# THE ATMOSPHERIC TRANSPORT AND DEPOSITION OF DIOXIN TO THE GREAT LAKES

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## Introduction

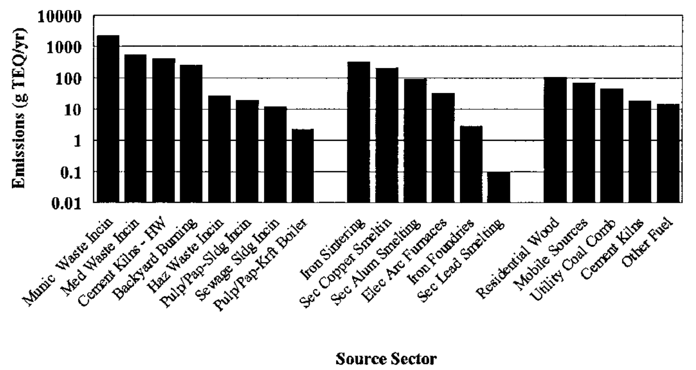
Dioxin is a compound of concern in the Great Lakes, and atmospheric deposition is an important loading pathway for it to the Lakes[1]. Thus, it is important to understand the relative importance of sources responsible for the atmospheric deposition of dioxin to the Lakes.

## Methodology

This analysis builds on earlier work analyzing the transport and deposition of dioxin to the Great Lakes[1,2,3]. A U.S. dioxin emissions inventory[3] for 1996 has been utilized consistent with a U.S. EPA inventory[4], except for the addition of several source categories (e.g., backyard burning and iron sintering). For Canada, a dioxin emissions inventory for 1995 was prepared by Environment Canada and the Canadian Federal-Provincial Task Force on Dioxins and Furans.[5] It has been assumed that these 1995 emissions are representative of 1996 emissions from Canada. Estimated emissions from backyard burning were added to the Canadian inventory. Speciation information was added to the Canadian inventory using congener profiles derived from the U.S. inventory. WHO-proposed mammalian toxic equivalency factors[6] were used throughout this analysis.

An overall summary of the emissions inventories for the U.S. and Canada is shown in Fig.1. The inventory contains over 5700 point sources. Area sources -- e.g., mobile sources and backyard burning -- were estimated at the county level in the U.S. Canadian area sources were estimated on a 50-km grid near the Great Lakes and a 100-km grid elsewhere.
The uncertainties in the estimated dioxin emissions in the U.S. and Canada are significant -- on the order of a factor of three on either side of the mid-range estimates for each source category shown in Fig. 1. In addition, the inventories used in this analysis have at least the following omissions: (a) the U.S. inventory does not contain estimated emissions from residential or commercial coal

Fig 1. Estimated 1996 Emissions of Dioxin from U.S. and Canadian Sources

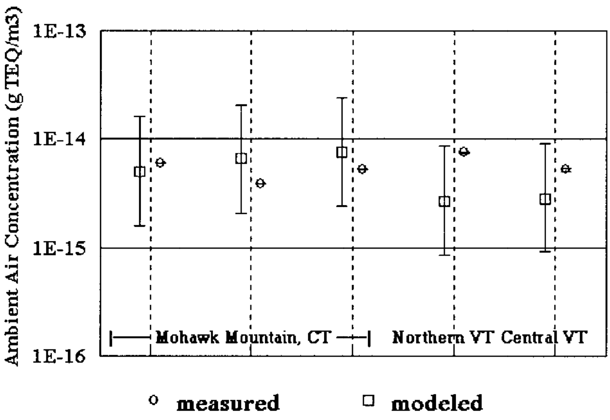


combustion, magnesium manufacturing, or small commercial incinerators; (b) neither the U.S. nor the Canadian inventories include emissions for open-burning of PVC-coated wires (e.g., structure and vehicle fires), asphalt production, landfill fires and landfill gas combustion, coke production, leaded gasoline combustion, and petroleum refining. While the information used in this analysis appears adequate to generate an estimate of source/receptor linkages, inventory improvement is necessary.

