Organization of Course

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DIOXIN CASE STUDY

Prepared in Conjunction with the

Commission for Environmental Cooperation's

Continental Pollutant Pathways Project

May 1997

(Note: This PDF Version was created November 2000, and is slightly different than the May 1997 original version. The only change is Figure 6, and its description in the text, which has been updated, to allow new electronic graphic images to be used in the document)

Case Study

Dioxin

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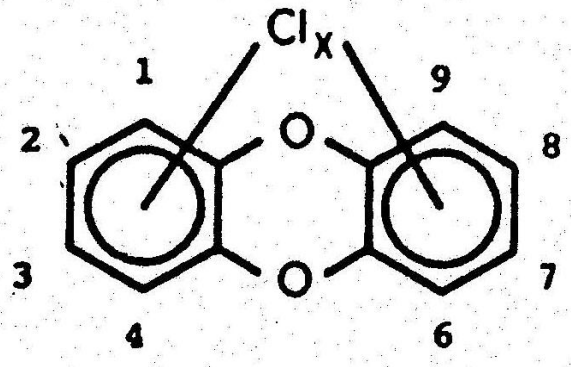
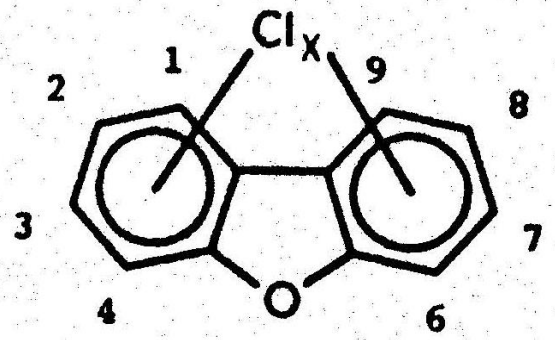
210 Different Congeners, 17 are "toxic"

2,3,7,8-TCDD is believe to be the most toxic





Structures of (left) polychlorinated-para-dioxins and (right) dibenzofurans.

Table 1. Toxic Equivalency Factors (TEF's) for PCDD/F Congeners

(U.S.EPA 1994a,b)

Dibenzo-*p*-dioxins		**Dibenzofurans**	
Congener(s)	**TEF**	**Congener(s)**	**TEF**
dibenzo-*p*-dioxin molecules with three or less chorine atoms (27 total)	0	dibenzofuran molecules with three or less chlorine atoms (59 total)	0
2,3,7,8-TCDD	**1**	**2,3,7,8-TCDF**	**0.1**
all other TCDD's (21 total)	0	all other TCDF's (37 total)	0
1,2,3,7,8-PeCDD	**0.5**	**2,3,4,7,8-PeCDF** **1,2,3,7,8-PeCDF**	**0.5** **0.05**
all other PeCDD's (13 total)	0	all other PeCDF's (26 total)	0
1,2,3,4,7,8-HxCDD **1,2,3,6,7,8-HxCDD** **1,2,3,7,8,9-HxCDD**	**0.1** **0.1** **0.1**	**1,2,3,4,7,8-HxCDF** **1,2,3,6,7,8-HxCDF** **1,2,3,7,8,9-HxCDF** **2,3,4,6,7,8-HxCDF**	**0.01** **0.01** **0.01** **0.01**
all other HxCDD's (7 total)	0	all other HxCDF's (12 total)	0
1,2,3,4,6,7,8-HpCDD	**0.01**	**1,2,3,4,6,7,8-HpCDF** **1,2,3,4,7,8,9-HpCDF**	**0.01** **0.01**
all other HpCDD's (1 total)	0	all other HpCDF's (2 total)	0
OCDD	**0.001**	**OCDF**	**0.001**

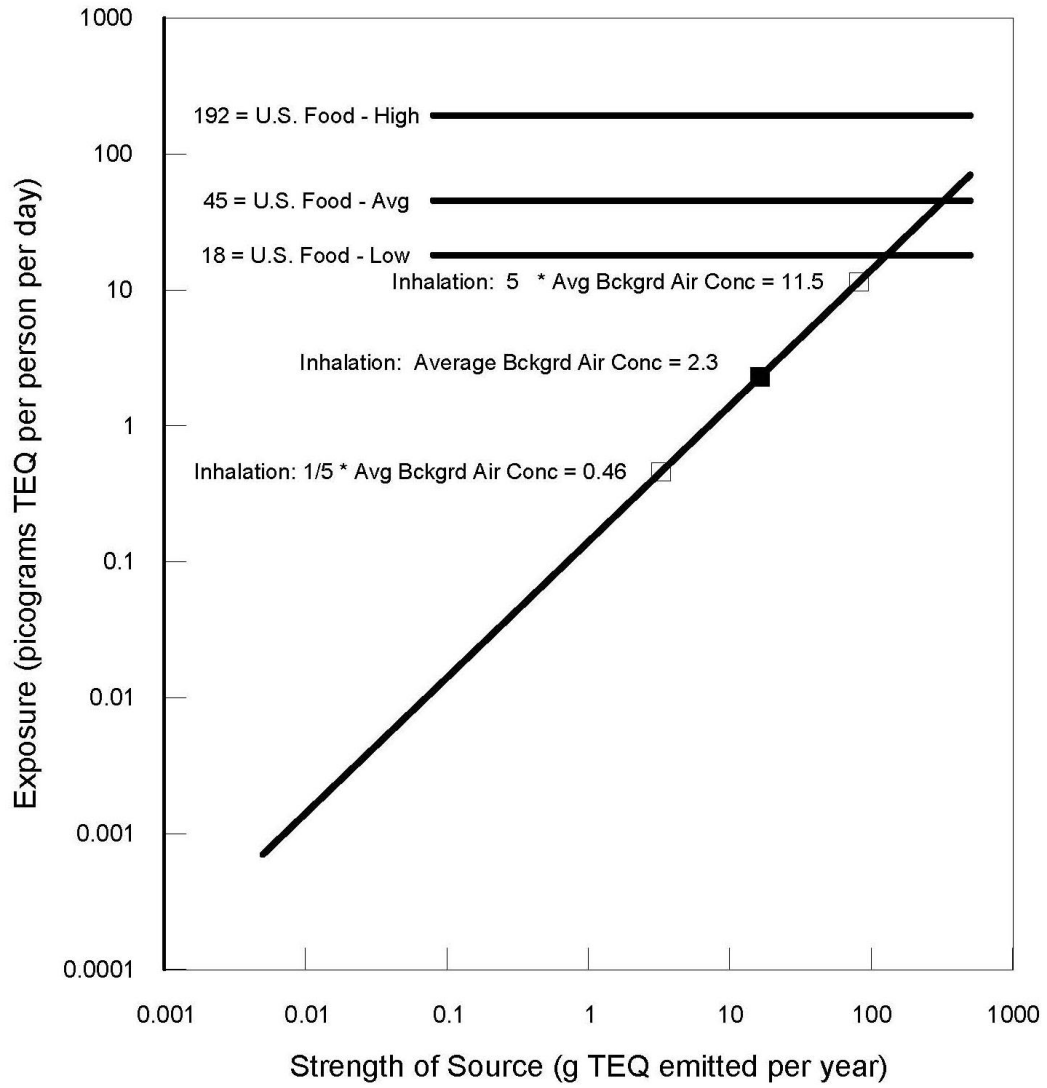
Abbreviations:

TCDD = Tetrachlorodibenzo-*p*-dioxin
PeCDD = Pentachlorodibenzo-*p*-dioxin
HxCDD = Hexachlorodibenzo-*p*-dioxin
HpCDD = Heptachlorodibenzo-*p*-dioxin
OCDD = Octachlorodibenzo-*p*-dioxin

Abbreviations:

TCDF = Tetrachlorodibenzofuran
PeCDF = Pentachlorodibenzofuran
HxCDF = Hexachlorodibenzofuran
HpCDF = Heptachlorodibenzofuran
OCDF = Octachlorodibenzofuran

Figure 3. Exposure to PCDD/F's from Food vs. Inhalation (U.S. Adults)

