Linkages Between Monitoring and Modeling of PBT's

Mark Cohen
NOAA Air Resources Laboratory
Silver Spring, Maryland, USA

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This talk will primarily deal with monitoring and modeling related to the *atmospheric* fate and transport of PBT's

- **Although analogous considerations are likely to be applicable to other situations…**

The Role and Potential Value of Models

1. **Models are mathematical and/or conceptual descriptions of real-world phenomena**

   - **They are necessarily a simplification – the real world is *very* complicated**

   - ***Hopefully* the most important aspects are treated sufficiently well…**

The Role and Potential Value of Models

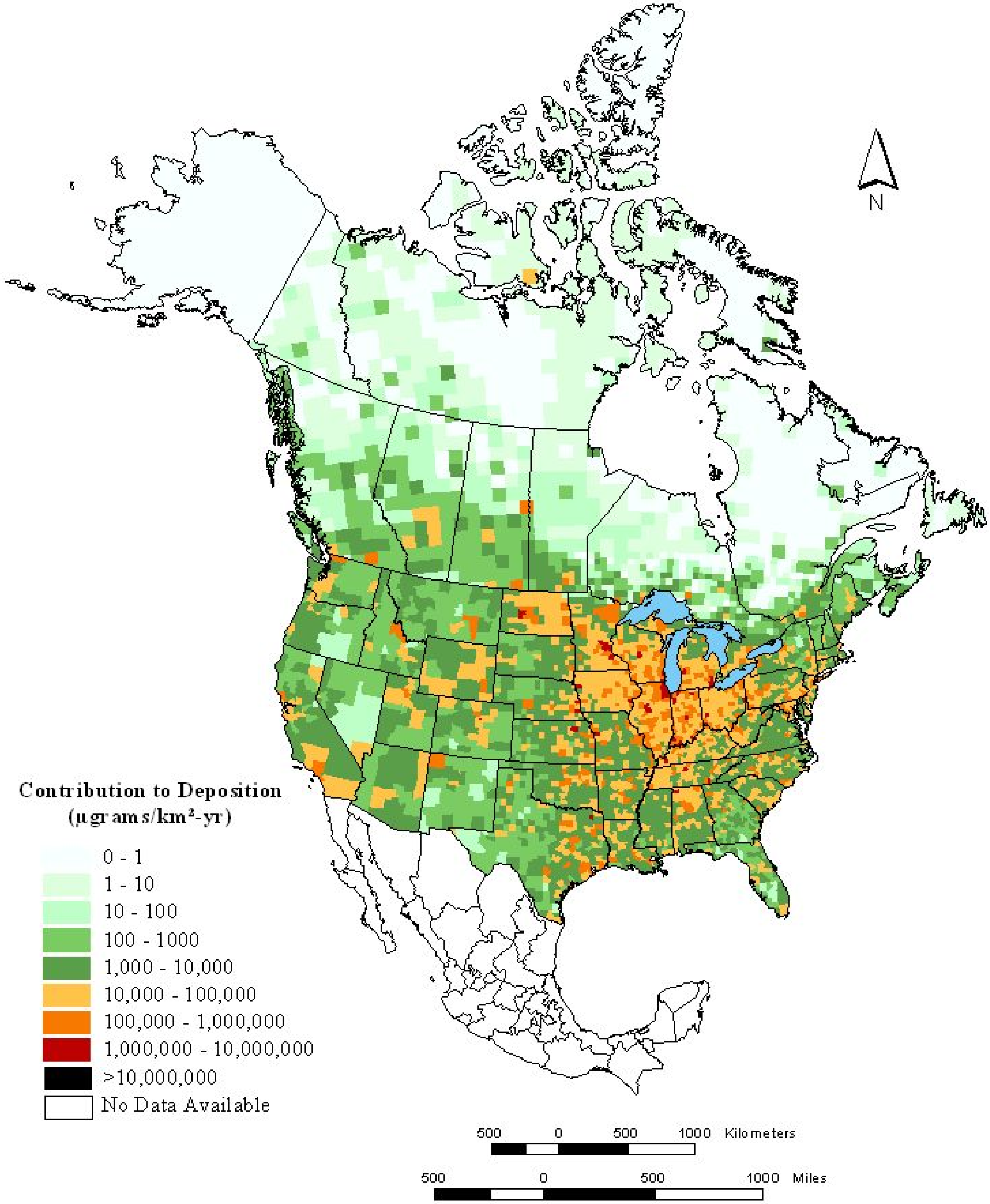
2. **Models are potentially valuable for:**

- **Examining large-scale scenarios that cannot easily be tested in the real world**

- **Interpreting measurements** (e.g., filling in spatial and temporal gaps between measurements)

- **Providing Source-Receptor Information** (maybe the only way to really get this…)

Estimated Contribution to the Atmospheric Deposition of Mercury to Lake Superior (µgrams/km²-yr)



The Role and Potential Value of Models

3. Models are a test of our collective knowledge

- They attempt to synthesize everything important that we know about a given system

- If a model fails, it means that we may not know everything we need to know…

The Role and Potential Value of Models

4. Whether we like it or not, models are used in developing answers to essentially all information necessary for policy decisions…

- EFFECTS (e.g., on human and wildlife health)

- CAUSES (e.g., environmental fate and transport of emitted substances)

- COSTS (e.g. for remediation)

Atmospheric monitoring can tell you the concentration of a compound is at a given location at a given time for a given media (air, precipitation, soil, surface water, etc.), but…

- **How representative are the measurements…**

  …with respect to *spatial* and *temporal* variations?

- **What are the reasons for variations among samples at a given site, or between samples at different sites?**

- **What are the main sources contributing to each observed measurement?**

- **We are generally *not* actually interested in the concentration or deposition at a single monitoring site…**

- **We are interested in the deposition to an *entire* water body, or to a particular ecosystem**

- ***We are just using the few monitoring sites that we might have to give us a clue as to what the total impact might be…***

Information obtained by monitoring cannot be fully utilized without modeling

AND

Modeling cannot be done credibly without using monitoring to ground-truth the results

Emissions

Meteorology

Atmospheric Fate processes (V/P, rxns, wet/dry deposition)

Evaluation of the model using ambient measurements

Model Results

What do modelers need from monitoring programs?

1. **At least some measurements somewhere, in order to ground-truth results.**

Some Monitoring Issues Identified for the Great Lakes (as of ~1996)

(Cohen, M., and P. Cooney, 1997, **The Transport and Deposition of Persistent Toxic Substances to the Great Lakes. 3.** ***The Use of Ambient Monitoring to Estimate the Atmospheric Loading of Persistent Toxic Substances to the Great Lakes*****.** Windsor, Ontario: IJC. Prepared for the International Joint Commission's International Air Quality Advisory Board)

Table 1. Compounds and Compound Groups Targeted in the Binational Virtual Elimination Strategy (BVES) for Persistent Toxic Substances in the Great Lakes Basin
(Envr. Canada and U.S. EPA, 1996) (Level indicated in parentheses)

METALS / ORGANOMETALLICS

Alkylated Lead (I)
including, but not necessarily limited to:
tetra-, tri- and di-ethyl lead,
tetra-, tri- and di-methyl lead

Cadmium and Cadmium Compounds (II)
including, but not necessarily limited to:
cadmium, cadmium oxide,
cadmium dichloride, cadmium sulfide

Mercury and Mercury Compounds (I)
including, but not necessarily limited to:
elemental mercury, mercury dichloride,
mercury oxide, monomethyl mercury, and
particulate mercury

Tributyltin Compounds (II)

ORGANOCHLORINE BIOCIDES

Aldrin / Dieldrin (I)
Chlordane (I)
DDT / DDD / DDE (I)
Endrin (II)
Heptachlor / Heptachlor Epoxide (II)
Hexachlorocyclohexanes (α,β,δ, and γ) (II)
Methoxychlor (II)
Mirex (I)
Pentachlorophenol (II)
Toxaphene (I)

INDUSTRIAL / MISCELLANEOUS

4-Bromophenyl Phenyl Ether (II)
3,3'-Dichlorobenzidene (II)
Hexachloro-1,3-Butadiene (II)
4,4'-Methylene bis (2-Chloroaniline) (II)
Octachlorostyrene (I)

CHLOROBENZENES

1,4-dichlorobenzene (II)
Tetrachlorobenzenes (several congeners) (II)
Pentachlorobenzene (II)
Hexachlorobenzene (I)

POLYCHLORINATED DIBENZO-P-DIOXINS and DIBENZOFURANS

2,3,7,8-TCDD and 2,3,7,8-TCDF (I)
1,2,3,7,8-PeCDD (I)
1,2,3,4,7,8-HxCDD (I)
1,2,3,6,7,8-HxCDD (I)
1,2,3,7,8,9-HxCDD (I)
1,2,3,4,6,7,8-HpCDD (I)
OCDD (I)
1,2,3,7,8-PeCDF (I)
2,3,4,7,8-PeCDF (I)
1,2,3,4,7,8-HxCDF (I)
1,2,3,6,7,8-HxCDF (I)
1,2,3,7,8,9-HxCDF (I)
2,3,4,6,7,8-HxCDF (I)
1,2,3,4,6,7,8-HpCDF (I)
1,2,3,4,7,8,9-HpCDF (I)
OCDF (I)

POLYCHLORINATED BIPHENYLS (PCB'S)

PCB's (I) [there are 209 PCB congeners]

POLYCYCLIC AROMATIC HYDROCARBONS

Benzo[a]Pyrene (I)
Dinitropyrenes (several congeners) (II)

plus PAH's as a group (II)
including but not limited to:
Phenanthrene, Anthracene
Benz[a]Anthracene, Perylene
Benzo[g,h,i]Perylene

To form a group of PAH's for this analysis, the following additional PAH's were added, consisting of the remaining compounds in the EPA's 16-PAH list & the ATSDR 17-PAH list:

Naphthalene, Acenaphthene
Acenaphthylene, Fluorene, Pyrene
Fluoranthene, Chrysene,
Benzo[b]Fluoranthene, Benzo[j]Fluoranthene
Benzo[k]Fluoranthene, Benzo[e]Pyrene
Dibenz[a,h]Anthracene,
Indeno[1,2,3-c,d]Pyrene

Great Lakes region monitoring issues for compounds of concern in the G.L.

- **Alkylated Lead**
- **4-Bromophenyl Phenyl Ether**
- **3,3'-Dichlorobenzidene**
- **4,4-Methylene bis(2-chloroanaline)**
- **Tributyltin**

	U.S.	CAN	Notes
Air	**NO**	**NO**	
Precipitation	**NO**	**NO**	
Lake-Water	**NO**		

Great Lakes region monitoring issues for compounds of concern in the G.L.

