

## **MODELLING THE ATMOSPHERIC CHEMISTRY, TRANSPORT, AND DEPOSITION OF SEMI-VOLATILE TOXIC POLLUTANTS**

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### **ABSTRACT**

We have investigated the atmospheric chemical and physical transformation and long range transport of toxic materials using the Models-3/CMAQ regional chemical transport modelling system. In this report, we focus on the behaviour of mercury and PCBs. For this work, we have added gas phase OH reactions and gas-particle partitioning of these substances to the existing model platform. The results show that long range transport on both particles and in the gas phase occurs to a significant extent for both materials. In the case of mercury, natural emission sources are sometimes larger than anthropogenic ones and in any case must be considered in order to understand the local concentrations.

**Key Words:** Atmospheric Transport, Deposition, Persistent Organic Pollutant, Mercury, Regional Atmospheric Model

### **1. INTRODUCTION**

The atmospheric transport and deposition of semi-volatile toxic materials continues to be a significant problem in many parts of the world. (Tsapakis et al., 2003) Long range transport of these compounds is a particular threat to environmentally sensitive areas such as the Arctic. These substances include mercury, pesticides and a wide variety of industrially-related toxins such as PCBs and dioxins. Due to their toxicity and persistence in the environment, many of these, such as PCBs and certain pesticides have been banned for industrial and commercial applications in North America. Despite this, they continue to enter the atmosphere in significant quantities, both from a small number of direct emission sources and from the soil and water residues that remain from previous use. Extensive studies of the movement of these compounds have shown that they are transported for very long distances from the point of emission. The mechanism for this transport is thought to be largely in the gas phase, but it is known that many of these materials partition to aerosols as well (Cousins and Mackay, 2001) and this provides an additional means for their transport.

WCAS has undertaken a program to investigate the atmospheric chemistry, transport and deposition of a series of toxic pollutants. For this presentation, we will focus on Mercury and PCBs. The objectives of the mercury studies are the assessment of the relative importances of anthropogenic and natural mercury emissions and the elucidation of the mechanisms and patterns of its long range transport. To ensure

proper treatment of the global background, we also explored the sensitivity of the model to the mercury boundary conditions. The objectives of the PCBs studies are to compare the roles and contributions of gas and particle phase transport mechanisms and to assess the effects of atmospheric chemistry and physical deposition in their removal.

## 2. METHODOLOGY

### 2.1. Models

The modelling tools used in these studies are based on the U.S. EPA's Models-3/*CMAQ* regional modelling system, driven by the *MM5* meteorology model. For the purposes of these studies, we use special versions of *CMAQ* chemical transport model (CTM) that were modified to handle mercury and PCBs. Details about the *CMAQ-Hg* model can be found in (Bullock and Brehme, 2000).

The *CMAQ* model has been expanded to simulate the transport, transformation and deposition of PCBs. The new *CMAQ* components describe gas/particle partitioning of PCBs and their chemical reactions with OH radicals. In this work, 22 PCB congeners, or specifically PCB-5, PCB-8, PCB-18, PCB-28, PCB-31, PCB-52, PCB-70, PCB-90, PCB-101, PCB-105, PCB-110, PCB-118, PCB-123, PCB-132, PCB-138, PCB-149, PCB-153, PCB-158, PCB-160, PCB-180, PCB-194, PCB-199, are studied.

PCBs are semi-volatile and partition between the gas and particle phases. In the current model, the major chemical transformations occur in the gas phase (OH reactions) and the major removal occurs in the particle phase (Atkinson R., 1996). Thus the partitioning process is a key factor that controls the behavior and fate of PCBs in atmosphere. In this work, the Junge-Pankow adsorption model is used to describe the gas/particle partitioning (Pankow J.F., 1987). According to this model, the fraction of a semi-volatile organic compound adsorbed to particles,  $\phi$ , depends on the vapor pressure of the substance at ambient temperature,  $P_L$ , and the specific surface area of the particles,  $\theta$  ( $\text{cm}^2/\text{cm}^3$ ):

$$\phi = c\theta / (P_L + c\theta) \quad (1)$$

where  $c$  is a parameter depending on the chemical being adsorbed and on the nature of the particle.

$$\log P_L = m_L / T + b_L \quad (2)$$

Falconer *et al.* (Falconer R.L., 1994), derived parameters for calculating the temperature dependence of  $P_L$  for 32 PCB congeners from available data and used this information to estimate the temperature dependence of 148 PCBs as a function of homolog and number of ortho-chlorines.

