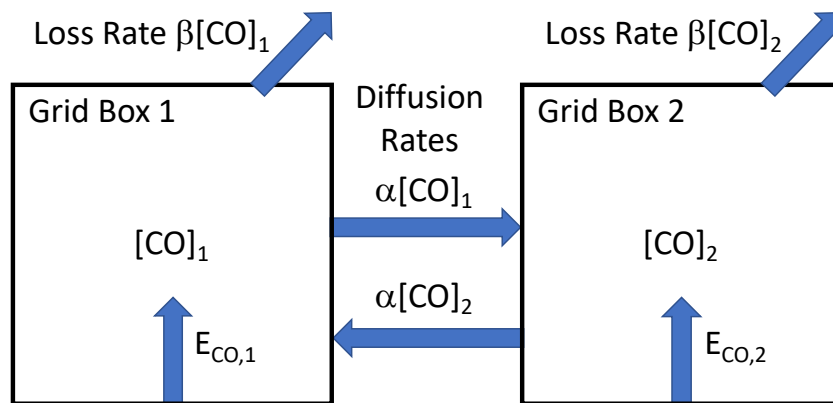


**Figure 14.** Two adjacent grad boxes from an air quality model (following the example of Hartel, 1988). Carbon monoxide (CO) is used here because its losses by chemical reaction and deposition are low. The concentrations of CO in boxes 1 and 2 are represented by $[CO]_1$ and $[CO]_2$, respectively. The emissions of CO are represented by $E_{CO,1}$ and $E_{CO2}$. The loss rates of CO are considered to be first-order and represented by a constant, $\beta$, multiplied by a concentration; therefore the losses of CO are $\beta[CO]_1$ and $\beta[CO]_2$, respectively. The "diffusion rates" between the grid boxes are given by an empirical constant multiplied by a concentration. The expression $\alpha[CO]_1$ gives the flowrate from box 1 to box 2 while $\alpha[CO]_2$ gives the flowrate from box 2 to box 1.

The net flow of CO from grid box 1 to grid box 2 will be given by:

$$CO\ Net\ flow = \propto ([CO]_1 - [CO]_2)$$

An expression for the net CO flow rate between grid boxes 1 and 2 may be derived. For this example, assume that $E_{CO,1} + E_{CO,2} = Constant$.

For box 1 the balance between the CO flowing into and out of the box is given below.

$$\text{Box 1: } E_{CO,1} + \alpha[CO]_2 = \alpha[CO]_1 + \beta[CO]_1$$

For Box 2 this balance is:

$$\text{Box 2: } E_{CO,2} + \alpha[CO]_1 = \alpha[CO]_2 + \beta[CO]_2$$

Add these two expressions and cancel $\alpha([CO]_1 + \alpha[CO]_2)$ from both sides and solve for $\beta$.

$$\beta = \frac{E_{CO,1} + E_{CO,2}}{\{CO]_1 + [CO]_2}$$

Substitute β back into the expression for Box 1 and solve for $\propto ([CO]_1 - [CO]_2)$. The result is:

$$\propto ([CO]_1 - [CO]_2) = \frac{E_{CO,1} \times [CO]_2 - E_{CO,2} \times [CO]_1}{\{CO\}_1 + [CO]_2}$$

This equation shows that the net flow of a trace gas, such as CO, from grid box 1 to grid box 2 may be estimated if the emission rates and the concentrations in both boxes are known.

**Cloud and Aqueous-Phase Chemistry**

Aqueous-phase chemistry has a major effect on the production atmospheric acidic compounds such as sulfate and organic acids. The first step in cloud aqueous-phase chemistry is to dissolve a gas-phase chemical species into the aqueous-phase. A first approximation is to assume that for dilute solutions there is an equilibrium between a dissolved species, *[X(aq)]*, and its gas-phase partial pressure $P_{X(g)}$. This relationship is known as Henry's law where $H_X$ is the Henry's law coefficient (Seinfeld and Pandis, 2016).

$$[X(aq)] = H_X \times P_{X(g)}$$

Note that in some formulations of Henry's law, the Henry's law coefficient is reported as the inverse of $H_X$.