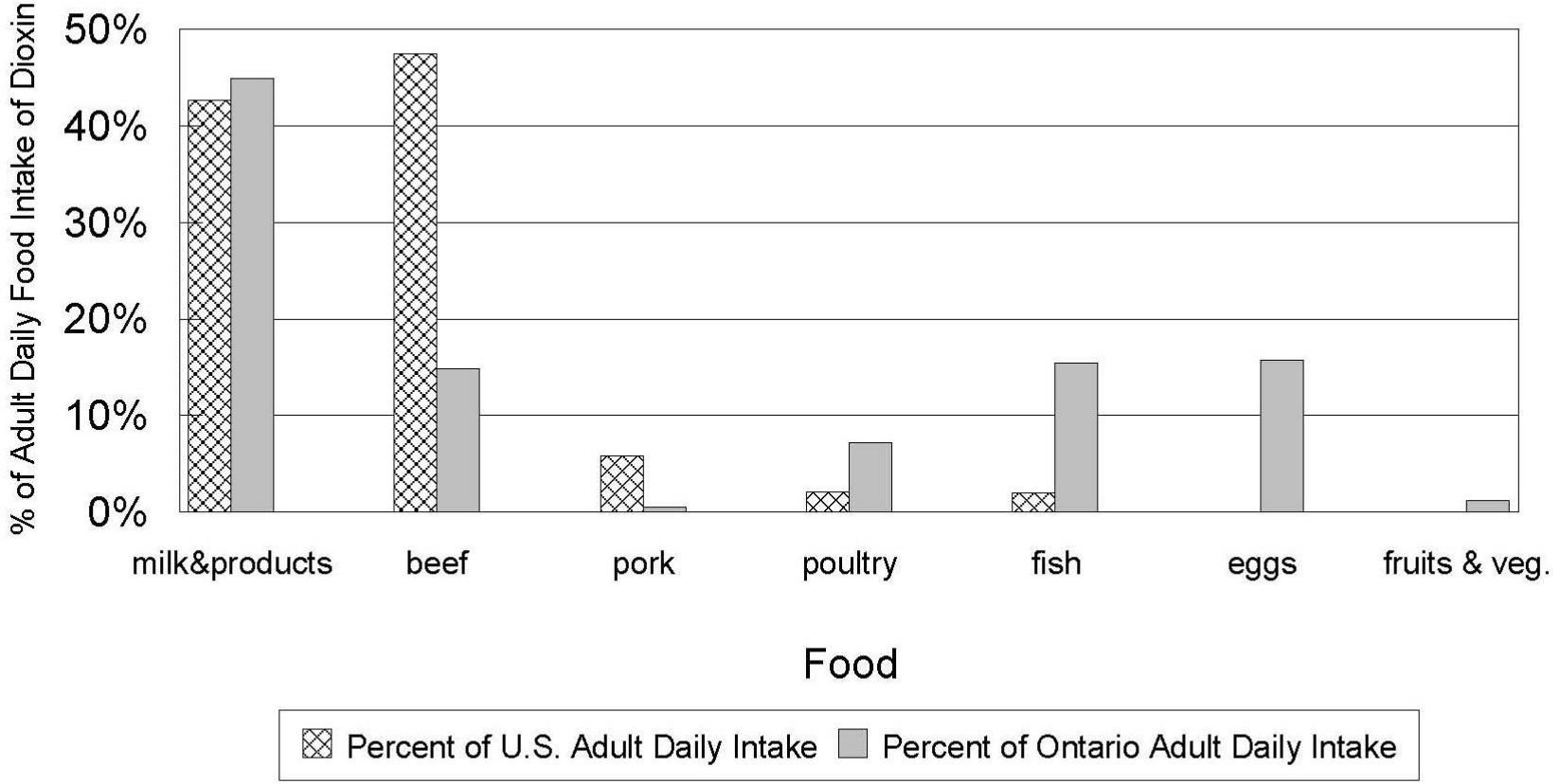


Food Data from Schecter et al., 1994c; Background Air Conc. from USEPA 1994a; Assumed Inhalation Rate: 23 m3/day; Inhalation 1 km from "Source" based on Dispersion Modeling in USEPA 1994a (stack height = 30.5 meters)

Human exposure to dioxin is largely through food consumption, rather than from inhalation

Figure 2. Relative Importance of Dioxin Exposure from Different Foods

(Estimates are based on extremely limited data and should be regarded as preliminary approximations only)



Note: Exposure from Egg Consumption Not Included in U.S. Data, Because of Lack of Data

U.S. Data: Schecter et al. (1994), Envr Health Persp 102(11): 962-966 (geometric mean of low & high estm's used)

Ontario Data: Birmingham et al. (1989), Chemosphere 19(1-6):507-512.

Summary of Atmospheric Deposition and Destruction Phenomenon Relevant to PCDD/PCDFs

	Gas-Phase PCDD/PCDF a significant fraction of the tetra- and penta- chloro PCDD/PCDFs exist in the vapor phase	Particle-Phase PCDD/PCDF essentially all of the hexa-, hepta- and octa-chloro PCDD/PCDFs exist in the particle phase
Wet Deposition	Depends on solubility of pollutant in water but, PCDD/PCDFs are not very soluble Thus, this is not a very important deposition pathway	In-Cloud: Rainout very efficient deposition mechanism Below-Cloud: Particle Scavenging by falling raindrops less efficient deposition mechanism Lagrangian time scale for air parcel encountering a rain event ~ 1 week

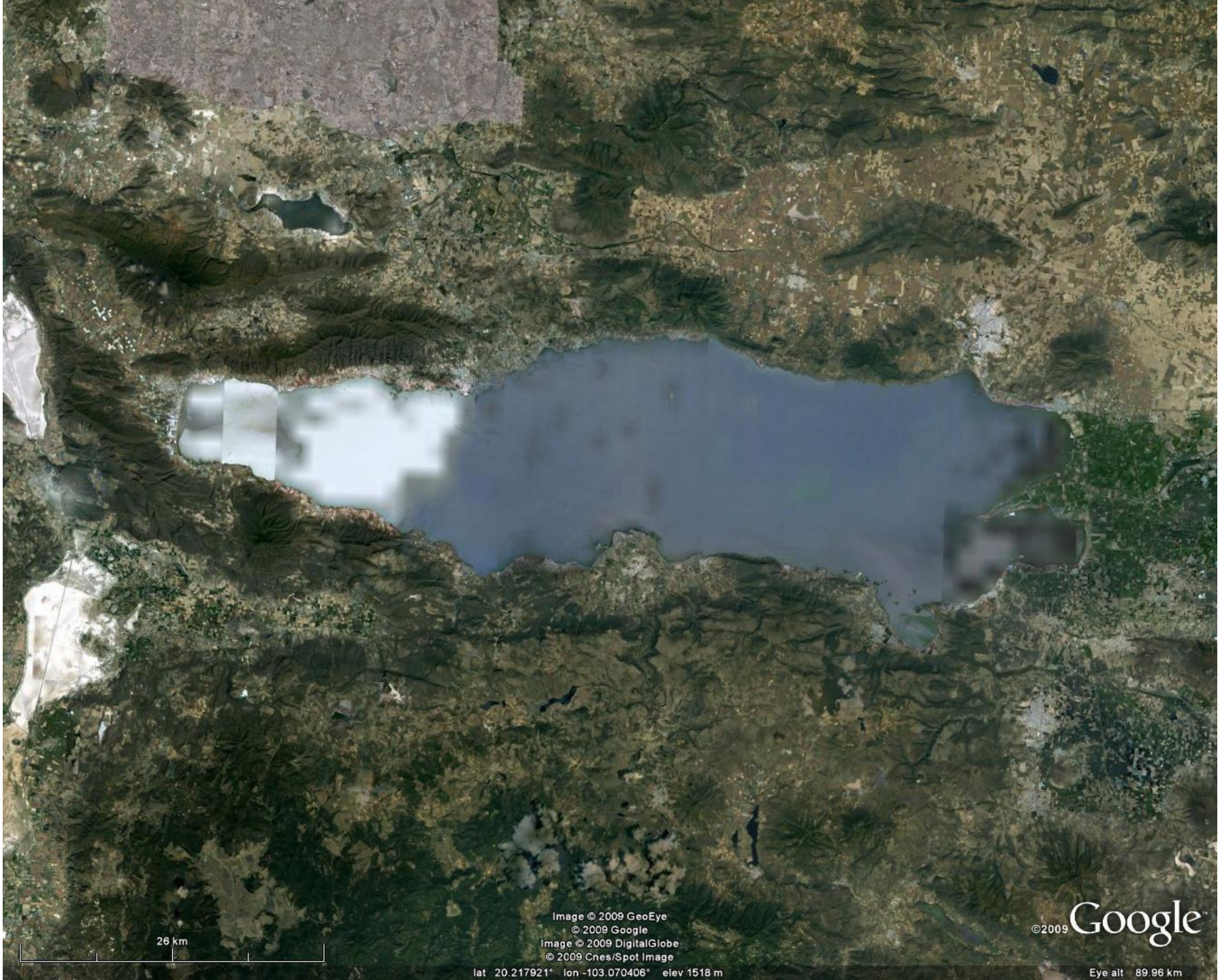
Summary of Atmospheric Deposition and Destruction Phenomenon Relevant to PCDD/PCDFs

