UNDERSTANDING AIR POLLUTION

The Past and the Future

Akula Venkatram

- 'Understanding'
- Air pollution problems
  - Acid deposition
  - Urban pollution
- The future
Empty skies proved that airports cause pollution, say researchers
By Michael McCarthy, Environment Editor and Phil Boucher

Eyjafjallajokull

Islandmountainglacier
Understanding

Basic physics and chemistry

Comprehensive or semi-empirical models

Simulations to formulate mitigation strategies

Observations
Acid Deposition

- Deposition of acidifying pollutants became a concern in the 1970s
- Acid deposition believed to be damaging lake and forest ecosystems in Scandinavia
Acid Deposition

- Wind
  - Transformation to sulfuric acid ($H_2SO_4$) and nitric acid ($HNO_3$)
  - Windborne ammonia gas and particles of cultivated soil partially neutralize acids and form dry sulfate and nitrate salts
- Nitric oxide (NO) and sulfur dioxide ($SO_2$) and nitric oxide
- Dry acid deposition (sulfur dioxide gas and particles of sulfate and nitrate salts)
- Wet acid deposition (droplets of $H_2SO_4$ and $HNO_3$ dissolved in rain and snow)
- Acid fog
  - Lakes in deep soil high in limestone are buffered
  - Lakes in shallow soil low in limestone become acidic
- Ocean
- Farm

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Acid Deposition

The early models were semi-empirical: Lagrangian trajectory models, statistical models for long-term concentrations

- Bolin and Persson, 1975
- Eliassen and Saltbones, 1975
- Fisher, 1975
- Venkatram et al., 1982
Semi-Empirical Models

- Parameters for chemistry, dry deposition, wet deposition
- Transport modeled using trajectories or 'wind roses'

\[ \frac{dp}{dt} = \frac{Q(t)}{h} - \lambda_p - kp \]
\[ \frac{dq}{dt} = -\lambda q + kp \]

Comparison of model predictions with observations of sulfur concentrations in rain averaged over 1982-1985. Venkatram et al. 1990
Issues with Semi-empirical Models

- Difficult to incorporate fundamental understanding into parameter values
  - Chemistry is generally simple
  - Transport does not account for wind shear
Comprehensive Models

- Designed to incorporate processes in as much detail as possible
- Designed to serve as numerical surrogates of governing system once it has been evaluated with observations
  - Used to conduct experiments that would be impossible in the real world
Comprehensive Models - Acid Deposition and Oxidant Model

- ADOM Framework
  - Transport
  - Dry Deposition
  - Wet Scavenging
  - Gas-Phase Chemistry
  - Aqueous-Phase Chemistry
  - Cloud Physics

- Meteorology
Acid Deposition - Gas Phase Chemistry

\[ \text{SO}_2 + \text{OH} \rightarrow \text{HOSO}_2 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2 \]
\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]

\[ \text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 \]
\[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O} \]
\[ \text{O} + \text{H}_2\text{O} \rightarrow 2\text{OH} \]
Acid Deposition - Aqueous Phase Chemistry

\[ \text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{O}.\text{SO}_2 \]
\[ \text{H}_2\text{O}.\text{SO}_2 \leftrightarrow \text{HSO}_3^- + \text{H}^+ \]
\[ \text{HSO}_3^- + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{SO}_4^{\text{vii}} + 2\text{H}^+ + \text{H}_2\text{O} \]
\[ \text{SO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{SO}_4^{\text{vii}} + 2\text{H}^+ \]

\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]
Role of $\text{H}_2\text{O}_2$

- Hydrogen peroxide oxidizes $\text{SO}_2$ in cloud water: wet removal of $\text{SO}_2$ is more efficient than that suggested by dissolution of $\text{SO}_2$
- Scavenging by rain is limited by the concentration of $\text{H}_2\text{O}_2$

**FIGURE 3**
Wet scavenging during oxidant-limited conditions

**FIGURE 6**
Reduction in emissions alters wet deposition

$r_s$ = Distance below which oxidant limitation applies.

