Measurements of Atmospheric Composition



N5550s

What is the atmosphere?

• Gaseous Envelope Surrounding the Earth



• Mixture of gases, also contains suspended solid and liquid particles (aerosols).

Aerosol = Dispersed Condensed Phase Suspended in a GasAerosols are the "visible" components of the atmospherePollution Haze over East CoastDust off West Africa



Clouds in the Atmosphere

- Clouds are made up of water droplets and/or ice crystals, much larger than typical aerosols (0.01-10 μm).
- Clouds are technically aerosols but have unique properties and are typically considered separately.



East Grand Forks: 17 July 2011



Citation Flight: 14 July 2011

Atmospheric Gases are "Visible" also, if you look at Ultraviolet (UV) or Infrared (IR) wavelengths

NO₂ Columns Observed from the SCIAMACHY Satellite Instrument





Gas Composition of Earth's Atmosphere



















August 2019: Atmospheric CO2 at Mauna Loa Observatory















August 2024: Atmospheric CO2 at Mauna Loa Observatory









Counties with Monitors Violating the 2008 8-Hour Ozone Standard





¹ 345 monitored counties violate the 2008 8-hour ozone standard of 0.075 parts per million (ppm). ² Monitored air quality data can be obtained from the AQS system at <u>http://www.epa.gov/ttn/airs/airsags/</u>

Air quality standard for surface ozone is 0.070 ppm or 70 ppb. In December 2020, EPA decided to retain the current ozone standards

Courtesy of http://www.epa.gov/glo/pdfs/2008_03_monitors_violating_2008.pdf

Counties With Monitors Projected to Violate Alternate 8-hour Ozone Standards of 0.070 and 0.075 parts per million in 2020



Air quality standard for surface ozone is 0.070 ppm or 70 ppb. In December 2020, EPA decided to retain the current ozone standards

Courtesy of http://www.epa.gov/glo/pdfs/2008_03_monitors_violating_2008.pdf

1.2 Number Density n_{χ} [molecules cm⁻³]

 $n_X = \frac{\# \text{ molecules of X}}{\text{unit volume of air}}$

Proper Measure For:

- Reaction Rates
- Optical Properties of Atmosphere

Column Concentration

$$\Omega = \int_{0}^{z_{t}} n_{x}(z) dz$$

Proper measure for absorption or scattering of radiation by atmosphere

 C_x - Mixing Ratio or Mole Fraction C_x [mol mol⁻¹]

 n_x and C_x are related by the ideal gas law:

$$n_X = n_a C_X = \frac{A_v P}{RT} C_X$$

Also define the mass concentration (g cm⁻³):

$$\rho_X = \frac{\text{mass of X}}{\text{unit volume of air}} = \frac{M_X n_X}{A_v}$$

 n_a = Air Density A_v = Avogadro's Number P = Pressure R = Gas constant $= A_v k k$ =Boltzmann Constant T = Temperature M_x = Molecular Mass of X

<u>Avogadro's Number</u> Number of constituents in one mole 6.02214129(27)×10²³ mol-1

This Weeks's Stratospheric Ozone Layer



Thickness of ozone layer is measured as a column concentration.



This Weeks's Stratospheric Ozone Layer



Ozone

absorption

spectrum

1 "Dobson Unit (DU)" = 0.01 mm ozone at STP = 2.69x10¹⁶ molecules cm⁻²

Thickness of ozone layer is measured as a column concentration.

Particular Matter (PM) Measurement Filter Samplers





Tapered Element Oscillating Micro-Balance (TEOM)







Scanning Mobility Particle Sizer (SMPS)

Differential Mobility Analyzer (DMA)



Aerosol Concentrations can be Expressed as mass per unit volume, typically in units of [µg m⁻³]

 $PM_{2.5} \equiv Particular Matter < 2.5 \ \mu m in diameter)$



PM_{2.5} in Fargo, North Dakota



Fine aerosol mass (2.5 µm particulate matter) measured in Fargo, North Dakota by month of the year. The box and whiskers give the 5, 25, 50, 75, and 95 percentiles. The solid line represents the monthly mean. The x axis denotes the month of the year, with the last box-and-whisker denoting the percentile for the whole period. The statistics are based on all valid, hourly averaged data from June 2000 through December 2003. The data are from the Air Quality System PM2.5 Mass Federal Reference Method (Hourly) program and were obtained from the VIEWS website (http://vista.cira.colostate.edu/views/Web/Data/). Creation of these plots and data is part IDL Simple example located at https://learn.aero.und.edu/pages.asp?PageID=162649.

