Modeling of Transport, Transformation and Deposition of PCBs, PCDD/Fs in Atmosphere

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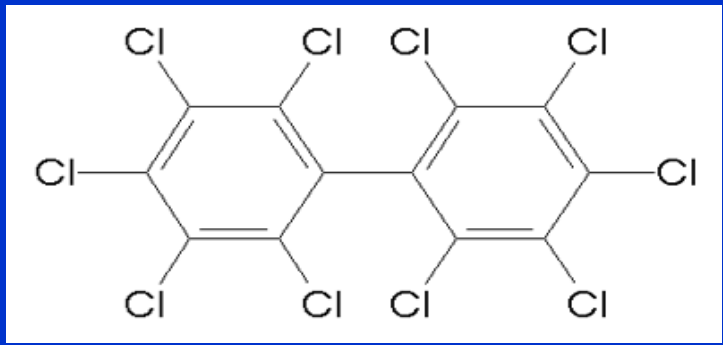
Introduction

- PCBs and PCDD/Fs are Persistent Organic Pollutants (POPs)
- POPs can be gaseous, semi-volatile or in aerosol form.
  - Remain in the environment for long periods of time and transport long distances.
  - Bio-accumulate, posing risks to human health and natural ecosystems.
- We have modified the SMOKE/CMAQ modeling system to include PCBs and PCDD/Fs
  - Added gas/aerosol partitioning and chemistry of PCBs and PCDD/Fs.
- Preliminary simulations in North America have been conducted.

Polychlorinated Biphenyls (PCBs):

- Characterized by two phenyl groups, with varying number of chlorine atoms (209 congeners).
- Used in hundreds of industrial and commercial applications
- More than one billion pounds of PCBs were manufactured in the North America.
- Production ceased in 1977.

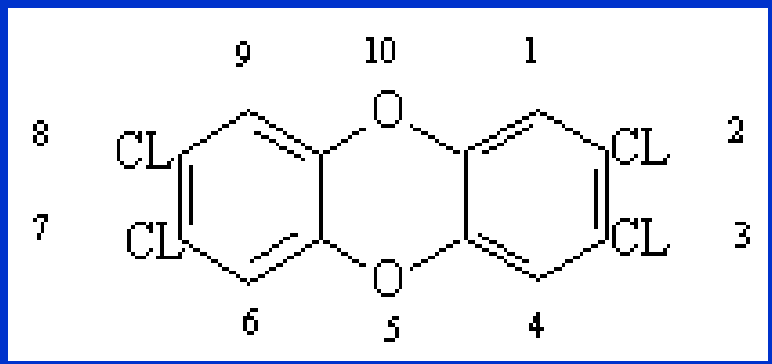


PCBs emission sources

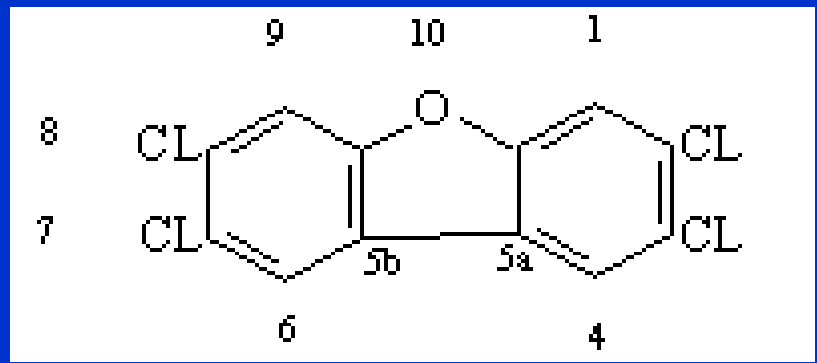
- Releases of commercial PCBs
  - Most common use of PCB in the past was in electrical transformers. Leaks or releases from electrical transformers containing PCBs
  - Improper disposal of PCB-containing consumer products and PCBs fluids
  - Poorly maintained hazardous waste sites containing PCBs
  - Old microscope oil and hydraulic fluids
- Combustion sources
  - Municipal waste combustion
  - Industrial woods combustion
  - Medical waste incineration
- Chemical manufacturing and processing sources
- Sediments in the bottom of lakes, river, or our ocean constantly release small amounts of PCBs into the environment.

PCDD/Fs

- Dioxin and furans: Polychlorinated dibenzo-p-dioxins and dibenzofurans pollutant group (PCDD/Fs)
- 210 different congeners.



2,3,7,8-TCDD



2,3,7,8-TCDF

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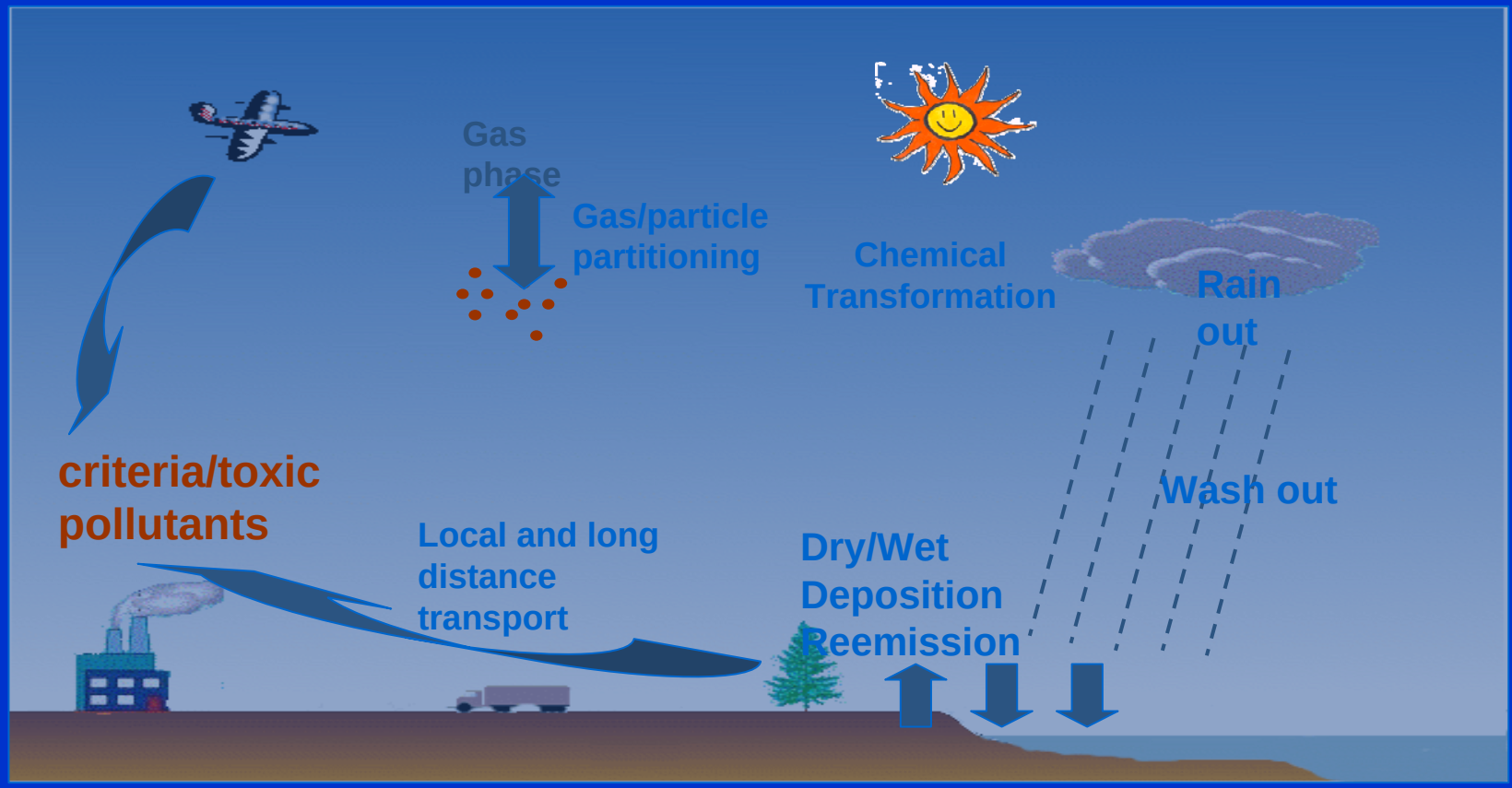
PCDD/Fs emission sources