The Junge-Pankow model needs the aerosol surface area, which is somewhat uncertain in most regional atmospheric models. In our work, the aerosol surface area is taken to be the sum of the Aitken mode and the accumulation mode calculated by

the *CMAQ* aerosol model. There are also uncertainties in the parameter *c* and in the low-temperature vapour pressure, but these are less important than those in the surface area.

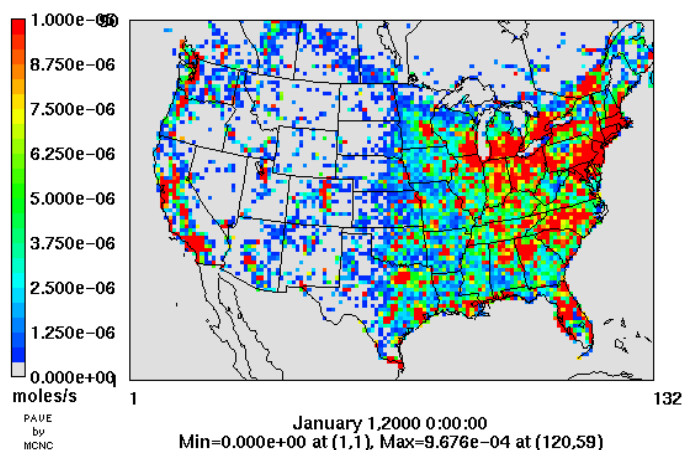
The possible chemical transformations of PCBs include photolysis and reaction with the hydroxyl (OH) radical, reaction with nitrate(NO<sub>3</sub>) radical and reaction with ozone(O<sub>3</sub>). At the present time, we have only implemented the reaction with OH. The rate constants used for the gas-phase reactions of OH with some PCB congeners are taken from the work of Atkinson (Atkinson R., 1996). In the future we will examine the importance of other reactions, including the photolysis of gas-phase PCDD/Fs and the reaction of gas-phase PCDDs with the NO<sub>3</sub> radical.

## 2.2. Emissions

Anthropogenic emissions of criteria species and the toxic pollutants were obtained from the US EPA, the US NEI emission inventory and the Canadian NPRI database. The data include waste incineration, power/energy generation, metallurgical processes, chemical manufacturing/processing and other high temperature sources.

The PCB emission inventory is not well developed; there are uncertainties in both emission factors and in the data based on human activities, such as open burning, traffic, manufacturing, etc.

In this work, we use the global emission data by (Breivik, 2002; Breivik et al., 2002) which have been developed using a mass-balance approach. The 22 PCB congeners are speciated from total PCB emissions and allocated to grid cells using the population surrogate using the SMOKE emission preprocessing model. The



result is shown in Figure 1.

Figure 1. Emission of PCBs at 0:00:00 January 1, 2000

Significant amounts of mercury are known to arise from natural sources. To obtain mercury emissions from natural sources, we created a model to describe the emission of mercury from vegetation, soil and water, using published measurements and laboratory data. Equation 3 is used to estimate Hg transpiration from vegetation (Xu et al., 1999).

$$F = E_c C_s$$

(3)

where, *F* is the Hg<sup>0</sup> flux, *E<sub>c</sub>* is the canopy transpiration and *C<sub>s</sub>* is the concentration of Hg<sup>0</sup> in the surface soil solution. For emission from bare soil and soil under vegetation canopy, we used Equations 4 and 5 respectively,

$$\ln F = -\frac{\beta}{T_s} + n \ln[Hg]_s + \gamma \quad (4)$$

$$\ln F = aR_{Gc} + b \ln[Hg]_s + c \quad (5)$$

where,  $[Hg]_s$  is Hg soil concentration,  $T_s$  is the soil temperature,  $R_{Gc}$  is the solar radiation reaching the soil under the canopy and  $\beta$ ,  $\gamma$ ,  $n$ ,  $a$ ,  $b$ ,  $c$  are constants. Emission from water was estimated using

$$F_w = K_w C_w \quad (6)$$

where,  $K_w$  is the mass transfer coefficient and  $C_w$  is the concentration of dissolved gaseous mercury in the water. Details of the natural mercury emission model can be found in (Gbor et al., 2004).