- **Pentachlorophenol**
- **Dinitropyrenes**
- **Perylene**

	U.S.	CAN	Notes
Air	**NO**	**Very Limited**	
Precipitation	**NO**	**NO**	
Lake-Water	**NO**		

Great Lakes region monitoring issues for compounds of concern in the G.L.

- **Toxaphene**

	U.S.	CAN	Notes
Air	**Very Limited**	**Very Limited**	(current status?)
Precipitation	**NO**	**NO**	
Lake-Water	**Very limited monitoring in a few lakes**		**None in Huron or Erie in last 5 years**

Great Lakes region monitoring issues for compounds of concern in the G.L.

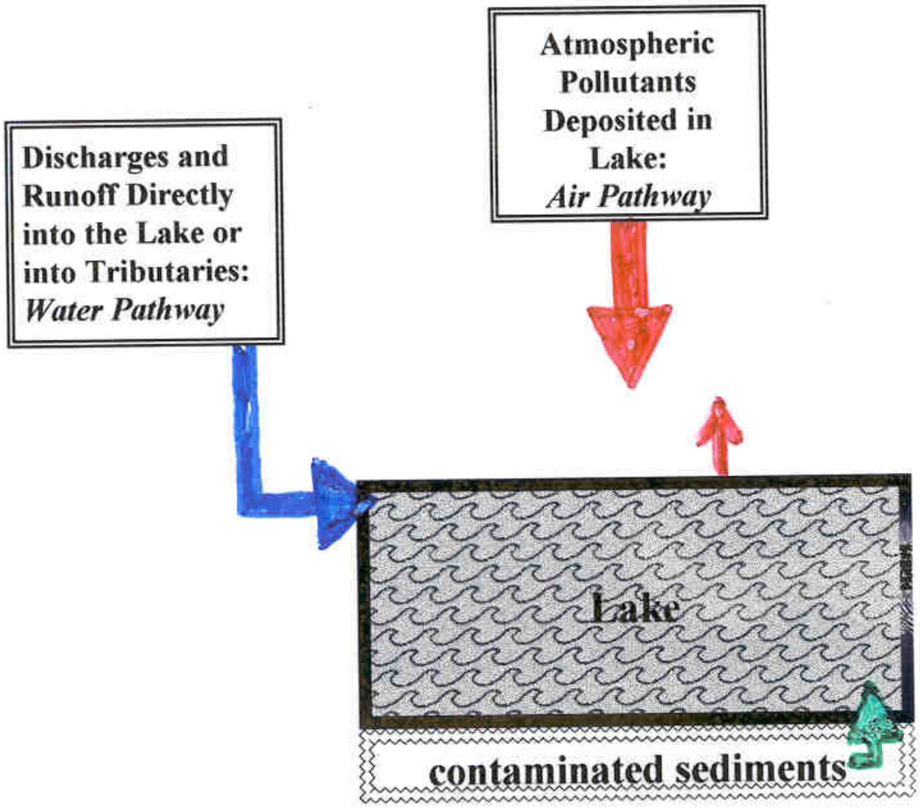
- **PCDD/F (dioxin)**

	U.S.	CAN	Notes
Air	**Very Limited**	**Very Limited**	No V/P
Precipitation	**NO**	**One site**	**The one Canada site now discontinued**
Lake-Water	**Very limited monitoring in a few lakes**		

Great Lakes region monitoring issues for compounds of concern in the G.L.

- **Aldrin**
- **Endrin**
- **Heptachlor**
- **Heptachlor Epoxide**
- **Methoxychlor**
- **Mirex**
- **Octachlorostyrene**

	U.S.	CAN	Notes
Air	**NO**	**IADN**	
Precipitation	**NO**	**IADN**	
Lake-Water	**limited monitoring in a few lakes**		



- ❑ For a given lake, WHICH POLLUTANTS are important?
- ❑ For a given lake and a given pollutant, WHICH PATHWAYS are important?
- ❑ For a given lake, a given pollutant, and a given pathway, WHICH SOURCES are important?

Estimates of the Percent of Great Lakes Loadings Attributable to the Atmospheric Deposition Pathway					
Pollutant	**Lake Superior**	**Lake Michigan**	**Lake Huron**	**Lake Erie**	**Lake Ontario**
DDT	97[a]	98[a]	97[a]	22[a]	31[a]
Lead	97[a]; 64[b]; 69[d]	99[a]	98[a]	46[a]	73[a]
Mercury	73[d]	> 80[j]	[k]	[k]	[k]
PCB's	90[a]; ~ 95[b,c]; 82[d]	58[a]	78[a]	13[a]	7[a]
PCDD/F	~100[e] ~80[f]	50-100[e] (PCDD) 5-35[e] (PCDF) 88[f]	86[f]	~40[f]	5-35 (PCDD)[e] < 5 (PCDF)[e]
Benzo(a)pyrene	96[a]	86[a]	80[a]	79[a]	72[a]
Hexachloro-benzene	99[f]	95[f]	96[f]	> 17[f]	40[f]
Atrazine	97[h]	~30[g]; 23[h]	~20[h]	~10-20[h]	~5[h]
Mirex	[k]	[k]	[k]	[k]	~5[a]

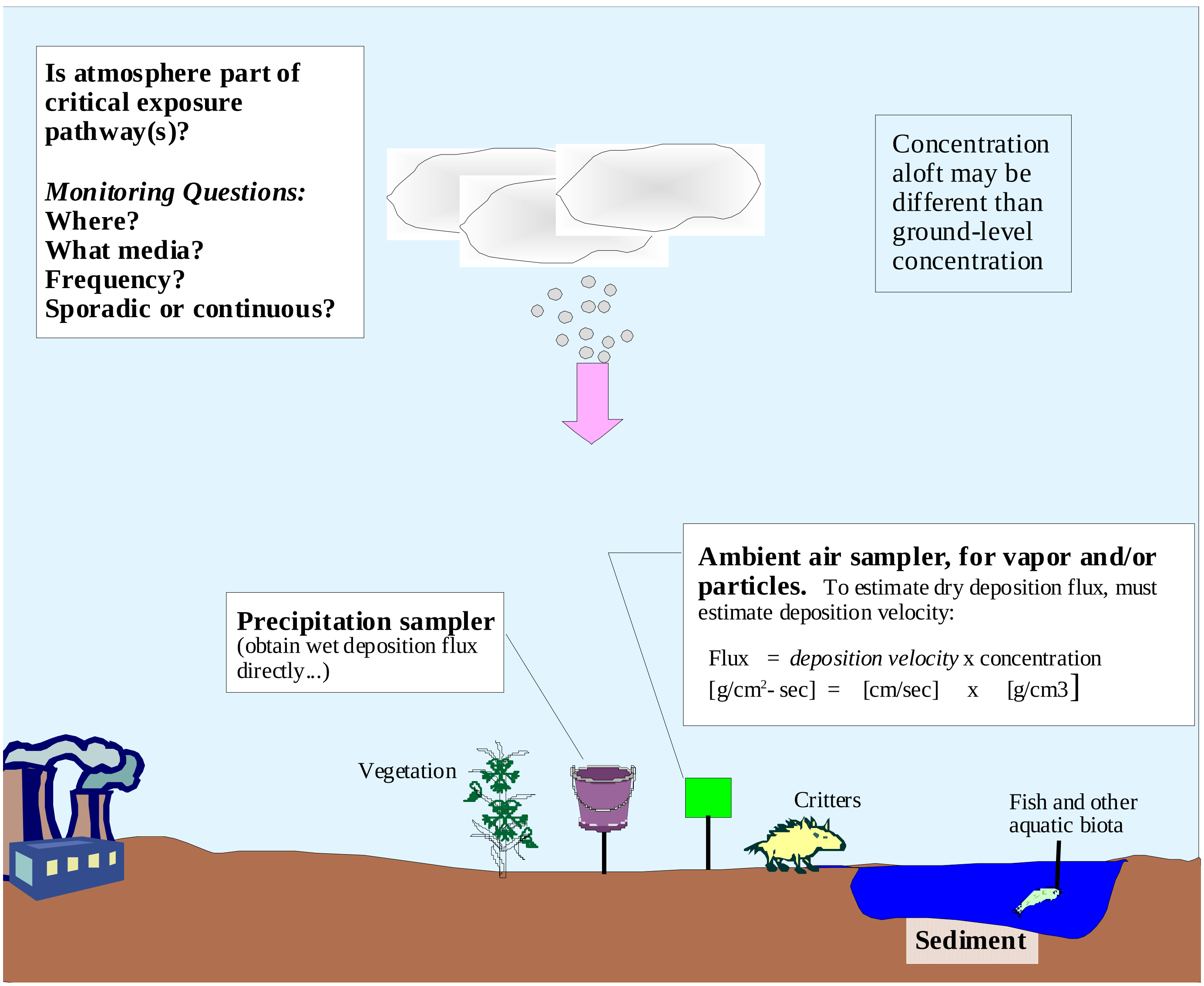
References and Notes

(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

What do modelers need from monitoring programs?

2. **Measurements of *atmospheric concentrations* are best to evaluate *atmospheric* models**

Atmospheric sampling in context…



What do modelers need from monitoring programs

3. **For regional and large-scale modeling, want sampling locations remote from intense local sources**

Hard to model PBT pollutants in big cities:

1. **Emissions inventory not precisely known**

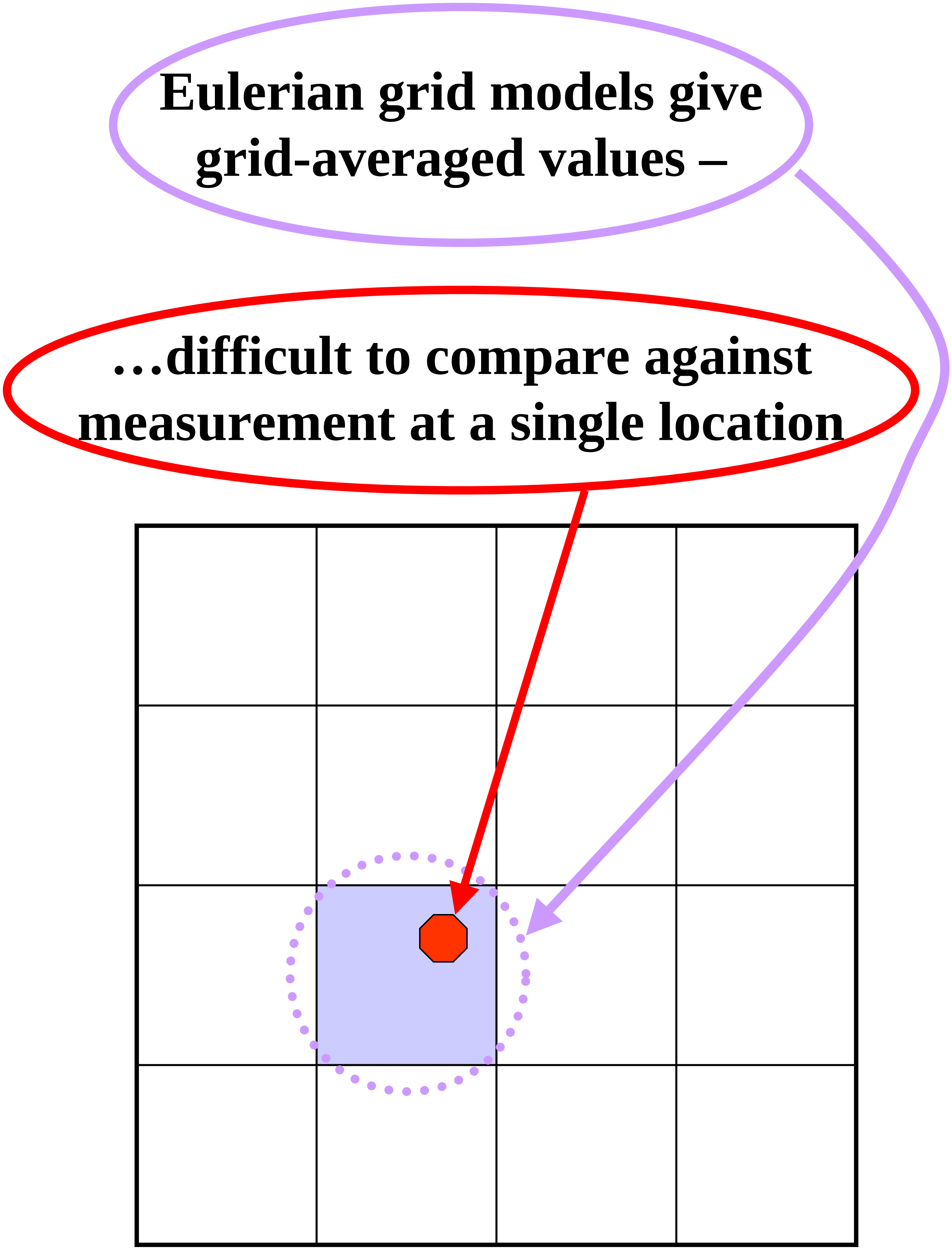
2. **Meteorology very complex**
   (flow around buildings)

So, measurements of PBT's in cities are generally not useful for comprehensive model evaluation

- **Sampling near intense sources?**
- **Must get the fine-scale met "perfect"**
- **Not really a relevant test**

Ok, if one wants to develop hypotheses regarding *whether or not this is actually a source* of the pollutant *(and you can't do a stack test for some reason!).*

	Case 1: Example PCB's	Case 2: Example PCDD/F
Emissions Inventory Status	**Poorly known**	**Moderately well known**
Comprehensive Modeling Possible?	**No (until inventory developed further)**	**Yes, to a certain extent**
Monitoring Strategy	**Short term upwind-downwind samples near suspected sources**	**Long-term samples at locations away from intense sources**
Modeling Strategy	**Back-trajectory studies to identify possible sources**	**Comprehensive modeling of all sources in inventory**


Eulerian grid models give grid-averaged values –
…difficult to compare against measurement at a single location

What do modelers need from monitoring programs?

