Modeling the Atmospheric Transport and Deposition of PCDD/F to the Great Lakes

MARK D. COHEN,*
ROLAND R. DRAXLER, AND
RICHARD ARTZ

NOAA Air Resources Laboratory, Silver Spring, Maryland 20910

BARRY COMMONER, PAUL BARTLETT, PAUL COONEY, KIM COUCHOT, ALAN DICKAR, HOLGER EISL, CATHERINE HILL, JAMES QUIGLEY, AND JOYCE E. ROSENTHAL†

Center for the Biology of Natural Systems, Queens College, Flushing, New York

DAVID NIEMI, DOMINIQUE RATTÉ, AND MARC DESLAURIERS

Pollution Data Branch, Environment Canada, Hull, Quebec, Canada

RACHELLE LAURIN

Ontario Ministry of the Environment, Toronto, Ontario, Canada

LARISSA MATHEWSON-BRAKE

Ontario Ministry of Natural Resources, Peterborough, Ontario, Canada

JOHN MCDONALD

International Joint Commission, Windsor, Ontario, Canada

Atmospheric deposition is a significant loading pathway for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (dioxin) to the Great Lakes. An innovative approach using NOAA's HYSPLIT atmospheric fate and transport model was developed to estimate the 1996 dioxin contribution to each lake from each of 5700 point sources and 42 600 area sources in a U.S./Canadian air emissions inventory. These unusually detailed source-receptor modeling results show that deposition to each lake arises from a broad geographical region, with significant contributions from up to 2000 km away. The source categories contributing most significantly to 1996 dioxin deposition appear to be municipal waste incineration, iron sintering, medical waste incineration, and cement kilns burning hazardous waste. Model-predicted air concentrations and deposition fluxes were consistent with ambient measurement data, within the uncertainties in each, but there may be a moderate tendency toward underestimation using midrange emissions estimates. The most likely reason for this tendency appears to be missing or underestimated emissions sources, but in-situ atmospheric formation of octachlorinated dibenzo-*p*-dioxin (OCDD) and heptachlorinated dibenzo-*p*-dioxin (HpCDD) may have also contributed. Despite uncertainties, the findings regarding the relative importance of different sources types and source regions appear to be relatively robust and may be useful in prioritizing pollution prevention efforts.

* Corresponding author phone: (301)713-0295 ext 122; fax: (301)-713-0119; e-mail: mark.cohen@noaa.gov.

† Current affiliation: Division of Environmental Health Sciences, Mailman School of Public Health, Columbia University, New York, New York.

Introduction

The polychlorinated dibenzo-*p*-dioxins and dibenzofurans pollutant group (PCDD/Fs or "dioxin") contains several potent carcinogens and endocrine disruptors, and human and wildlife exposure to these compounds is an issue of broad concern (*1*). The atmospheric fate of PCDD/F has recently been reviewed (*2*). Dioxin contamination in the Great Lakes is an ongoing problem (*3*) and estimates of the percent of dioxin loading to the Great Lakes attributable to atmospheric deposition are presented in Table 1. These estimates suggest the atmosphere is the most important loading pathway for Lakes Superior, Michigan, and Huron. For Lakes Erie and Ontario, while the atmosphere is not the dominant source, it is significant. Thus, it is critical to determine the following: (a) the amount of such deposition to the lakes; (b) the relative importance of contributions from local, regional, national, continental, and global source regions; and (c) the relative importance of different source categories.

There are several methodological approaches available to develop information on the atmospheric deposition pathway, including semiempirical loading estimates (*6, 7*), receptor-based approaches (e.g., back-trajectory calculations) (*8*−*13*), and comprehensive modeling. In the *comprehensive modeling* approach, one attempts to simulate the transport, dispersion, transformation, and deposition of pollutant emitted from each source in a comprehensive emissions inventory using an atmospheric model. This approach has been used to estimate the deposition of toxaphene (*14*), heavy metals (*15, 16*), mercury (*17*), dioxin (*4*), and atrazine (*18*) to the Great Lakes. Only one other previously published attempt to comprehensively model the long-range atmospheric transport of dioxin could be found (*19*). The modeling system presented here is somewhat unique, as unusually detailed source-receptor information is developed in the analysis. This analysis is for 1996; the primary impediment to carrying out the analysis for a more recent year is the lack of more up-to-date geographically resolved emissions inventories.