### 3. SIMULATION

The mercury simulations were carried out on a domain covering eastern North America, with 75 x 70 grid squares, 36 km grid size and 21 vertical sigma layers, for the period from May 1 to September 30, 2000. The PCB simulations were carried out on a domain covering North America, with 132 x 90 grid squares, 36 km grid size and 15 vertical sigma layers, for the period from January 1 to July 28, 2000. Version 3.6 of the PSU/NCAR *MM5* meteorology model and the Pleim-Xiu Land Surface Model (LSM) (Xiu and Pleim, 2001) were used to generate the meteorology data, which were then processed using *MCIP*. The natural mercury emission model was incorporated into *MCIP*. The mercury and PCB emissions were merged with anthropogenic mercury and criteria emissions using *SMOKE*. The gridded emissions output from *SMOKE* were fed to the modified *CMAQ* model to simulate the behaviour of the toxic substances in the atmosphere. The models were run for several scenarios to examine the effects of reducing or eliminating various combinations of the anthropogenic and natural mercury emissions.

## 4. RESULTS AND DISCUSSIONS

### 4.1. Mercury

The comparison between natural and anthropogenic mercury emissions is shown in Figure 2. High anthropogenic mercury emissions occur in the north eastern part of the U.S., while natural emissions dominate in the northern and western part of the domain. Emissions from the lakes and ocean were obtained using the natural mercury emission model. The anthropogenic emission averaged over the whole domain for the modelling period was  $1.4 \text{ ngm}^{-2}\text{h}^{-1}$  while the natural emission was  $2.9 \text{ ngm}^{-2}\text{h}^{-1}$ . This is consistent with the estimate that natural emissions are about twice the anthropogenic emissions on a global scale (Seigneur et al., 2004).

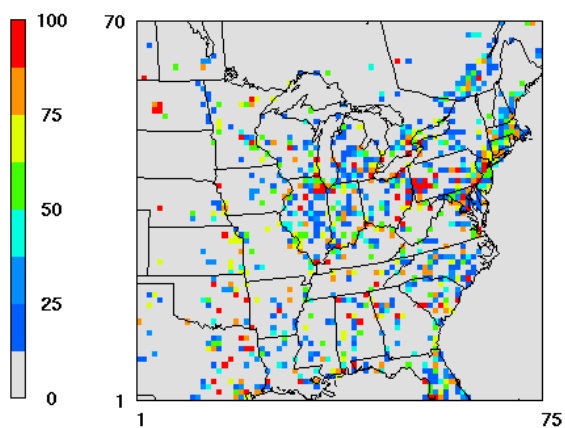


Figure 2. Percent of mercury emissions contributed by anthropogenic emissions for each grid cell from May to September, 2000

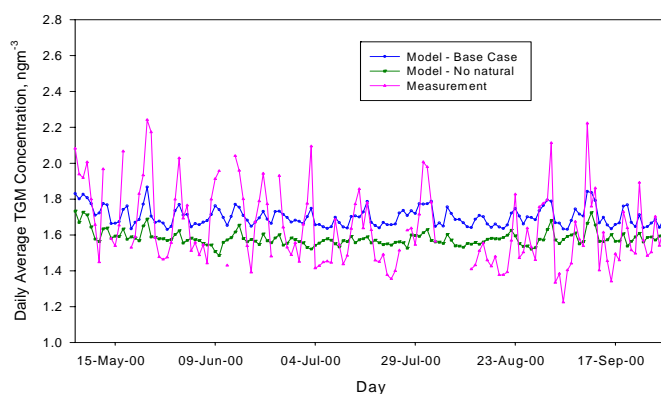


Figure 3. Modeled and measured daily average TGM for Egbert, Ontario, from May to September, 2000.

