# Atmospheric Constituents - Evolution

## Composition of the Atmosphere

- Evolution of Earth’s Atmosphere
- Cool Earth Theory

## Science Concepts

- Newton’s Laws of Motion
  - First Law
  - Second Law
- Acceleration of Gravity
- Centripetal Acceleration
- Photodissociation
- Photosynthesis

## The Earth System (Kump, Kastin & Crane)

- Chap. 10 (pp. 187-196)
- Chap. 11 (pp. 207-238)
**Evolution of the Atmosphere**

**Several Theories**

- Earth was formed as a molten mass (hot)
- Earth was formed by accretion, gravitational collection of meteorites and interplanetary dust (cool)

**Cool Earth Theory**

Assume for our argument that Earth was formed by accretion and thus was an aggregate of dust and meteorites

<table>
<thead>
<tr>
<th>EON</th>
<th>ERA</th>
<th>PERIOD</th>
<th>EPOCH</th>
<th>AGE (10^6)y</th>
<th>ATMOSPHERIC EVOLUTION</th>
<th>IMPORTANT EVENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precambrian</td>
<td>Hadean</td>
<td></td>
<td>4600 - 3800</td>
<td>4350 BP</td>
<td>Earth 80% formed&lt;br&gt;Original atmosphere contained interstellar cloud gases from which our Solar System was formed&lt;br&gt;- Hydrogen, helium, nitrogen, oxygen, neon, carbon oxides, as well as a long list of trace gases</td>
<td>4570 BP&lt;br&gt;- Oldest known solar system material&lt;br&gt;4440 BP&lt;br&gt;- Oldest lunar crust rocks retrieved by the Apollo mission</td>
</tr>
</tbody>
</table>
Evolution of the Atmosphere

Cool Earth Theory (Con’t)

• What happened to these original gases?
  - Forces
    > Vector quantity - Have a direction as well as a magnitude
  - Newton's Laws
    > First Law
      ‡ An object's velocity (direction or speed) will remain unchanged unless acted upon by a force
    > Second Law
      ‡ Object's acceleration = \frac{\text{net force}}{\text{object's mass}}
Evolution of the Atmosphere

Cool Earth Theory (Cont’d)

† Acceleration is defined as the change in velocity with time and it also is a vector

\[ a = \frac{\text{(Change in velocity)}}{\text{(Change in time)}} = \frac{(V_2 - V_1)}{(t_2 - t_1)} \]

† Acceleration, i.e., a change in velocity can be change in direction or speed or both

- Forces acting on an atmospheric gas molecule

> Gravitational force - attraction toward planet

† Force of attraction between two objects - in this case the gas molecule and the planet

\[ \text{Const} \times \frac{(\text{Mass of planet}) \times (\text{Mass of molecule})}{(\text{Distance})^2} \]

where “Distance” is the distance between the centers of the two objects. In this case, approximately the planet’s radius.
Evolution of the Atmosphere

Cool Earth Theory (Con’t)

- Forces acting on an atmospheric gas molecule (Con’t)

> Centripetal force - “center seeking” force; force needed to accelerate a molecule around a corner

‡ Centripetal force needed to accelerate molecule around a spherical planet depends on motion of the gas molecule

\[
\text{(Mass of molecule)} \times \left(\text{Velocity of molecule}\right)^2 \times (\text{Radius of rotation})
\]

where the “Radius of rotation” is, in this case, approximately the radius of the planet. Note this is the same as the “Distance” in the gravitational force.
Evolution of the Atmosphere

Cool Earth Theory (Con’t)

- Forces acting on an atmospheric gas molecule (Con’t)
  > Centripetal force (Con’t)
    ‡ Note the (velocity of molecule) has two parts
      § Velocity due to Earth’s rotation and velocity relative to the Earth
      § Velocity relative to the Earth has two components
        ◊ Velocity due to wind, i.e., macroscale molecular motion
        ◊ Velocity related to the gas’ temperature, i.e., microscale molecular motion
Evolution of the Atmosphere

Cool Earth Theory (Con’t)

- Is force toward enough to keep gas molecule, i.e., is the force of gravity strong enough to attract the molecule so it will stay as part of the planet’s atmosphere

  ?

