Steady State Box Model
A defined volume of air (the box) receives pollution from a source, while pollution is removed at the same time by a sink process.

In a “steady state” the concentration (and the total amount) of the pollutant inside the box does not change (is constant).

Box Model Formula

\[
q = \frac{S \times \tau}{V}
\]

- \( V \) = Volume of box
- \( S \) = Source rate
- \( = \) Sink rate
- \( \tau \) = residence time (\( \tau \): tau)
- \( q \) = steady state concentration of pollutant in box

If we know the source rate of a pollutant and its residence time in the atmosphere, we can calculate its concentration in a given volume.

Sources and Sinks

Sources:
Everything that introduces pollutants into the air in the box
- direct emissions (cars, industry, …)
- transport by wind
- chemical formation

Sinks:
Processes that remove or convert pollutants
- wind blows pollutants away (ventilation)
- chemical conversion
- pollutants are deposited on the ground (rainfall)
An Example: Your next party

![Diagram showing number of guests arriving and leaving over time.]

Box Model Formula

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- \( S \) = Source rate
- \( \tau \) = Sink rate
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- \( q \) = steady state concentration of pollutant in box

Source/Sink Rates

\[ S = \frac{\text{Amount of substance emitted/lost in time interval } t}{\text{time interval } t} \]

In a steady state the source and the sink rates are equal.

Party:
- Source rate: People arriving per hour
- Sink rate: People leaving per hour

Let’s say \( S = 5 \) guests/hour
Residence time

\[ \tau = \text{average period of time that a molecule of a pollutant is in the box before it is removed} \]

Party:
How long does a guest on average stay in your home.
Let’s say \( \tau = 2 \text{ hours} \)

Box Model Formula

\[ q = \frac{S \times \tau}{V} \]

Your party at steady-state:
\( S = 5 \text{ guests/hour} \)
\( \tau = 2 \text{ hours} \)
\( V = 1 \)

Average number of guests in your house?
\( q = S \times \tau = 5 \text{ guests/hour} \times 2 \text{ hours} = 10 \text{ guests} \)
Sources of aerosols

- Biological: seeds, pollen, spores (1-250 μm); bacteria, algae, fungi, viruses (<1 μm)
- Solid Earth: dust, volcanoes
- Oceans: sea-salt
- Anthropogenic (~20% mass): fires (soot and ash); dust from roads; wind erosion of tilled land; fuel combustion; industrial processes
- Chemical formation: gas (SO₂, HNO₃, hydrocarbons,) condensing onto existing particles, or forming new particles.

SEA SPRAY

Dust Storm off West Africa (sept. 2005)

http://visibleearth.nasa.gov/view_rec.php?id=20238
Mount St. Helens (Fall, 1982)

Peter Frenzen, available from Mount Saint Helens National Volcanic Monument Photo Gallery

Prescribed Burn in Big Horn National Forest, Wyoming (1981)

Fig. 5.7. U.S. Forest Service, available from National Renewable Energy Lab.

Urban Aerosol

- Power generation
- Diesel
- Automobiles
- Construction
Dry Deposition

Aerosols are taken up by surfaces, i.e. ground, buildings, plants.

Factors that govern dry deposition rates:
- Level of atmospheric turbulence
- Chemical properties of depositing species
- Nature of surface itself

Wet Deposition

Aerosols are taken up into water droplets, which are then deposited.

Particle concentrations in the atmosphere

Polluted environments PM₁₀ ~ 100 µg/m³

Take a volume of 1 m³ of air (bathtub size)
⇒ Mass of 100 µg of particles = 0.0001 grams (10 billion or more particles)

Marine background ~ 10 µg/m³
Arctic ~ 1 µg/m³
Visibility impairment in Mt. Rainier National Park

Clear day: VR=240km
VR = visibility range
Hazy day: VR=80km

Wavelengths vary over many orders of magnitude

http://www.nrao.edu/whatisra/mechanisms.shtml

Wavelengths
Visible light (0.4 - 0.7 μm)

<table>
<thead>
<tr>
<th>Energy</th>
<th>λ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.4</td>
</tr>
<tr>
<td>blue</td>
<td>green yellow</td>
</tr>
</tbody>
</table>

Ultraviolet
0.1 - 0.4 μm

Infrared (heat)
0.7 - 100μm
Gas (Rayleigh) Scattering
Redirection of radiation by a gas molecule without a net transfer of energy to the molecule

What is white light?
Sum of all wavelengths in the visible region.
Radiation Scattering by a Sphere

Visibility

Visibility is defined as the ability to distinguish a perfectly black surface from a white background.