SPECIFIC ISSUES FOR AEROSOL CONCENTRATIONS

• A given aerosol particle is characterized by its size, shape, phase, and chemical composition – large number of variables!

- Measures of aerosol concentrations must be given in some integral form, by summing over all particles present in a given air volume that have a certain property
- The aerosol size distribution must be treated as a continuous function



Typical U.S. aerosol size distributions by volume

Courtesy of Daniel J. Jacob

Major Aerosol Modes



Courtesy of Singh: Figure 5.4

Partial Pressure P_x [Pa]

Dalton's Law:
$$P_X = C_X P = \frac{RT}{A} n_X$$

Proper Measure for Phase Change (Such as Condensation of Water Vapor)

Thought experiment: consider a pan of water with a lid:



Now heat the pan:



Courtesy of Daniel J. Jacob



PHASE DIAGRAM FOR WATER



RUNAWAY GREENHOUSE EFFECT ON VENUS

Due to accumulation of water vapor from volcanic outgassing early in its history

...did not happen on Earth because farther from Sun; as water accumulated it reached saturation and precipitated, forming the oceans



WHY CAN YOU SEE YOUR BREATH ON COLD MORNINGS?

Draw mixing lines (dashed) to describe dilution of your breath plume w/outside air



Courtesy of Daniel J. Jacob

RAOULT'S LAW

P_x – **Partial Pressure**



Water Saturation Vapor Pressure over Pure Liquid Water Surface



Water Saturation Vapor Pressure over Aqueous Solution of Water Mixing Ratio X_{H2O}

An atmosphere of relative humidity *RH* can contain at equilibrium aqueous solution particles of water mixing ratio

$$x_{H2O} = \frac{P_{H2O,SAT}}{P_{H2O,SAT}^{o}} = \frac{RH}{100}$$

AEROSOL PARTICLES MUST SATISFY SOLUBILITY EQUILIBRIA

Consider an Aqueous Sea Salt (NaCl) Particle. It must satisfy:

$$\begin{aligned} x_{Na+} x_{Cl-} &\leq K_s \text{ (solubility equilibrium) #1} \\ x_{Na+} &= x_{Cl-} \text{ (electroneutrality) } \\ x_{Na+} &+ x_{Cl-} + x_{H2O} = 1 \text{ (closure) } \end{aligned}$$

Where X is some molecule or atom.

This requires: Can you derive this requirement? $RH \ge 00(1 - 2K_s^{\frac{1}{2}})$ Deliquescence Relative Humidity

At lower RH, the particle starts out dry. Hint: Substitute #2 in #3, solve for X_{H2O} and substitute #1.

Atmospheric Haze

Haze: A suspension in the air of extremely small, dry particles invisible to the naked eye and sufficiently numerous to give the air an opalescent appearance. Courtesy of Federal Meteorological Handbook No. 1 - Surface Weather Observations and Reports September 2005 Chapter 8 (http://www.ofcm.gov/fmh-1/pdf/H-CH8.pdf).

Clear Day

Haze Day



Great Smoky Mountains Nation Park Courtesy of EPA (http://www.epa.gov/visibility/)

Atmospheric Mist

Haze: Temperature/Dew Point Temperature spread greater than 4 ^oF. Visibility 5/8 miles to 7 miles.

Mist: Temperature/Dew Point Spread less than or equal to 4 ^oF . Visibility 5/8 miles to 7 miles.

Courtesy of Automated Surface Observing System manual (http://www.weather.gov/asos/pdfs/aum-toc.pdf)





What defines the difference between Haze and Mist?