  (Force of gravity) greater than (Centripetal force)

- Conclusions

  > As mass of planet increases, the gravitational force toward increases

  > As rotation of planet increases, the force needed increases

  > As the planet’s temperature increases, the force needed increases

  > As molecule’s mass increases, the gravitational force toward increases

*Climate and Global Change Notes*
# Evolution of the Atmosphere

## Cool Earth Theory (Con’t)

<table>
<thead>
<tr>
<th>EON</th>
<th>ERA</th>
<th>PERIOD</th>
<th>EPOCH</th>
<th>ATMOSPHERIC EVOLUTION</th>
<th>IMPORTANT EVENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precambrian (Con’t)</td>
<td>Hadean (Con’t)</td>
<td></td>
<td>4600 - 3800</td>
<td>• Original atmosphere lost to space, Earth’s surface too warm; gravity insufficient to hold early hot gases</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Began creating a new atmosphere by impact degassing and volcanic outgassing</td>
<td>4050 BP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Continued collisions directly provided gases as frozen material melted and vaporized; also collisions released CO₂ from the Earth’s surface (impact degassing) probably primary method</td>
<td>- Planet collides with Earth to form Moon</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Volcanic activity emitted gases (volcanic outgassing or degassing) once thought to be the primary process</td>
<td>3800 BP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Causes Earth to rotate about an axis that is tilted w.r.t. the Earth’s orbital plane</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>- Nearly every lunar rock is older than nearly every Earth rock</td>
</tr>
</tbody>
</table>
Cool Earth Theory (Con’t)

- Sample possible new gases; hydrogen, helium, nitrogen, oxygen, neon, carbon compound gases

> Group I gases (lightest)

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Molecular Wt</th>
<th>Volcanic Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>H₂</td>
<td>2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Helium</td>
<td>Hé₂</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

> Group II gases

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Molecular Wt</th>
<th>Volcanic Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>14</td>
<td>1</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>16</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>18</td>
<td>79</td>
</tr>
</tbody>
</table>

Climate and Global Change Notes
Evolution of the Atmosphere

Cool Earth Theory (Con’t)

- Possible new gases; hydrogen, helium, nitrogen, oxygen, neon, carbon compound gases (Con’t)

> Group III gases (heaviest)

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Molecular Wt</th>
<th>Volcanic Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Sulfide</td>
<td>H₂S</td>
<td>34</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>CO₂</td>
<td>44</td>
<td>12</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>SO₂</td>
<td>64</td>
<td>6</td>
</tr>
</tbody>
</table>

- Note volcanic gases lead to an atmosphere of mostly water vapor and carbon dioxide with lesser amounts of sulfur dioxide and nitrogen

- Impacts during the accretion period adds nitrogen by the melting of frozen ammonia, NH₃ contained in planetesimals (small proto-planets); the NH₃ is split apart to elemental H₂ and N₂ during the collision
Cool Earth Theory (Con’t)

- CO₂ more abundant than today, thus surface warmer than today temperature 85°- 110°C (185°-230°F)

> Conclusions applied to Earth

‡ Group I gases too light so they fly off
‡ Group III gases heavy enough so they remain
‡ Group II gases? - Because Earth was relatively cool, most stay

> Conclusions applied to other planets

‡ Uranus - large, excessively cold (-215°C) (Hydrogen-Methane atmosphere)
‡ Jupiter - large, moderately cold (-110°C) (Hydrogen-Helium atmosphere)
‡ Earth - small, cool (15°C) (Water Vapor-Carbon Dioxide atmosphere with some Sulfur Dioxide and Nitrogen)
‡ Mercury - small, very hot (260°C) (No atmosphere)
### Evolution of the Atmosphere

#### Cool Earth Theory (Con’t)

Earth doesn’t have water vapor-carbon dioxide atmosphere. Why not?

<table>
<thead>
<tr>
<th>EON</th>
<th>ERA</th>
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<th>EPOCH (10^6y)</th>
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<th>IMPORTANT EVENTS</th>
</tr>
</thead>
</table>
| Precam-brian (Con’t) | Archean (archaios = ancient) | 3800 - 2500 | • Impacts and volcanic activity slowed  
• Earth began to cool  
• Water began to condense and form oceans  
• CO₂ dissolved in oceans and most deposited as limestone  
• Radioactive decay of potassium-40 by electron capture formed small amount inert gas argon  
   - One of the processes heating the Earth’s core | 3500 BP  
• Earliest evidence of life  
• 1st life existed near surface of ocean (needed light), but not too near the surface because no oxygen and thus, no ozone, there was too much uv light |
# Evolution of the Atmosphere

## Cool Earth Theory (Con’t)

<table>
<thead>
<tr>
<th>EON</th>
<th>ERA</th>
<th>PERIOD</th>
<th>EPOCH</th>
<th>AGE (10⁶y)</th>
<th>ATMOSPHERIC EVOLUTION</th>
<th>IMPORTANT EVENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precambrian</td>
<td>Archean</td>
<td>(Con’t)</td>
<td>(Con’t)</td>
<td>3800 - 2500</td>
<td>3500 BP&lt;br&gt;• Oxygen began to be added to atmosphere&lt;br&gt; - Photodissociation; produces 1-5% of oxygen&lt;br&gt; 2H₂O + uv light $\Rightarrow$ 2H₂ + O₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2700 BP&lt;br&gt;• 1st oxygen producing bacteria (cyanobacteria)&lt;br&gt; - CO₂ + H₂O $\Rightarrow$ CH₂O + O₂&lt;br&gt; • Photosynthesis; plants; one celled plankton; produces 95-99% of oxygen&lt;br&gt; - 6CO₂ + 6H₂O $\Rightarrow$ C₆H₁₂O₆ + 6O₂</td>
<td></td>
</tr>
</tbody>
</table>
### Evolution of the Atmosphere