The equilibrium between $H_2O$, the hydrogen ion, $H^+$, and the hydroxide ion, $OH^-$ is very important for aqueous-phase chemistry. Water dissociates and has the following equilibrium expression where $K_w'$ is the equilibrium constant for $H_2O$ while *[H₂O]*, *[H⁺]* and *[OH⁻]* are the concentrations of $H_2O$, $H^+$ and $OH^-$, respectively (Seinfeld and Pandis, 2016).
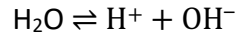
$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_w' = \frac{[H^+][OH^-]}{[H_2O]}$$

However, the number of $H_2O$ molecules that actually dissociate is very small, so $[H_2O]$ is relatively constant and the most common form of this equation is given below with $K_w$ as the effective equilibrium constant for $H_2O$.

$$K_w = [H^+][OH^-]$$

At 298 K, $K_w$ = 1.0 × 10⁻¹⁴ M² (Moles) and following the above equation, *pH* and *pOH* are defined as follows.

$$pH = -log_{10}[H^+]$$

$$pOH = -log_{10}[HO^-]$$

$$pH + POH = 14$$

Pure water has a pH of 7.0 and a pOH of 7 at 298 K.

*CO₂ and its Aqueous-Phase Absorption*
Carbon dioxide, $CO_2$, is a good example of a gas that dissolves in water to produce a number of chemical species. Carbon dioxide interacts with water through the following equilibrium reactions (Seinfeld and Pandis, 2016).

$$CO_2(g) + H_2O \rightleftharpoons CO_2 \bullet H_2O$$
$$CO_2 \bullet H_2O \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^=$$
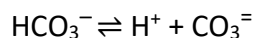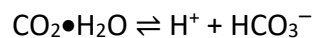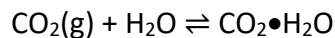
The first reaction produces a complex between a liquid water molecule and $CO_2$. The complex can react further to produce a hydrogen ion and a bicarbonate ion, $HCO_3^-$. The bicarbonate ion may react with to produce another hydrogen ion and a carbonate ion, $CO_3^=$. Note that electrical charge is conserved in each of these reactions and that these reactions show that when $CO_2$ dissolves in pure liquid water the solution become acidic.

If equilibrium equations are written for these reactions the following equations result where $H_{CO2}$ is the Henry's law coefficient for $CO_2$.

$$H_{CO_2} = \frac{[CO_2 \bullet H_2O]}{p_{CO_2}}$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2 \bullet H_2O]}$$

$$K_2 = \frac{[H^+][CO_3^=]}{[HCO_3^-]}$$

These equilibrium equations may be rewritten as follows.

$$[CO_2 \bullet H_2O] = H_{CO_2} p_{CO_2}$$

$$[HCO_3^-] = \frac{H_{CO_2} K_1 p_{CO_2}}{[H^+]}$$

$$[CO_3^=] = \frac{H_{CO_2} K_1 K_2 p_{CO_2}}{[H^+]^2}$$

The total carbon dioxide dissolved in water, $[CO_2]_T$, is the sum of $[CO_2 \bullet H_2O]$, $[HCO_3^-]$ and $[CO_3^=]$.

$$[CO_2]_T = H_{CO_2} p_{CO_2} \left( 1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} \right)$$

Note that this final equation confirms that the total carbon dioxide dissolved in water is inversely related to [H⁺]. Therefore, at high [H⁺] the pH of the water is low and carbon dioxide will be less soluble. If a basic substance such as ammonia is added to the water the pH is reduced and carbon dioxide becomes more soluble in the resulting solution.

**Extending the Evaluation of Forecast Skill to Air Quality Modeling Process Modules**

Evaluation of an air quality modeling system includes an assessment of the combined and relative effects of meteorology, emissions, and all the modules in the air quality model (Stockwell, 2020).

There are two classes of model evaluation:

Operational evaluation – This will be discussed in detail in the unit, Evaluation of Meteorological and Air Quality Simulations with Observations. An operational evaluation involves a direct comparison between simulated and observed concentrations. This evaluation provides an estimate of the accuracy of a model's simulations.

Diagnostic evaluation – A diagnostic evaluation determines how well the modules comprising the model are performing. This requires collecting much more detailed observations of meteorological and chemical processes that affect pollutant formation and distribution in addition to the simulated concentrations.