PCDD/F is a chemical group with 210 different congeners. In this analysis, emissions were estimated and atmospheric modeling was conducted on a congener-specific basis. However, for brevity, we have generally presented combined results for all congeners using the toxic equivalent (TEQ) formulation (*20*). Human-health toxic equivalency factors (TEFs) proposed by the World Health Organization (*21*) have been used, but the results would not vary significantly if the slightly different wildlife TEFs were used.

This paper presents an innovative and powerful approach for developing source-receptor information, extending and updating earlier work (*4, 22, 23*) analyzing the impacts of dioxin atmospheric emissions on the Great Lakes. The article proceeds in four sections: (1) the emissions inventory used as input to the analysis; (2) the basic model for simulating the atmospheric fate and transport of a single congener emitted from a single source; (3) a numerically efficient methodology to simulate complex congener mixtures emitted from multiple sources; and (4) results for the overall modeling

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TABLE 1. Estimates of the Fraction of Great Lakes Dioxin Loadings Attributable to the Atmospheric Deposition Pathway

pollutant	Lake Superior	Lake Michigan	Lake Huron	Lake Erie	Lake Ontario
PCDD/F (TEQ)	~100 (*5*); ~80 (*4*)	~88 (*4*)	~86 (*4*)	~40 (*4*)	
total PCDD		50−100 (*5*)			5−35 (*5*)
total PCDF		5−35 (*5*)			<5 (*5*)

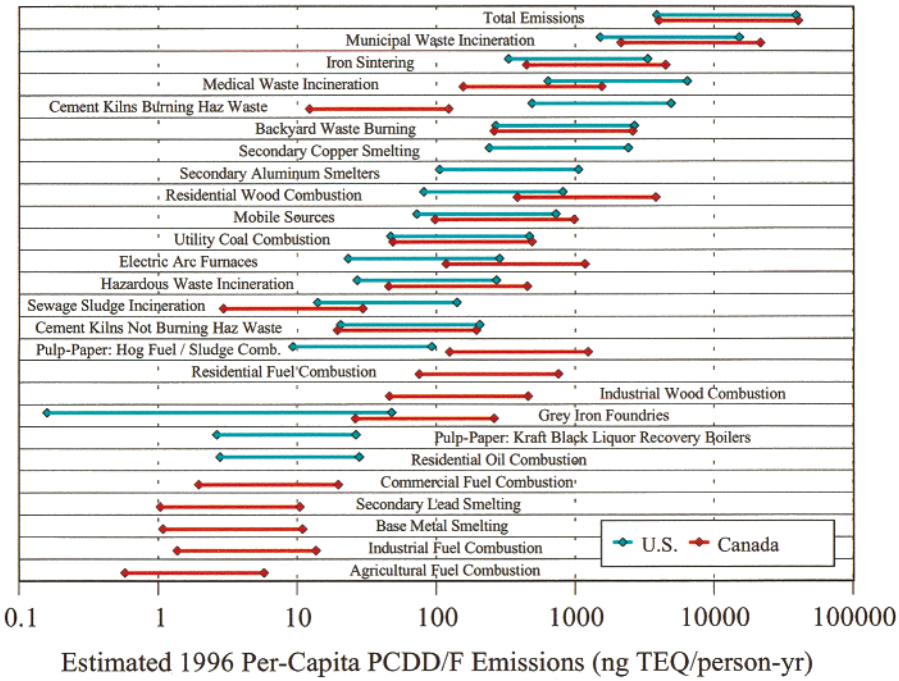

FIGURE 1. Estimated per-capita 1996 dioxin emissions from U.S. and Canadian source categories.

system. Additional details for most components of the analysis are provided as Supporting Information (SI), but for brevity, further references to SI will be only occasionally noted.

Emissions Inventory

The U.S. inventory used in the analysis (*23*) was built from a previously prepared 1993 inventory (*4*) to include several new source categories, to estimate emissions with a higher degree of spatial resolution, and was updated to reflect 1996 emissions. A 1995 emissions inventory for Canada was used (*24*), believed to be similar to 1996 emissions. Speciation information for all sources and emissions from backyard burning were added to the Canadian inventory. Overall summaries of the emissions inventories for the U.S. and Canada are shown in Figures 1 and 2. The inventories have a few emissions categories that cannot be directly compared (e.g., U.S. residential oil combustion vs Canadian residential fuel combustion). The Canadian inventory has a few source categories (e.g., agricultural fuel combustion) not included in the U.S. data, but these categories appear to be relatively insignificant.

