

## A THREE-DIMENSIONAL MODEL ASSESSMENT OF THE GLOBAL DISTRIBUTION OF HEXACHLOROBENZENE

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### Introduction

The distributions of persistent organic pollutants (POPs) in the global environment have been studied typically with box/fugacity models with simplified treatments of atmospheric transport processes<sup>1</sup>. Such models are incapable of simulating the complex three-dimensional mechanisms responsible for long-range transport, such as penetrating convection, tropospheric jets, and synoptic weather systems<sup>2,3,4</sup>. These mechanisms can distribute POPs much more rapidly around the globe than slow winds confined to the surface. Moreover, many POPs react with atmospheric hydroxyl radical (OH), the distribution of which varies significantly with space and time. Three-dimensional models of the global atmosphere have long been available for studying the distributions of highly volatile tracers, yet their use in POPs exposure assessment has been rare. The purpose of this study is to examine the global distribution of hexachloro-benzene (HCB), a typical volatile POP, with an advanced 3-D radiative-dynamical-chemical model to examine the relative roles of different physical and chemical processes in determining its distribution.

### Methods and Materials

The atmospheric model used for this study is the Global Balance Environment (GLOBE) model recently developed and copyrighted by MCNC<sup>5</sup>. GLOBE is a comprehensive model of the troposphere, stratosphere, and mesosphere that simultaneously computes atmospheric circulation and pollutant chemistry and transport. It is highly efficient, requiring only 92 seconds per simulated day on a single processor of a Microway Alpha UP2000 Linux system. The model consists of a spectral meteorological model with 11 zonal waves coupled on-line to a grid, *chemical transport model with a resolution of 6° latitude x 11.25° longitude x 1.2 km altitude*. The model employs an enhanced version of the global balance system that conserves energy, while allowing advection of zonal mean vorticity and temperature by the mean meridional circulation. It includes a detailed radiative transfer code, efficient parameterizations of gravity waves, breaking planetary waves, equatorial Kelvin waves, cumulus convection (based on the Kuo scheme) and large-scale condensation, plus extensive inorganic and hydrocarbon chemistry.

GLOBE computes an annually averaged inter-hemispheric exchange time of 1.2 years, comparable to that predicted by primitive equation general circulation models<sup>6,7</sup>. Moreover, it predicts a total atmospheric lifetime for CH<sub>3</sub>CCl<sub>3</sub> of 4.0 years, within 20% of the lifetime of 4.8 years, inferred from analysis of its global distribution<sup>8</sup>. GLOBE has simulated successfully the observed inter-hemispheric gradient of CH<sub>2</sub>Cl<sub>2</sub> using data from the Reactive Chlorine Emissions Inventory (RCEI)<sup>9,10,11</sup>.

# TRANSPORT & FATE

Total annual mean global emissions of HCB were assumed to be 92,000 kg/yr, based on the upper limits for the HCB emission factors for metals manufacturing and combustion from Bailey<sup>11</sup>. Various surrogates were used to obtain the spatial distribution of HCB emissions as follows:

HCH (hexachlorocyclohexane) pesticide use (3107 kg yr):  $\alpha$ -HCH from the Canadian Global Emissions Interpretation Centre<sup>13</sup>

Non-HCH pesticide use (3356 kg/yr): CH<sub>4</sub> from animals from Fung et al.<sup>14</sup>

Chemical manufacturing (1309 kg yr): CH<sub>2</sub>Cl<sub>2</sub> + C<sub>2</sub>Cl<sub>4</sub> + C<sub>2</sub>HCl<sub>3</sub> from RCEI<sup>10</sup>

Metals manufacturing (16,442 kg/yr): CO from EDGAR (Emissions Database for Global Atmospheric Research) I20 category<sup>15</sup>

Combustion (62,818 kg/yr): anthropogenic HCl from RCEI<sup>16</sup>

Biomass burning (4956 kg/yr): biomass burning CH<sub>4</sub> from Fung et al.<sup>14</sup>

HCB was assumed to react only with atmospheric OH radicals with a temperature-dependent rate coefficient of  $4.9 \times 10^{-10} e^{-(2920/T)}$ <sup>17</sup>, where T is temperature. The Henry's Law constant for HCB, needed for calculating its uptake by clouds and precipitation, and its vapor pressure were obtained from the temperature-dependent extrapolations of Paasivirta et al.<sup>18</sup> Losses to the surface and re-volatilization from the surface were not included in these simulations to isolate the role of atmospheric processes in determining the distribution of HCB.