Both types of evaluation utilize statistical methods to evaluate air quality and meteorological models and their component modules. These statistics include: accuracy (the agreement between simulations and measurements), bias (the extent to which the model or module may have systematic errors that result in over or under predictions, skill scores (does the simulation show an increase in accuracy of its simulations relative to persistence or another reference forecast), and the degree of correlation and shared variance between simulations and observations. Figure 15 shows that model evaluation is a key part of modeling system research programs.
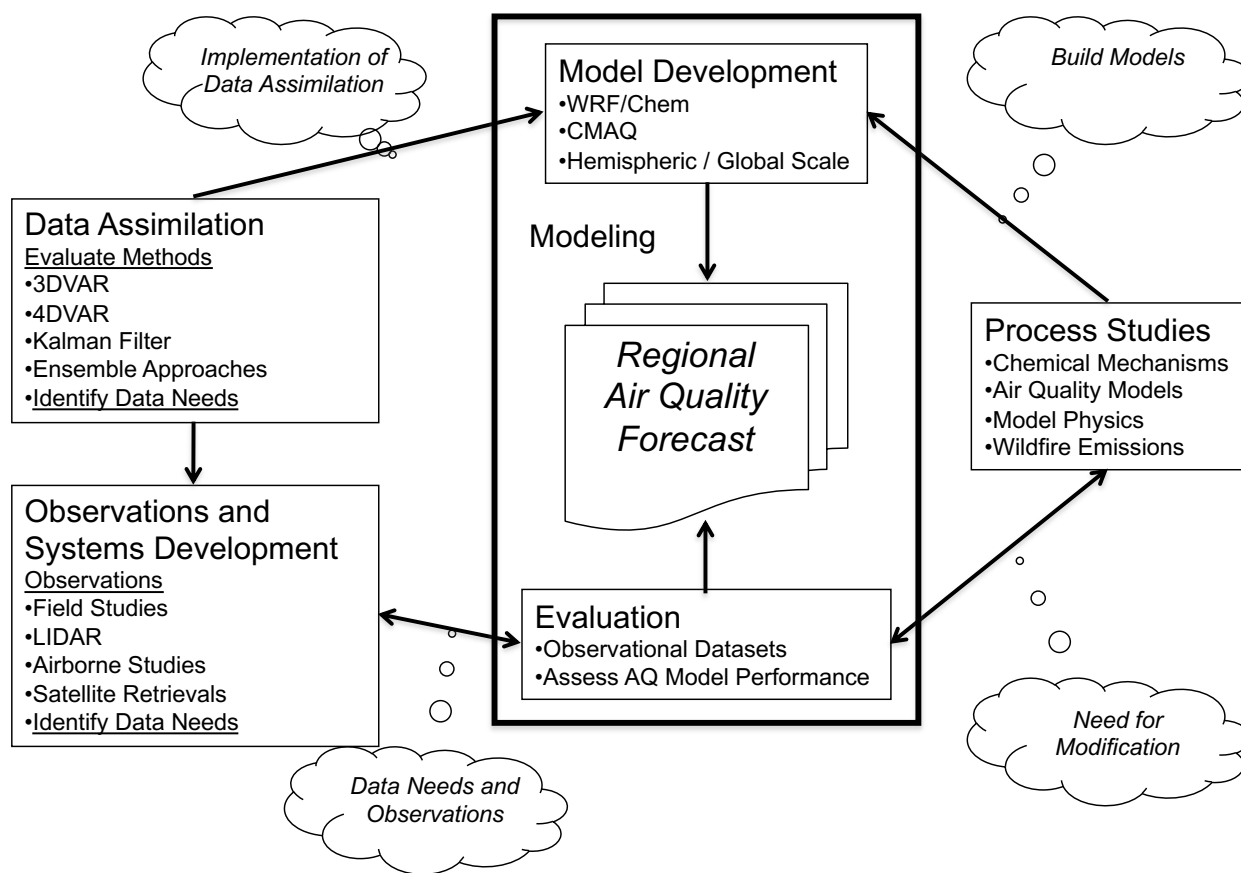


**Figure 15.** Research needs for an air quality modeling system research program.

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WRF Model – General Information
https://www.mmm.ucar.edu/weather-research-and-forecasting-model

WRF Users Page https://www2.mmm.ucar.edu/wrf/users/

WRF Data Assimilation System Users Page
https://www2.mmm.ucar.edu/wrf/users/wrfda/index.html

**Assignments**

**Meteorological Forecast Model:** Examine the referenced webpages and sub-webpages for WRF and report on a feature of special interest to you. You may be interested in downloading a free meteorology textbook by Stull (2017), see the references above..

*WRF References*
WRF Model – General Information
https://www.mmm.ucar.edu/weather-research-and-forecasting-model

WRF Users Page
https://www2.mmm.ucar.edu/wrf/users/

WRF Data Assimilation System Users Page
https://www2.mmm.ucar.edu/wrf/users/wrfda/index.html

**Chemistry:** For this problem, define incremental ozone reactivity, $IR_{O3}$, to be the change in ozone concentrations $\Delta[O_3]$, divided by a change in the emissions of a particular organic compound $\Delta[VOC_i]$.

$$IR_{O_3} = \frac{\Delta[O_3]}{\Delta[VOC_i]}$$

Discuss why would you expect different classes of organic compounds to have different values of $IR_{O3}$?