Figure 3 shows a comparison between model and measurements of Total Gaseous Mercury (TGM) for the Egbert, Ontario site, which is a rural area north of Toronto. The model reproduced the concentration trends quite well ( $R = 0.8162$ ). Neglecting natural emission reduced the correlation ( $R = 0.5115$ ). Similar results were obtained for all three monitoring sites within the domain. The effect of global background on mercury concentration is illustrated in Figure 4. The background contributes over 80% of the average TGM concentration in the domain. This illustrates the global nature of mercury pollution. Elemental mercury has atmospheric residence time of about 1 to 2 years and as such can be transported through long distances. Though the global background contributes significantly to total gaseous mercury in the atmosphere, local anthropogenic emissions may have a greater importance for

mercury deposition near the sources. Figure 5 shows the effects of local emissions on deposition of mercury. It shows dry deposition of elemental, divalent and particulate mercury attributed to anthropogenic emissions in Canada. The spread of elemental mercury deposition (Figure 5a) is wider than that of divalent mercury (Figure 5b), illustrating the larger transport distance of elemental mercury, compared to divalent and particulate mercury. It also indicates that anthropogenic emissions have a more direct effect on locations closer to the emission sources. Anthropogenic emissions in Canada are about 10 times less than those in the U.S., but mercury is transported in both directions across the U.S./Canada border, depending on the synoptic weather. These results show that regional as well as global cooperation is required if the problem of mercury pollution is to be resolved.

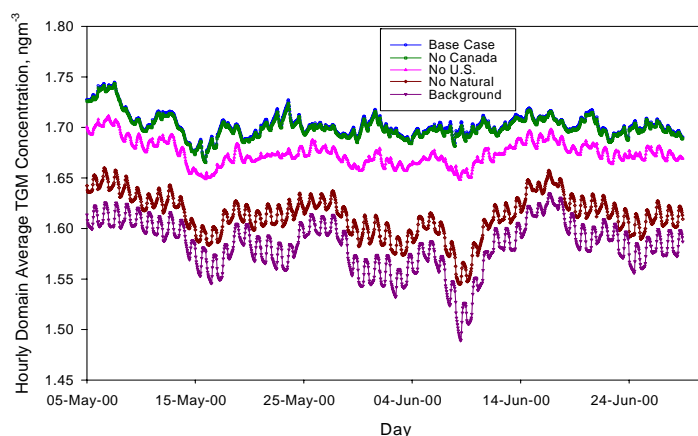


Figure 4. Average TGM concentration in domain for different scenarios.

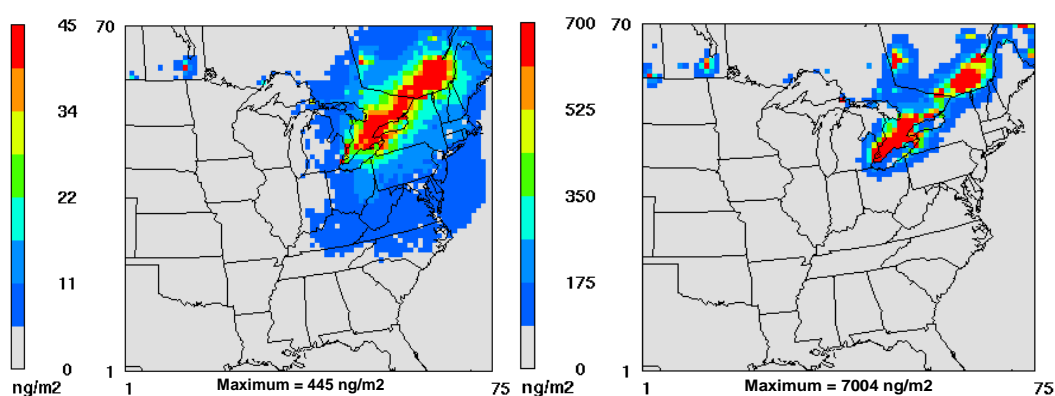


Figure 5. Total deposition of (a) elemental and (b) sum of divalent and particulate mercury in domain due to anthropogenic emissions in Canada. Note: Maximum colour scale is 10% of the maximum grid value.

## 4.2. PCBs

The modelled concentration distributions of all PCB congeners are similar since their emissions are speciated proportionally from total emission data. Figure 6 shows the gas- and particle-phase concentration and deposition of the PCB-8 congener. Compared with the distribution of emissions shown in Figure 6, these concentration data show that considerable regional transport of these materials occurs. For example, a plume of high concentration extends from the northeastern US into the Atlantic ocean and from the southwestern US into the Gulf of Mexico. High concentrations occur in the eastern continental US and Canada including the densely populated Great Lakes area. California also has high concentrations. (Although they are probably significant, emissions from Mexico were ignored in this work due to lack of quantitative emission data.) most of the concentration of PCB-8 is in the gas phase due to its relatively high vapour pressure. As the number of chlorine atoms in the PCB molecule increases, the amount partitioning to particles also increases.