*Fractional change in cumulative wet sulfur deposition for April ’82, 1981, as a result of a 50% reduction in $\text{SO}_2$ emissions.*
Role of $H_2O_2$

- Revealed in long-term concentrations
Role of Non-precipitating Clouds

Simulation of a 12 day period in 1998 showed that

- Sulfur in rain was estimated well
- Total ambient sulfur estimated well
- Sulfate in air underpredicted
- \( \text{SO}_2 \) in air overpredicted

Hypothesis

*Oxidation in cloud results in ambient sulfate when the cloud evaporates*
Role of Non-precipitating Clouds - results from Karamchandani and Venkatram, 1992

Sulfur in Rain

Total Ambient Sulfur (as Sulfate)

Observed Concentration (mg/l) vs ADOM Prediction (mg/l)

Observed Concentration (μg/m³) vs ADOM Prediction (μg/m³)

Data points are categorized as 'w/o non-precip. stratus' and 'w non-precip. stratus'.
Role of Non-precipitating Clouds - results

Ambient $SO_2$

- w/o non-precip. stratus
- w non-precip. stratus

Ambient Sulfate

- w/o non-precip. stratus
- w non-precip. stratus
Models are used to estimate the contributions of pollution sources to visibility reduction.

Visibility is reduced by scattering of light by aerosols.
Results from simulations

- Established culpability of different sources to acid deposition

<table>
<thead>
<tr>
<th>Receptor Source</th>
<th>US</th>
<th>Canada</th>
</tr>
</thead>
<tbody>
<tr>
<td>US</td>
<td>70%</td>
<td>70%</td>
</tr>
<tr>
<td>Canada</td>
<td>30%</td>
<td>30%</td>
</tr>
</tbody>
</table>

- Showed the importance of sulfate formation in non-precipitating clouds
Urban Air Pollution Modeling

- Non-uniform surface characteristics and buildings
- Complex flow and turbulent fields

*Use flat-terrain models with modifications in plume spread*
St Louis Experiment

- Conducted in 1963-65
- Zinc Cadmium Sulfide particles released close to the surface
- Doses sampled at 30-50 locations on arcs ranging from 800 m to 16 km from the source along the estimated plume centerline
- Meteorology measured at three surface stations and an instrumented TV tower in the middle of the city
- Resulted in 26 daytime and 16 evening hour-long experiments
Analysis of Data

- McElroy and Pooler derived horizontal spreads from arc doses, and vertical spreads from maximum ground-level concentrations.
- They presented these spreads as functions of stability parameters.
- Briggs (1973) presented analytical forms that fit the data.
- Used in ISC model as urban dispersion curves.
St Louis Model Performance

Briggs Curves

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Day

Evening

Observed concentration (µs/m³)

Estimated concentration (µs/m³)
Current Urban Pollution Problems

Environmental Justice
Freeways through neighborhoods

Need models for ~1 m scale dispersion!
Sources Near Residents
Urban Field Experiments

Tracer studies designed to study dispersion at scales of meters to kilometers in urban areas.

- CE-CERT parking lot study, April-May 2001
- Dugway Proving Grounds Model Study- July 2001
- Summer and winter Barrio Logan field studies- August and December 2001
- Wilmington shoreline study- September 2003, 2004

*Funded by CEC and ARB to examine Environmental Justice Issues*
Dugway Experiment
Meteorological Measurements
Sampling Sites

- 74 sites
Wilmington/Long Beach Field Study

Locations of sodar and sonic tower

Wilmington Park
Elementary School

LADWP tracer release
sonic mini-sodar
Model Results using Boundary Layer Information and Initial Spread

\[ r^2 = 0.64 \quad \text{Fac2} = 61\% \quad \text{Bias} = 1.29 \]
Model Results - Highway Modeling

(a) Observed NO concentration (ppb) vs Estimated NO concentration (ppb), Sonic-5

- $e_f = 0.57 \text{ gm/km}$
- $r^2 = 0.64$
- $fac2 = 84$

(b) Observed NO concentration (ppb) vs Estimated NO concentration (ppb), Sonic-20

- $e_f = 0.51 \text{ gm/km}$
- $r^2 = 0.65$
- $fac2 = 91$

e)

d) Observed NO concentration (ppb) at unit 2 vs Estimated NO concentration (ppb) at unit 1

Sonic-5

- 200

- 190

- 180

- 170

- 160

- 150

- 140

- 130

- 120

- 110

- 100

- 90

- 80

- 70

- 60

- 50

- 40

- 30

- 20

- 10

- 0

Sonic-20

- 200

- 190

- 180

- 170

- 160

- 150

- 140

- 130

- 120

- 110

- 100

- 90

- 80

- 70

- 60

- 50

- 40

- 30

- 20

- 10

- 0
Freeway concentration contributions

1-3 Butadiene Concentrations
Simple models work well

BUT...