	Gas-Phase PCDD/PCDF a significant fraction of the tetra- and penta- chloro PCDD/PCDFs exist in the vapor phase	Particle-Phase PCDD/PCDF essentially all of the hexa-, hepta- and octa-chloro PCDD/PCDFs exist in the particle phase
Dry Deposition	Depends on physical chemical properties of pollutant: e.g., adsorption to soil, adsorption to vegetation, solubility in water, etc... Depends on local meteorological conditions: e.g., wind speed, turbulence, and temperature And depends on nature of land surface: e.g., urban, agricultural, forest, desert, water	Primarily depends on particle size: Small particles have a lot of surface area, but they have a low deposition velocity Big particles have appreciable deposition velocity because of gravity, but, they don't have much surface area Somewhat dependent on local meteorological conditions: e.g., wind speed and temperature Not very dependent on nature of land surface
Atmospheric Transformation	gas-phase PCDD/PCDF somewhat vulnerable to hydoxyl radical reaction; gas-phase PCDD/PCDF less vulnerable to photolysis (but, the rate of this process is relatively uncertain)	particle-phase PCDD/PCDF appear to be much less vulnerable to photolytic or chemical destruction

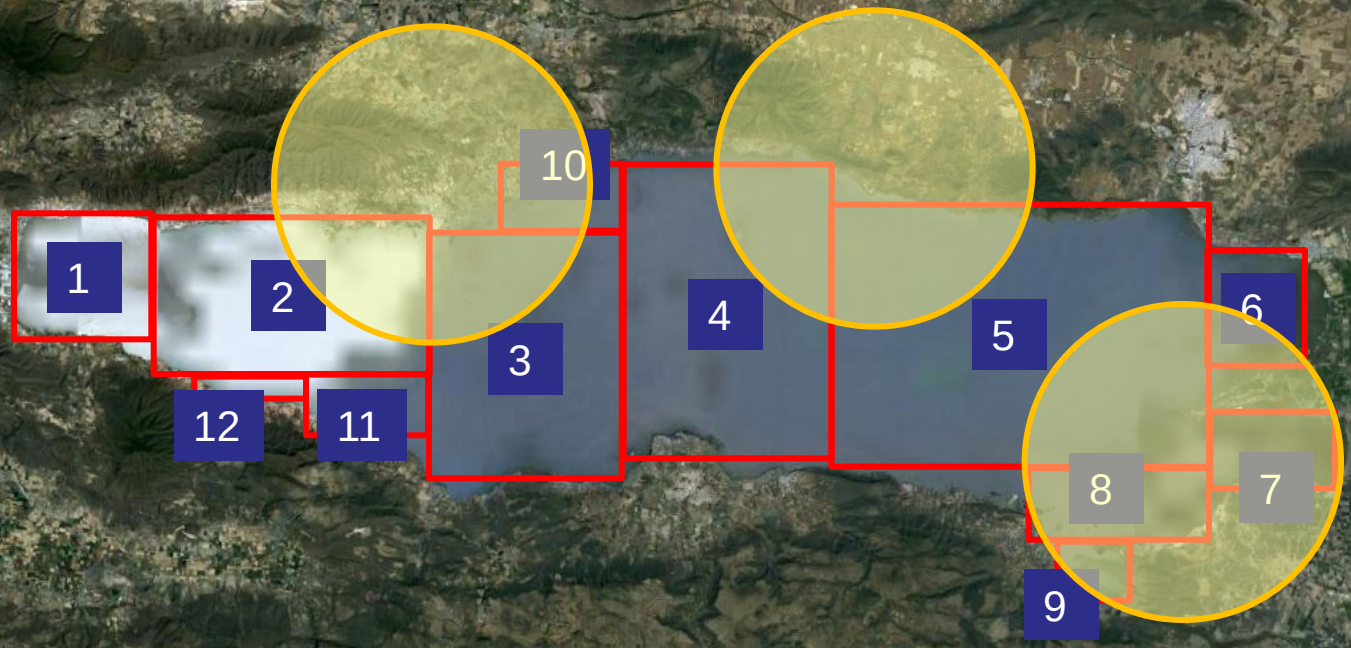
In 1993, we obtained the HYSPLIT model (version 3)

Several modifications made to simulate PCDD/F & Hexachlorobenzene

- **Deposition accounting for specific point and area receptors**
- **Vapor/particle partitioning for semivolatile compounds**
- **Atmospheric chemistry – reaction with OH and photolysis**
- **Particle size distribution for particle-associated material**
- **Particle deposition estimated for each particle size**
- **Enhanced treatment of wet and dry deposition**
- **Accounting for five different deposition pathways**
  - **Dry -- gas**
  - **Dry -- particle**
  - **Wet -- below cloud high RH (droplets present below cloud)**
  - **Wet -- below cloud low RH (dry particles present below cloud)**
  - **Wet -- in cloud**


26 km
Image © 2009 GeoEye
© 2009 Google
Image © 2009 DigitalGlobe
© 2009 Cnes/Spot Image
lat 20.217921° lon -103.070406° elev 1518 m
©2009 Google
Eye alt 89.96 km

Deposition from a given puff is assigned to a receptor, based on the overlap with that receptor, for each time step