## Results and Discussion

The GLOBE model was run for 5 years with HCB to obtain a stationary state with respect to seasonal variations. The total atmospheric lifetime of HCB averaged over the last three years of the simulation was 2.4 years. Figure 1 shows the calculated distribution of surface concentrations of HCB for July and December of the fifth year of model simulation. High concentrations in several areas are apparent, especially in the results for July. These "hot spots" coincide with areas of high emissions. Concentrations of HCB increase with latitude in both hemispheres, and vary inversely with OH radical concentrations and with temperature through its loss reaction. The mean HCB abundance in the Northern Hemisphere is about twice that in the Southern Hemisphere. The calculated inter-hemispheric ratio is in accord with observations made mainly during the early 1980s<sup>19</sup>. However, the calculated global abundance of HCB is about a factor of two lower than those observations. To some extent, this may reflect the large uncertainty in HCB emissions factors and possibly missing sources of HCB in the inventory<sup>12</sup>. On the other hand, it is possible that the difference may be due at least in part to a decline in emissions since the measurements were made. For example, it has been estimated that HCB concentrations near the Great Lakes have been decreasing by 5-10% per year<sup>12, 20</sup>. This implies a 1.6 to 2.6 fold decrease in concentrations over a 10-year period. Our results point to the need for better characterization of HCB emissions and global atmospheric concentration trends. Moreover, a more comprehensive simulation that includes treatments of surface reservoirs (e.g., soil, natural water bodies) and loss processes may be required to better account for temporary storage and re-volatilization of HCB from compartments other than air.

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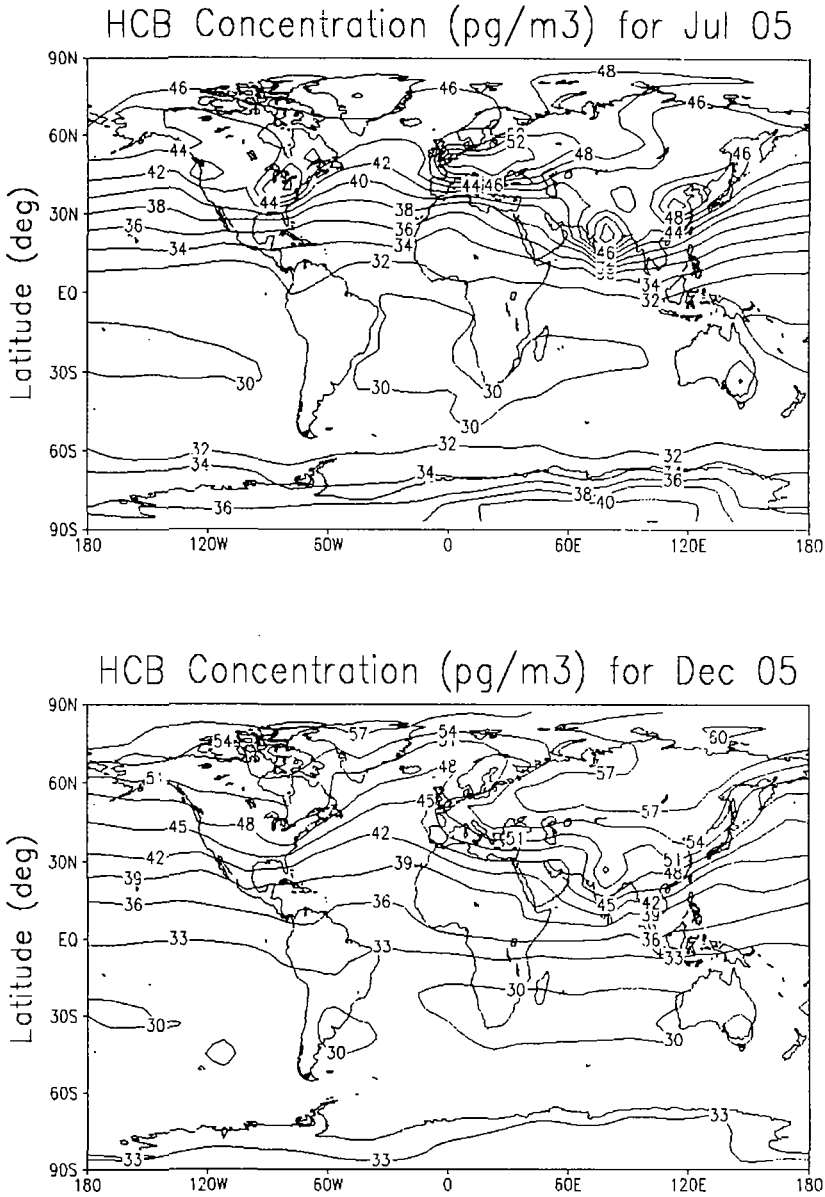


Figure 1.