Atmospheric Processes: Transport of Air Toxics, Source-Receptor Relationships

Dr. Mark Cohen
NOAA Air Resources Laboratory
SSMC3, R/ARL, Room 3316
1315 East West Highway, Silver Spring MD, 20910
ph: 301-713-0295 x122; fax: 301-713-0119
mark.cohen@noaa.gov

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WHAT DO YOU WANT TO KNOW?

1. Is a given pollutant causing a problem?

2. If so, is the atmospheric pathway significant relative to other loading pathways, and what is the contribution from the atmospheric pathway?

3. SOURCE RECEPTOR RELATIONSHIPS -- If the atmospheric pathway is significant, what is the geographic scale of the problem -- what fraction of the loading is due to local contributions? what fraction due to regional contributions? what fraction due to more distant sources? What are the most significant source categories contributing to the atmospheric loading?

Obviously, the reason why you want to know about source-receptor relationships is that you want to eventually be able to do something about the problem.

The answers to the above questions will obviously depend on

- what pollutant you are considering,
- where you are considering it, and
- when you are considering it...

And, you might be interested in trends in the above information –

- has deposition been increasing or decreasing?
- what might the impact be of a change in the emissions from one or more sources in the future?
<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Lake Superior</th>
<th>Lake Michigan</th>
<th>Lake Huron</th>
<th>Lake Erie</th>
<th>Lake Ontario</th>
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<tr>
<td>DDT</td>
<td>97&lt;sup&gt;a&lt;/sup&gt;</td>
<td>98&lt;sup&gt;a&lt;/sup&gt;</td>
<td>97&lt;sup&gt;a&lt;/sup&gt;</td>
<td>22&lt;sup&gt;a&lt;/sup&gt;</td>
<td>31&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>Lead</td>
<td>97&lt;sup&gt;a&lt;/sup&gt;; 64&lt;sup&gt;b&lt;/sup&gt;; 69&lt;sup&gt;d&lt;/sup&gt;</td>
<td>99&lt;sup&gt;a&lt;/sup&gt;</td>
<td>98&lt;sup&gt;a&lt;/sup&gt;</td>
<td>46&lt;sup&gt;a&lt;/sup&gt;</td>
<td>73&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>Mercury</td>
<td>73&lt;sup&gt;d&lt;/sup&gt;</td>
<td>&gt; 80&lt;sup&gt;f&lt;/sup&gt;</td>
<td>K</td>
<td>K</td>
<td>K</td>
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<tr>
<td>PCB’s</td>
<td>90&lt;sup&gt;a&lt;/sup&gt;; ~ 95&lt;sup&gt;b,c&lt;/sup&gt;; 82&lt;sup&gt;d&lt;/sup&gt;</td>
<td>58&lt;sup&gt;a&lt;/sup&gt;</td>
<td>78&lt;sup&gt;a&lt;/sup&gt;</td>
<td>13&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>PCDD/F</td>
<td>~100&lt;sup&gt;e&lt;/sup&gt;</td>
<td>50-100&lt;sup&gt;e&lt;/sup&gt; (PCDD)</td>
<td>86&lt;sup&gt;f&lt;/sup&gt;</td>
<td>~40&lt;sup&gt;f&lt;/sup&gt;</td>
<td>5-35 (PCDD)&lt;sup&gt;e&lt;/sup&gt;</td>
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<td></td>
<td>~80&lt;sup&gt;f&lt;/sup&gt;</td>
<td>5-35&lt;sup&gt;f&lt;/sup&gt; (PCDF)</td>
<td>88&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>&lt;5 (PCDF)&lt;sup&gt;f&lt;/sup&gt;</td>
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<tr>
<td>Benzo(a)pyrene</td>
<td>96&lt;sup&gt;a&lt;/sup&gt;</td>
<td>86&lt;sup&gt;a&lt;/sup&gt;</td>
<td>80&lt;sup&gt;a&lt;/sup&gt;</td>
<td>79&lt;sup&gt;a&lt;/sup&gt;</td>
<td>72&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>Hexachlorobenzene</td>
<td>99&lt;sup&gt;f&lt;/sup&gt;</td>
<td>95&lt;sup&gt;f&lt;/sup&gt;</td>
<td>96&lt;sup&gt;f&lt;/sup&gt;</td>
<td>&gt; 17&lt;sup&gt;f&lt;/sup&gt;</td>
<td>40&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>Atrazine</td>
<td>97&lt;sup&gt;h&lt;/sup&gt;</td>
<td>~30&lt;sup&gt;h&lt;/sup&gt;; 23&lt;sup&gt;h&lt;/sup&gt;</td>
<td>~20&lt;sup&gt;h&lt;/sup&gt;</td>
<td>~10-20&lt;sup&gt;h&lt;/sup&gt;</td>
<td>5&lt;sup&gt;h&lt;/sup&gt;</td>
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<td>Mirex</td>
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<td>~5&lt;sup&gt;a&lt;/sup&gt;</td>
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**References and Notes**