- Waste incineration
  - Incineration of municipal solid waste, hazardous waste, medical waste, sewage sludge
- Power/energy generations
  - Motor vehicle, wood, oil, coal
- High temperature sources
  - kilns, cigarette smoking etc.
- Uncontrolled and minimally controlled sources
  - Combustion of landfill gas and landfill fires, accidental fires, backyard barrel burning and residential yard waste burning etc
- Metal smelting and refining
- Chemical manufacture and processing



Fate of POPs in atmosphere

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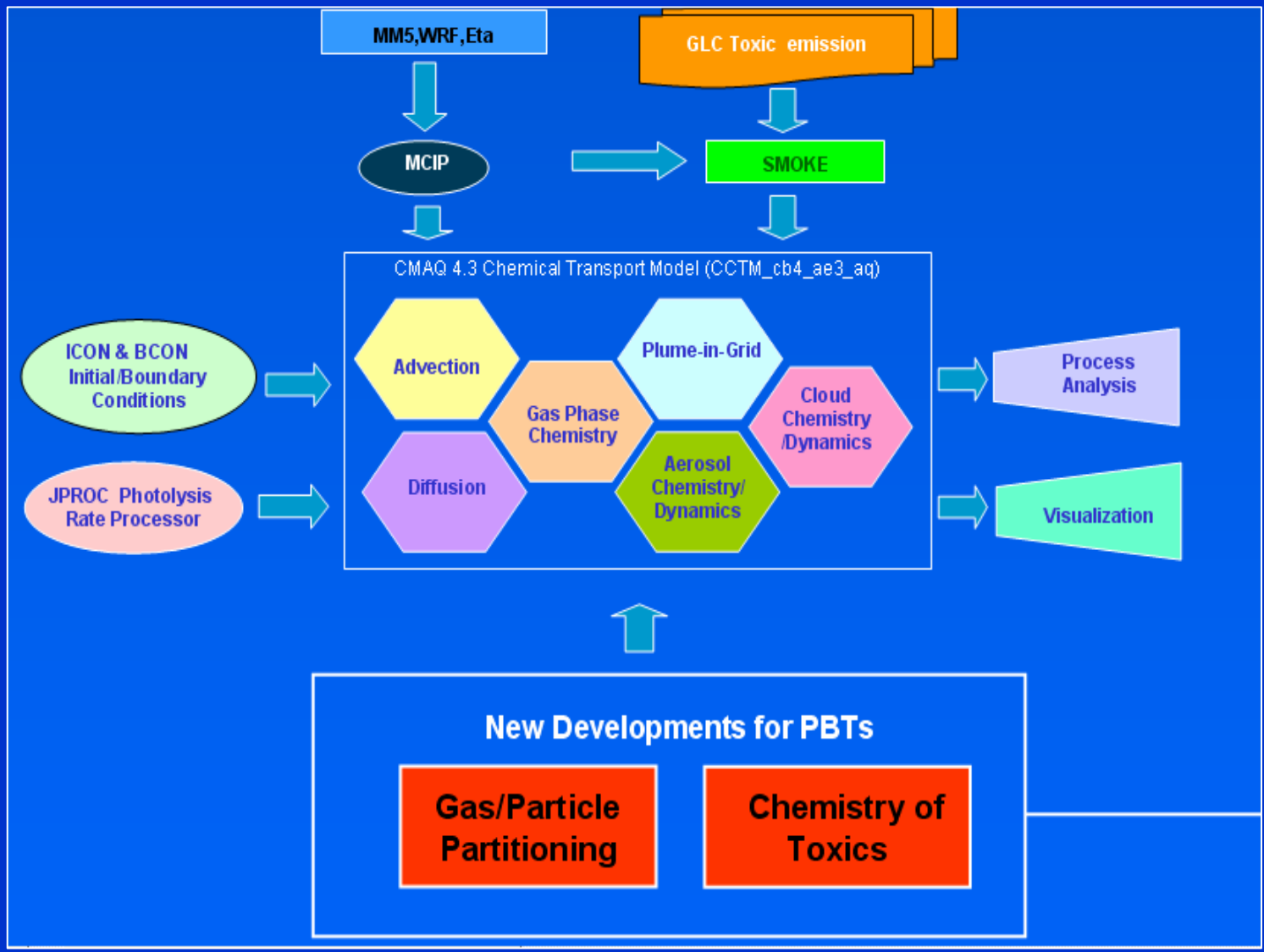
Model Development


MM5,WRF,Eta
GLC Toxic emission
MCIP
SMOKE
CMAQ 4.3 Chemical Transport Model (CCTM_cb4_ae3_aq)
ICON & BCON Initial/Boundary Conditions
JPROC Photolysis Rate Processor
Advection
Plume-in-Grid
Gas Phase Chemistry
Cloud Chemistry /Dynamics
Diffusion
Aerosol Chemistry/ Dynamics
Process Analysis
Visualization
New Developments for PBTs
Gas/Particle Partitioning
Chemistry of Toxics

Model modification and new components

- SMOKE/CMAQ model system has been modified to include 22 PCBs congeners and 17 PCDD/Fs congeners.
- Gas/partitioning of PCBs and PCDD/Fs added
- Gas phase chemical transformation
- Dry and wet removal of particle phase and wet removal of gas phase PCBs and PCDD/Fs are included.

PCBs and PCDD/Fs congeners in the model

PCBs		PCDD/Fs	
PCB-5	PCB-118	2,3,7,8-TCDD	1,2,3,6,7,8-HxCDF
PCB-8	PCB-123	1,2,3,7,8-PeCDD	1,2,3,7,8,9-HxCDF
PCB-18	PCB-132	1,2,3,4,7,8-HxCDD	2,3,4,6,7,8-HxCDF
PCB-28	PCB-138	1,2,3,6,7,8-HxCDD	1,2,3,4,6,7,8-HpCDF
PCB-31	PCB-149	1,2,3,7,8,9-HxCDD	1,2,3,4,7,8,9-HpCDF
PCB-52	PCB-153	1,2,3,4,6,7,8-HpCDD	OCDF
PCB-70	PCB-158	OCDD	
PCB-90	PCB-160	2,3,7,8-TCDF	
PCB-101	PCB-180	1,2,3,7,8-PeCDF	
PCB-105	PCB-194	2,3,4,7,8-PeCDF	
PCB-110	PCB-199	1,2,3,4,7,8-HxCDF	