The most important removal process is wet deposition, even for congeners like PCB-8 which has only two chlorine atoms and is mostly found in the gas phase. The maximum wet deposition of particle-phase PCB-8 in the domain is 2.393E-08 kg/hectare while maximum wet deposition of gas-phase PCB-8 is 3.852E-10 kg/hectare and the dry deposition of gas-phase PCB-8 is only 6.791E-12 kg/hectare.

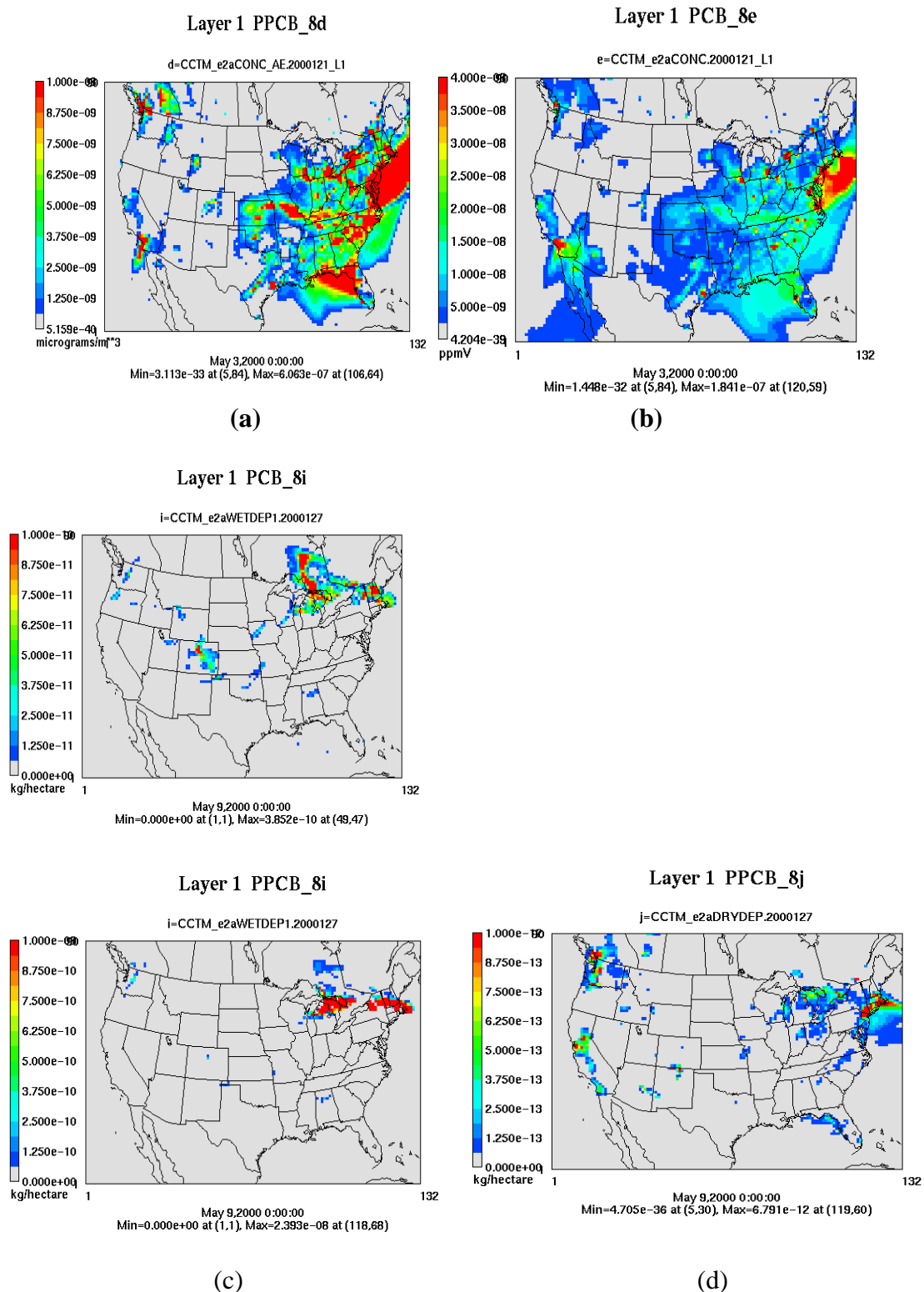


Figure 6. Concentration and deposition of gas and particle phase PCB-8 at 0:00GMT May 9, 2000. (a) concentration of gas-phase PCB-8; (b) concentration of particle-phase PCB-8; (c) wet deposition of gas-phase PCB-8; (d) wet deposition of particle-phase PCB-8; (e) dry deposition of particle-phase PCB-8



Figure 7 shows the comparison of modeling results with measured gas-phase PCB data from the Integrated Atmospheric Deposition Network(IADN). The model results show fair agreement with the measurements. For most stations, the model results are over estimated except for one remote station (EGH).