A modified version of the NOAA HYSPLIT[7] (Hybrid Single Particle Lagrangian Integrated Trajectory) model was used to simulate the atmospheric fate and transport of dioxin from sources in the United States and Canada to the Great Lakes. HYSPLIT is a Lagrangian model, in which puffs of pollutant are emitted from user-specified locations, and are then advected, dispersed, and subjected to destruction and deposition phenomena throughout the model domain. Similar to many atmospheric fate and transport models, HYSPLIT uses gridded meteorological data obtained from other sources. For these simulations, we used archived output from NOAA's Nested Grid Model (NGM), a primitive equation meteorological simulation model.

The modeling of the atmospheric fate of a dioxin performed here includes simulation of vapor/particle partitioning, wet and dry deposition, reaction with the hydroxyl radical, and photolysis. The methodology involves simulations of the fate and transport of specific dioxin congeners from unit-source-strength sources at a range of different source locations. The locations were chosen to coincide with the major source regions identified in the inventory and to provide comprehensive geographical coverage of the modeling domain (U.S. and Canada). A total of 84 such *standard source locations* were used for each of 4 different congeners (2378-TCDF, 2378-TCDD, 23478-PeCDF, and OCDD). These simulations produce *transfer coefficients* (mass deposited/mass emitted) from each modeled source location to each Great Lake. Transfer coefficients for sources in locations other than those explicitly modeled are estimated using a spatial interpolation technique. The technique uses an average of the four closest explicitly simulated locations, weighted by distance and orientation. Transfer coefficients for congeners not explicitly simulated are estimated using a congener interpolation methodology which is based upon the species' vapor/particle partitioning characteristics. Estimation of *ambient concentrations* at a given receptor location are made in an analogous way. Conceptually, the overall modeling analysis consists of "multiplying" the geographically resolved emissions inventory with the geographically resolved transfer coefficients. In this way, we can estimate the contribution of each source and source region to atmospheric deposition of any given receptor. This methodology assumes the linear independence

**Fig 2. Comparison of Model Predictions with Ambient Measurements at Month-Long Sample Sites**



of the atmospheric fate/transport of dioxin emitted from different sources, an assumption that appears to be valid due to the fact that dioxin's fate processes in the atmosphere can be well characterized by first-order kinetic rate expressions (i.e., rate = k*c, where k is a rate constant and c is the concentration of dioxin) and because of dioxin's trace concentrations in the atmosphere.

**Results and Discussion**

For dioxin, in 1996, appropriate 30-day rural ambient air measurements at two sites each in Vermont and Wisconsin and one site in Connecticut are available[3]. A comparison of the modeling predictions with these ambient measurements is presented in Fig. 2. The model predictions are consistent with the ambient measurements, within the uncertainty of each. The uncertainty range in the modeling results was derived solely from an estimate of the source-by-source uncertainty in the emissions inventory; the overall range would be somewhat greater than this if we were to include all other aspects of the modeling uncertainty.

An example of the detailed source-receptor linkage from each U.S. county and Canadian grid square to dioxin deposition to Lake Superior is presented in Fig. 3. An overall summary of the relative contributions from different distances is presented in Fig. 4. A substantial contribution of atmospheric deposition of dioxin occurs from relatively distant sources for Lake Superior (also true for