Gas/Particle Partitioning Models

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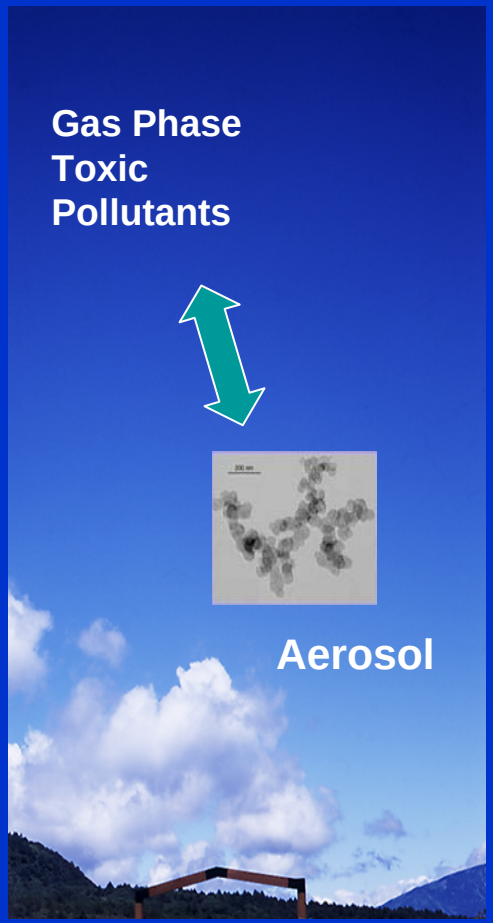
Junge-Pankow adsorption model (J-P Model)[1,2]



$$\phi = c\,\theta\,/(\,p_L + c\,\theta\,)$$

$$\log\ p_L = m_L / T + b_L$$

φ: fraction on aerosol;
θ: aerosol surface area concentration
P_L: saturation vapor pressure
T: temperature;
c, m_L and b_L: constants [3]

1. Junge C.E. 1977. in Fate of Pollutants in the Air and Water Environments (Edited by Suffet I. H.) : J. Wiley, New York
2. Pankow, Atmos. Env. Vol.21, No.11, 2275-2283, 1987
3. R. L. Falconer and T. F. Bidleman, Atmos. Env. Vol. 28, No. 3, 547-554, 1994

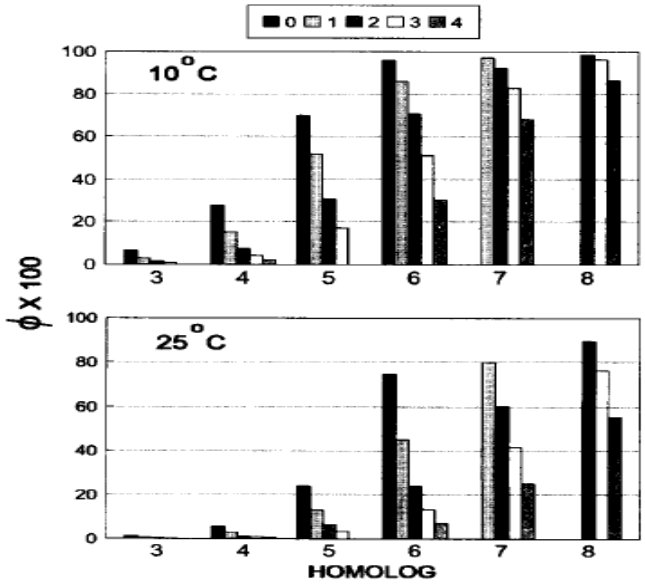


Fig. 3. Percent particulate PCBs ($\Phi \times 100$) in urban air at 10 and 25° C by homolog (number) and ortho-chlorine (shade).

J-P model results by Falconer R. L. 1994, using aerosol surface area of

1.1X10^{-5} cm^2/cm^3 for urban air

1.5x10^{-6} cm2/cm3 for average continental background air

4.2x1^{-7} cm2/cm3 for clean continental background air

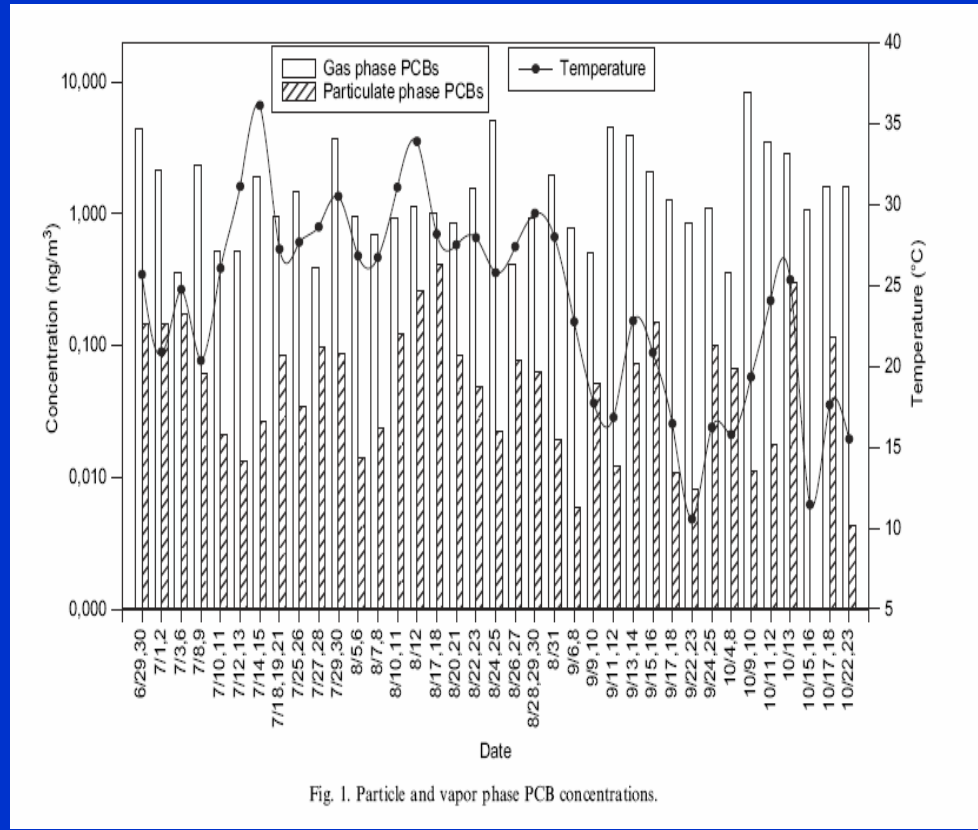


Fig. 1. Particle and vapor phase PCB concentrations.