#### Cool Earth Theory (Con’t)

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</tr>
</thead>
</table>
| Precambrian (Con’t) | Proterozoic (proteros = before; zoe = life) |        |         | 2500 - 545 | 2000 BP  
• 1st evidence of oxygen in atmosphere  
• Oxygen reached about 1% of present value  
700 BP  
• Oxygen reached about 10% of present value  
• Ozone began to reach amounts sufficient to begin to shield surface from UV radiation | Huronian Glaciations  
900 BP  
• Length of day ~18 h  
Late Proterozoic Glaciations |
### Evolution of the Atmosphere

#### Cool Earth Theory (Con’t)

<table>
<thead>
<tr>
<th>EON</th>
<th>ERA</th>
<th>PERIOD</th>
<th>EPOCH (10^9y)</th>
<th>ATMOSPHERIC EVOLUTION</th>
<th>IMPORTANT EVENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phanerozoic</td>
<td>Paleozoic</td>
<td>Cambrian</td>
<td>545 - 505</td>
<td></td>
<td>• Abundant marine organism fossils</td>
</tr>
<tr>
<td></td>
<td>- Age of Ancient Life (paleo = ancient; zoe = life)</td>
<td>Ordovician</td>
<td>505 - 438</td>
<td></td>
<td>• 1st fish fossil</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Silurian</td>
<td>438 - 408</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Devonian</td>
<td>408 - 360</td>
<td></td>
<td>• 1st land plant fossils</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mississippian</td>
<td>360 - 320</td>
<td>• Oxygen reached its present value</td>
<td>• Extensive coal deposits developed worldwide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pennsylvanian</td>
<td>320 - 286</td>
<td></td>
<td>• Appalachian &amp; Ouachita Mountains formed by continental collision with Africa</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Permian</td>
<td>286 - 245</td>
<td></td>
<td>• Permo-Carboniferous Glaciations</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Land masses joined to form single supercontinent called Pangea</td>
</tr>
</tbody>
</table>
## Evolution of the Atmosphere

### Cool Earth Theory (Con’t)

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</thead>
<tbody>
<tr>
<td>Phanerozoic</td>
<td>Mesozoic - Age of Middle Life (meso = middle; zoe = life)</td>
<td>Triassic</td>
<td>245 - 208</td>
<td></td>
<td>• 1st dinosaurs&lt;br&gt;• North America begins to separate from Africa</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jurassic</td>
<td>208 - 144</td>
<td></td>
<td>• Atlantic Ocean begins to form between North America &amp; Africa</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cretaceous</td>
<td>144 - 66.4</td>
<td></td>
<td>• Dinosaurs become extinct&lt;br&gt;Rocky Mountains begin forming</td>
<td></td>
</tr>
</tbody>
</table>
### Evolution of the Atmosphere

#### Cool Earth Theory (Con’t)

<table>
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<th>EON</th>
<th>ERA</th>
<th>PERIOD</th>
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<th>ATMOSPHERIC EVOLUTION</th>
<th>IMPORTANT EVENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phanerozoic (Con’t)</td>
<td>Cenozoic - Age of Recent Life (ceno = recent; zoe = life)</td>
<td>Tertiary</td>
<td>Paleocene</td>
<td>66.4 - 57.8</td>
<td>• Mammals become dominant land animals</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Eocene</td>
<td>57.8 - 36.6</td>
<td>• Alps form in Europe</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oligocene</td>
<td>36.6 - 23.7</td>
<td>• Himalaya Mountains begin to form</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Miocene</td>
<td>23.7 - 5.3</td>
<td>• Antarctic Ice Sheet develops</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pliocene</td>
<td>5.3 - 1.6</td>
<td>• Humans appear for the first time</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pleistocene</td>
<td>1.6 - 0.01</td>
<td>Late Proterozoic Glaciations - Northern hemisphere</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Holocene</td>
<td>0.01 - present</td>
<td>Civilization modified atmosphere</td>
<td>• Human civilization develops&lt;br&gt;• Length of day ~24 h Tides caused by Moon slow Earth’s rotation</td>
</tr>
</tbody>
</table>
Evolution of the Atmosphere

Cool Earth Theory Summary

- Earth with no atmosphere
- Atmosphere of water vapor and carbon dioxide with some nitrogen formed by impact and volcanic outgassing; no oxygen
- Impacts and volcanic activity slowed; Earth cooled; water vapor condensed; oceans formed
- Oceans absorbed much of the carbon dioxide which helped cool the Earth
Evolution of the Atmosphere