See Discussion at Blog - June 18, 2021 - Brief Low Visibility (Morning Haze Layer)

Uptake of Water by Aerosols (NaCl)



Courtesy of Daniel J. Jacob

<u>Efflorescence</u>, spontaneous loss of water by a hydrated salt, which occurs when the aqueous vapor pressure of the hydrate is greater than the partial pressure of the water vapour in the air.

Uptake of Water (NH₄)₂SO₄, NH₄HSO₄ and H₂SO₄



Relative volume change of (NH₄)₂SO₄, NH₄HSO₄ and H₂SO₄ particles at 298 K as a function of RH. V is the particle volume at a given RH and V0 is the volume of the dry particle. The data used in the figure were produced using the extended aerosol inorganics model (E-AIM, http://www.aim.env.uea.ac.uk/aim/aim.php) Courtesy of Peng et al., 2022

Deliquescence and Effloresence $RH \ge 100(1 - 2K_s^{\frac{1}{2}})$ **Deliquescence Relative Humidity**

K_s(NaCl) = 0.015625 ⁻⁻ 75 % Relative Humidity

	Relative Humidity (RH)	
	Deliquescence	Effloresence
Ammonium Sulfate ((NH ₄) ₂ SO ₄)	78 – 82 %	30 - 48 %
Sodium Chloride (NaCl)	73 – 77 %	41 – 51 %
Ammonium Nitrate (NH ₄ NO ₃)	60 - 66 %	25 – 36 %

Chao Peng, Lanxiadi Chen, Mingjin Tang, A database for deliquescence and efflorescence relative humidities of compounds with atmospheric relevance, Fundamental Research, Volume 2, Issue 4, 2022, Pages 578-587, ISSN 2667-3258, https://doi.org/10.1016/j.fmre.2021.11.021. (https://www.sciencedirect.com/science/article/pii/S2667325821002612)

Atmospheric Ammonium Nitrate



The center shows aerosol mass fraction as a function of the total mass of NR-PM1 measured from the Twin Otter. Ammonium nitrate is in blue, organic species in green, and sulfate and chloride in red and pink, respectively. The bar chart on the left corresponds to the average of the mass fractions when the total aerosol mass is $< 2 \ \mu g \ m^{-3}$ (clean conditions). The bar chart to the right corresponds to the average of the mass fractions when the total aerosol mass is $> 17.5 \ \mu g \ m^{-3}$ (polluted conditions) and altitude is $< 900 \ m \ a.g.l.$ (below the boundary layer). (https://doi.org/10.5194/acp-18-17259-2018)





Pyrocumulus in California on August 10, 2013. Courtesy of Nicholas Carletta

Variation in particle size with relative humidity. This is for a salt (NaCl) that has a deliquescing at 0.75.

Courtesy of Singh: Figure 5.1

Aerosol Residence Time



Who issues Air Quality Alerts?

The National Oceanic and Atmospheric Administration (NOAA), in partnership with the Environmental Protection Agency (EPA), issues daily air quality forecast guidance as part of a national Air Quality Forecasting Capability. NOAA's National Weather Service (NWS) currently provides forecast guidance for ozone and smoke based on numerical atmospheric predictions updated twice daily. (Source – https://www.weather.gov/phi/air_quality).



Air Quality Alert

OKZ019-024>030-060115-Logan-Canadian-Oklahoma-Lincoln-Grady-McClain-Cleveland-Pottawatomie-Including the cities of Guthrie, Yukon, Concho, El Reno, Mustang, Oklahoma City, Chandler, Stroud, Prague, Meeker, Davenport, Wellston, Chickasha, Tuttle, Purcell, Newcastle, Blanchard, Norman, Moore, and Shawnee 808 PM CDT Wed Sep 4 2019 ...AIR QUALITY ALERT IN EFFECT FROM 7 AM TO 8 PM CDT THURSDAY... The following statement was issued by the Oklahoma Department of Environmental Quality. An Air Quality Alert for Ozone has been issued for Thursday, September 5th for the Oklahoma City Metropolitan area due to

expected high concentrations of ozone. Persons with existing heart or respiratory ailments should reduce physical exertion and outdoor activity.