Measured PCBs concentration at Chicago, IL, June to Oct. 1995,

Tasdemir, Y. et. al. 2004

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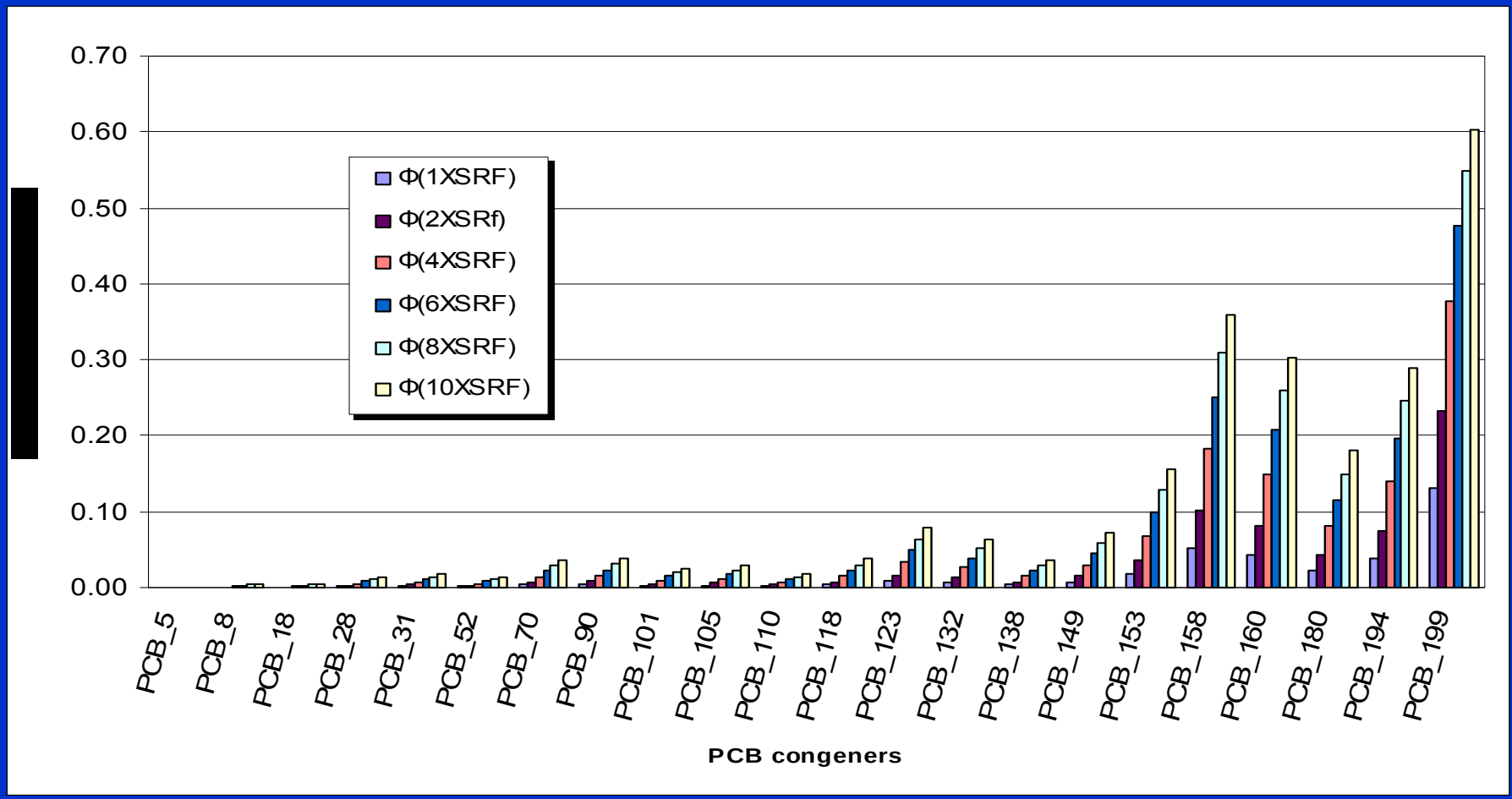

Φ of PCB_S calculated by J-P adsorption partitioning model IIT,Chicago, 15:00GMT, April 30, 2000

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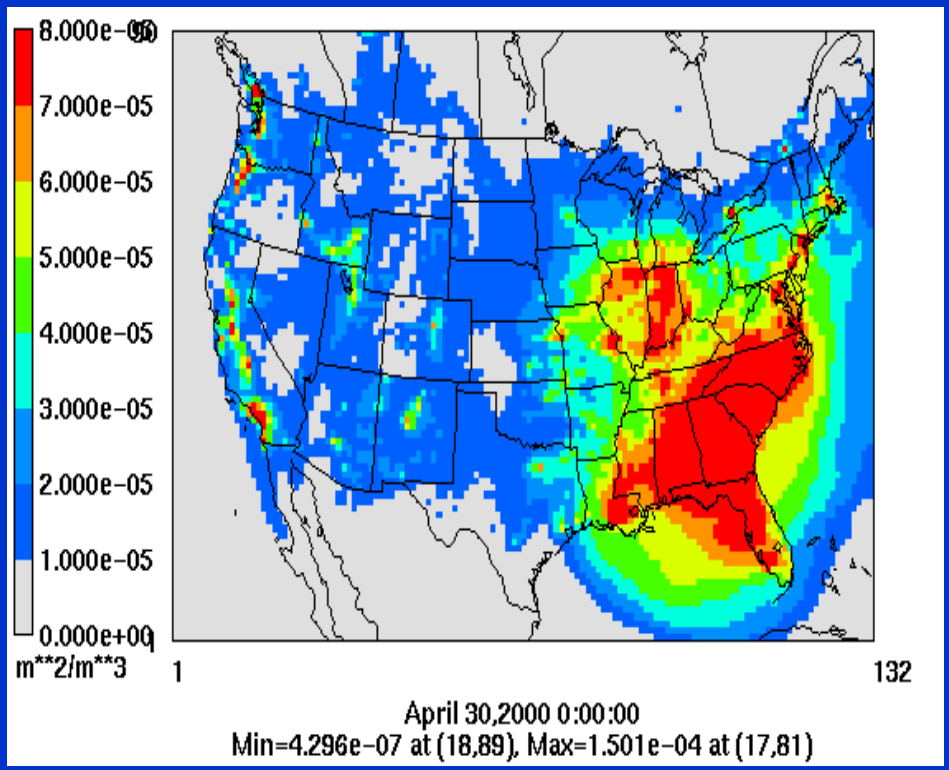


- Averaged aerosol surface area by CMAQ for April 30-May 2,2000.

Some authors use following for J-P adsorption partitioning model:

urban air:

$1.1X10^{-5}cm^2/cm^3$

average continental background:

$1.5X10^{-6}cm2/cm3$

clean continental background:
$4.2X10^{-7}cm2/cm3$

K_{OA} absorption model

- Absorption of gas-phase compounds into an organic film coating the particle is important
- Vapour pressure P_L can be replaced with the octanol-air partitioning coefficient (K_{OA})
- Gas/particle partitioning can be described by gas/particle partitioning coefficient (Yamasaki and et al., 1982) :

$$Kp = \frac{F / TSP}{A}$$

Where Kp(m3μg-1) is a temperature dependent partitioning constant, TSP(μgm-3) is the concentration of total suspended particulate material, and F(ng/m-3) and A(ng/m-3) are the particulate and gaseous concentrations of the compound of interest. In our work, PM_{10} is used as TSP.

- The measured data and showed that the highly correlated regression of the following form can often be obtained,

$$\log Kp = m \log p_L^0 + b$$

- Theory study Pankow(1994a;1994b) proposed that absorption of gas-phase compounds into an organic film coating the particle makes an important contribution to the overall particle-gas partitioning process. Pankow's expression for *Kp* based on absorption is