Cool Earth Theory Summary (Con’t)

• Life added oxygen, methane and more nitrogen
  - Oxygen by converting some of the carbon dioxide
  - Nitrogen added by bacteria
  - Methane as a by-product of soil, ocean and coastal methanogenic bacteria;
    still an active process, but much more active process in the past

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}
\]

• New category of planet - small, cool, with life (Nitrogen-Oxygen atmosphere
  with lesser amounts of argon and methane

Climate and Global Change Notes
Atmospheric Constituents - Today

**Composition of the Atmosphere**

Atmospheric Constituents
- Homosphere
  - Gases
  - Particulates
  - Pollutants
    - Smog
    - Ozone
    - Mitigation
    - Cleansing
    - Wet Deposition
      - Acid Rain
    - Dry Deposition
    - Air Quality Index
  - Heterosphere

**Science Concepts**

- Gasoline Oxidation
- Smog Chemistry
- Ozone-Temperature Relationship
- pH Scale

**The Earth System (Kump, Kastin, & Crane)**

- Chap. 3 (p. 44)
### Atmospheric Constituents

#### Homosphere

- Major constituents are constant in this layer; lowest 80 km of the atmosphere
- Non-variable atmospheric constituents

<table>
<thead>
<tr>
<th>Name</th>
<th>% By Volume (Average - Moist air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>76.9</td>
</tr>
<tr>
<td>Oxygen</td>
<td>20.7</td>
</tr>
<tr>
<td>Argon</td>
<td>0.93 or 9.3 x 10^{-1}</td>
</tr>
<tr>
<td>Neon</td>
<td>0.0018 or 1.8 x 10^{-3}</td>
</tr>
<tr>
<td>Helium</td>
<td>0.00052 or 5.2 x 10^{-4}</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.00005 or 5.0 x 10^{-5}</td>
</tr>
</tbody>
</table>

- Variable atmospheric constituents

<table>
<thead>
<tr>
<th>Name</th>
<th>% By Volume (Average - Moist air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Vapor</td>
<td>1.4 (up to 4%)</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.035 or 3.5 x 10^{-2}</td>
</tr>
<tr>
<td>Methane</td>
<td>0.00017 or 1.7 x 10^{-4}</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>0.00003 or 3.0 x 10^{-5}</td>
</tr>
<tr>
<td>Ozone</td>
<td>0.000004 or 4.0 x 10^{-6}</td>
</tr>
<tr>
<td>Particles</td>
<td>0.000001 or 1.0 x 10^{-6}</td>
</tr>
<tr>
<td>Chlorofluorocarbons</td>
<td>0.00000001 or 1.0 x 10^{-8}</td>
</tr>
</tbody>
</table>
Atmospheric Constituents

Homosphere (Con’t)

- Variable atmospheric constituents (Con’t)
  - Source is surface of Earth
  - Water vapor
    > Maximum near surface
    > Maximum over water surface
    > Maximum in warm regions
Atmospheric Constituents

Homosphere (Con’t)

• Variable atmospheric constituents (Con’t)

- Air Pollutants

  > “The presence of substances in the atmosphere, particularly those that do not occur naturally. These substances are generally contaminants that substantially alter or degrade the quality of the atmosphere. The term is often used to identify undesirable substances produced by human activity, that is, anthropogenic air pollution. Air pollution usually designates the collection of substances that adversely affects human health, animals, and plants; deteriorates structures; interferes with commerce; or interferes with the enjoyment of life.” (Glossary of Meteorology; http://amsglossary.allenpress.com/glossary/)

http://www.epa.gov/air/oaqps/eog/course422/ap3.html

Climate and Global Change Notes
Atmospheric Constituents

Homosphere (Con’t)

• Variable atmospheric constituents (Con’t)
  - Carbon Oxides
    > CO₂
      † Maximum over cities
      ‡ Natural causes
        § Respiration; forest fires; volcanic activity
      ‡ Human causes
        § Combustion of fossil fuels

Atmospheric Constituents

Gasoline Combustion
Number of pounds of carbon dioxide emitted into the air for each mile driven in a passenger car that gets 22 mpg: 0.9

Number of pounds of carbon dioxide produced by burning 1 gallon of gasoline: 19

Gasoline is a hydrocarbon such as “heptane” or C\(_7\)H\(_{16}\). “Burning” gasoline means to oxidize or to chemically combine it with oxygen. Ideally when gasoline combines with oxygen it produces carbon dioxide (CO\(_2\)) and water (H\(_2\)O).