The inventory contains ~5700 point sources and ~42 600 area sources. Contacts with facilities, industry groups, and/or regulatory agencies provided information about activity levels (e.g., tons per year burned in an incinerator), processes, and pollution control equipment for individual facilities in each significant source category. Source categories treated as area sources—e.g., mobile sources—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. Emissions from residential wood combustion were assumed to vary seasonally. For municipal waste incinerators, information on significant changes in the emissions from a given facility, e.g., due to closing or change in pollution control technology, was factored into the analysis. For other sources in the inventory, emissions were assumed to be uniform and continuous throughout the year. The lack of temporal resolution obviated the use of short-term measurements in the comparison of model predictions against ambient measurements. Figure 1 shows an approximate range of emissions for each source category. Based on the variations in available stack test data, and uncertainties in the activity levels and emissions factors used, this range was estimated to be a factor of 10 for most source categories. In a few cases, information was available to support a more specific uncertainty estimate.

There are substantial uncertainties in dioxin emissions estimates, because of inherent variability in emissions, infrequent testing, and inadequate characterization of many sources. While total U.S. emissions for most source categories are relatively consistent with U.S. EPA inventories (*25, 26*) as shown in Table 2, variations within and among the different inventories indicate the magnitude of emissions uncertainty. While the available information appears adequate to generate an initial estimate of source/receptor linkages, further improvement of emission inventories is necessary to increase the accuracy of this or other modeling analyses.

Because of difficulties in estimating emissions, the U.S. and Canadian inventories used here do not include all potentially significant source categories. The U.S. inventory does not contain emissions estimates for magnesium manufacturing, small commercial incinerators, residential or commercial coal combustion, or several other fuel combustion categories. Neither inventory contains estimates for structure and vehicle fires (e.g., involving open-burning of wires insulated with poly(vinyl chloride)), asphalt production, landfill fires, combustion of landfill gas in venting or energy