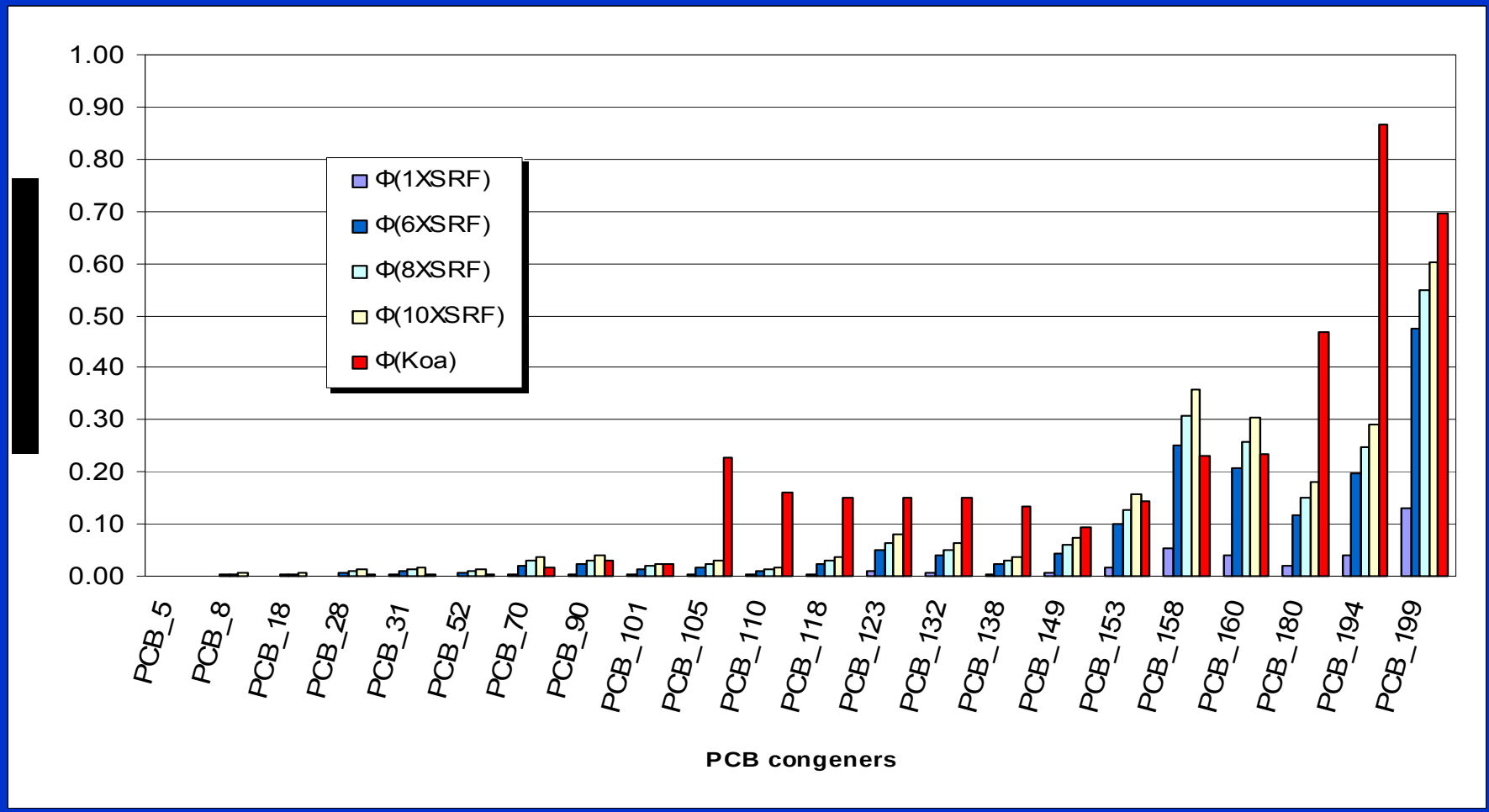
$$K_P = 10^{-6} RTf_{om} / M_{om}\gamma_{om} p_L^0$$

- Finizio et al., 1997;Harner and Bidleman, 1996;Harner and Bidleman, 1998) suggested use octanol-air partition coefficient K_{OA} as an alternative to vapour pressure for describing absorption to aerosols:

$$K_P = 10^{-9} K_{OA} f_{om} (\gamma_{oct} / \gamma_{om})(M_{oct} / M_{om}) / \rho_{oct}$$

$$LogK_{OA} = A + B/T$$

- Harner et.al (Harner, T. et al. 1996)measured KOA over the temperature range of -10oC to +30oC for selected PCBs.
- For other PCBs, K_{OA} can be calculated by relative retention time (RRT)(Harju, M. t., Haglund, P., & Naikwadi, K. P. 1998).
- The K_{OA} of any PCDD/Fs congeners at any temperature can be obtained by correlating measured Koa values at a specific temperature against reported retention time indices (RTI) for dioxins and furans (Donnelly et al., 1987; Hale et al., 1985; Harner, 2000).



Comparison of K_{OA} model and J-P partitioning model
IIT, Chicago, 15:00GMT, April 30, 2000

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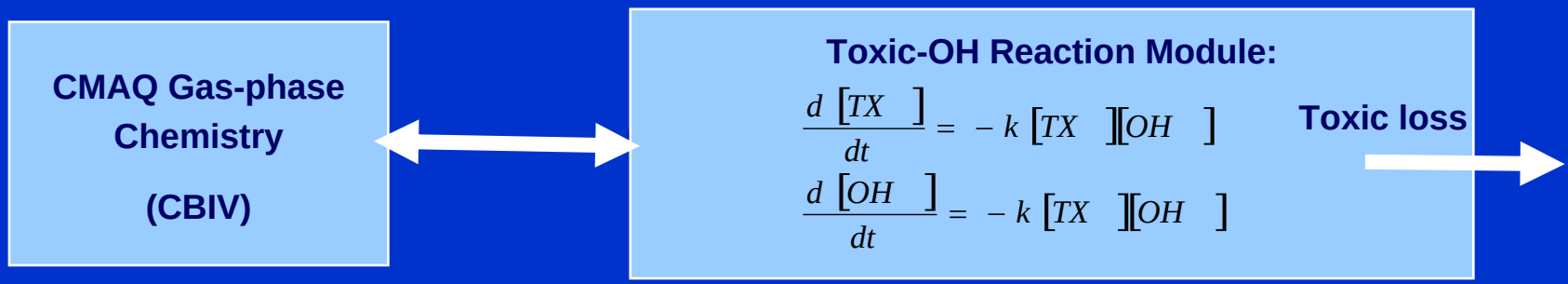
Chemical Transformations of PCBs, PCDD/Fs

- Four possible routes: phtolysis, reaction with OH, NO_3 radical and O_3.
- However, probably the only important tropospheric loss process for gas-phase PCBs, PCDD/Fs.

POPs + OH -> Products



1.Roger Atkinson, Issues in Environmental Sciences and Technology 1997, No.6, The Royal Society of Chemistry
2.R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 1,1, 1989
3.R. Atkinson and S. M. Aschmann, Environ. Sci. Technol., 19, 462, 1985
4.P. N. Anderson and R. A. Hites, Environ. Sci. Technol., 30, 1756, 1996
5.P. N. Anderson and R. A. Hites, Environ. Sci. Technol., 30, 301, 1996

Table Measured rate constants for the gas-phase reaction of the OH radical with PCBs at room temperature

Congeners	10^{12} x $cm^3 molecule^{-1} s^{-1}$	Temperature(K)	Reference
PCB1	2.82 ± 0.38 $2.7^{+0.7\,a}_{-0.6}$	295±1 298	Atkinson and Aschmann [2,3] Anderson and Hites [4]
PCB7	$2.6^{+0.7\,a}_{-0,5}$	298	Anderson and Hites [4]
PCB15	2.0 ± 0.5^{a}	298	Anderson and Hites [5]
PCB31	$1.2^{+0.3\,a}_{-0.2}$	298	Anderson and Hites [4]
PCB33	$1.0^{+0.4\,a}_{-0,5}$	298	Anderson and Hites [4]
PCB44	$0.8^{+0.4a}_{-0.2}$	298	Anderson and Hites [4]
PCB95	$0.4^{+0.3a}_{-0.2}$	298	Anderson and Hites [4]
PCB110	$0.6^{+0.5a}_{-0.3}$	298	Anderson and Hites [4]

[a] Rate constants calculated at 298K from measurements carried out at elevated temperatures in the range 322-366K

Table Estimated room temperature rate constants for the gas-phase PCBs [1]

No. Cl atmos	0	1	2	3	4	5	6
$k^{OH}(10^{12}\,cm^3 molecule^{-1} s^{-1})$	6.8	3.2-4.6	1.4-3.1	1.0-2.1	0.35-1.7	0.3-0.9	0.16-0.5

PCDD/Fs rate constant

- Atkinson R., 1996, Atmospheric Chemistry of PCBs, PCDDs and PCDFs: Issues in Envrionmental Sciences and Technology, v. 6, p. 53-72.
- Kwok,ESC, R Atkinson, J Arey, 1995, Rate Constants for the Gas-Phase Reactions of the OH Radical with Dichlorobiphenyls, 1-Chlorodibenzo-p-dioxin, 1,2-Dimethoxybenzene, and Diphenyl Ether: Estimation fo OH Radical Reaction Rate Constants for PCBs, PCDDs, and PCDFs: Environ.Sci.Technol., v. 29, p. 1591-1598.
- Meylan,WM, P H Howard. Chemosphere 26, 2293. 1993.
- Meylan,WM, P H Howard. AOPWIN:Atmospheric Oxidation Program, v1.82 for Microsoft Windows 3.1;Syracuse Research Corporation: Syracuse, NY. 1996.