C:\hysplit4\receptors\recp_data.txt

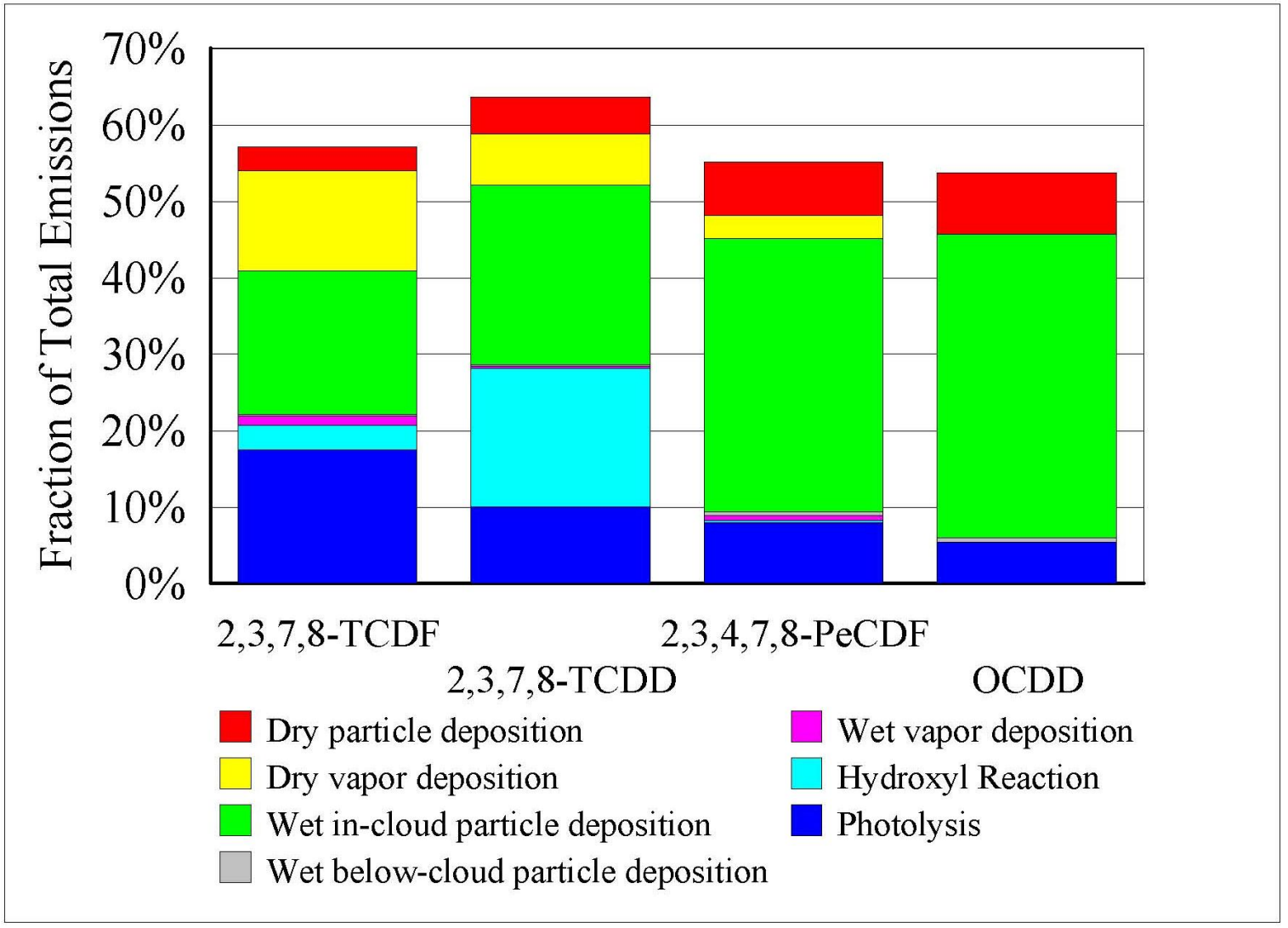
minimum longitude of rectangle	maximum longitude of rectangle	minimum latitude of rectangle	maximum latitude of rectangle

```
'Lake_Chapala', 1,-103.418,-103.343,20.223,20.289 /
'Lake_Chapala', 2,-103.343,-103.194,20.211,20.288 /
'Lake_Chapala', 3,-103.194,-103.085,20.163,20.285 /
'Lake_Chapala', 4,-103.085,-102.974,20.177,20.331 /
'Lake_Chapala', 5,-102.974,-102.766,20.173,20.311 /
'Lake_Chapala', 6,-102.766,-102.714,20.233,20.290 /
'Lake_Chapala', 7,-102.766,-102.693,20.173,20.211 /
'Lake_Chapala', 8,-102.861,-102.759,20.140,20.174 /
'Lake_Chapala', 9,-102.844,-102.803,20.111,20.140 /
'Lake_Chapala',10,-103.156,-103.085,20.285,20.324 /
'Lake_Chapala',11,-103.256,-103.194,20.180,20.211 /
'Lake_Chapala',12,-103.319,-103.256,20.199,20.211 /
```

You can add your own receptors!

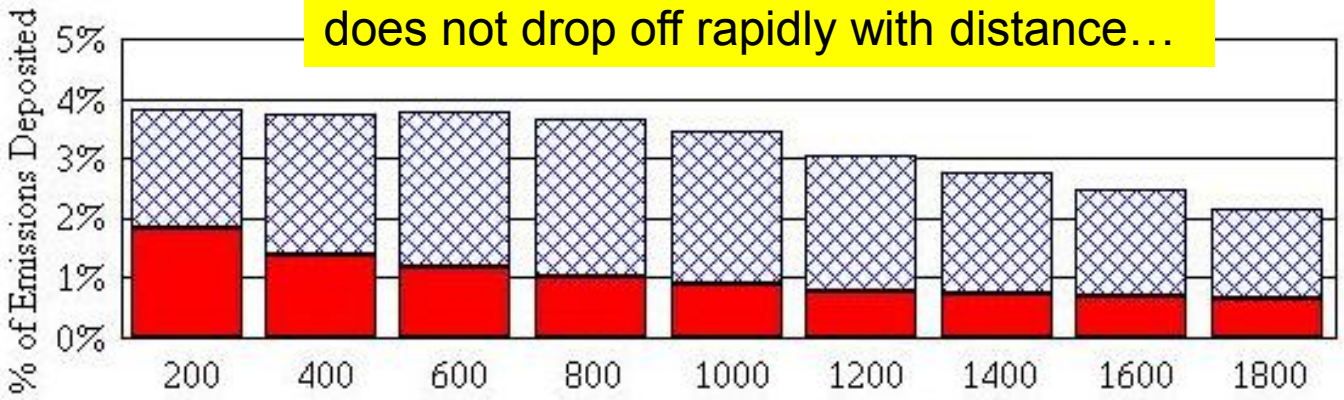
Also, in addition to "area" receptors, like a lake, point receptors can be added, e.g., corresponding to measurement site locations

This is particularly useful for model evaluation

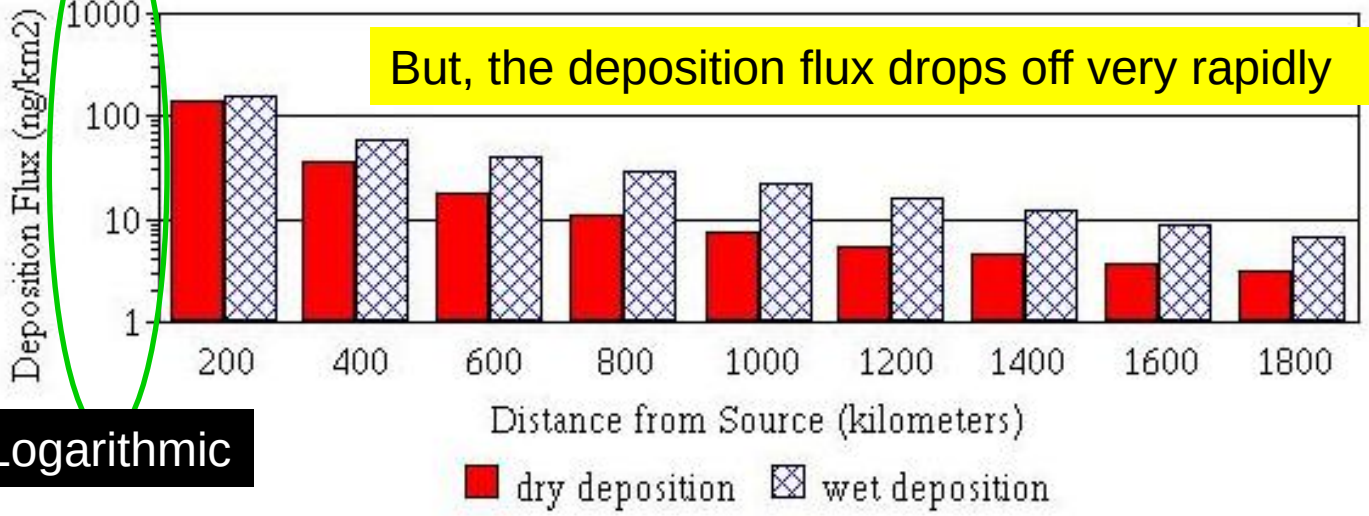


Fraction of emissions of four dioxin congeners accounted for in different fate pathways anywhere in the modeling domain for a hypothetical 1996 year-long continuous source near the center of the domain.

The fraction of emissions deposited does not drop off rapidly with distance…



But, the deposition flux drops off very rapidly



Logarithmic

Deposition amount and flux of 2,3,7,8-TCDD in successive, concentric, annular 200-km-radius-increment regions away from a hypothetical 1996 year-long continuous source near the center of the modeling domain [40° N, 95° W).

Rate of destruction of PCDD/F congeners by photolysis is particularly uncertain….