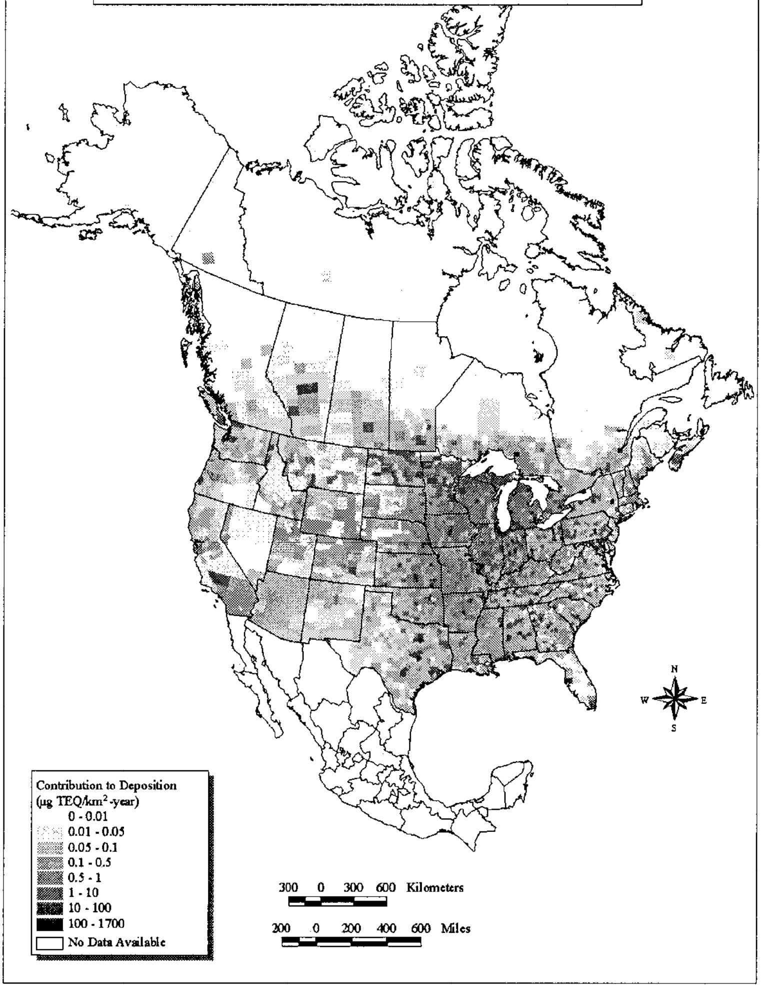
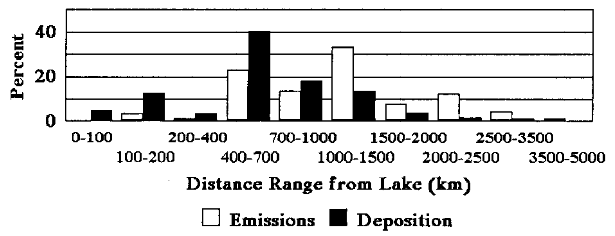


Fig 3. Modeled Contributions to 1996 Atmospheric Deposition of Dioxin to Lake Superior (ug TEQ deposited/km2-yr)

Lake Huron). A more significant fraction – on the order of 50% -- of the deposition to Lakes Michigan, Erie, and Ontario originates from within 100 km of the lake. The estimated total dioxin deposition fluxes (grams TEQ/year) to each lake and the uncertainty range (in parentheses) due solely to the estimated uncertainties in the emissions are the following: 25 (8-80) for Lake Superior, 52 (16 - 160) for Lake Michigan, 32 (10-100) for Lake Huron, 27 (9-86) for Lake Erie, and 18 (6-56) for Lake Ontario. While the results vary from lake to lake, *on a per-capita basis*, the U.S. contribution is on the order of twice that of the Canadian contribution, except for Lake Ontario, where the two are comparable. There is significant – perhaps even comparable – uncertainty in the modeling methodology in addition to the uncertainty in the emissions. The largest such uncertainty may be the choice of algorithm used to estimate dry deposition to water bodies. The approach used in this analysis is that proposed by Slinn and Slinn[8], with a correction for humidity-induced particle growth near the water surface. Future work will attempt to characterize this and other non-emissions-related modeling uncertainties.

This analysis has included only sources in the United States and Canada. Sources in other regions will not likely add significantly to the loading of dioxin to the Great Lakes, but this will be tested in future work.

**Fig 4. Percent of Total Emissions or Total Deposition of Dioxin Arising from Within Different Distance Ranges from Lake Superior**



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