Removal processes

- Particle phase: same as CMAQ
- Gas phase: same as CMAQ. Henry's law constants of PCBs and PCDD/Fs are by Sander (1999) and Cohen (2002) respectively.
- Dry removal process of gas phase is ignored. There may be partitioning and other exchange processes between surface (soil and water surface) and air.

Sander,R. Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry. 1999.

Cohen,M, et.al, 2002, Modeling the Atmospheric Transport and Deposition of PCDD/F to the Great Lakes: Environ.Sci.Technol., v. 36, p. 4831-4845.

Modeling Results

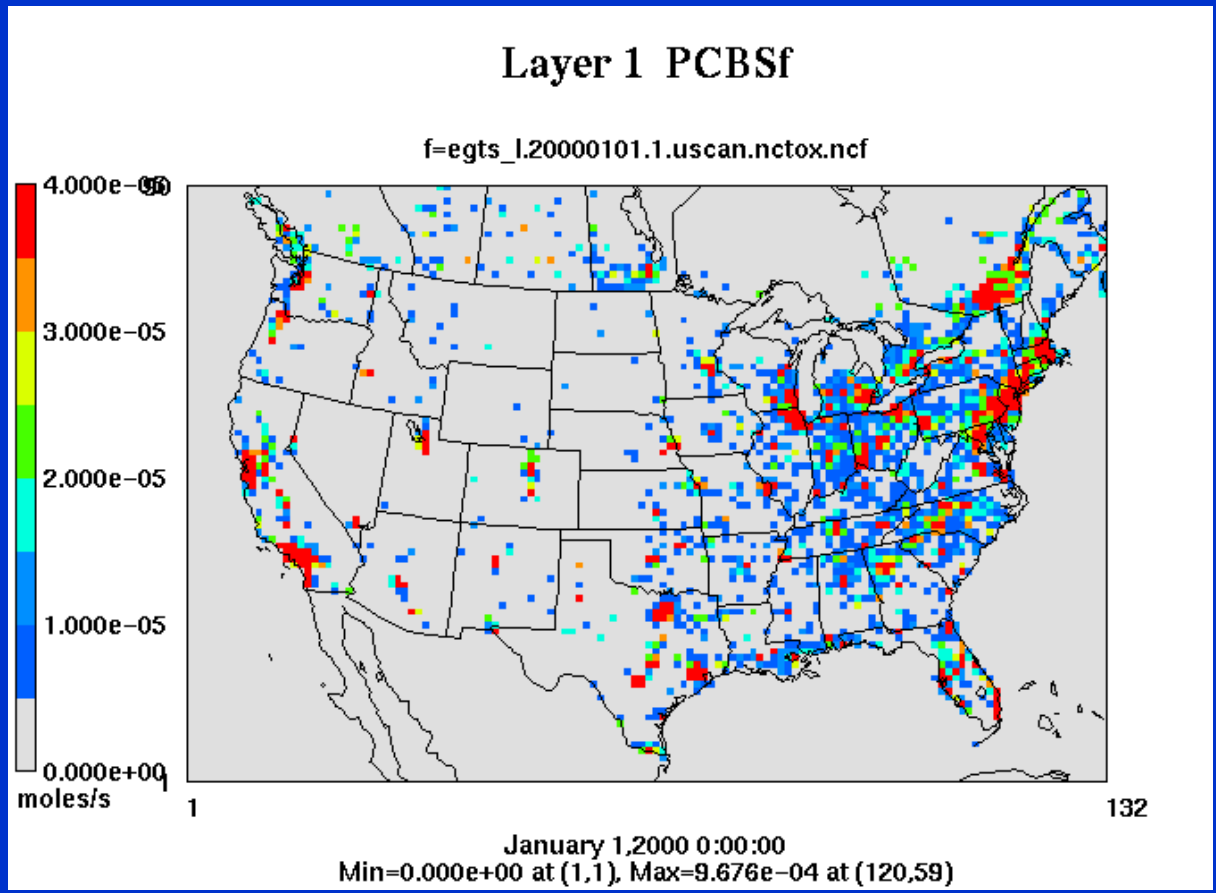
PCBs Emissions

Two approaches:

- Emission factors, need more check.
  - US EPA 1999 NEI HAPS.
  - No Canadian emission inventory. PCBs emission of open household burning estimated based on population.
- Mass balance approach, currently used

  global emission of 22 PCB congeners from 1930 to 2000[1][2] , the total emission of countries allocated by population to model grids.

1. Breivik, K. et. al., Towards a global historical emission inventory for selected PCB congerners – a mass balance approach 1. Global production and consumption. The Science of the Total Environment, 290 (2002) 181-198
2. Breivik, K. et. al., Towards a global historical emission inventory for selected PCB congerners – a mass balance approach 2. Emssions. The Science of the Total Environment, 290 (2002) 199-224



PCBs Emission Distribution (moles/s)

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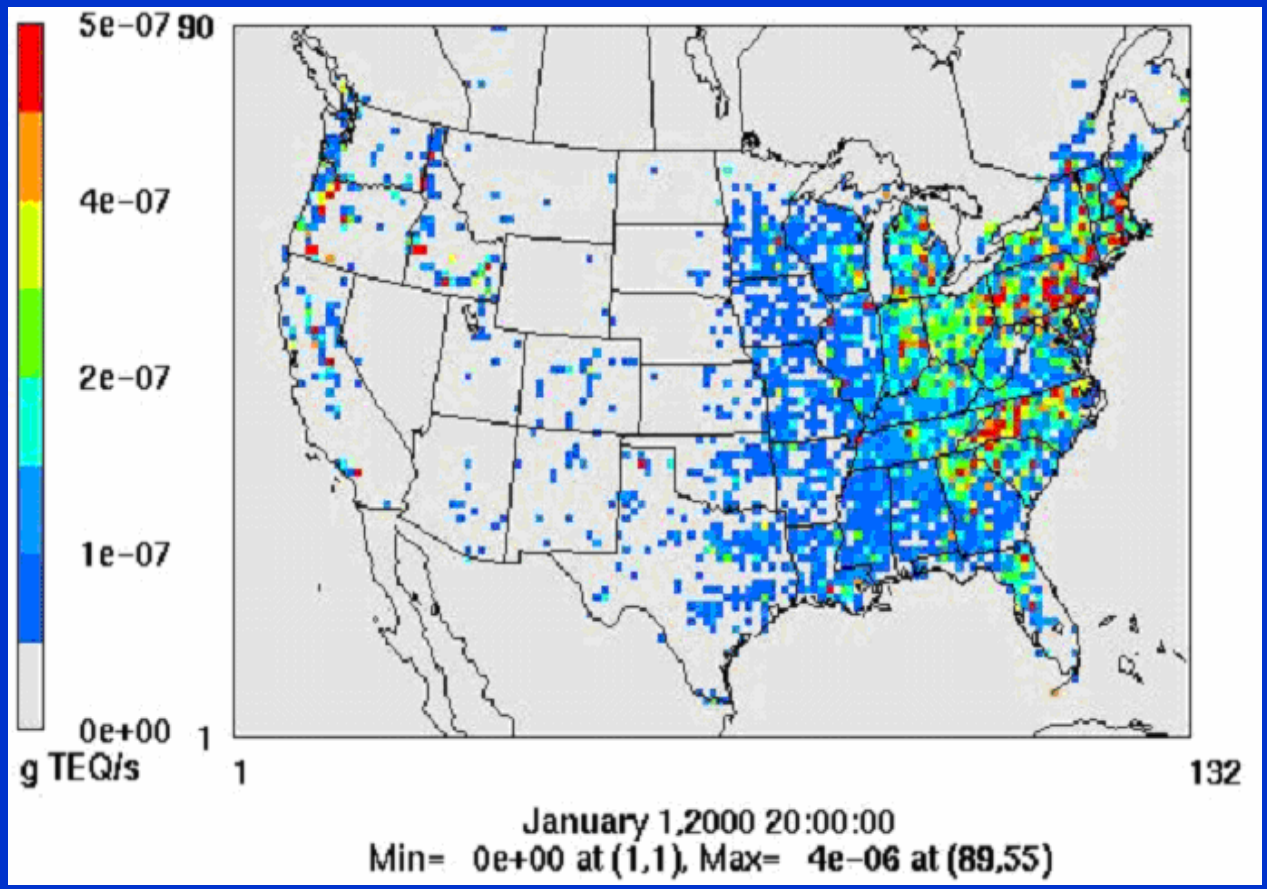
PCDD/Fs emission inventories and data processing using SMOKE