4. Process-related information, if possible: e.g.,

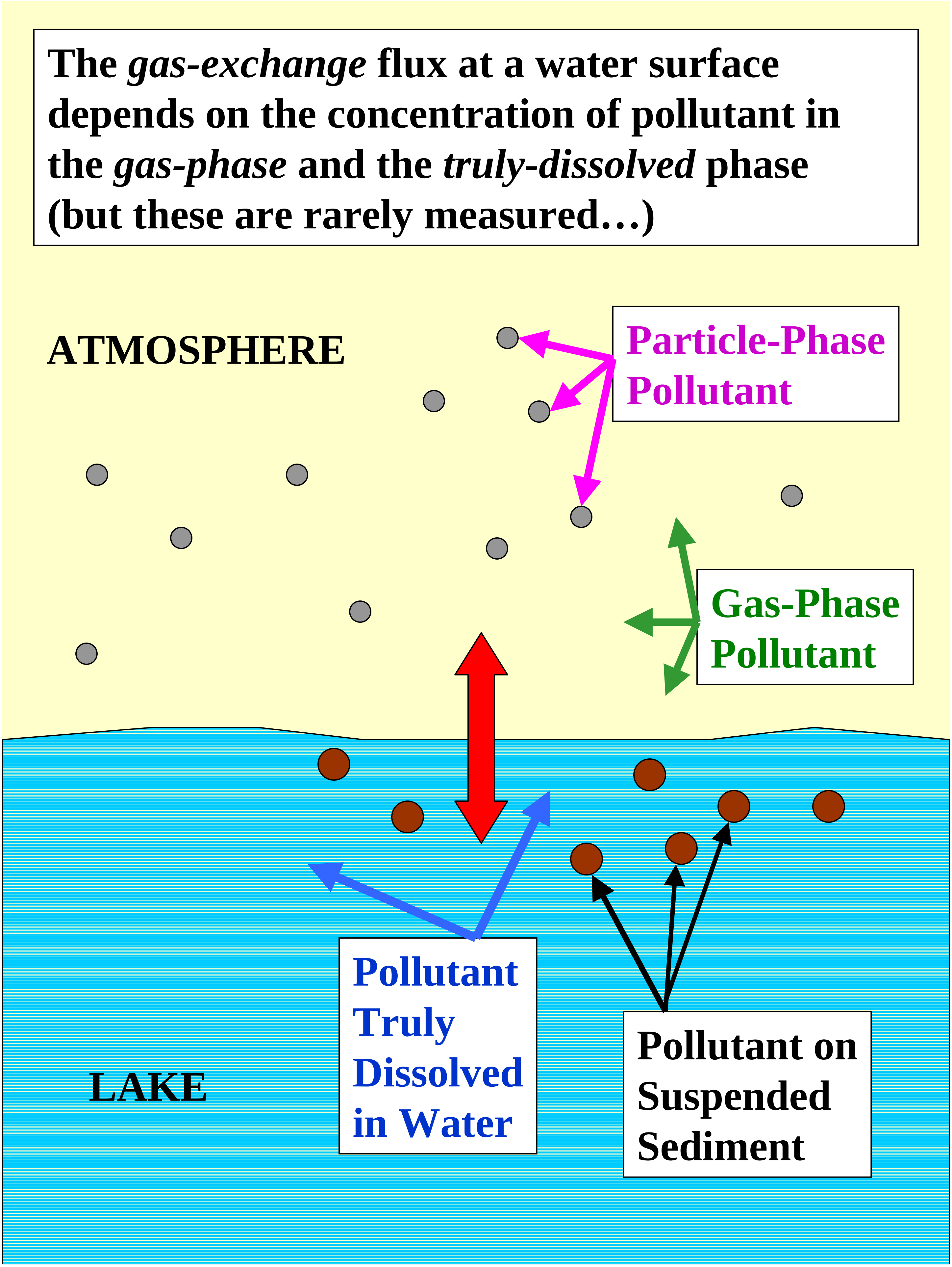
*** vapor/particle partitioning**

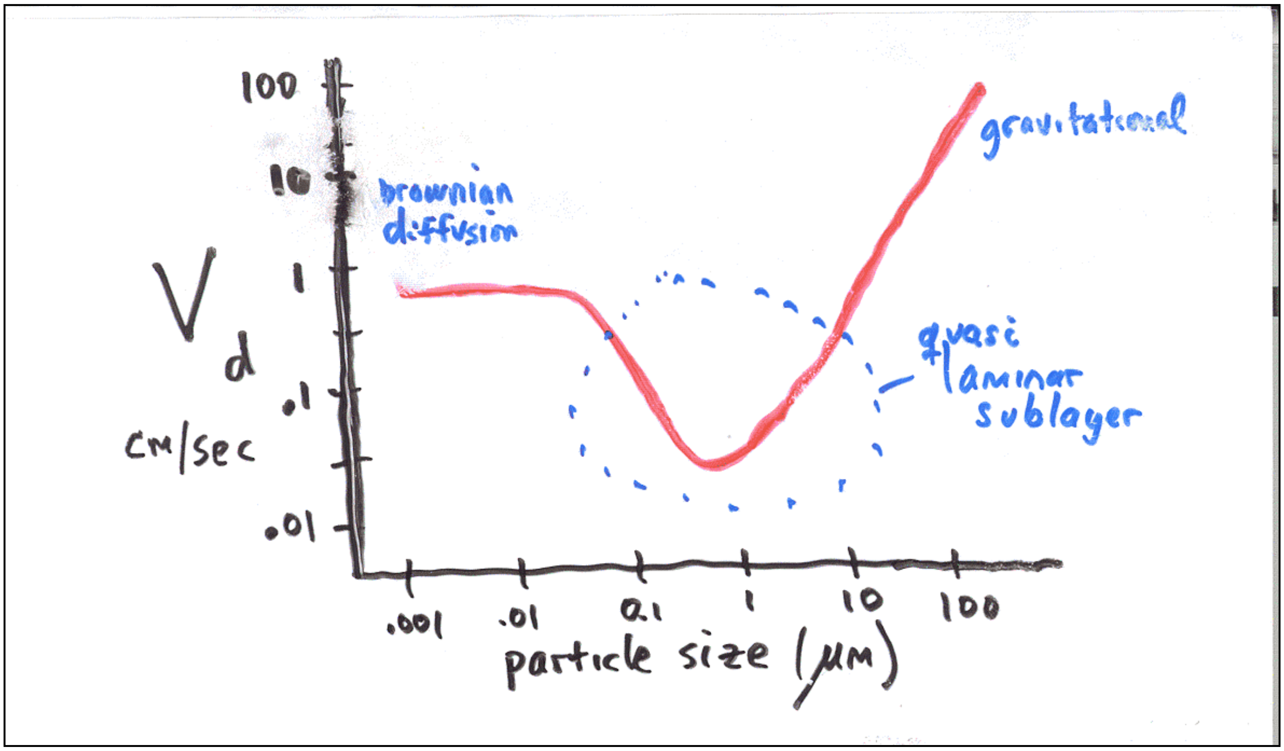
*** particle size distribution**

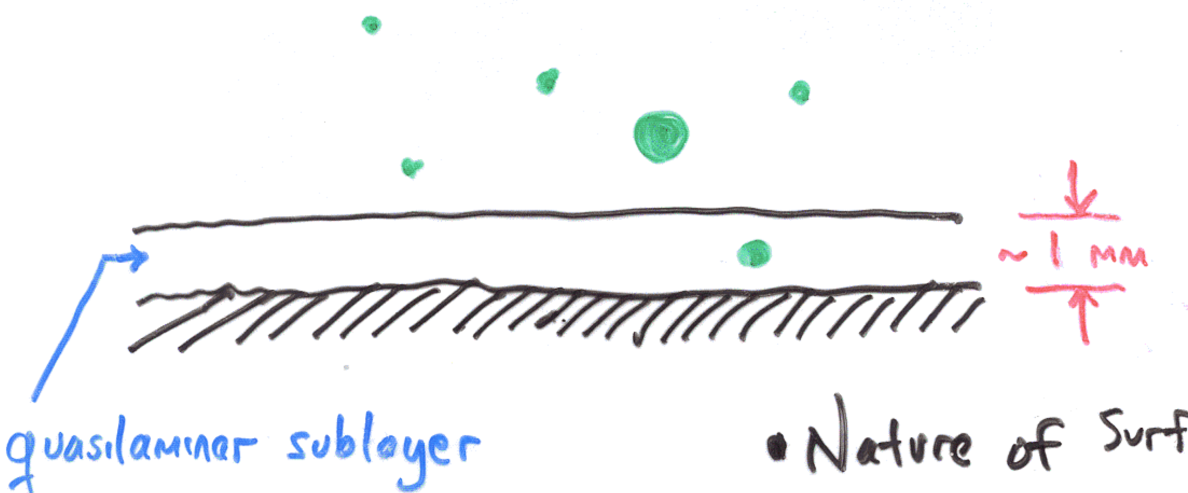
*** speciation**

*** for estimation of lake deposition flux, may need aqueous concentrations (etc.)**

*** data for elevations other than "ground level"**


The *gas-exchange* flux at a water surface depends on the concentration of pollutant in the *gas-phase* and the *truly-dissolved* phase (but these are rarely measured…)
ATMOSPHERE
Particle-Phase Pollutant
Gas-Phase Pollutant
LAKE
Pollutant Truly Dissolved in Water
Pollutant on Suspended Sediment



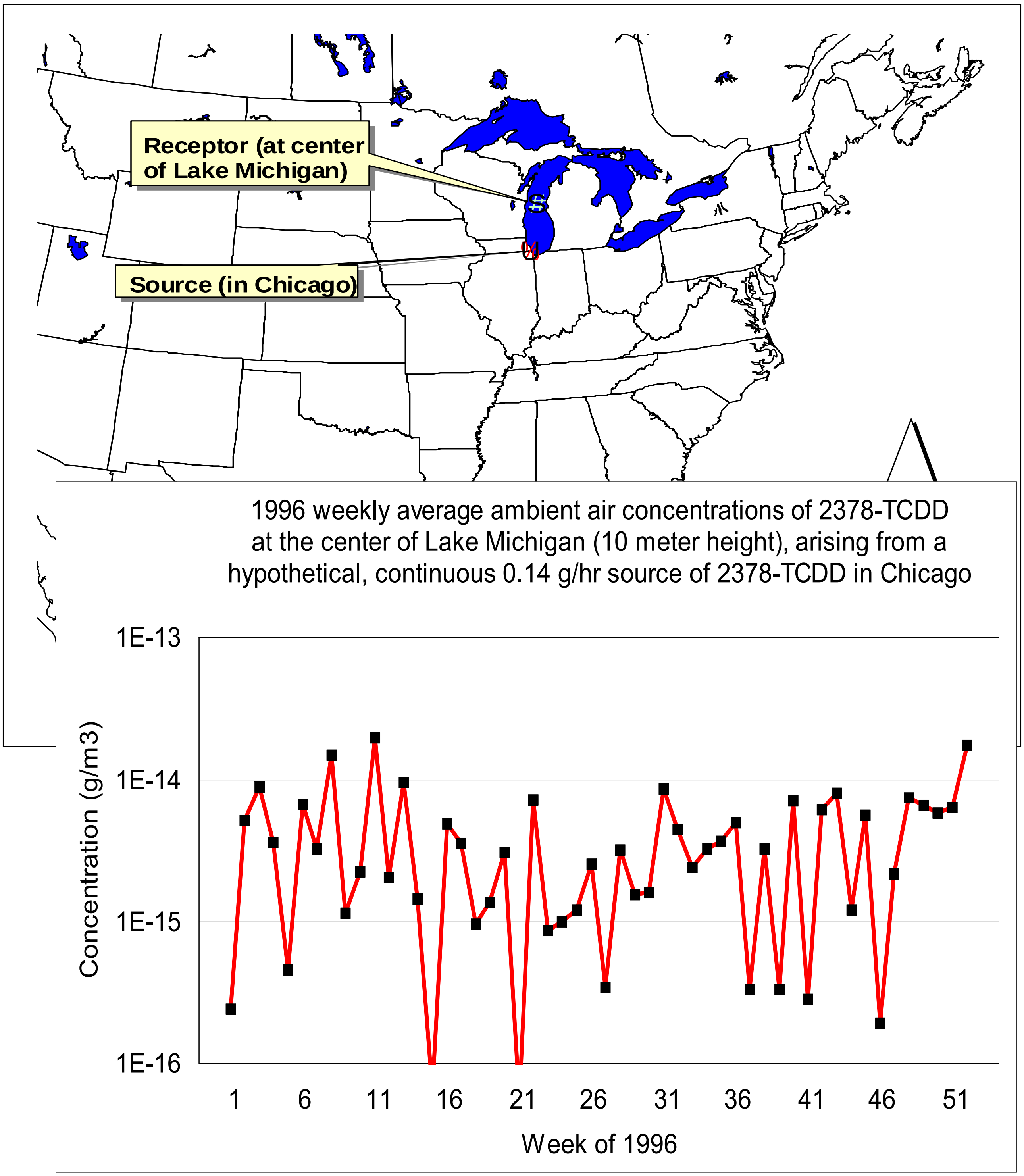


- Nature of Surface
  - water
  - vegetation...
- species-specific particle size distributions
- Hygroscopic Growth near water surface
- particle size dependence

What do modelers need from monitoring programs?

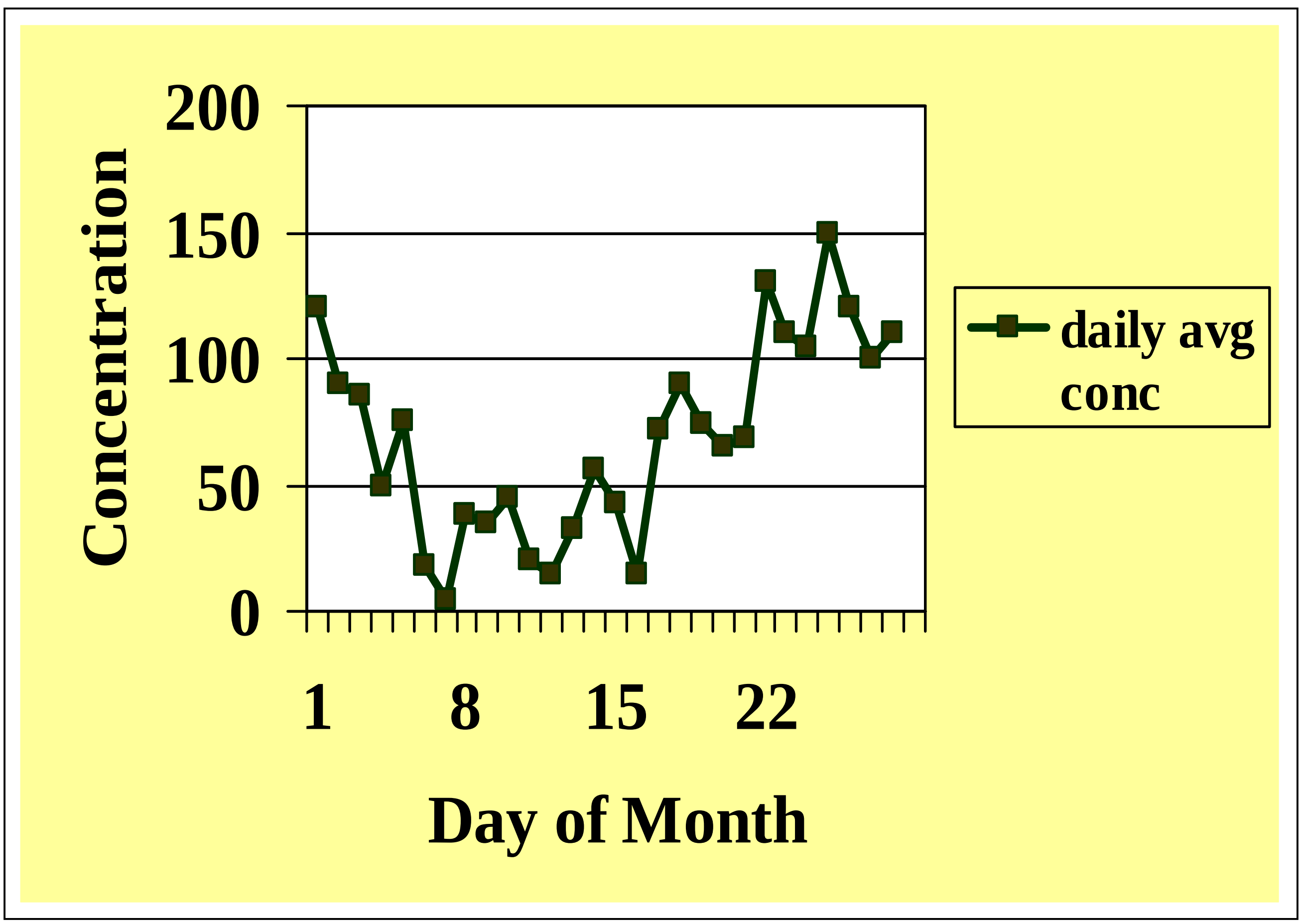
5. If only a few measurements, long-term samples *may* be better than a few short measurements

source-receptor relationships can be very episodic...