\[
\text{Heptane} + \text{Oxygen} \rightarrow \text{Carbon Dioxide} + \text{Water}
\]

\[
\text{C}_7\text{H}_{16} + 11\text{O}_2 \rightarrow 7\text{CO}_2 + 8\text{H}_2\text{O}
\]

Carbon (C) “weighs” 12 atomic units; hydrogen (H) 1 atomic unit; and oxygen (O) 16 atomic units. So

\[
\begin{align*}
\text{C}_7\text{H}_{16} & + 11\text{O}_2 \rightarrow 7\text{CO}_2 + 8\text{H}_2\text{O} \\
100 \text{ units} & + 352 \text{ units} \rightarrow 308 \text{ units} + 144 \text{ units}
\end{align*}
\]

Gasoline weighs ~ 5.666 lb per gal. Thus,

\[
\begin{align*}
\text{C}_7\text{H}_{16} & + 11\text{O}_2 \rightarrow 7\text{CO}_2 + 8\text{H}_2\text{O} \\
5.666 \text{ lb} & + 19.94 \text{ lb} \rightarrow 17.45 \text{ lb} + 8.15 \text{ lb}
\end{align*}
\]
Atmospheric Constituents

Homosphere (Con’t)

- Variable atmospheric constituents (Con’t)
  - Carbon Oxides (Con’t)
    > CO
      † Odorless, colorless, poisonous gas; causes headaches, drowsiness, fatigue, can result in death
      † Natural causes
        § Forest fires; oxygen combining with methane and VOCs
      † Human causes (2/3 in U.S. from transportation)
        § Incomplete combustion of fossil fuels; low air-to-fuel ratios in the engine; poorly tuned engine; metals processing and chemical manufacturing and residential wood burning
        § Woodstoves, gas stoves, cigarette smoke and unvented gas and kerosene space heaters are sources of CO indoors

http://www.epa.gov/air/oaqps/eog/course422/ap5.html

Climate and Global Change Notes
**Atmospheric Constituents**

**Homosphere (Con’t)**

- Variable atmospheric constituents (Con’t)
  - Carbon Oxides (Con’t)
    - CO (Con’t)
      † Image from NASA’s Measurements Of Pollution In The Troposphere (MOPITT) instrument
      † Note fires in western Montana and Idaho in August 2007 have increased CO across North and South Dakota, Minnesota, Iowa and Wisconsin
      † Black areas are where clouds prevented measurements
      † Fires produce large amounts of CO that remains in the atmosphere for about two months on average while gray smoke particles disappear after about a week

[Image from NASA’s Measurements Of Pollution In The Troposphere (MOPITT) instrument](http://earthobservatory.nasa.gov/Newsroom/NewImages/images.php3?img_id=17751)
Atmospheric Constituents

Homosphere (Con’t)

- Variable atmospheric constituents (Con’t)
  - Volatile Organic Compounds (VOCs)
    - Highly reactive organic compounds
    - Hydrocarbons
      ‡ Gasoline, benzene, formaldehyde, methane, etc.
    - Natural causes
      ‡ Terpenes; >0.1% ppm; vegetation emissions
    - Human causes
      ‡ Incomplete fuel combustion, evaporation of fuel, solvents (e.g., painting, cleaning agents), chemical production, fuel refining

Primary Sources

- Transportation 46%
- Fuel Combustion (Stationary) 29%
- Industrial Processes 16%
- Solid Waste Disposal 2%
- Miscellaneous 7%
Atmospheric Constituents

Homosphere (Con’t)

- Variable atmospheric constituents
  - VOCs (Con’t)
    - Hydrocarbons (Con’t)
      ‡ Methane (CH$_4$)
      § Natural causes - Natural gas; Formed by decay of organic material in oxygen-starved environments such as swamps, rice patties, stomachs of cattle
      § Human causes (estimated 60%) - Fossil fuel production, animal husbandry, rice cultivation, biomass burning and waste management

http://www.epa.gov/methane/sources.html
Atmospheric Constituents

Homosphere (Con’t)

- Variable atmospheric constituents (Con’t)
  - Nitrogen Oxides (NO, NO\textsubscript{2}, NO\textsubscript{x})

  > Natural causes
    † Soil bacteria, volcanoes, lightning (5%)
    § “We know that lightning is the most important source of NO\textsubscript{x} in the upper troposphere, where our weather takes place,” Koshak continues. "NO\textsubscript{x} indirectly influences our climate because it partly controls the concentration of ozone (O\textsubscript{3}) and hydroxyl radicals (OH) in the atmosphere. Ozone is an important greenhouse gas, and OH is a highly reactive molecule that controls the oxidation of several greenhouse gases.”