- Simple models for dispersion provide adequate concentration estimates if mean wind and turbulence velocities are known.

**Point sources:**

\[ C \sim \frac{Q}{u_{dil}x^2} \]

\[ u_{dil} = \frac{\sigma_w \sigma_v}{U} \]
Estimating model inputs from urban routine measurements

One or two level measurements of winds and $\sigma_T$ can be used to estimate urban parameters.
Results - Stable Conditions

\[ u_* = C_D u \left( 1 - \frac{2u_0}{C_{D/2} u} \right)^{1/2} \]

\[ \sigma_w = 1.6u_* \]

\[ \sigma_v = 1.9u_* \]
Results - Unstable Conditions
Dispersion Models

- Simpler models are not appropriate for estimating concentrations within a kilometer from source when plume is still in the urban canopy

- Need numerical and/or physical models
Impact of distributed generators

Palm Springs site
Laboratory modeling

- TSI PIV/PLIF System: INSIGHT
- 3G Software, Blue Sky Laser
- 400mJ, Laser Arm, 2M Camera

City Layout
Average Velocity Field
8 Buildings set 3 degrees off per
20 Hz pump speed sampled for
From Simple to Complex

Long Beach
- Renaissance Hotel
- E Ocean Blvd

Los Angeles
- AON Center
- Biltmore Millennium Hotel
- Pershing Square
Is Urban Canopy Layer “Convective”?

\[ C(x, 0, 0) = \frac{Q \cdot f(x)}{\sqrt{2\pi\sigma_y\sigma_z} \cdot U} \]

\[ f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{p} \exp\left(-\frac{t^2}{2}\right) dt \]

\[ p = \frac{\ln\left(\frac{x}{x_i}\right)}{\ln\left(s_g\right)} \quad \text{where} \quad x_i: \quad F^{1/3} x_i^{2/3} - w_d x_i + h_s U = 0 \]

\[ \sigma_y = \frac{\sigma_v x}{U}, \quad \sigma_z = \frac{\sigma_w x}{U} \quad w_d = 0.5w_s \]
Impact of individual buildings

Flow behind a distributed generator

Chimney effect of a tall building
Performance of Numerical Models

J.J. Baik, S.B. Park SNU
Summary

Understanding of air pollution problems is gained through

- Basic science
- Field studies and laboratory experiments
- Modeling/Simulation

How is this going to change in the future?
Past and Future

Per capita income

Air Quality

Kuznet's curve

London, 1952

Delhi, now

Beijing, now
The Future

- Measurement techniques will become more sophisticated and perhaps less/more expensive.

- Models will become more comprehensive and output will be more realistic with increase in computational power.
On Using Comprehensive Models

- Inevitable errors in numerous model inputs make model evaluation a difficult exercise
- Numerical errors
- Finite grid sizes create false effects-mixing and chemistry
- Responses of the complex model are very difficult to interpret
  - Need to draw generalizations based on model results that are “messy” as reality
Future of Modeling

- Need both comprehensive as well as simpler semi-empirical models
- Simple models provide insight that is more difficult to obtain from complex models
- Might need simple models to interpret results from complex models
Acknowledgements

- Collaborators over the past 30 (?) years
  - Prakash Karamchandani, Marko Princevac, David Pankratz, Dennis Fitz

- Students- Jing Yuan, Tao Zhan, Wenjun Qian, Qiguo Jing, Si Tan, Karim Alizad, Sam Pournazeri

- EPRI, USEPA, CEC, CARB, NSF, Ontario Environment, Umweltbundesamt
Model Performance

**Release behind power plant**

- $m_g = 0.64$, $s_g = 4.02$
- $r^2 = 0.46$

**Initial spread and limited mixing**

- $m_g = 1.08$, $s_g = 1.69$
- $r^2 = 0.92$
Field study next to major highway in Raleigh, North Carolina,