(a) Strachan and Eisenreich (1988), percentages of total inputs; (b) Hoff et al. (1996); (c) Net loss of PCB’s to the atmosphere of 1600 kg/year; total non-atmospheric inputs of approximately 70 kg/year; (d) Dolan et al. (1993); (e) Pearson et al. (1998); (f) Cohen et al. (1995); (g) Rygwelski et al. (1999); (h) Schottler and Eisenreich (1997); (j) Mason and Sullivan (1997); (k) no estimates could be found
TRANSPORT and FATE of ATMOSPHERIC POLLUTANTS

- **vapor-particle partitioning** at low relative humidity
- **vapor-droplet partitioning** in clouds (and/or at high relative humidity)
- **chemical transformations** producing new compounds (may be more or less toxic) due to reactions and photolysis in the vapor phase, on the surface of particles, and/or within droplets (note: this may involve interaction with compounds from other emissions sources)

- **wet deposition** of particle phase and vapor phase material, from inside clouds and as the precipitation collects material as it falls through the atmosphere

- **dry deposition** of particle phase and vapor phase material, depends on meteorology (e.g., wind speed) and characteristics of surface

- **re-emission** (grasshopper effect) for some pollutants
Estimates based primarily on atmospheric reactions with OH and O₃, for vapor phase fraction, and a 3 - 14 Day estimated half-Life for particle-phase fraction of a given compound.

*Approximate Atmospheric Half-Life (Days)*

Typical, average travel distance in the atmosphere is approximately 400 km per day.

For long-lived compounds capable of being re-emitted, these half-lives are for the first "hop" only.
## Illustrative Examples of Certain Aspects of Atmospheric Behavior of Pollutants

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>Vapor-Particle Partitioning</th>
<th>Relative water solubility</th>
<th>Important Deposition Modes</th>
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<tbody>
<tr>
<td></td>
<td>vapor</td>
<td>intermediate</td>
<td>particle</td>
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<tr>
<td>é hexachlorobenzene</td>
<td>T</td>
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<td>é other chlorobenzenes</td>
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<td>é light PAH’s (e.g., anthracene)</td>
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<td>é elemental mercury</td>
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<td>é aldrin/dieldrin</td>
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<td>é mirex</td>
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<td>é endrin</td>
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<tr>
<td>é heptachlor</td>
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<td>é hexachloro-1,3-butadiene</td>
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<td>é octachlorostyrene</td>
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<td>é hexachlorocyclohexanes (e.g., lindane)</td>
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<td>é pentachlorophenol</td>
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<td>é reactive gaseous mercury (e.g., HgCl₂)</td>
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<td>é 4,4’-methylene bis(2-chloroaniline)</td>
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<td>é TCDD/F and PeCDD/F</td>
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<td>é DDT / DDD / DDE</td>
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<td>é toxaphene</td>
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<td>é some PAH’s (e.g., fluoranthene, chrysene)</td>
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<td>é methoxychlor</td>
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<td>é PCB’s</td>
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<td>é cadmium</td>
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<td>é particulate mercury</td>
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<td>é HxCDD/F, HpCDD/F, OCDD/F</td>
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<td>é heavy PAH’s (e.g., benzo-a-pyrene)</td>
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**NOTE:**
two-way gas exchange at terrestrial and water surfaces can be important

(Vd for small particles?)
| Methodological Approaches for Analysis of the Atmospheric Deposition Pathway |
|---|---|---|---|---|
| 1. **Semi Empirical Loading Estimates** | Emissions of Pollutants to the Air | Atmospheric Transport and Fate | Ambient Monitoring | Atmospheric Deposition to a Great Lake |
| 2. **Receptor-Based Analysis** | | | |
| 3. **Comprehensive Atmospheric Fate and Transport Modeling** | | | |
Precipitation sampler (obtain wet deposition flux directly...)