  > Human causes
    † Automobile engines (50%), coal power plants (50%)
Atmospheric Constituents

Homosphere (Con’t)

- Variable atmospheric constituents (Con’t)
  
  - Sulfur Compounds (SO₂, H₂S)
    
    > Natural causes (2/3)
      ‡ Volcanoes and sea spray, decay of organic material

    > Human causes (1/3)
      ‡ Burning fossil fuels (wood, sulfur containing coal, oil and natural gas); petroleum refineries, cement manufacturing and metal processing facilities

http://www.epa.gov/air/oaqps/eog/course422/ap5.html

U.S. SO₂ Sources

Climate and Global Change Notes
Atmospheric Constituents

Homosphere (Con’t)

- Variable atmospheric constituents (Con’t)
  - Ozone

  > Three atoms per molecule instead of the normal two atoms per molecules
  > Derived from the Greek word ozein which means “to smell”
  > Maximum near 25 km
  > Secondary maximum near ground

Fahey, D.W., Twenty Questions and Answers About the Ozone Layer. http://vortex.nsstc.uah.edu/atmchem/recent_events/upperstrat03_recovery.html
Atmospheric Constituents

Homosphere (Cont.)

- Variable atmospheric constituents (Cont’t)
  - Ozone (Cont’t)
    - Secondary maximum near ground (Cont’t)
      - Photochemical smog ($O_3$, $NO_2$, etc.)
        - Brownish haze, particularly over cities in the summertime
      - Primary component is ozone
    - Creation
      \[
      NO_2 + \text{uv} \rightarrow NO + O \\
      O + O_2 + M \rightarrow O_3 + M
      \]
      where $M$ is a catalyst
    - The NO plus VOCs and sunlight replenish the NO$_2$
      \[
      \text{VOC} + NO + \text{uv} \rightarrow NO_2 + \text{other products}
      \]
      Thus, the process can begin again

“If you thought trees were upstanding citizens of nature, you may want to think again.”

“Measurements show that at high temperatures, trees and some other plants discharge the chemical isoprene” (a VOC), thus, contributing to smog formation. Deciduous trees may increase their output by ten fold as the temperature rises from 86°F to 95°F.

Atmospheric Constituents

Homosphere (Con’t)

- Variable atmospheric constituents (Con’t)
  - Ozone (Con’t)
    > Secondary maximum near ground (Con’t)

‡ Photochemical smog (Con’t)

§ Note, three elements play a roll in O₃ production NOₓ, ultraviolet (uv) sunlight and VOCs

§ Destruction
  \[
  O_3 + NO \Rightarrow NO_2 + O_2
  \]
Atmospheric Constituents

Homosphere (Con’t)

- Variable atmospheric constituents (Con’t)

  - Particulates (Aerosols)
    - Larger than ~1 µm
      † Windblown dust
      † Sea salt from sea spray and bursting bubbles
    - Smaller than 1 µm
      † Conversion of sulfur dioxide (SO₂) (released from volcanic eruptions) to sulfate particles
      † Formation of soot and smoke during burning processes

http://earthobservatory.nasa.gov/Library/Aerosols/aerosol.html
Atmospheric Constituents

Homosphere (Con’t)

- Variable atmospheric constituents (Con’t)

  - Particulates (Aerosols) (Con’t)

    - Dust fills this scene over the Gulf of Oman on 18 February 2003, captured by the Moderate Resolution Spectroradiometer (MODIS on the Terra satellite. At top left is Iran, then Pakistan, then India at bottom right. At bottom left is Oman.

  [Image source: visibleearth.nasa.gov/view_rec.php?id=5017]
Atmospheric Constituents

Homosphere (Con’t)

- Variable atmospheric constituents (Con’t)
  - Particulates (Aerosols) (Con’t)
    - Burning of savanna grasslands in South Africa
    - CO₂ and soot particulates are components of the emissions

http://earthobservatory.nasa.gov/Library/BiomassBurning/
Atmospheric Constituents

Homosphere (Con’t)

• Variable atmospheric constituents (Con’t)
  - Particulates (Aerosols) (Con’t)
  
    > January 1, 2006 fires and dust storm over New Mexico, Texas and Oklahoma
    > Dust storm is the light shade of tan, partially obscuring the view of the darker ground
    > Fires are marked in red

Atmospheric Constituents

Homosphere (Con’t)

- Variable atmospheric constituents (Con’t)
  - Particulates (Aerosols) (Con’t)
    > Aerosol optical thickness measures how much aerosols filter incoming sunlight
    > NASA satellite data seems to indicate there are less aerosols now than in the early 90s
    > Thus, allowing more sunlight to reach Earth’s surface
    > Note very small pockets of red (increased aerosol optical thickness), mostly near land in the Northern Hemisphere
    > Blue areas (decreased aerosol optical thickness) dominate
    > This decline in the dimming power of aerosols over the past decade may have made the greenhouse warming trend more evident in the past decade than in previous decades

Atmospheric Constituents

Homosphere (Con’t)