- US
  - Point, area, and non-road source 1999, US EPA
- Canada
  - Point source 2000 NPRI Canada
  - Gridded area and non-road source 1995 converted to county level
  - Congener emission profiles
  - Waste incineration
  - Power/energy generation
  - Other high temperature sources
  - Metallurgical processes
  - Chemical manufacture/processing sources



PCDD/Fs Emission Distribution (g I-TEQ/s)

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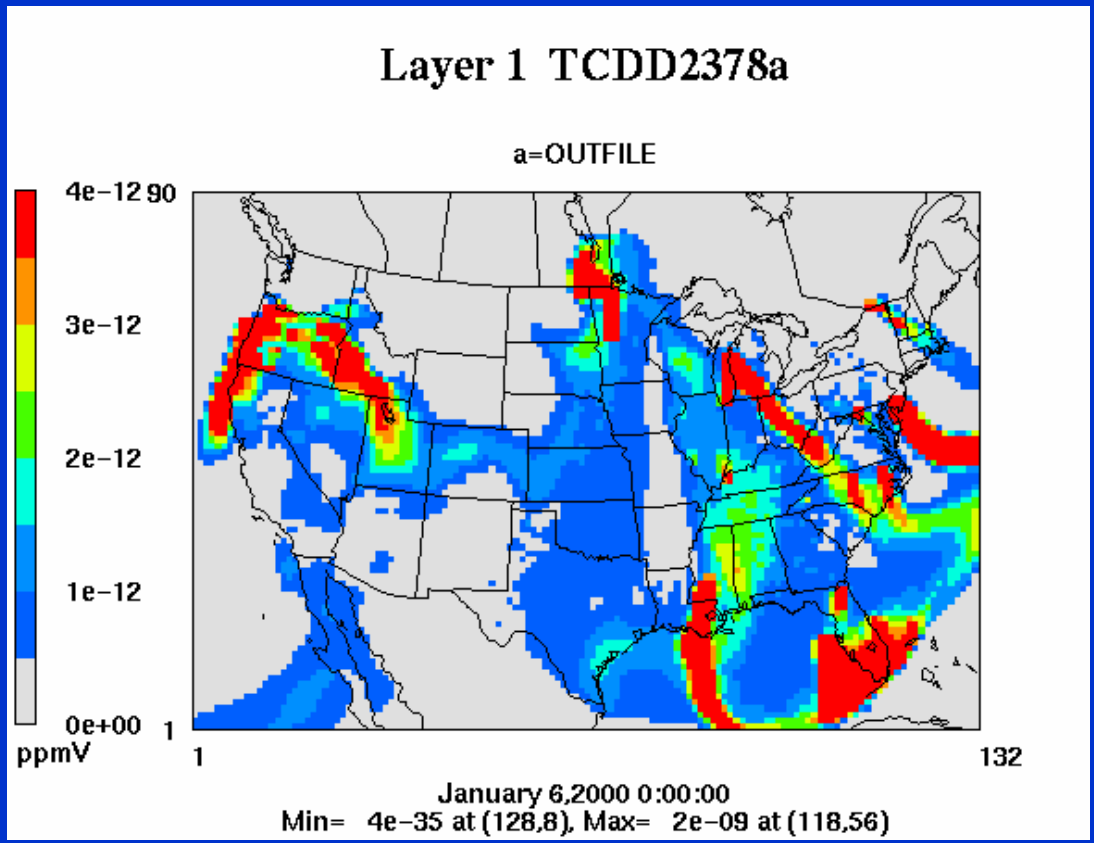
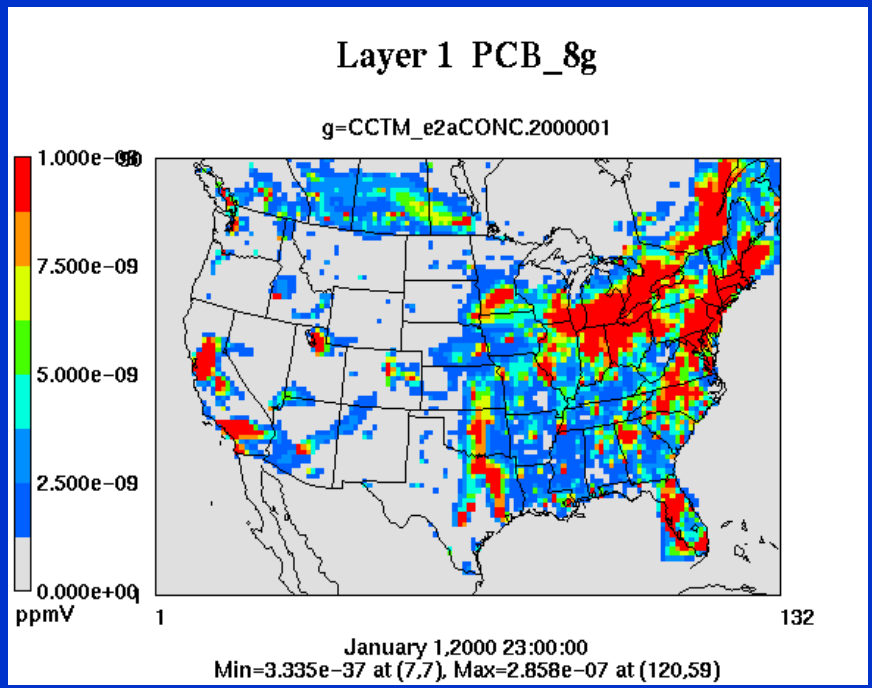
Modeling setup

- Projection: Lambert
- Domain: US36_132X90
- Grid: 36km
- Vertical levels: 15
- Meteorology model: MM5
- Year: 2000

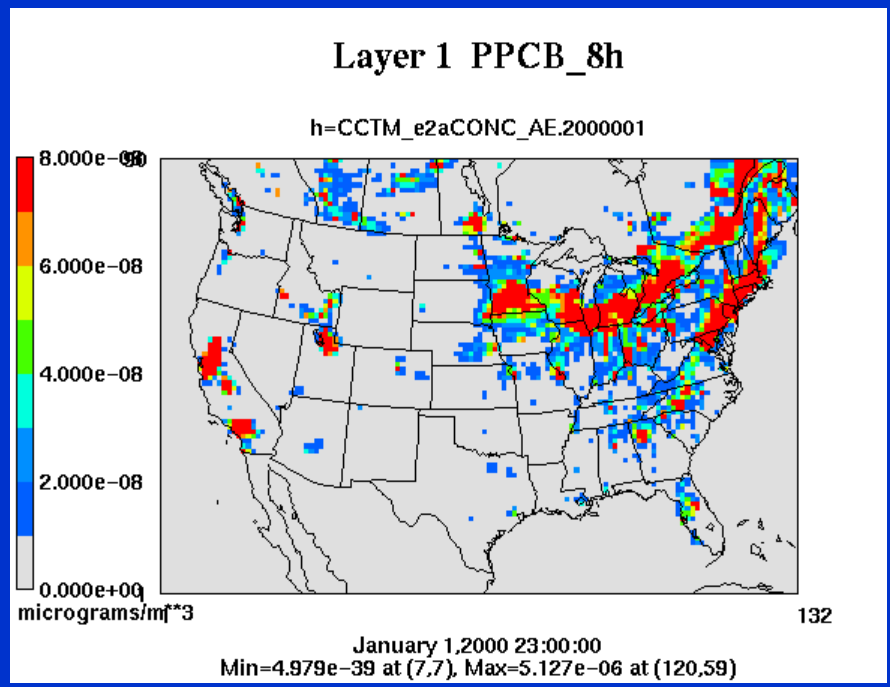
Example 2378TCDD gas phase concentration