**Emissions:** Suppose you have a single grid-box in the PBL that is 12 km by 12 km by 1 km. You have a source of CO with an emission rate of 10 kg hr$^{-1}$. Assume that CO has a molecular weight of 28 g mole$^{-1}$ and Avogadro's number is $6.023 \times 10^{23}$ molecules mole$^{-1}$. What is the emissions rate of CO in the grid-box in units of molecules cm$^{-3}$?

**Deposition:** You have a mixing ratio of $O_3$ that is 60 ppbV over a uniform wheat field with a temperature of 298 K and a reference surface layer of 10 m. Suppose that the deposition velocity for $O_3$ under these conditions is 0.5 cm s$^{-1}$. What is the deposition flux of $O_3$ to the field in units of molecules cm$^3$ s$^{-1}$. Assume these conditions remain constant, what would be the deposition of ozone in terms of grams to an area of 10 km by 10 km over 24 hours?

Repeat this problem for an ammonia concentration of 400 ppbV over a cattle feedlot at 298 K and a reference surface layer of 10 m. Assume the deposition velocity for $NH_3$ is 5.0 cm s$^{-1}$. Calculate the deposition flux of $NH_3$ to the field in units of molecules cm$^3$ s$^{-1}$. Assume these conditions remain constant, what would be the deposition of $NH_3$ in terms of grams to the feedlot with an area of 2 km by 2 km over 24 hours?

**Transport and Dispersion**: (1) Please fill in the details needed to derive the following gradient diffusion approximation equation.

$$\propto ([CO]_1 - [CO]_2) = \frac{E_{CO,1} \times [CO]_2 - E_{CO,2} \times [CO]_1}{\{CO\}_1 + [CO]_2}$$

(2) Perform a sensitivity study for the equation derived in this session. Determine the relative effect of differences in CO concentrations and emission rates between the two grid boxes. You may prefer to do this in terms of relative concentrations and emission rates. Discuss your findings.

**Multi-phase: Aerosol, Cloud, Chemistry and Physics:** A number aerosol distribution may be approximated by the following equation where $r$ is the particle radius ($\mu m$), $N(r)$ is the cumulative particle number distribution ($cm^{-3}$) for particles larger than $r$, $R_i$ is the mean particle radius ($\mu m$), $n_i$ is the nth integral of the $i^{th}$ normal function and $log(\sigma)$ is a measure of the particle polydispersity (Jaenicke, 1988).

$$\frac{dN(r)}{d(log\ r)} = \sum_{i=1}^{3} \frac{n_i}{\sqrt{2\pi}\ log(\sigma_i)} exp\left\{-\frac{(log\ (r/R_i))^2}{2(log(\sigma_i))^2}\right\}$$

Given the values listed in the table below plot the particle number distributions for marine, rural and urban aerosols and discuss.

| Aerosol | Range | $i$ | $n_i$ (cm$^{-3}$) | $R_i$ (cm$^{-3}$) | $log(\sigma)$ |
|---|---|---|---|---|---|
| Marine | I | 1 | $1.33 \times 10^2$ | 0.0039 | 0.657 |
| | II | 2 | $6.66 \times 10^1$ | 0.133 | 0.210 |
| | III | 3 | $3.06 \times 10^0$ | 0.29 | 0.396 |
| Rural | I | 1 | $6.55 \times 10^3$ | 0.00739 | 0.225 |
| | II | 2 | $1.47 \times 10^2$ | 0.0269 | 0.557 |
| | III | 3 | $1.99 \times 10^3$ | 0.0419 | 0.266 |
| Urban | I | 1 | $9.93 \times 10^4$ | 0.00651 | 0.245 |
| | II | 2 | $1.11 \times 10^3$ | 0.00714 | 0.666 |
| | III | 3 | $3.64 \times 10^4$ | 0.0248 | 0.337 |

For the range: I is the Aitken mode, II is the accumulation mode and III is the coarse mode.

**Cloud and Aqueous-Phase Chemistry**

If at atmospheric pressure and a temperature of 208 K; $H_{CO2} = 3.4 \times 10^{-2}$ Moles atm$^{-1}$, $p_{CO2} = 350$ ppbV; $K_1 = 4.3 \times 10^{-7}$ Moles liter$^{-1}$ and $K_2 = 4.7 \times 10^{-11}$ Moles liter$^{-1}$ use the following equations (as derived above) to plot the total dissolved concentration of dissolved $CO_2$ as a function of pH. Careful: you may need to adjust units as you do your calculations.

$$[CO_2]_T = H_{CO_2}p_{CO_2}\left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right) \qquad pH = -log_{10}[H^+]$$