Ambient air sampler, for vapor and/or particles. To estimate dry deposition flux, must estimate deposition velocity:

\[
\text{Flux} = \text{deposition velocity} \times \text{concentration}
\]

\[
\text{[g/cm}^2\text{-sec]} = \text{[cm/sec]} \times \text{[g/cm}^3\text{]}
\]

Monitoring Questions:
Where?
What media?
Frequency?
Sporadic or continuous?

Concentration aloft may be different than ground-level concentration

Is atmosphere part of critical exposure pathway(s)?

Vegetation
Critters
Fish and other aquatic biota
Sediment
SUMMARY
Short Range! Long Range Transport

ⅰ From the Perspective of the Source (e.g., a given incinerator)

- dispersion, transformation, and deposition generally serve to reduce impacts as distance from the source increases:
  - *but, for some pollutants, re-emission can lengthen the effective transport distance and even cause an eventual buildup at distances far from the source*

- in general, the biggest impacts are nearby:
  - *but, this represents only a small fraction of the emissions*

- each pollutant behaves differently:
  - *wide range of estimated lifetimes/transport distances/re-emissions rates*

- we have some idea of the fate and transport of pollutants:
  - *but, there are a lot of uncertainties*

ⅱ From the Perspective of the Receptor (e.g., the Great Lakes)

- the contributions from individual sources will tend to be very *episodic*

- on a source by source basis, all things being equal, nearby sources will have a greater impact than far-away sources:
  - *but the number of sources can increase as you go away from the receptor; so there is a competition – less impact per source, but more sources; [worldwide sources may be significant for some pollutants (e.g., HCB)]*

- geographical distribution (distance/orientation) is important:
  - *but for many pollutants of concern in the Great Lakes, our characterization of sources remains relatively uncertain...*

- Dioxin examples for the Great Lakes
  - *for Lake Michigan, about 40% comes from within 100 km of the lake, but more than half comes from much further away (100-1500 km). For the other Great Lakes, even less local impact.*
Figure 11. Deposition amount and flux of 2,3,7,8-TCDD in successive, concentric, annular 200-km-radius-increment regions away from a continuous 1996 year-long source at the center of the modeling domain. The deposition amount has been divided by the total amount emitted in the simulation to give the fraction of the emissions deposited in any given concentric region. The deposition flux for each region has been normalized to correspond to an emissions rate of 1 gram/year.
1996 weekly average ambient air concentrations of 2378-TCDD at the center of Lake Michigan (10 meter height), arising from a hypothetical, continuous sources of 2378-TCDD in Chicago.

Note: daily averages are even more variable, and hourly averages vary even more than the daily averages.
Figure 10. Weekly estimates of deposition to Lakes Superior and Ontario arising from a hypothetical, continuous source of 2,3,7,8-TCDD at the center of the modeling domain. The values plotted are the ratios between the weekly deposition rate, D(t), and the weekly emissions rate, E(t), from the hypothetical source.
Figure 5. Fraction of 1996 Dioxin Emissions Deposited in the Great Lakes
(grams TEQ deposited per year / grams TEQ emitted per year)

Overall Transfer Coefficient
(fraction deposited)

0.000004 - 0.000007
0.000007 - 0.000001
0.00001 - 0.000002
0.000002 - 0.000004
0.000004 - 0.000007
0.000007 - 0.00001
0.00001 - 0.00002
0.00002 - 0.00004
0.00004 - 0.00007
0.00007 - 0.0001
0.001 - 0.002
0.002 - 0.004
0.004 - 0.007
0.007 - 0.01
0.01 - 0.02
0.02 - 0.04
0.04 - 0.07
Figure 1. Estimated per-capita 1996 emissions from U.S. and Canadian source categories (g TEQ/person-yr)