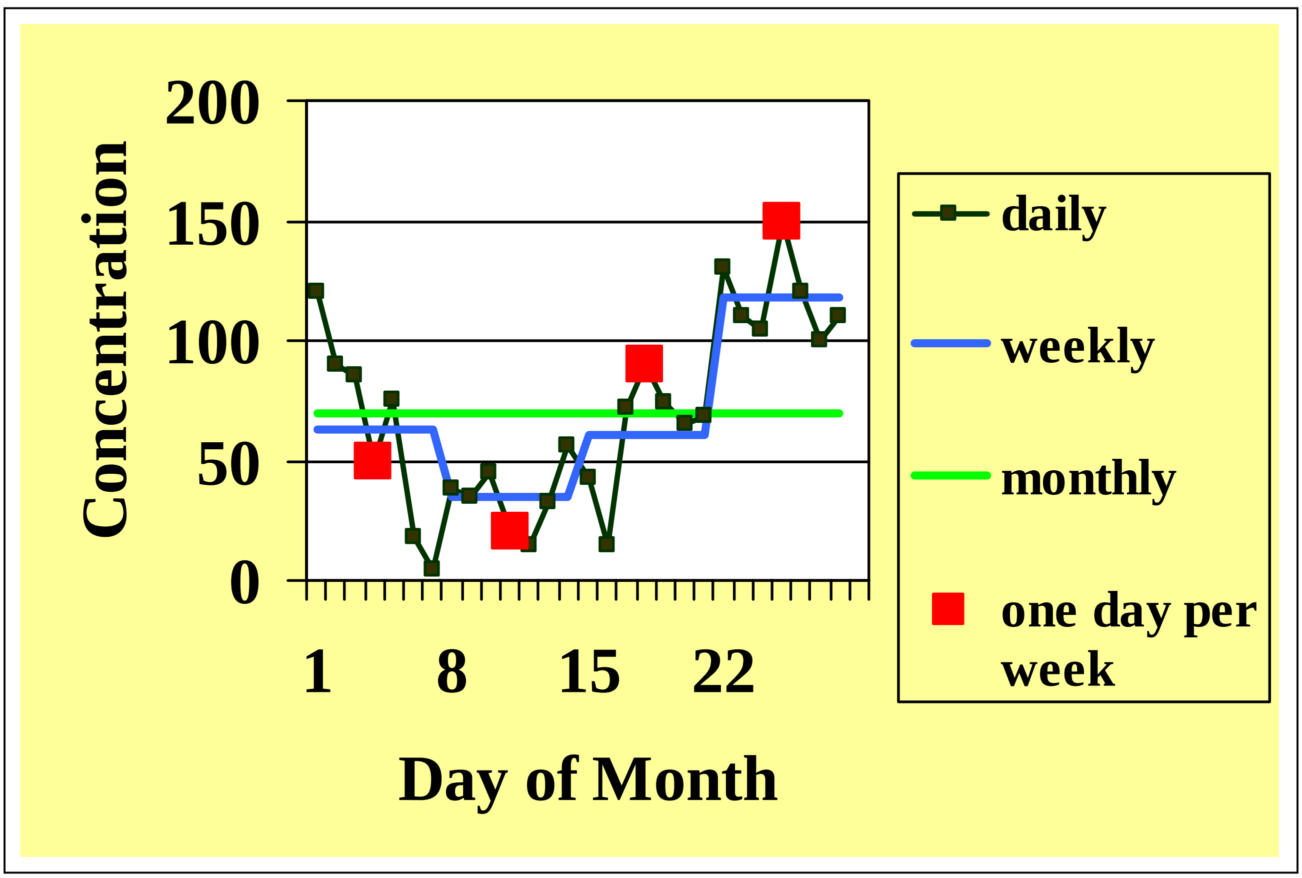
Suppose the "actual" daily average concentrations for a given pollutant at a given location were the following, over a 28 day period

Note: there would most likely be diurnal variations as well (not seen in daily averages)



Measurement frequency and period:

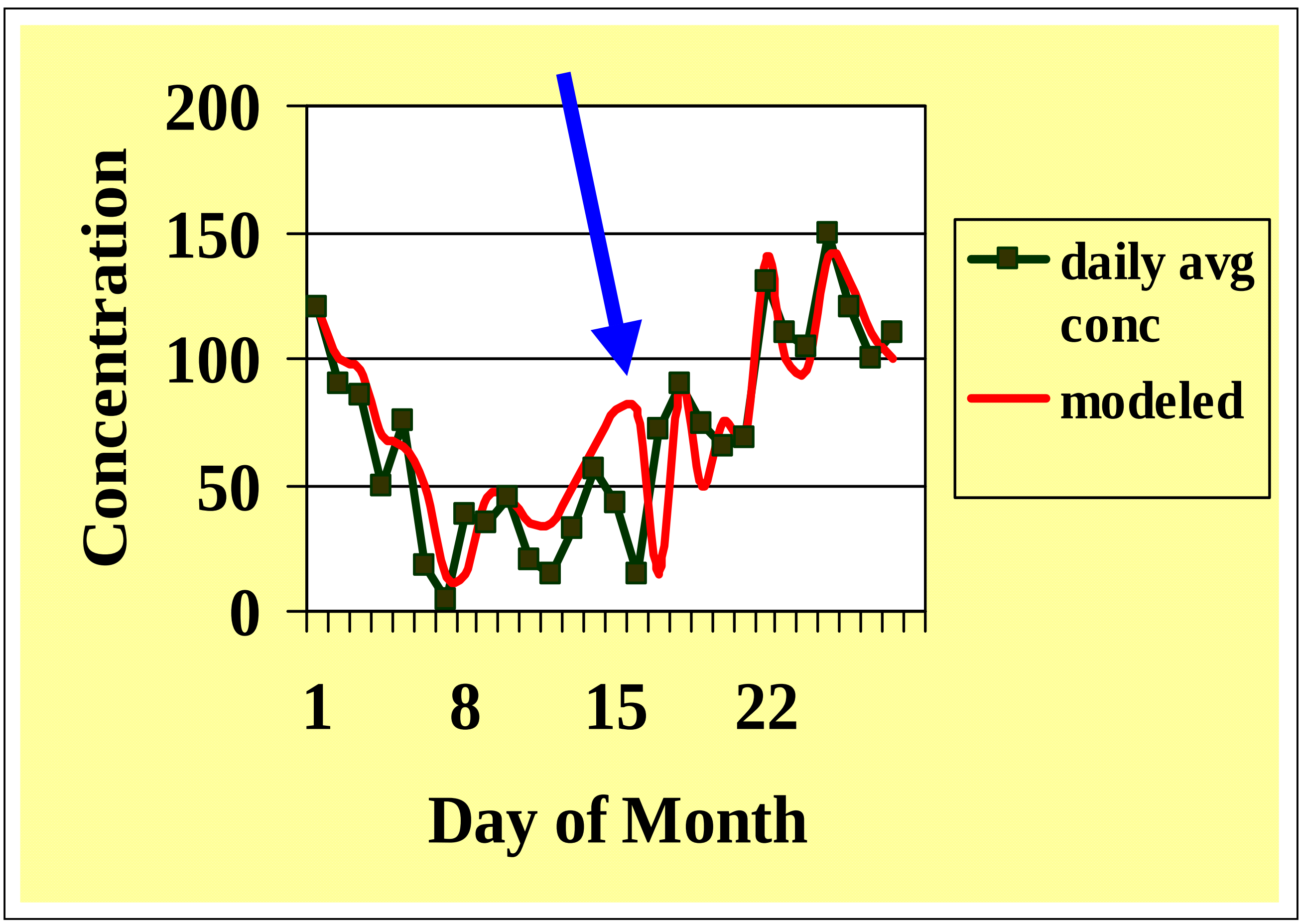
24-hr measurements each day?
Integrated weekly measurements?
Integrated monthly measurements?
One day per week?



Modeled vs. Measured Values

sometimes you can miss the timing a little, but still more or less be doing an "ok" simulation.

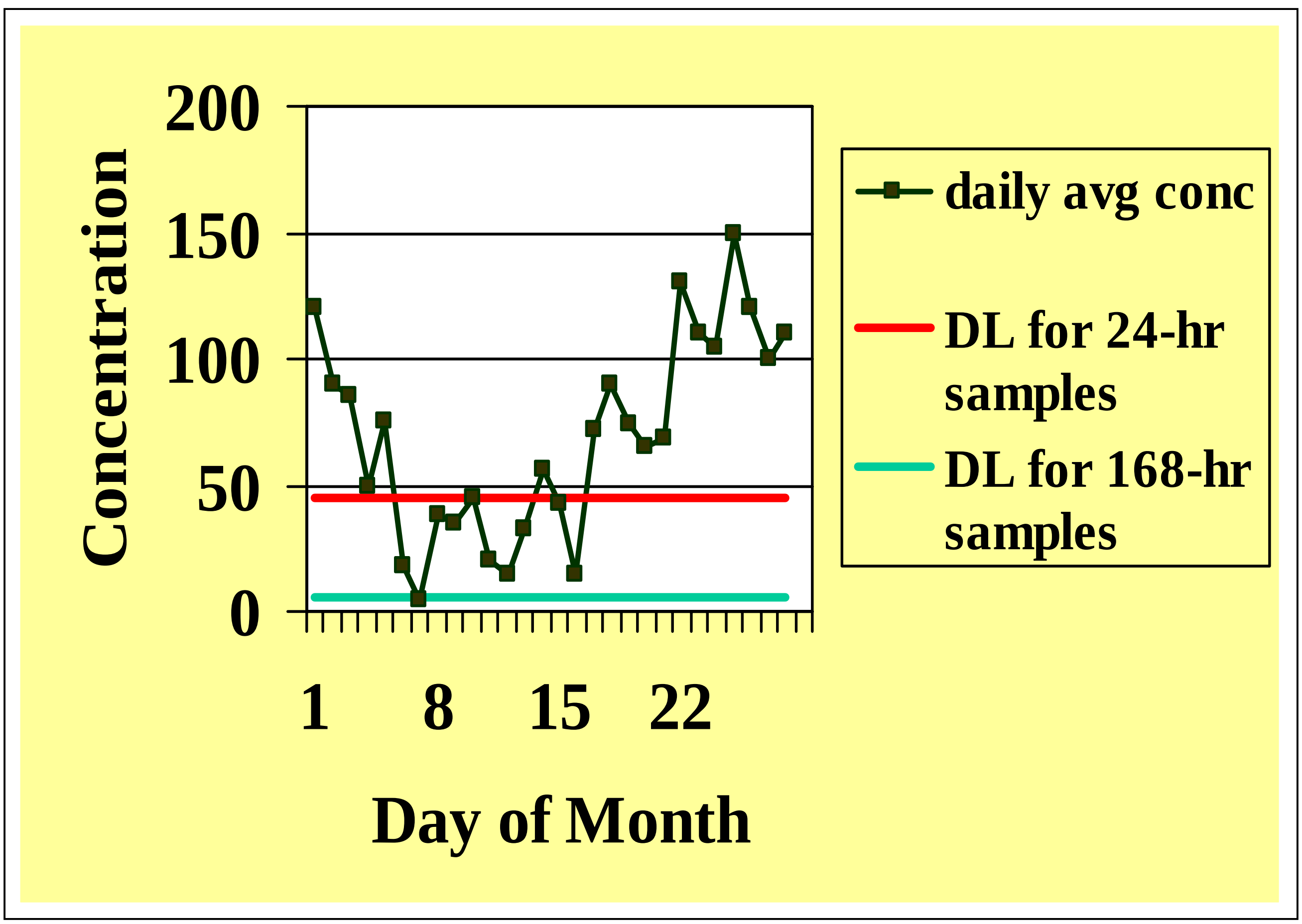
If you only take a few short term measurements, there is a danger of being overly disappointed in the results…



DETECTION LIMIT ISSUES

Short-term measurements generally have higher (worse) detection limits (“DL”) compared to longer-term samples

If you can only collect a few samples, you don’t want to “waste” them on “NON-DETECTS”



What do modelers need from monitoring programs?