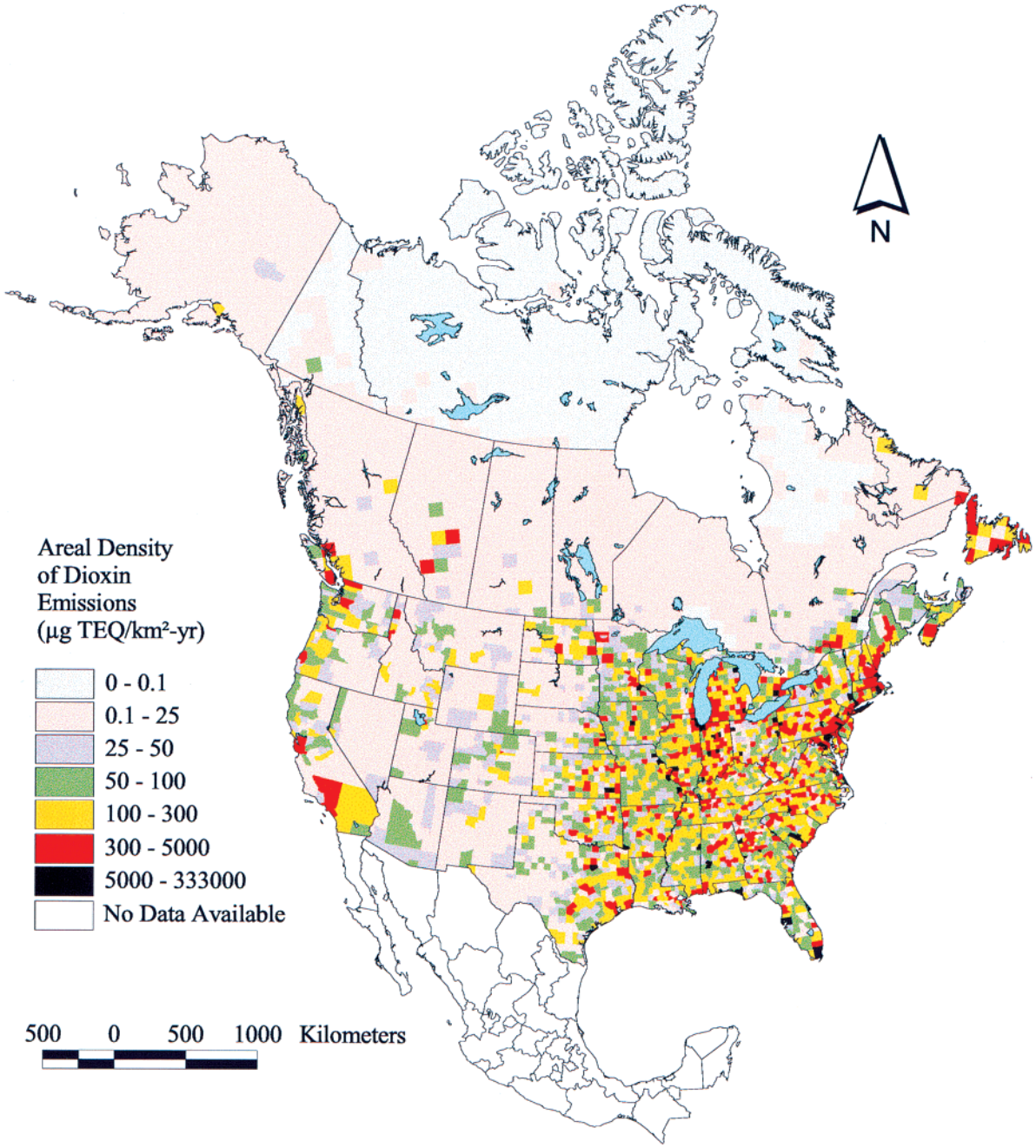

FIGURE 2. Geographical distribution of U.S. and Canadian 1996 dioxin emissions.

reclamation systems, coke production, combustion of leaded gasoline in on-road and off-road vehicles and aircraft, petroleum refining operations, chemical plant flares, or forest fires.

Modeling Dioxin Emissions from a Single Source

In short-range modeling (<50 km) of PCDD/F using Gaussian-plume dispersion models, only a small fraction of the emitted dioxin is transformed or deposited within the modeling domain. This is consistent with the finding that long-range transport of dioxin can occur (*27*, *28*). This section presents a modeling methodology to simulate the atmospheric behavior of a given congener of dioxin emitted from a single source over a range of length scales, up to and including long-range transport.

The *HYSPLIT* Atmospheric Fate and Transport Model. NOAA's *HYSPLIT_4* (Hybrid Single Particle Lagrangian Integrated Trajectory model, Version 4) was used, with the modifications described below. 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. It was developed at the U.S. National Oceanic and Atmospheric Administration (NOAA) to model releases of radioactive materials and is used for emergency response at NOAA (*29*). The development, validation, and operation of HYSPLIT are summarized elsewhere (*30*−*32*). It has been used to simulate many different atmospheric processes, including regional ozone formation (*33*, *34*), sulfur transport and deposition in the U.S. (*35*, *36*), and dispersion of pollutants from Persian Gulf oil fires (*37*, *38*).

Meteorological Data. HYSPLIT uses gridded meteorological data computed by an external model. For the simulations presented here, output from NOAA's Nested Grid Model (*NGM*) was used (*39*). Analysis-mode simulations (i.e.,

TABLE 2. 1996 U.S. Emissions Inventory Used in This Analysis Compared to Two Different U.S. EPA 1995 Inventories[g]

source category	1996 (this analysis) central	1996 (this analysis) range	1995 (*26*) central	1995 (*25*) central	1995 (*25*) range
municipal waste incineration	1280	*400–4000*	1250	1100	*492–2460*
medical waste incineration[a]	540	*170–1700*	497	477	*151–1510*
backyard burning	225	*70–710*	628	1000[c,d]	*316–3162*
power/energy generation	170	*50–540*	278[d]	234[e]	*87–640*
cement kilns	430	*140–1400*	177	171	*54–540*
landfill fires	*b*		1000[c]	1000[c,d]	*316–3162*
forest and brush fires	*b*		200[c]	2080	*64.5–645*
ferrous metal smelting and refining	300	*100–1000*	95[e]	130[c,d]	*41–411*
nonferrous metal smelting and refining	300	*90–900*	317[e]	560	*177–1767*
other	45	*14–141*	103[e]	45[e]	*16–130*
total quantified emissions[f]	3300	*1000–10000*	3111	2745	1026–7539
total for highly uncertain estimates			1434[c]	2180[c,d]	*689–6894*
total emissions in inventory	3300	*1000–10000*	4546[e]	4925[e]	*1716–14433*[e]