- Municipal Waste Incineration
- Iron Sintering
- Medical Waste Incineration
- Cement Kilns Burning Haz Waste
- Backyard Waste Burning
- Secondary Copper Smelting
- Secondary Aluminum Smelters
- Residential Wood Combustion
- Mobile Sources
- Utility Coal Combustion
- Electric Arc Furnaces
- Hazardous Waste Incineration
- Sewage Sludge Incineration
- Cement Kilns Not Burning Haz Waste
- Pulp-Paper: Hog Fuel / Sludge Combustion
- Residential Fuel Combustion
- Industrial Wood Combustion
- Grey Iron Foundries
- Pulp-Paper: Kraft Black Liquor Recovery Boilers
- Residential Oil Combustion
- Commercial Fuel Combustion
- Secondary Lead Smelting
- Base Metal Smelting
- Industrial Fuel Combustion
- Agricultural Fuel Combustion

Estimated 1996 Per-Capita PCDD/F Emissions (g TEQ/person-yr)
Figure 2. Total Dioxin Emissions for 1996
Figure 3. Estimated Contributions to the 1996 Atmospheric Deposition of Dioxin to Lake Superior (µgrams TEQ/km²-yr)
Figure 5. Percent of total 1996 emissions and deposition of dioxin arising from within different distance ranges from Lake Superior.
Figure 6. Percent of total 1996 emissions and deposition of dioxin arising from within different distance ranges from Lake Michigan.
Figure 4. Fraction of estimated 1996 PCDD/F atmospheric deposition contributions to Lake Superior from U.S. and Canadian sources arising from different source categories.
Figure 12. Contribution of Different Source Sectors to Atmospheric Deposition of Dioxin
( pg TEQ deposition / km² ) / ( person - year )

(Each country's annual deposition flux contribution amount normalized by their total population)

United States
Canada

"incin" = waste incineration; "metals" = metallurgical processing; "fuel" = fuel combustion
Figure 9. Model-estimated total 1996 deposition for different PCDD/F homologue groups to Lake Superior.
Figure 6. Comparison of model predictions with ambient measurements at month-long sample sites. Sample locations and dates (all dates 1996): A. Mohawk Mtn CT (5/14- 6/13); B. Mohawk Mtn CT (8/14-9/13); C. Mohawk Mtn CT (10/22-11/22) D. Northern VT (8/1-8/28); E. Central VT (8/1-8/28).
Figure 11. Relative contribution of the seventeen 2,3,7,8-substituted PCDD/F congeners to the overall model-predicted deposition to Lake Superior.
Figure 10. Measured 1994 and 1997 fluxes to Siskiwit Lake on Isle Royale (Baker and Hites, 2000) and 1990 fluxes to Lake Superior (Pearson et al., 1997, 1998), compared to 1996 modeled fluxes. Non-detects in the measurements are plotted with a mid-point value at 1/2 the detection limit (DL), with a range of 0 to the DL. Model estimates shown using dry deposition methodologies A and E. Measurements in Isle Royale and Lake Superior were each reported at 2 sediment sampling sites.
Approximate range of uncertainties in estimating total 1996 PCDD/F deposition to Lake Superior

- red square: central estimate
- black diamond: min or max in simulations
- white triangle: inferred min or max
- green range: range in estimates

- emissions
- interpolation
- 28 vs. 84 std. pts.
- photolysis
- wet dep.
- dry dep.
Some questions to be answered for an atmospheric monitoring program:

1. **What pollutants do you try to measure?**
   - What pollutants are causing a problem?
   - What pollutants are suspected of causing a problem?
   - What pollutants do you need to measure to assess whether a potential problem may exist?
   - Caution: don’t just assume you’ll only measure what is “always” measured...
   - Be careful with cost accounting in your decisions, i.e., distinguish between analytical costs and other sampling costs – i.e., don’t assume you can’t include “analytically expensive” pollutants, as the total cost for sampling these may not be that much more than for “cheaper” pollutants.