- Variable atmospheric constituents (Con’t)
  - Particulates (Aerosols) (Con’t)
    - Irritating
      - Soot, dust, smoke, pollen, salt, etc.
    - Dangerous
      - Asbestos fibers, arsenic, sulfuric acid, PCBs, oil, pesticides, etc.
    - Diameter > 10 \( \mu \text{m} \)
      - Settle within a day
    - Diameter < 1 \( \mu \text{m} \)
      - Can remain for several weeks
      - Penetrate lung’s defenses
    - Natural causes
      - Volcanoes, forest fires, dust storms, ocean waves
    - Human causes
      - Paper mills, power plants, manufacturing processes, combustion engines, fireplaces, open burning
Atmospheric Cleansing

- Wet deposition; atmospheric removal by precipitation
  - Hydroxyl radical (OH•); partial molecule; unpaired electrons
  - OH• wants to find a hydrogen (H) atom to make water (H₂O)
  - Most urban pollution contains hydrogen
  - Example

\[
\begin{align*}
\text{CH}_4 + \text{OH}• & \rightarrow \text{CH}_3• + \text{H}_2\text{O} \\
\text{CH}_3• + \text{O}_2 & \rightarrow \text{CH}_3\text{O}_2• \\
\text{CH}_3\text{O}_2• + \text{NO} & \rightarrow \text{CH}_3\text{O}• + \text{NO}_2 \\
\text{CH}_3\text{O}• + \text{O}_2 & \rightarrow \text{HCHO} + \text{HO}_2•
\end{align*}
\]

HCHO is more ($\approx 10^6$ more) water soluble than CH₄. Thus, clouds and rain will now more likely absorb the hydrocarbon molecule. Many pollutants behave somewhat similarly.

- OH• may be created by one of the destruction mechanisms of ozone

\[
\begin{align*}
\text{O}_3 + \text{uv} & \Rightarrow \text{O}_2 + \text{O} \quad \text{ (uv light < 0.31 } \mu\text{m)} \\
\text{O} + \text{H}_2\text{O} & \Rightarrow \text{OH}• + \text{OH}•
\end{align*}
\]
Atmospheric Cleansing (Con’t)

- Wet deposition (Con’t)
  - Acid Rain
    > Acidity and alkalinity of a substance is measured by the pH scale, a continuous scale from 0 (acid) to 14 (basic).
    > pH is a log-10 scale, a pH of 3 is 10 times more acidic than a pH of 4
    > Pure water is neutral (pH 7.0)
  - Changes the pH of aquatic habitats
  - Affects plants directly and indirectly
  - Affects buildings, statues, etc.
  - Precipitation is not considered acidic unless the pH is less than 5.6 because normal rainfall is slightly acidic

http://www.lbl.gov/Education/ELSI/pollution-main.html

Atmospheric Constituents

Climate and Global Change Notes
Atmospheric Cleansing (Con't)

- Wet deposition (Con’t)
  - Acid Rain (Con’t)
  > Acid Water Significant Values
    ‡ pH of 11.0 - 11.5: Rapidly lethal to all fish.
    ‡ pH of 10.5 - 11.0: Highly lethal to salmonids. Prolonged exposure is lethal to carp and perch.
    ‡ pH of 9.0 - 10.5: Harmful to salmonids and perch if present for long periods.
    ‡ pH of 8.2 - 9.0: Not harmful to most fish, but indirect effects may occur at this level due to chemical changes in the water.
    ‡ pH of 6.5 - 8.2: Optimal for most organisms.
    ‡ pH of 5.5 - 6.0: Fresh water shrimp absent. Not harmful to most fish, unless free carbon dioxide is high (>100 ppm).
    ‡ pH of 5.0 - 5.5: Bottom-dwelling bacteria (decomposers) begin to die. Mats of fungi begin to replace bacteria in the substrate. Plankton begin to disappear. Snails and clams absent.
    ‡ pH of 4.5 - 5.0: Most fish eggs will not hatch.
    ‡ pH of 4.0 - 4.5: Most insects, frogs, and all fish absent.
    ‡ pH of 3.5 - 4.0: Lethal to salmonid fishes.
    ‡ pH of 3.0 - 3.5: Most fish cannot survive for more than a few hours, although some invertebrates and plants can be found at such low levels.
Atmospheric Cleansing (Con’t)

- Dry deposition
  - Sedimentation; gravitational fallout; collision between particles and objects (e.g., vegetation, structures, etc.)