To help understand uncertainties, sensitivity analyses can be very useful

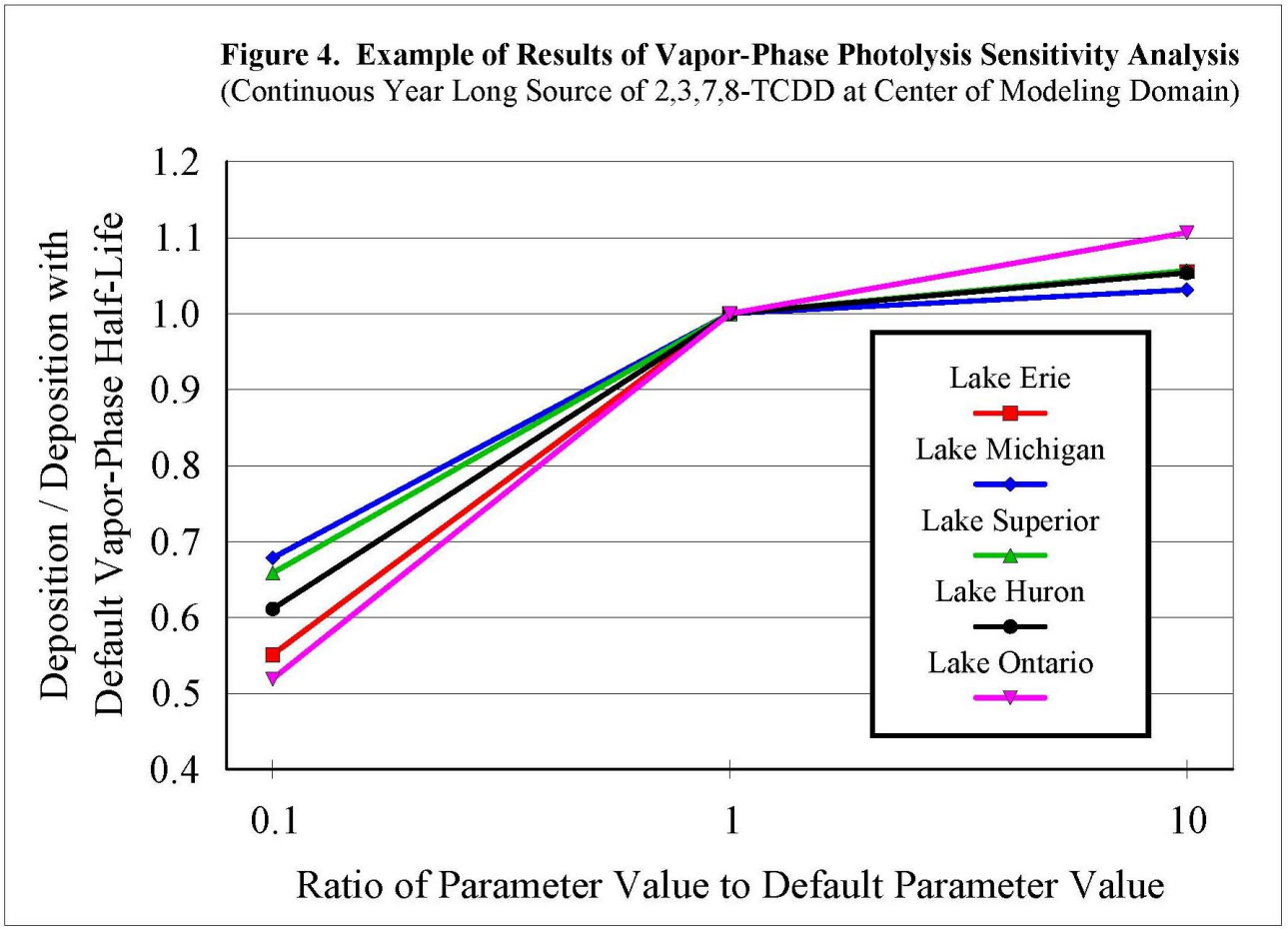


Figure 2. Particle Size Distribution Used in Modeling

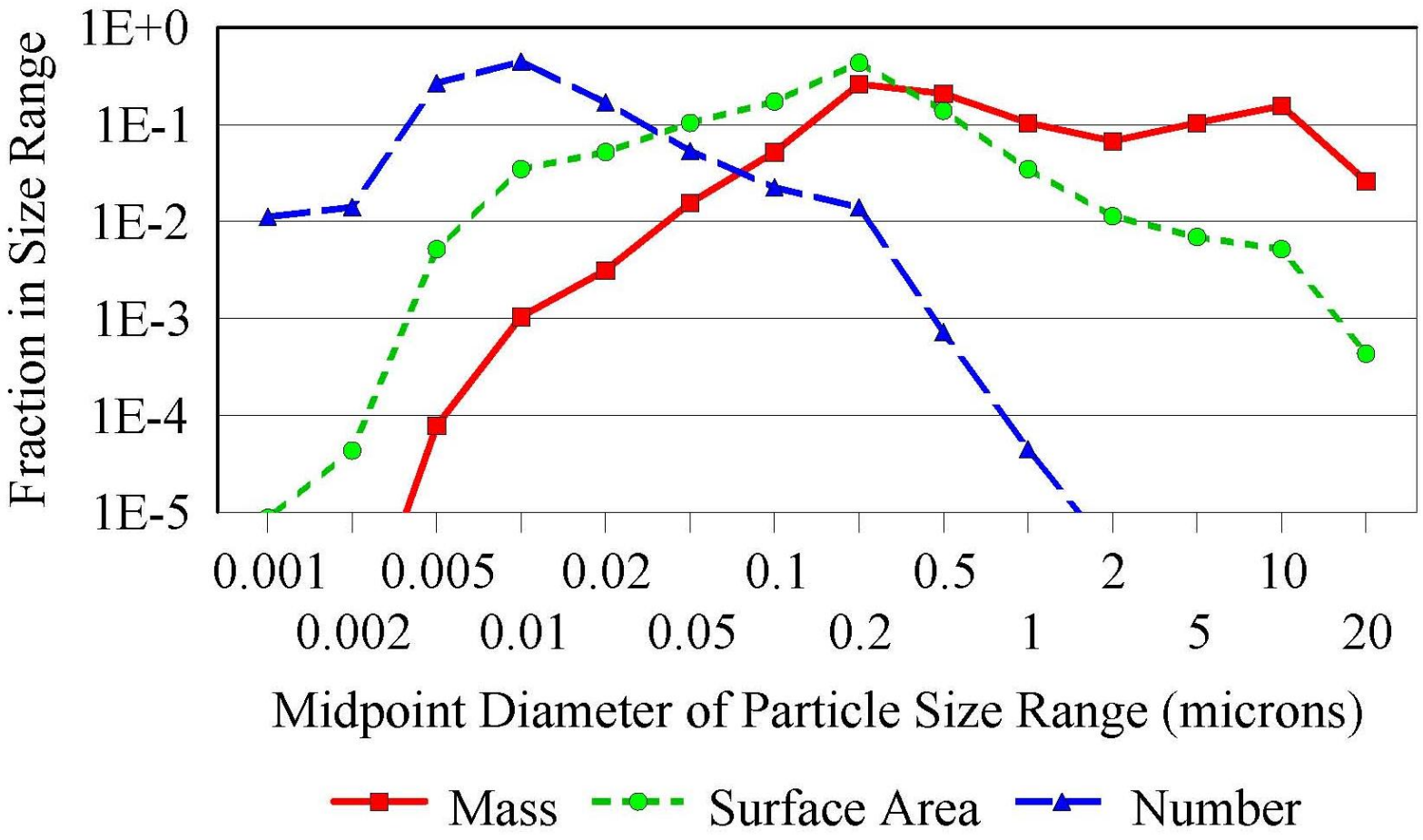
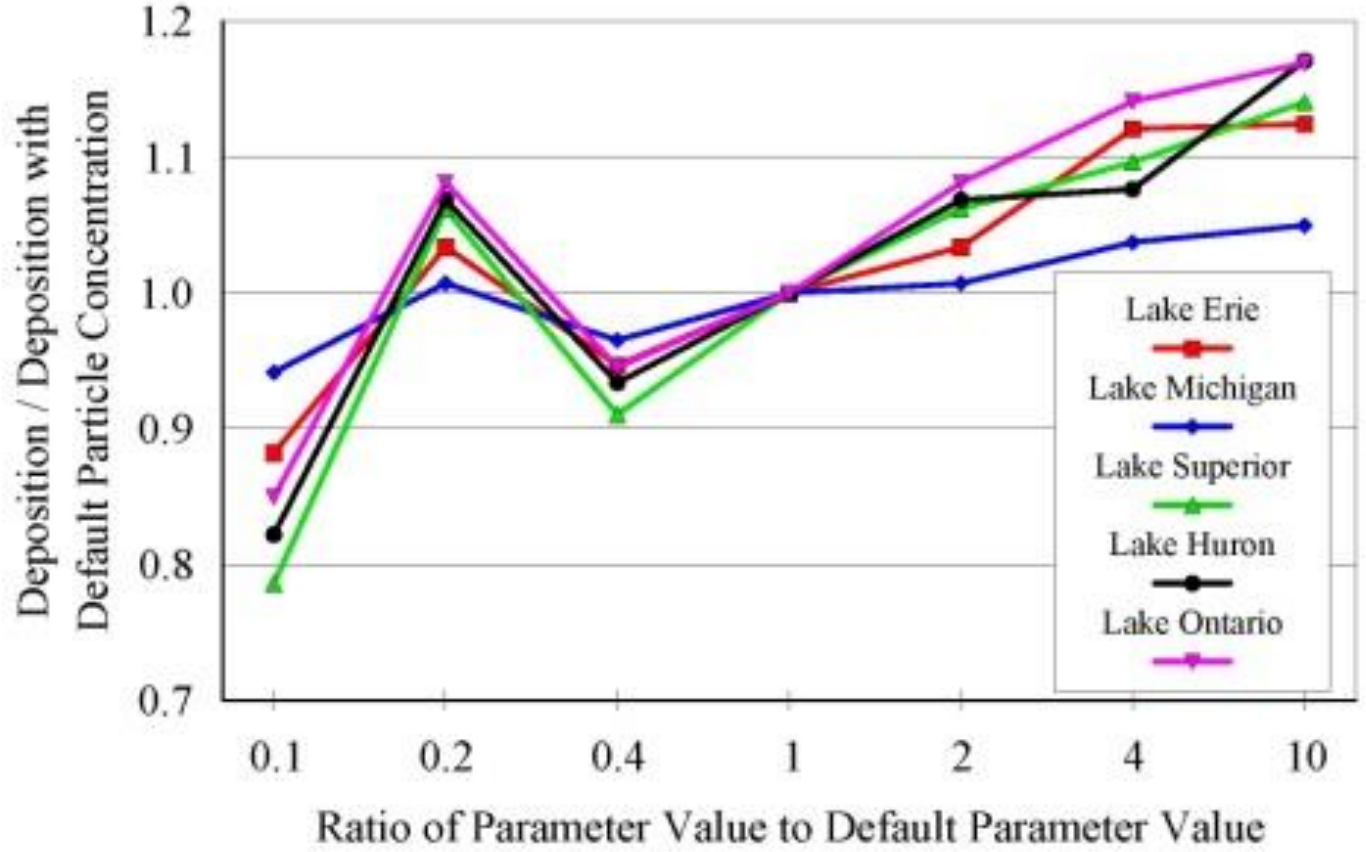