2. **What are you going to try to use the monitoring data for?**
   - Screening level assessment of magnitude of problem?
   - Trend analysis?
   - A source of data for back-trajectory calculations?
   - A comprehensive modeling analysis (monitoring data are used for model evaluation)

3. **What atmospherically relevant media? (air (gas and/or particles), size resolved measurements for particulate? precipitation, fog, passive media (e.g., pine needles...)**
   - What media are significant concentrations expected in?
   - What are the relative costs of monitoring for the pollutant in different media
   - How easy will it be to use the information later (passive media may be more difficult)

4. **How long do you sample for (1 hour samples?, 1 day samples?, 1 month samples?, etc.)**
   - How long do you have to sample for to get measurable amounts?
   - How long will analyte be stable in sampling system?
   - Short-term samples better for back-trajectory analyses...

5. **Are sample periods continuous or sporadic, e.g., 1 day every month, or every day? If sporadic, what is frequency of sampling?**
   - If sporadic, may not get good answer for average concentrations.
   - If sporadic, may miss episodic phenomenon
   - If continuous, may cost too much...
   - Which is better: one 1-day sample per month or one 30-day sample per month? It depends...

6. **Where do you sample? How many locations?**
   - What spatial gradients exist or are expected?
   - Are there existing sampling sites that can be “exploited” (e.g., power already provided, etc.)
   - Adequate “fetch”; representative of general area?

7. **Ground level samples only, or elevated samples?**
   - Are dramatic vertical gradients expected? Do you need to know them?
   - Most samples are at ground level (~ 2 meters height)... Costs more for tower samples; aircraft samples even more expensive

8. **What else should you measure to help you interpret what you get?**
   - Meteorological conditions at the site (temperature, precipitation, wind speed, wind direction...)
   - Total particulate matter
   - Other pollutants and/or compounds (e.g., ozone, crustal elements, other tracers, etc.)

9. **What quality control and quality assurance steps need to be taken?**
   - Very important – if there are problems, you want to know right away...
   - Field and laboratory procedures... (spikes, blanks...)
QUESTIONS to SPEAKERS

1. Why care about air toxics deposition and accumulation in park ecosystems?
   For some toxics, atmospheric deposition may be a significant or even the most significant loading pathway into a given park ecosystem.

2. Effects of air toxics (and at what concentrations)?
   Data are very limited, because we haven’t looked all that hard for most compounds. However, ecosystems contamination by mercury, dioxin, PCB’s and PAH’s (these are examples – there are others) are probably mostly driven by the atmospheric pathway...

3. Air toxics distribution and effects in the western US?
   Why limit discussion to western U.S.?
   Data are very limited; we don’t know all that much yet...

4. Recommendations for monitoring of air toxics in specific media in parks?
   Measure a range of toxics in a variety of media, especially at the top of the food chain. Conduct screening level risk-assessments to find out which compounds are most likely to be causing adverse affects in park ecosystems...

5. "Advance work" before an air toxics monitoring plan can be devised?
   Air toxics monitoring can proceed in stages. Screening level analyses can begin by measuring a suite of compounds in the atmosphere in a variety of locations
   Using these data and data on concentrations in various media (including biota), develop plan to measure the most important compounds at a sufficient number of locations to characterize the problem

6. What trends can we predict in toxic emissions, deposition and impacts?
   Emissions trends hard to assess, because emissions inventories (U.S., elsewhere) are of poor quality. Some pollutants may be increasing, some decreasing...
   Deposition trends should follow emissions trends (more or less) (can be a lag due to grasshopper effect)
   Impacts can be further lagged behind emissions and deposition trends due to accumulation in sediments, soil, or other ecosystem “reservoirs”

7. What do we need to know – research and knowledge gaps?
   Which compounds are causing problems in the parks?
   Of these, how important is the atmospheric pathway?
   Temporally and geographically resolved emissions inventories
   Atmospheric fate and transport behavior of these compounds?
   Relative importance of different sources and source regions?
   Technical and economic options for reducing or eliminating these emissions?