PCB8 model results



Gas phase



Particle phase

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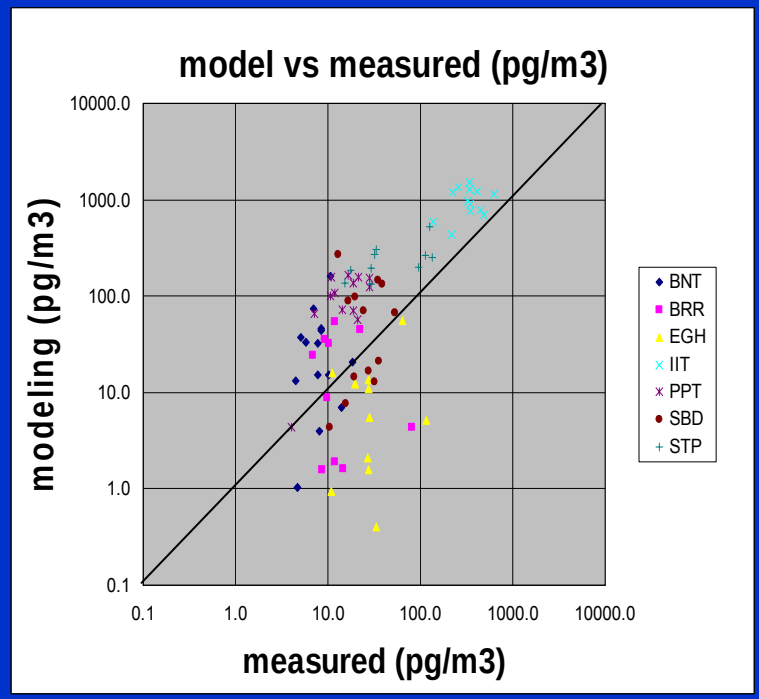
Comparison with measurements

IADN PCBs monitoring stations

twice/month, daily average



Modeled *vs* measured gas-phase PCB concentrations for 0:00GMT Jan. 1, 2000 to 0:00GMT July 28, 2000.

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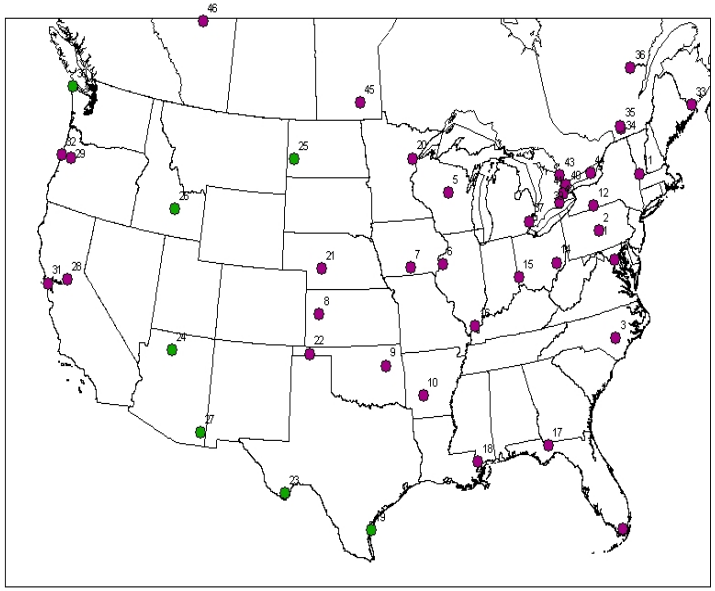
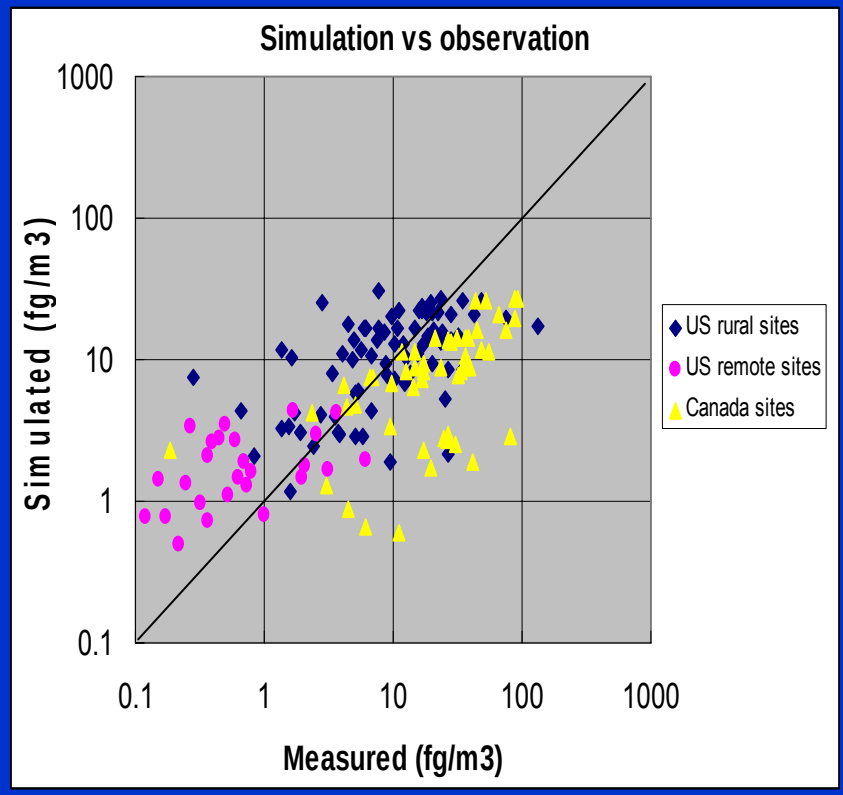


- US NDAMN (National Dioxin Air Monitoring Network)
  - Quarterly average data
  - 32 stations
- Canadian NAPS (National Air Pollution Surveillance)
  - Two daily data average data per month
  - 18 stations



Modeled *vs* measured PCDD/F air concentrations for the months 1-2, 4- 5, 8-9, 11-12 of 2000.

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Summary

- CMAQ model have been expanded for PCBs and PCDD/Fs. The reaction with OH and two gas/particle models, J-P adsorption and K_{OA} absorption model have been added to CMAQ.
- Removal and chemical transformation of PCBs/PCDD/Fs depend on the partitioning processes very much. Aerosol surface area is important for J-P adsorption gas/particle partitioning model. The current J-P model in CMAQ underestimated particle fraction of PCBs. K_{OA} absorption model produce more reasonable gas/particle portioning results.

- For PCBs, the estimated emission inventory by Breivik and the approach of allocating emission by population is generally acceptable. More detailed spatial location information is necessary for better modeling result .
- For PCDD/Fs some point sources and the area source in some states are still questionable. Canadian area emissions for recent year is expected.
- Basically, preliminary simulation results for PCBs and PCDD/Fs are acceptable. To verify the model, more comparison works with measurements are needed