Expressed as visibility length.

Particles decrease visibility!

Good Visibility

Poor Visibility

Visibility impairment in Mt. Rainier National Park

Clear day: VR=240km

VR = visibility range

Hazy day: VR=80km
Processes Affecting Visibility

Particles and Visibility

Visibility at National Parks

http://vista.cira.colostate.edu/improve/Education/VisConcepts.swf
Visibility in the US

Typical visual ranges
• Western U.S.: 90-180 km (50-100 miles), ~ one-half of what it would be without human-made air pollution.
• Eastern U.S.: 30-60 km (15-40 miles), or about one-third of the visual range under natural conditions.

IMPROVE web site:
http://vista.cira.colostate.edu/views/Web/GraphicViewer/seasonal.htm

from "Introduction to Visibility" by William C. Malm
Air Quality Standards for Particulate Matter (PM)

**PM₁₀**: (particles smaller than 10 μm)
- 24 hour average: 150 μg/m³

**PM₂.₅**: (particles smaller than 2.5 μm)
- 24 hour average: 35 μg/m³
- Annual average: 15 μg/m³

PM = Particulate Matter = particles = aerosols

Air Quality Guide for Particle Pollution

<table>
<thead>
<tr>
<th>AQI Level</th>
<th>Air Quality Index (AQI)</th>
<th>Health Advisory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good</td>
<td>0 – 50</td>
<td>None</td>
</tr>
<tr>
<td>Moderate</td>
<td>51 – 100</td>
<td>Unusually sensitive people should consider reducing prolonged or heavy exertion.</td>
</tr>
<tr>
<td>Unhealthy for sensitive groups</td>
<td>101 – 150</td>
<td>People with heart or lung disease, older adults, and children should reduce prolonged or heavy exertion.</td>
</tr>
<tr>
<td>Unhealthy</td>
<td>151 – 200</td>
<td>People with heart or lung disease, older adults, and children should reduce prolonged or heavy exertion.</td>
</tr>
<tr>
<td>Very unhealthy (alert)</td>
<td>201 – 300</td>
<td>People with heart or lung disease, older adults, and children should avoid all physical activity outdoors. Everyone else should avoid prolonged or heavy exercise.</td>
</tr>
</tbody>
</table>

An AQI of 100 for particles up to 2.5 micrometers in diameter corresponds to a level of 35 micrograms per cubic meter (averaged over 24 hours). An AQI of 100 for particles up to 10 micrometers in diameter corresponds to a level of 150 micrograms per cubic meter (averaged over 24 hours).

Health effects of aerosol particles

“Our bodies natural defenses help us to cough or sneeze larger particles out of our bodies. But those defenses don’t keep out smaller particles, those that are smaller than 10 microns, or micrometers, in diameter, or about one-seventh of the diameter of a single human hair. These smaller particles get trapped in the lungs, while the smallest are so minute they can pass through the lungs into the blood stream, just like essential oxygen.”

Quote from the American Lung Association:
http://lungaction.org.reports/sota05_heffects.html
UW MESA Air Pollution Study

http://depts.washington.edu/mesaair/

U.S. SO₂ emissions (1996)

Sulfur content: Coal 1 - 6% S  
               Oil 1 - 2% S  
               Gas ~ 0.5% S

U.S. NOₓ emissions (2001)

Stern, Chemosphere 58 (2005)