Figure 3. Example of Results of Particle Concentration Sensitivity Analysis
(Continuous Year Long Source of 2,3,7,8-TCDD at Center of Modeling Domain)



Dry Deposition and Surface Exchange

Process Information:
1. Dry Deposition - Resistance Formulation

$$V_d = \frac{1}{R_a + R_b + R_c + R_a R_b V_g} + V_g$$

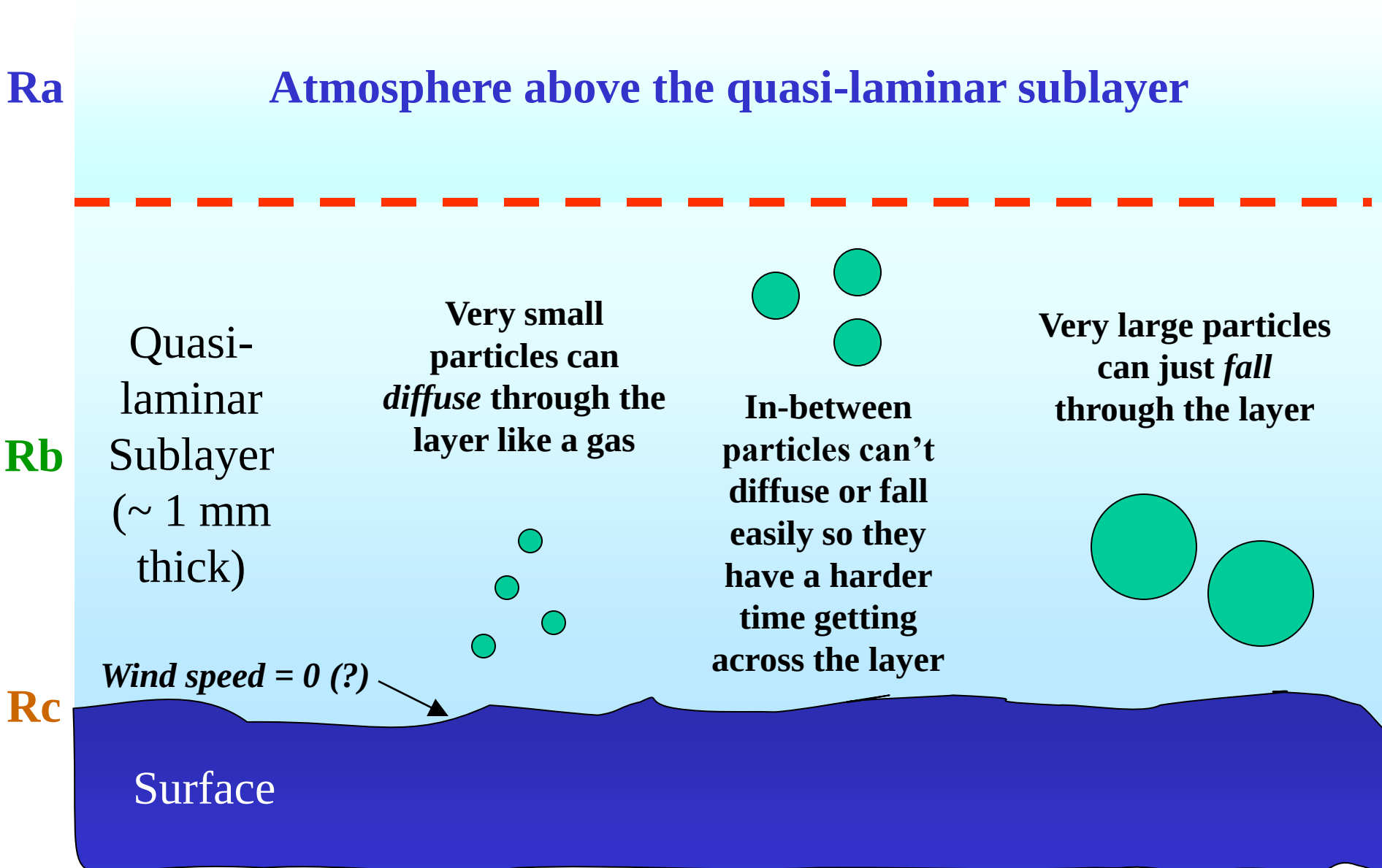
in which

- R_a = aerodynamic resistance to mass transfer;
- R_b = resistance of the quasi-laminar sublayer;
- R_c = overall resistance of the canopy/surface (zero for particles)
- V_g = the gravitational settling velocity (zero for gases).

Dry Deposition

- depends intimately on vapor/particle partitioning and particle size distribution information
- resistance formulation [R_a, R_b, R_c...]
- for gases, key uncertainty often R_c (e.g., “reactivity factor” f_0)
- for particles, key uncertainty often R_b
- How to evaluate algorithms when phenomena hard to measure?