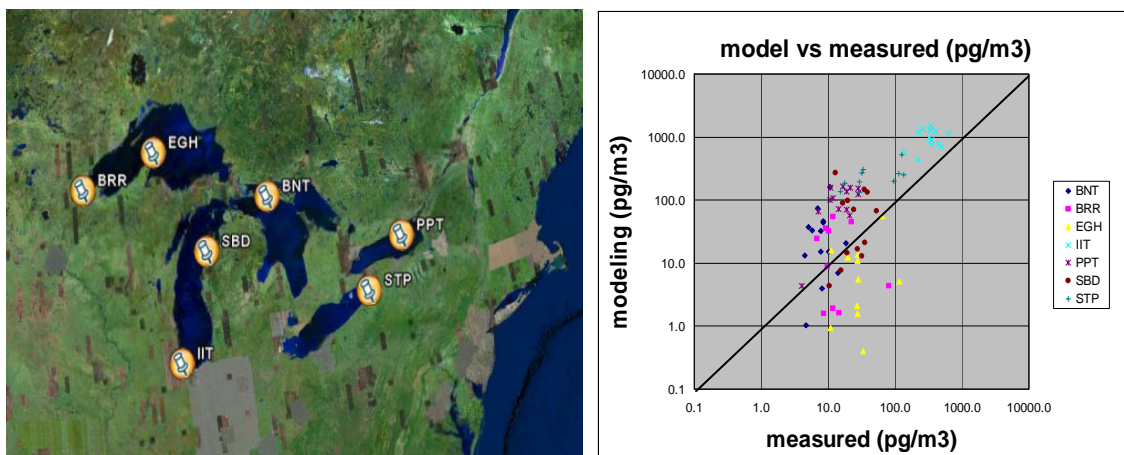


Figure 7. Comparison of modelling results with measured gas-phase PCBs data from the Integrated Atmospheric Deposition Network(IADN) for the period of January – August, 2000

## 5. CONCLUSIONS

The atmospheric transport and deposition of mercury and PCBs, which are representative of several varieties of semi-volatile toxic materials, were studied using modified versions of EPA's *CMAQ* model.

Mercury emissions from natural sources were found to be very important, contributing

about two-thirds of the total emission in the domain. Anthropogenic emissions were concentrated mainly in urban centers and areas with large combustion facilities. Good correlation was found between model simulations of total gaseous mercury and measurements, especially if natural emissions are considered. The results also show that long range transport of anthropogenic mercury is very important throughout North America, but transport distances differ for the common mercury species (elemental, divalent and particulate). Furthermore, the global background was found to contribute significantly to the amount of mercury in the domain. Therefore global efforts are required if the impact of mercury pollution on our ecosystem is to be minimized.

The *CMAQ* model has been expanded to include OH chemistry and gas-particle partitioning of PCBs. The Junge-Pankow model was used to describe the adsorption partitioning. Emissions data have been spatially allocated to the model grid by population. For most monitoring stations of the IADN, the simulations show generally acceptable agreement with measurement, but more detailed information about the location of the emission sources would lead to better model performance.

The results show that there exists significant regional scale transport. Deposition of the particle phase material is the most important removal process of PCBs in the atmosphere.

The aerosol surface area is important in the Junge-Pankow gas/particle partitioning model, which is unfortunate, because there are still uncertainties in the aerosol component of the *CMAQ* model. In particular, the description of the primary emission may not be complete and accurate. There is also some uncertainty in the secondary organic aerosol formation. Preliminary comparison with measured results shows that the model underestimates the total aerosol surface area concentration. Although it is still unclear, this might be due to averaging over a relatively coarse grid, which would reduce peak concentrations. As a consequence of this, the removal of particle phase of PCBs may be underestimated. Further comparison with measured deposition data is in progress.

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