6. Clear and accurate documentation of Detection Limit issues

What do modelers need from monitoring programs?

7. Data that has already undergone “troubleshooting”

(e.g., typo’s have been fixed, field and/or lab glitches have been removed or appropriately noted)

What do modelers need from monitoring programs?

8. **Data that is easily available, e.g., downloadable from the web (like MDN)**

EXTRA SLIDES

PARAMETERS TYPICALLY USED TO ESTIMATE THE NET ATMOSPHERIC DEPOSITION TO A GIVEN LAKE OR LAKE AREA
(all the parameters below will vary in time and space; thus, averages are used)

	Parameter	How Obtained (in typical situation)
Wet Deposition	Concentration of the Pollutant in Precipitation	Measured
	Precipitation Rate	Measured
Dry Deposition of Particle-Phase Pollutant	Concentration of the Pollutant in the Air Near the Lake Surface	Measured
	Vapor/Particle Partitioning Characteristics	Measured or estimated
	Dry Deposition Velocity of Particle-Associated Pollutant	Typically estimated; often a constant value is assumed
Net Dry Deposition Flux of Vapor Phase Pollutant	Concentration of the Pollutant in the Air Near the Lake Surface	Measured
	Vapor/Particle Partitioning Characteristics	Measured or estimated.
	Pollutant conc. truly dissolved in the near-surface lake water	Measured or estimated from the total water concentration of the pollutant
	Henry's Law Constant	Based on existing laboratory measurements; temperature dependent
	Temperature	Measured
	Air-Water Mass Transfer Coefficient	Estimated, using correlation-based semi-empirical theories derived from experimental measurements.

Rain Bucket

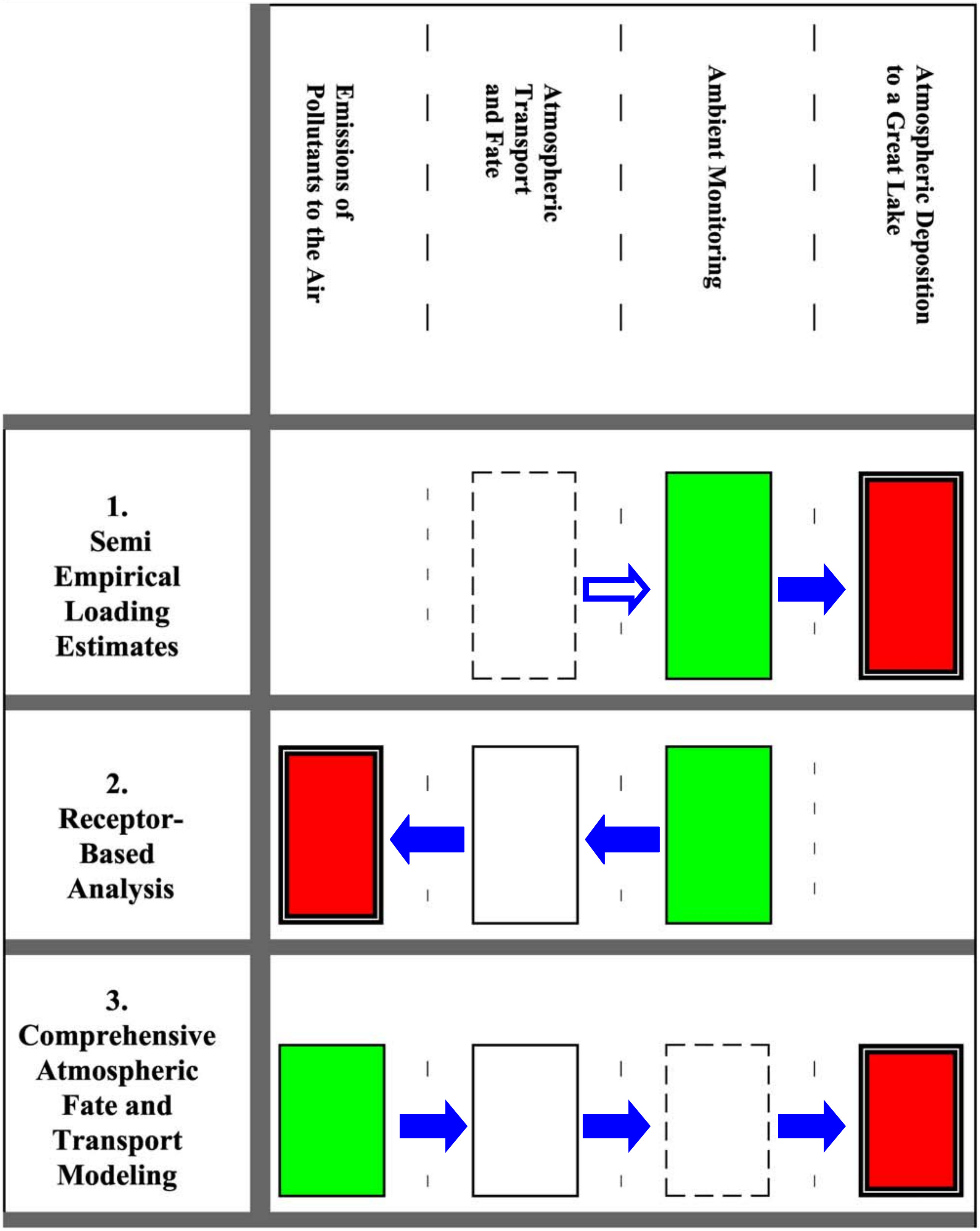
V/P?

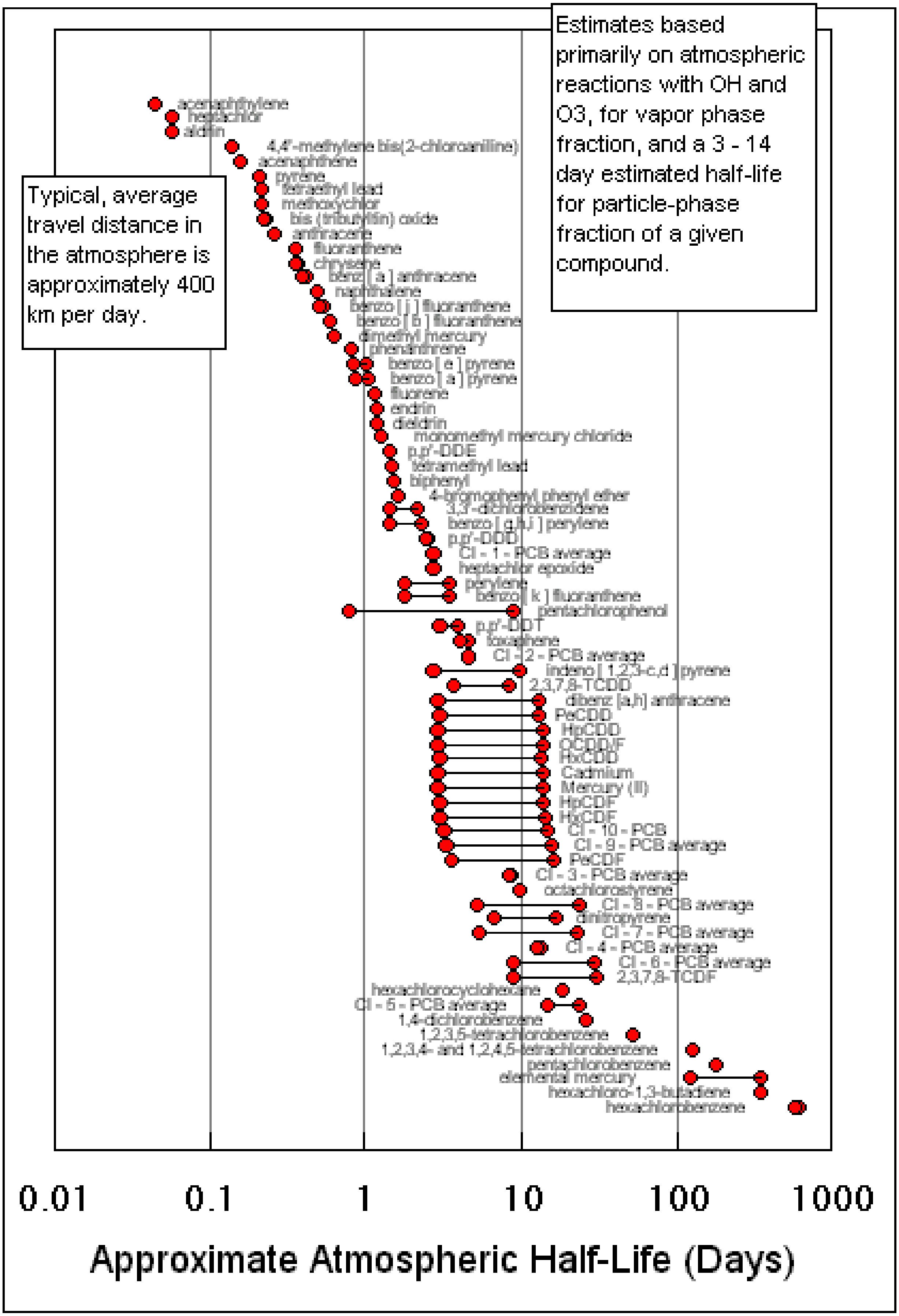
?