Uptake of gases in water

Gas molecules can enter a water droplet through the surface

pH Scale

Figure 10.3
Acidity of acid rain

Uptake of CO₂ in water leads to Carbonic Acid

\[ H₂CO₃ \rightarrow \text{at } \sim 360 \text{ ppmv CO}_₂ \]

natural rain is acidic

pH (natural rain) \sim 5.6

acid (+ H₂SO₄) rain pH \sim 5 - 4

acid fog minimum reported pH \sim 1.7
Liming of a Lake in Sweden

Influence on Ecosystems

Forrests

Effects depend on the “buffering capacity” of soil

Damage leaves

Acid rain weakens trees

Aluminum (toxic)

Removal of nutrients

Nutrients: Ca, Mg, K

Acidified Forest, Oberwiesenthal, Germany (1991)
Acidified forest near Most, Czechoslovakia (1987)

Effects on Aquatic Ecosystems

http://www.epa.gov/airmarkets/acidrain/effects/surfacewater.html#fish

Sandstone Figure in 1908 and 1968, Westphalia, Germany
Acid Rain Program in the US

- Created under 1990 Clean Air Act Amendments
- Also NOx reductions
- Over 10 year period (1995-2005): SO$_2$ emissions from power plants down by 7 million tons (41% reduction compared to 1980 levels).
- Reduction in acid deposition (~30% reduction in NE US 1990-2005).
Reduction in acid rain deposition (sulfate): ~35% over 1990-2005

National Atmospheric Deposition Network
http://nadp.sws.uiuc.edu/amaps2/so4dep
Costs of 1990 Clean air act amendment

- Initially estimated to be ~$10 billion/year
- Actual costs ~$1-2 billion/year
- cap and trade is more economical than strict regulations.
  Scrubbers turned out to be cheaper than expected and unexpected gains from switching to low sulfur coal.

Cost-effectiveness of Acid Rain Program

- Costs = $3 billion/year.
- Benefits = $122 billion/year [PM → human health; visibility; ecosystems]
- 40-to-1 benefit/cost ratio!

**Now:** SO$_2$ and NO$_x$ emissions from power plants were planned (2005) to be regulated as part of the Clean Air Interstate Rule (CAIR). (Also a clean air mercury rule) 3.7 million ton SO$_2$ cap (2010), 1.5 million ton NO$_x$ cap (2010). Was supposed to go into effect January 1, 2009, but...
  → went to DC circuit court and eliminated July 11, 2008, due to a fundamental argument about the cap and trade approach (among other arguments)

Clean Air Interstate Rule

The Clean Air Interstate Rule would have covered 28 eastern states and the District of Columbia. Air emissions in these states contribute to unhealthy levels of ground-level ozone, fine particles or both in downwind states. The rule uses a cap and trade system to reduce the target pollutants—sulfur dioxide (SO$_2$) and nitrogen oxides (NO$_x$)—by 70 percent.
Problems with CAIR

North Carolina and some electric-power producers opposed aspects of the regulation. The major objection to CAIR was the inability of the EPA to guarantee each state would reduce its emissions sufficiently to prevent interference with air quality downwind. The emissions trading systems set up by CAIR was to reduce emissions overall, and prevent transport of pollution generally, but the EPA couldn’t promise that each state would reduce emissions sufficiently.

➢ July 11, 2008
North Carolina vs. EPA
Court found “more than several fatal flaws in the rule” and vacated the rule in its entirety

➢ December 23, 2008
Court granted rehearing. The EPA needs to replace it with a new rule that fits the court’s view of the agency’s powers under the Clean Air Act.

EPA proposes transport rule

July 6, 2010

- Will replace CAIR when final
- Addresses problems with CAIR by largely eliminating interstate trading
- Will improve air quality in the eastern U.S. by reducing power plant emissions from 31 states and D.C.
- By 2014, would reduce power plant SO2 emissions by 71%, and NOx emissions by 52%, over 2005 levels.
Clean Air Mercury Rule

On March 15, 2005, EPA issued the Clean Air Mercury Rule to permanently cap and reduce mercury emissions from coal-fired power plants for the first time ever.

On February 8, 2008, the D.C. Circuit Court vacated the Clean Air Mercury Rule (New Jersey vs. EPA). The plaintiffs maintained that cap-and-trade contributed to "hot spots" for mercury.

EPA intends to propose air toxics standards for coal- and oil-fired electric generating units by March 15, 2011 and finalize a rule by November 16, 2011.