Pollution Budget

http://www.epa.gov/air/oaqps/eog/course422/ap7b1.html
**FPA Air Quality Index (AQI)**

- An index for reporting daily air quality
- Focuses on health effects that can happen within a few hours or days after breathing polluted air
- Five major air pollutants regulated by the Clean Air Act: ground-level ozone, particulate matter, carbon monoxide, sulfur dioxide, and nitrogen dioxide

<table>
<thead>
<tr>
<th>Index Value</th>
<th>Descriptors</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to 50</td>
<td>Good</td>
<td>Green</td>
</tr>
<tr>
<td>51 to 100</td>
<td>Moderate</td>
<td>Yellow</td>
</tr>
<tr>
<td>101 to 150</td>
<td>Unhealthy for Sensitive Groups</td>
<td>Orange</td>
</tr>
<tr>
<td>151 to 200</td>
<td>Unhealthy</td>
<td>Red</td>
</tr>
<tr>
<td>201 to 300</td>
<td>Very Unhealthy</td>
<td>Purple</td>
</tr>
<tr>
<td>301 to 500</td>
<td>Hazardous</td>
<td>Maroon</td>
</tr>
</tbody>
</table>

- **Good** => Air quality is considered satisfactory and air pollution poses little or no risk.
- **Moderate** => Air quality is acceptable; however, for some pollutants there may be a moderate health concern for a very small number of individuals. For example, people who are unusually sensitive to ozone may experience respiratory symptoms.

http://www.epa.gov/airnow/aqibroch/aqi.html#2
Atmospheric Constituents

EPA Air Quality Index (Cont’d)

<table>
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- **Unhealthy for Sensitive Groups** => Certain groups of people are particularly sensitive to the harmful effects of certain air pollutants. For example, children and adults who are active outdoors and people with respiratory disease are at greater risk from exposure to ozone, while people with heart disease are at greater risk from carbon monoxide. The general public is not likely to be affected when AQI is in this range.

- **Unhealthy** => Everyone may begin to experience health effects. Members of sensitive groups may experience more serious health effects.

- **Very Unhealthy** => Trigger a health alert, meaning everyone may experience more serious health effects.

- **Hazardous** => Trigger health warnings of emergency conditions. The entire population is more likely to be affected.

http://www.epa.gov/airnow/aqibroch/aqi.html#2
Atmospheric Constituents

EPA Air Quality Index (Con’t)

• Reported on TV and in Newspapers

Pollutant: Ozone
Today's Forecast: 130
Quality: Unhealthy for Sensitive Groups

Children and people with asthma are the groups most at risk.

http://www.epa.gov/airnow/aqibroch/eqi.html#2
### EPA Air Quality Index (Con’t)

#### Air Quality Index (AQI): Particulate Matter (PM)

<table>
<thead>
<tr>
<th>Index Values</th>
<th>Levels of Health Concern</th>
<th>PM$_{2.5}$</th>
<th>Cautionary Statements$^*$</th>
<th>PM$_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 50</td>
<td>Good</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>51 - 100**</td>
<td>Moderate</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>101 - 150</td>
<td>Unhealthy for Sensitive Groups</td>
<td>People with respiratory or heart disease, the elderly, and children should limit prolonged exertion.</td>
<td>People with respiratory disease, such as asthma, should limit outdoor exertion.</td>
<td></td>
</tr>
<tr>
<td>151 - 200</td>
<td>Unhealthy</td>
<td>People with respiratory or heart disease, the elderly, and children should avoid prolonged exertion; everyone else should limit prolonged exertion.</td>
<td>People with respiratory disease, such as asthma should avoid outdoor exertion; everyone else, especially the elderly and children, should limit prolonged exertion.</td>
<td></td>
</tr>
</tbody>
</table>

PM$_{2.5}$ => Particles up to 2.5 microns in diameter  
PM$_{10}$ => Particles up to 10 microns in diameter

http://www.epa.gov/airnow/aqibroch/aqi.html#2
### Atmospheric Constituents

**EPA Air Quality Index (Con't)**

**Air Quality Index (AQI): Particulate Matter (PM)**

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<th>PM$_{10}$</th>
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</thead>
<tbody>
<tr>
<td>201 - 300</td>
<td>Very Unhealthy</td>
<td>People with respiratory or heart disease, the elderly, and children should avoid any outdoor activity; everyone else should avoid prolonged exertion.</td>
<td></td>
<td>People with respiratory disease, such as asthma, should avoid any outdoor activity; everyone else, especially the elderly and children, should limit outdoor exertion.</td>
</tr>
<tr>
<td>301 - 500</td>
<td>Hazardous</td>
<td>Everyone should avoid any outdoor exertion; people with respiratory or heart disease, the elderly, and children should remain indoors.</td>
<td></td>
<td>Everyone should avoid any outdoor exertion; people with respiratory disease, such as asthma, should remain indoors.</td>
</tr>
</tbody>
</table>

PM$_{2.5}$ => Particles up to 2.5 microns in diameter

PM$_{10}$ => Particles up to 10 microns in diameter

http://www.epa.gov/airnow/aqibroch/aqi.html#2
Atmospheric Constituents

Heterosphere

- Above 80 km