Summary of Air and Water Monitoring Issues Identified for BVES Compounds in the Great Lakes Region		
Compound or Group	**Air and Precipitation Monitoring Issues**	**Water Monitoring Issues**
Alkylated Lead 4-Bromophenyl Phenyl Ether 3,3'-Dichlorobenzidene 4,4'-Methylene bis (2-chloroaniline) Tributyltin	Not included in any of the air or precipitation monitoring programs identified	Not included in any of the water monitoring programs identified
Pentachlorophenol Dinitropyrenes Perylene	Limited air monitoring identified in Canada only No precipitation monitoring	Not included in any of the water monitoring programs identified
PAH's in general	Spatial representativeness issue: PAH's are emitted primarily in urban areas.	No monitoring in Lake Huron in the last five years
PCDD/F (dioxins and furans)	Limited number of Great Lakes monitoring stations in Canada only, near Lakes Erie and Ontario; No monitoring identified near Lakes Superior, Michigan, or Huron; Spatial representativeness: monitoring primarily in urban locations, although, e.g., air monitoring at Pt. Petre. Only one site (Dorset) for precipitation monitoring	Monitoring by Envr. Canada for 2,3,7,8-TCDD in Lake Erie (1994, 1995) and Lake Superior (1996, 1997); Monitoring by Cook and Burkhard (US EPA) in Lake Michigan in 1994 No monitoring in Lake Huron or Lake Ontario in the last five years
Mercury	Limited number of monitoring location; Little or no gas-phase speciation data being collected	Systematic measurements only identified for Lake Michigan
Toxaphene	Monitoring only at 2 sites (Eagle Harbor and Pt. Petre) No current measurements in precipitation could be identified	No monitoring in Lake Huron or Lake Erie in the last five years

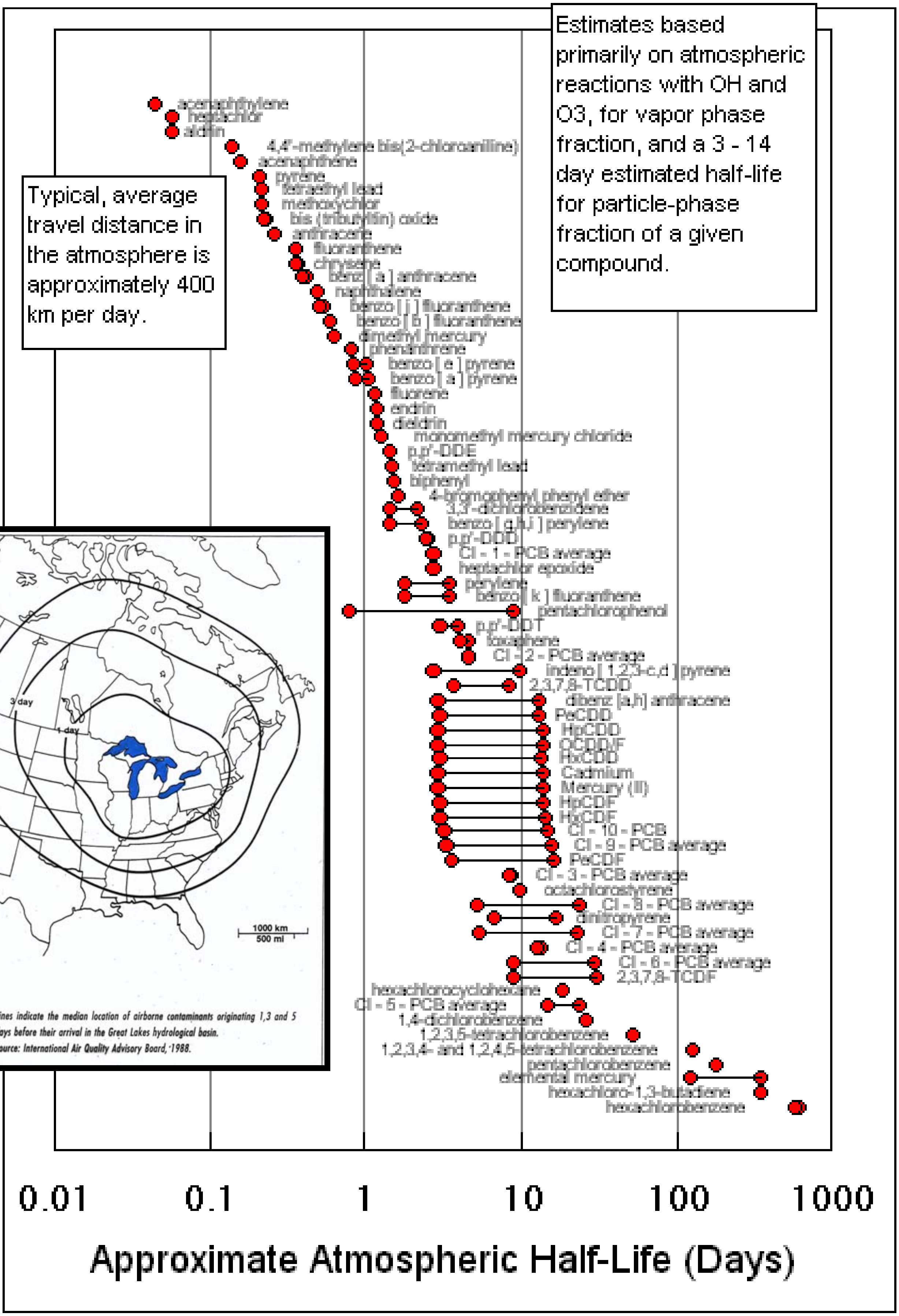
Summary of Air and Water Monitoring Issues Identified for BVES Compounds in the Great Lakes Region		
Compound or Group	**Air and Precipitation Monitoring Issues**	**Water Monitoring Issues**
Aldrin Endrin Heptachlor & Heptachlor Epoxide Methoxychlor Mirex Octachlorostyrene	Measured at some or all Canadian IADN stations, but not at U.S. sampling sites in the Great Lakes Region	No monitoring in Lake Huron in the last five years
DDT/DDD/DDE	Spatial representativeness: high concentrations in the air at South Haven — are there other hot spots in the Great Lakes region?	
Hexachloro-1,3-butadiene	Not part of IADN, but, measured in other programs in Can. & U.S. It may be possible to estimate loadings for many of the Lakes; No data near Lake Superior.	No monitoring in Lake Huron in the last five years
1,4-dichlorobenzene tetrachlorobenzenes pentachlorobenzenes	Limited air measurements in the Great Lakes region	For all, no monitoring in Lake Huron in the last five years For 1,4-DCB, none in Lk. Mich. either
PCB's	Different sets of PCB's being monitored in different programs Since one or more lakes may be volatilizing PCB's, representativeness of shoreline monitoring stations is in question	Different sets of PCB's being monitored in different programs

Methodological Approaches for Analysis of the Atmospheric Deposition Pathway





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.
Typical, average travel distance in the atmosphere is approximately 400 km per day.
acenaphthylene
heptachlor
aldrin
4,4'-methylene bis(2-chloroaniline)
acenaphthene
pyrene
tetraethyl lead
methoxychlor
bis (tributyltin) oxide
anthracene
fluoranthene
chrysene
benz [a] anthracene
naphthalene
benzo [j] fluoranthene
benzo [b] fluoranthene
dimethyl mercury
phenanthrene
benzo [e] pyrene
benzo [a] pyrene
fluorene
endrin
dieldrin
monomethyl mercury chloride
p,p'-DDE
tetramethyl lead
biphenyl
4-bromophenyl phenyl ether
3,3'-dichlorobenzidene
benzo [g,h,i] perylene
p,p'-DDD
Cl - 1 - PCB average
heptachlor epoxide
perylene
benzo [k] fluoranthene
pentachlorophenol
p,p'-DDT
toxaphene
Cl - 2 - PCB average
indeno [1,2,3-c,d] pyrene
2,3,7,8-TCDD
dibenz [a,h] anthracene
PeCDD
HpCDD
OCDD/F
HxCDD
Cadmium
Mercury (II)
HpCDF
HxCDF
Cl - 10 - PCB
Cl - 9 - PCB average
PeCDF
Cl - 3 - PCB average
octachlorostyrene
Cl - 8 - PCB average
dinitropyrene
Cl - 7 - PCB average
Cl - 4 - PCB average
Cl - 6 - PCB average
2,3,7,8-TCDF
hexachlorocyclohexane
Cl - 5 - PCB average
1,4-dichlorobenzene
1,2,3,5-tetrachlorobenzene
1,2,3,4- and 1,2,4,5-tetrachlorobenzene
pentachlorobenzene
elemental mercury
hexachloro-1,3-butadiene
hexachlorobenzene
0.01
0.1
1
10
100
1000
Approximate Atmospheric Half-Life (Days)



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.
Typical, average travel distance in the atmosphere is approximately 400 km per day.
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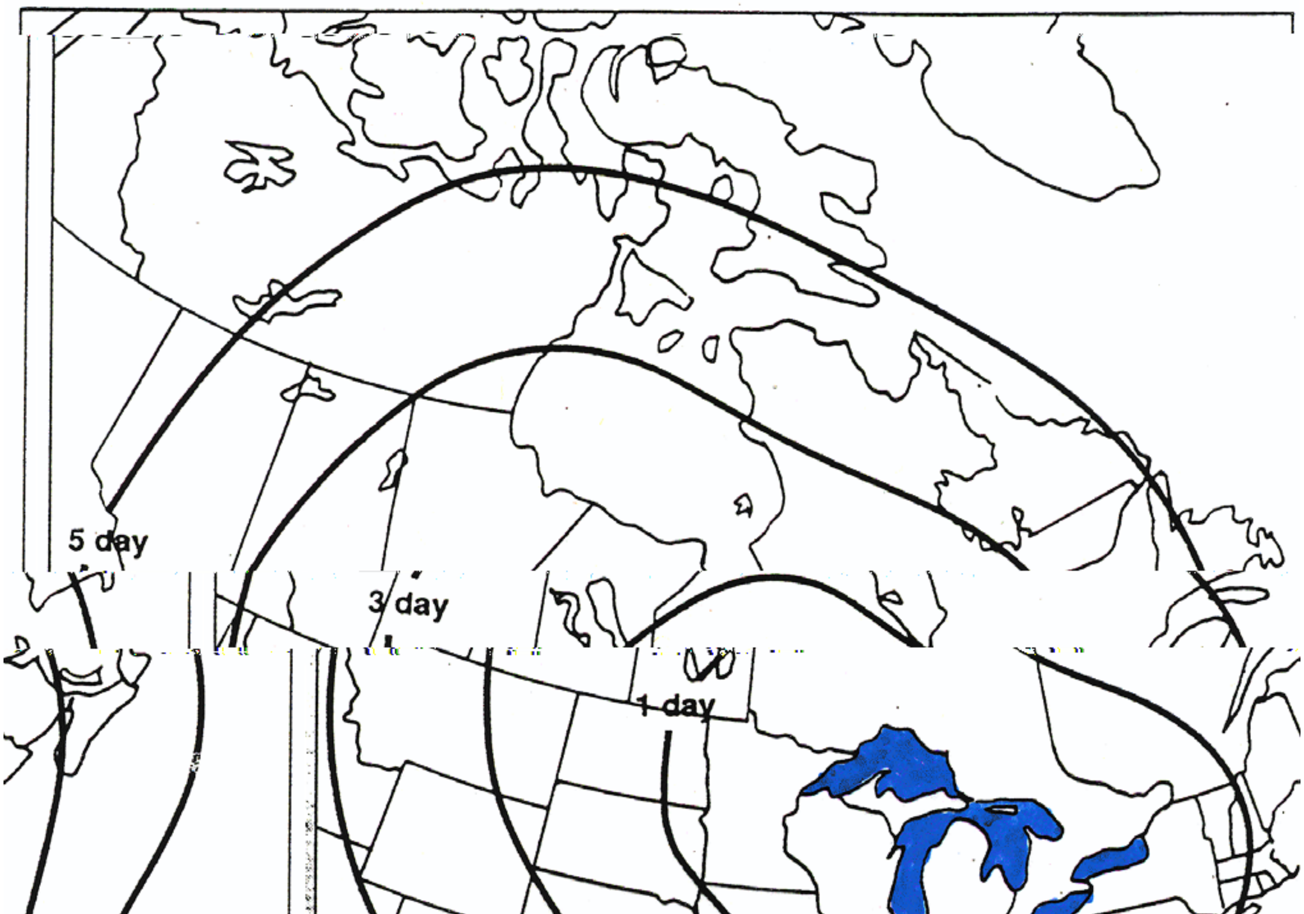
acenaphthene
pyrene
tetraethyl lead
methoxychlor
bis (tributyltin) oxide
anthracene
fluoranthene
chrysene
benz [a] anthracene
naphthalene
benzo [j] fluoranthene
benzo [b] fluoranthene
dimethyl mercury
phenanthrene
benzo [e] pyrene
benzo [a] pyrene
fluorene
endrin
dieldrin
monomethyl mercury chloride
p,p'-DDE
tetramethyl lead
biphenyl
4-bromophenyl phenyl ether
3,3'-dichlorobenzidene
benzo [g,h,i] perylene
p,p'-DDD
Cl - 1 - PCB average
heptachlor epoxide
perylene
benzo [k] fluoranthene
pentachlorophenol
p,p'-DDT
toxaphene
Cl - 2 - PCB average
indeno [1,2,3-c,d] pyrene
2,3,7,8-TCDD
dibenz [a,h] anthracene
PeCDD
HpCDD
OCDD/F
HxCDD
Cadmium
Mercury (II)
HpCDF
HxCDF
Cl - 10 - PCB
Cl - 9 - PCB average
PeCDF
Cl - 3 - PCB average
octachlorostyrene
Cl - 8 - PCB average
dinitropyrene
Cl - 7 - PCB average
Cl - 4 - PCB average
Cl - 6 - PCB average
2,3,7,8-TCDF
hexachlorocyclohexane
Cl - 5 - PCB average
1,4-dichlorobenzene
1,2,3,5-tetrachlorobenzene
1,2,3,4- and 1,2,4,5-tetrachlorobenzene
pentachlorobenzene
elemental mercury
hexachloro-1,3-butadiene
hexachlorobenzene
5 day
3 day
1 day
1000 km
500 mi
Lines indicate the median location of airborne contaminants originating 1,3 and 5 days before their arrival in the Great Lakes hydrological basin.
Source: International Air Quality Advisory Board, 1988.
0.01
0.1
1
10
100
1000
Approximate Atmospheric Half-Life (Days)