Particle dry deposition phenomena



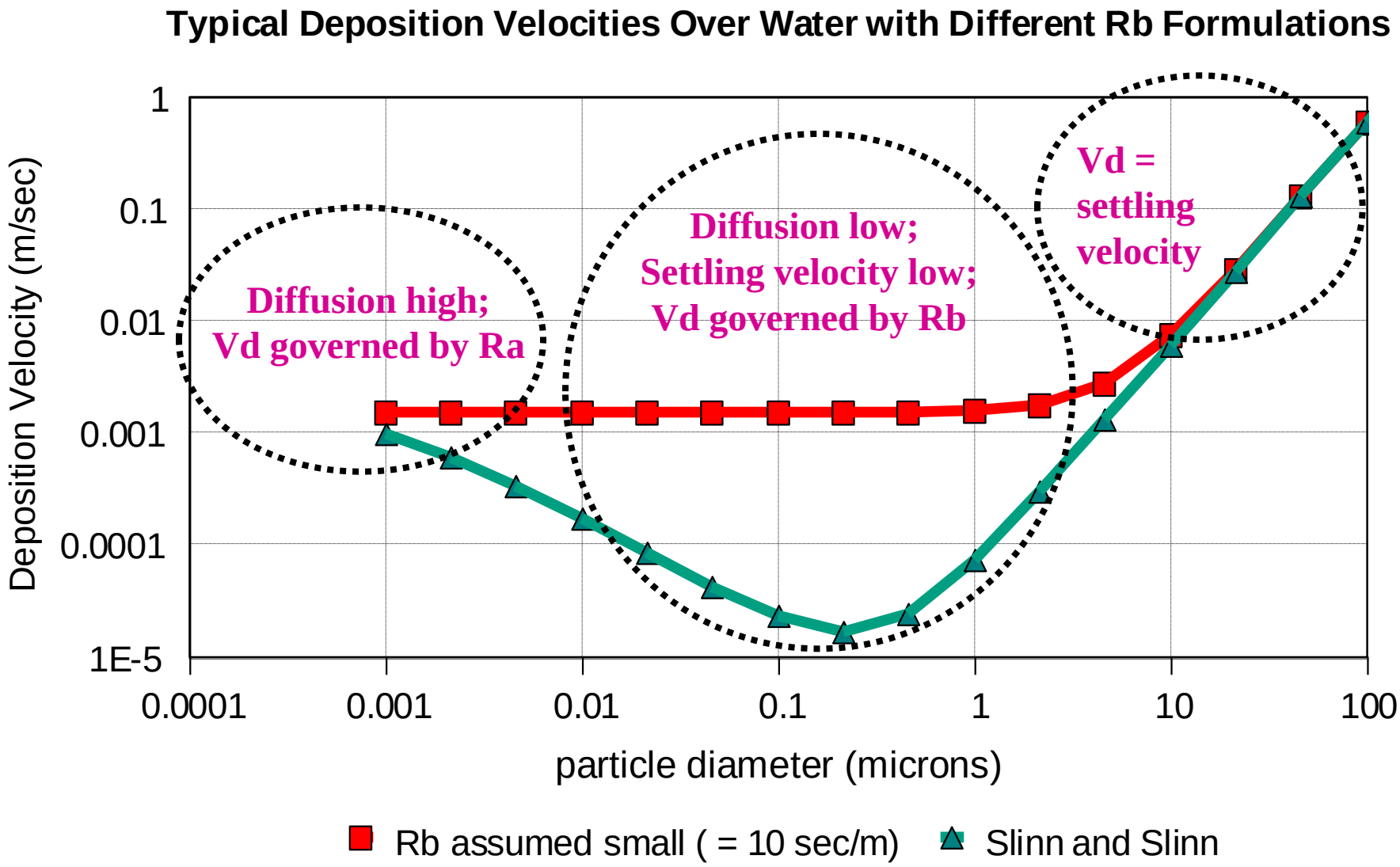

Typical Deposition Velocities Over Water with Different Rb Formulations
Deposition Velocity (m/sec)
1
0.1
0.01
0.001
0.0001
1E-5
0.0001
0.001
0.01
0.1
1
10
100
particle diameter (microns)
Diffusion high;
Vd governed by Ra
Diffusion low;
Settling velocity low;
Vd governed by Rb
Vd =
settling
velocity
Rb assumed small (= 10 sec/m)
Slinn and Slinn

Table 3. Alternative Dry Deposition Methodologies Used in this Modeling Analysis

Dry Deposition Method		Water Surfaces		Land or Vegetative Surfaces	
		Particles	Vapor	Particles	Vapor
		(if no entry in table, then use of default methodology is implied)			
A	default				
A′	default with no RH correction	no correction for hygroscopic growth of particle near water surface			
B	modified HYSPLIT_3 resistance methodology	Same as A for land/vegetative surfaces, except that exponent on *Sc* in R_b formulation is -0.5, instead of -0.67			
C	ADOM-II for particles	same as B, with addition of 0.01 cm/sec phoretic velocity component	same as B	different functional dependence on *St* in R_b formulation; addition of 0.01 cm/sec phoretic velocity component; exponent on *Sc*: - 0.5 for z0 < 10cm, and -0.7 for z0 > 10 cm	
D	Williams (1982) for particles depositing to water	Williams (1982)	same as B		
E	HYSPLIT_4 resistance methodology	similar to B, except that R_b set to 10 sec/m (a relatively low value)	same as B	a different functional dependence on *St* in R_b formulation	essentially the same as A

Figure 5. Variations in simulated 1996 deposition of 2,3,7,8-TCDD and OCDD to Lake Michigan with alternative dry deposition methodologies. "TCDD" = 2,3,7,8-TCDD; "Milw" indicates source in Milwaukee, WI; "center" indicates source at center of modeling domain; "SF" indicates source in San Francisco, CA.