[redacted]

Source-Receptor relationships are highly variable;
thus: need long-term simulations to develop representative averages

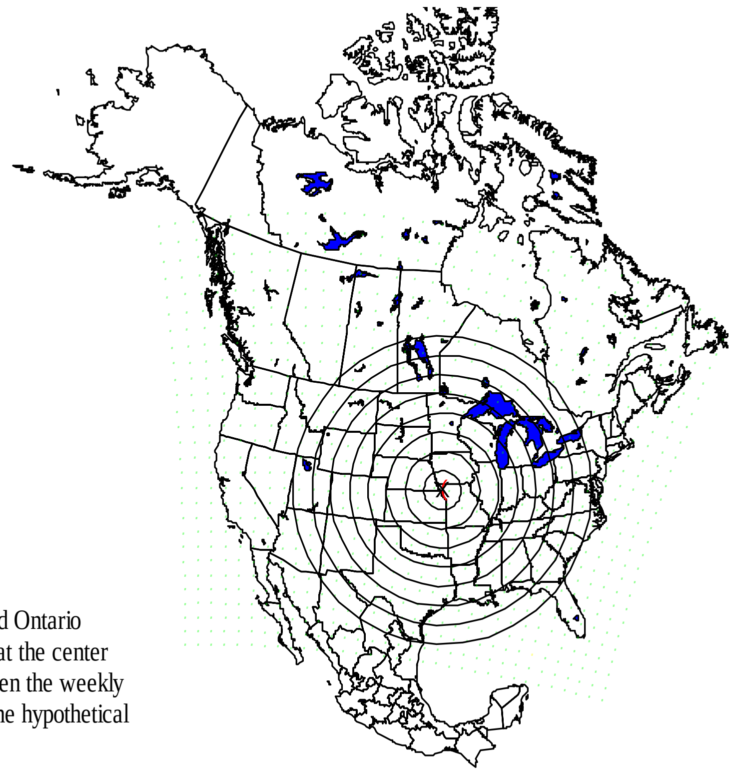
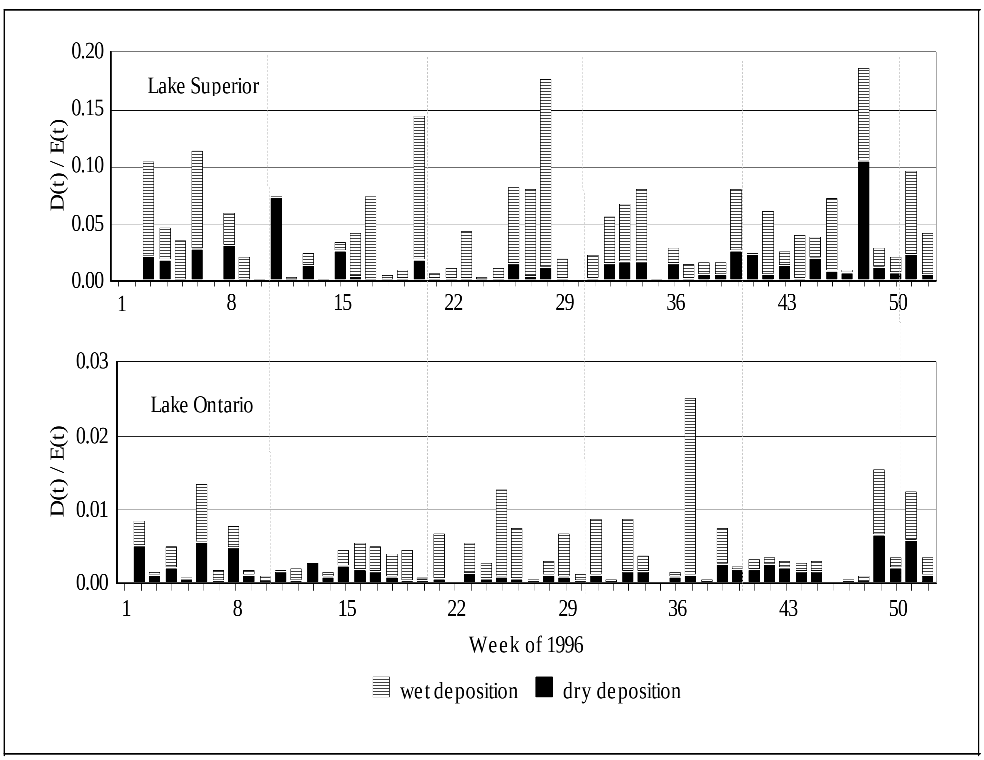
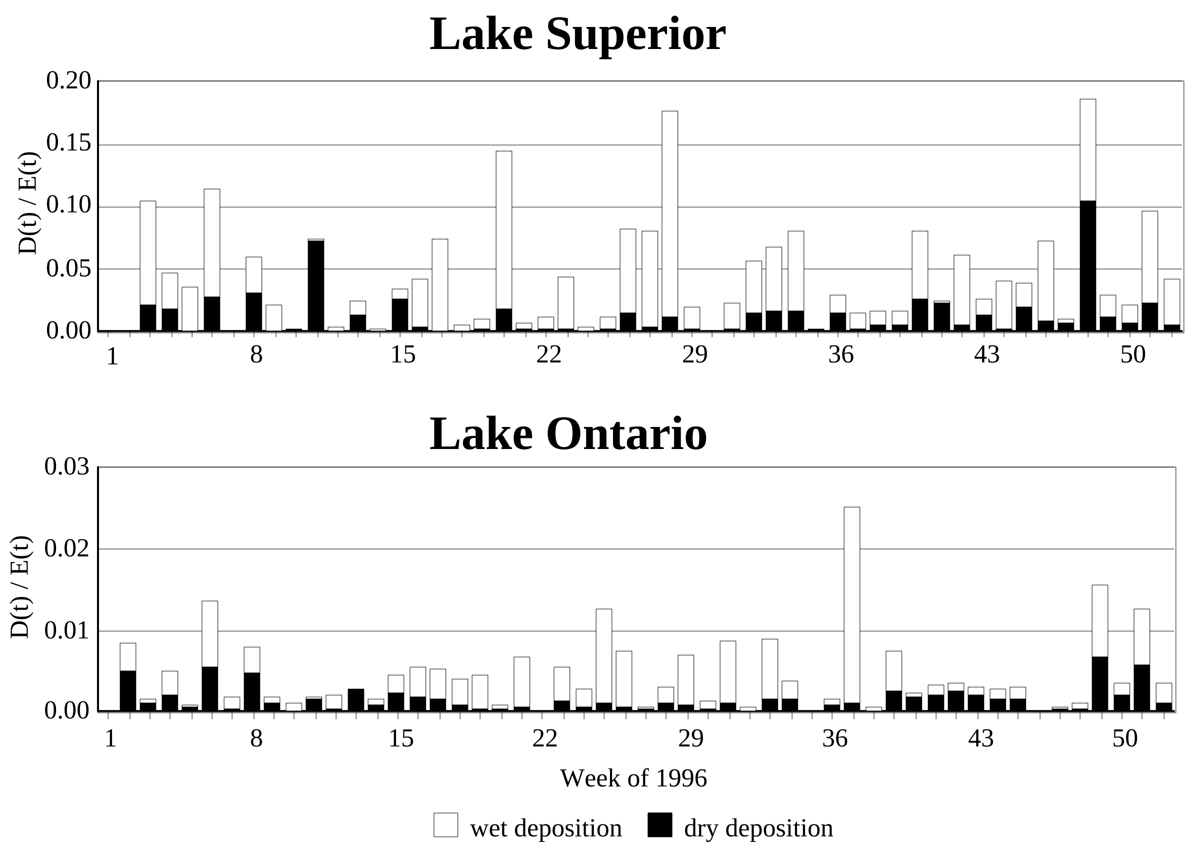


Figure 10. Weekly estimates of deposition to Lakes Superior and Ontario arising from a hypothetical, continuous source of 2,3,7,8-TCDD at the center of the modeling domain. The values plotted are the ratios between the weekly deposition rate, D(t), and the weekly emissions rate, E(t), from the hypothetical source.



Highly episodic deposition even for a continuous source … thus: long term simulations are necessary (that is why we do 1 year simulations)



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.

Sampling *close to* or *far away* from sources?