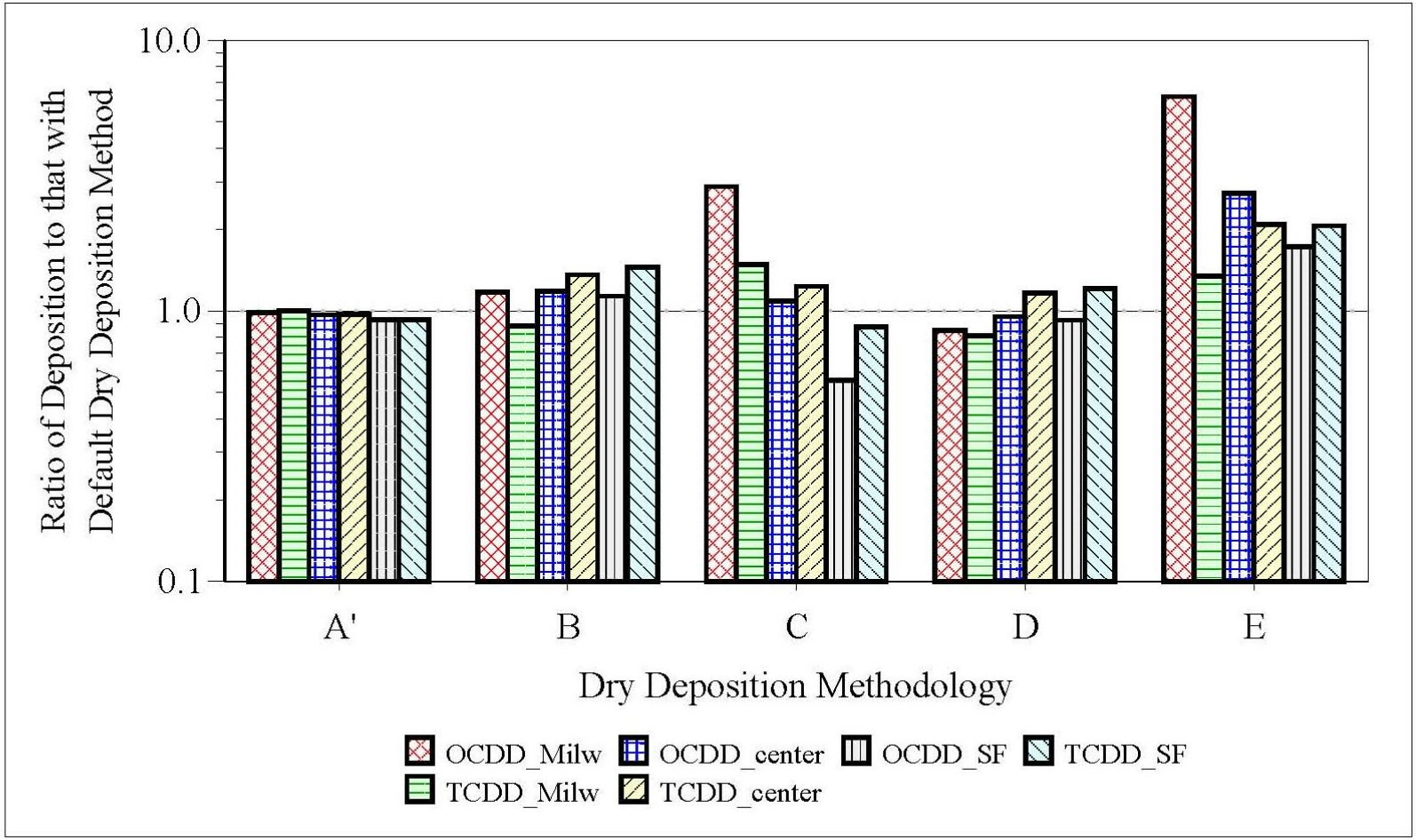
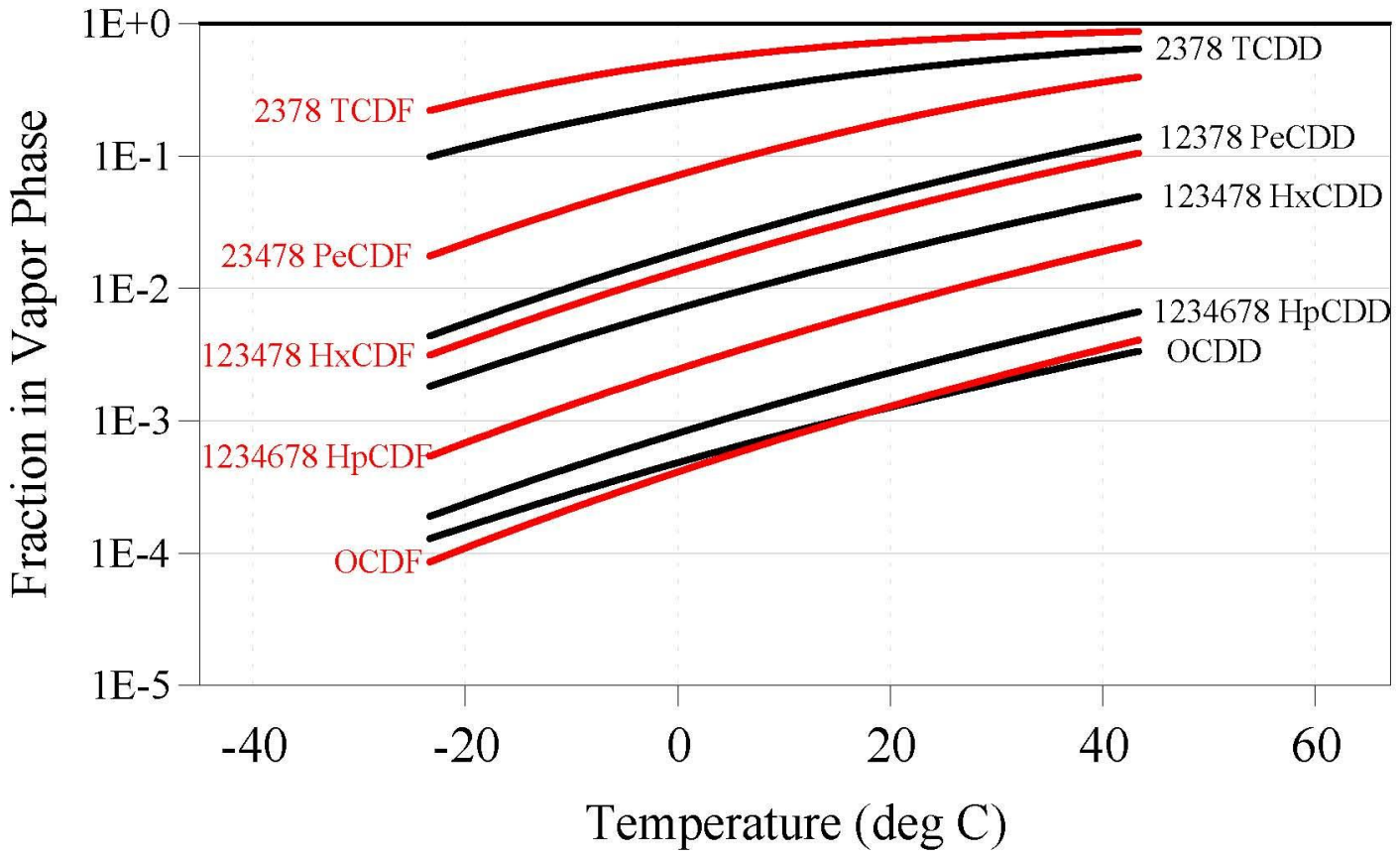


Figure 1. Estimated vapor/particle partitioning characteristics of selected PCDD/F congeners



The aerosol surface area used in these calculations is 3.5e-06 cm2/cm3, equivalent to "Background + Local Sources".

More Information on Vapor / Particle Partitioning

- **In the atmosphere, pollutants can exist, generally, in the vapor phase or associated with particles, i.e., the aerosol phase.**

- **For semivolatile compounds there can be there can be significant fractions associated with either phase.**

- ***This phenomenon is of crucial importance in determining the fate of semivolatile compounds in the atmosphere, because each of the deposition and destruction mechanisms depend a great deal on the physical form of the pollutant.***

- **The vapor/particle partitioning phenomenon was first introduced by Junge (1977), and has been extended and reviewed by many…**

The theory of vapor-particle partitioning postulates that for any species in the atmosphere, there is an equilibrium between vapor phase and the particle phase that depends primarily on:

- **the physical-chemical properties of the species of interest,**
- **the nature of the atmospheric aerosol,**
- **and the temperature.**

As proposed by Junge (1977), the vapor-particle partitioning of <u>exchangeable</u> material can be estimated from the following equation:

$$\Phi = c S_t / (p(T) + cS_t)$$

where

Φ = the fraction of the total mass of the species absorbed to the particle phase (dimensionless)

S_t = the total surface area of particles, per unit volume of air (cm^2/cm^3)

p(T) = the saturation vapor pressure of the species of interest (atm), at the ambient temperature (T)

c = an empirical constant, estimated by Junge (1977) to be approximately 1.7×10^{-4} atm-cm

The most thermodynamically stable form of many semivolatile species at ambient temperatures is typically a solid, but, Bidleman (1988) has argued that it is the "non-equilibrium" or subcooled liquid phase which controls the dynamic equilibrium partitioning of such compounds between the vapor phase and the atmospheric aerosol. Thus, the subcooled liquid vapor pressure at the ambient temperature should be used in the above equation.

This vapor pressure can be approximately estimated from the following equation:

$$\ln (P_l/P_s) = \Delta S_f (T_m - T) / RT$$

where

P_l = subcooled liquid vapor pressure (atm) at temp. T
P_s = solid vapor pressure (atm) at temperature T
ΔS_f = entropy of fusion (atm m^3/mole deg K)
(approximately equal to 6.79 R)
T_m = melting temperature of the solid compound (deg K)
T = ambient temperature (deg K)
R = the gas constant (atm m^3/mole deg K)

The solid vapor pressure at the temperature of interest can be estimated from the reported solid vapor pressure at a standard temperature with the Clausius-Clapeyron equation using the enthalpy of vaporization, according to the following equation:

$$\ln (P^s_1 / P^s_2) = (\Delta H / R) (1/T_2 - 1/T_1)$$

where

P^s_1 = solid vapor pressure (atm) at temperature T_1
P^s_2 = solid vapor pressure (atm) at temperature T_2
ΔH = enthalpy of vaporization (J/mole)
Note: according to Trouton's Rule, ΔH can be approximately estimated by the following relation: $\Delta H / T_{boil}$ = 84 J/(mol degK) (Mackay et al 1986).
R = gas constant (J/mole degK [=] (atm m^3/mole deg K)
T_2 = temperature 1 (deg K)
T_1 = temperature 2 (deg K)

- Thus, the vapor particle partitioning for a given compound in the atmosphere can be estimated from the first of the above two equations, with P_l from the second equation used for P(T).

- The only species-specific physical-chemical property data required to make a vapor/particle partitioning estimate according to the above simplified approach are the species' solid vapor pressure at one temperature, and the species' boiling and melting temperatures.

- It is typically assumed that semivolatile compounds in the atmosphere are "fully exchangeable", i.e., that the compound can move freely between the vapor and particle phases, depending on the dictates of thermodynamics.

- To the extent that a portion of the material is "locked-up" within particles *and is not available for exchange*, this assumption would be in error.