[a] Including crematoria. [b] Not included in inventory. [c] EPA regarded this estimate as "highly uncertain." [d] For the purposes of this table, a factor of 10 range was assumed for these estimates. This seemed reasonable as the uncertainty range for most of the "more certain" estimates was approximately this large, and the range for these highly uncertain estimates must be at least this large, if not larger. [e] Includes some "quantified emissions" and some "highly uncertain" estimates. [f] "Quantified emissions" defined by EPA as being those with no more than a certain maximum uncertainty; emissions estimates with higher uncertainty were tabulated separately (see "total for highly uncertain estimates" in the above table). [g] Central estimates are given and ranges in emissions estimates (when available) are italicized.

after the weather actually happened) rather than forecasts were used, so that meteorological observations could be utilized to improve model accuracy. The data provided to HYSPLIT from the NGM include wind speed and direction, amount and type of precipitation, temperature, humidity, and other meteorological information. The modeling domain used in this analysis and the location of NGM grid points are shown in Figure 3. The gridded data had a 2-h temporal resolution, 180 km horizontal resolution, and 11 vertical levels from the surface up to an elevation of 6000 m. Such temporal and spatial resolution has been found to be adequate in this type of analysis (*36, 40, 41*) but evidence also exists that greater spatial resolution may improve estimation accuracy for dry (*42, 43*) and wet deposition (*44*). A small improvement in accuracy might also be obtained by using observed precipitation data instead of NGM-estimated values (*36*). It is unlikely that the use of higher resolution meteorological data or observed precipitation data would significantly change the overall results presented here, but this could be tested in future work.

Vapor-Particle (V/P) Partitioning. A fundamental factor influencing the atmospheric fate of any compound is its phase distribution behavior in the atmosphere (*45*), and V/P partitioning of PCDD/Fs has recently been reviewed (*46*). We have used the conventional adsorption-based formulation of the V/P phenomenon (*45, 47, 48*) and have assumed that the subcooled liquid-phase vapor pressure is most relevant to equilibrium partitioning (*45*). As an illustration, Table 3 lists V/P partitioning characteristics estimated with this methodology for typical conditions, using congener-specific physical-chemical properties (see SI: Table 2) (*48, 49*). We have assumed that atmospheric PCDD/F is completely "exchangeable" between the vapor and particle phases. This is consistent with ambient measurements (*50, 51*) which found that the proportion in the two phases was dependent on temperature but that the total atmospheric concentration was not. While there is uncertainty in the simulation of this phenomenon, the methodology used here yields results that are consistent with the available experiment data and alternative methods for prediction (e.g., refs *46, 52, 53*).

Aerosol Characteristics. Bidleman (*45*), citing a study by Whitby (*54*), reviewed data on aerosol surface area and suggested the following typical values (cm^2 surface area per cm^3 of air): 4.2×10^{-7} (clean continental background); 1.5×10^{-6} (average background); 3.5×10^{-6} (background + local sources); 1.1×10^{-5} (urban). While the characteristics of the atmospheric aerosol vary with location and time, the size distribution is relatively uniform (*55*). For this analysis, we assumed that the aerosol was the same everywhere, with a surface area of 3.5×10^{-6} cm^2 per cm^3 of air and a typical size distribution, divided into 14 segments (see SI for details). A sensitivity analysis showed that the simulation results were not significantly affected by variations in the particle concentration (see SI for details regarding this and other sensitivity analyses).

TABLE 3. Characteristics of 2,3,7,8-Substituted PCDD/F Congeners

PCDD/F congener	typical fraction on particles[a] (%)	TEF for humans/mammals (*21*)	first-order rate constant for reaction with OH at 298.15 K (cm^3/molec-s) (*60, 61*)
2,3,7,8-TCDF	30.2	0.1	1.6E-013
2,3,7,8-TCDD	58.8	1	2.0E-012
1,2,3,7,8-PeCDF	84.0	0.05	7.5E-014
2,3,4,7,8-PeCDF	84.0	0.5	7.5E-014
1,2,3,7,8-PeCDD	95.5	1	1.7E-012
1,2,3,6,7,8-HxCDF	95.8	0.1	3.6E-013
1,2,3,7,8,9-HxCDF	96.3	0.1	3.4E-014
2,3,4,6,7,8-HxCDF	96.3	0.1	3.0E-013
1,2,3,4,7,8-HxCDF	96.7	0.1	3.0E-013
1,2,3,7,8,9-HxCDD	98.4	0.1	1.4E-012
1,2,3,6,7,8-HxCDD	98.4	0.1	1.4E-012
1,2,3,4,7,8-HxCDD	98.4	0.1	1.2E-012
1,2,3,4,6,7,8-HpCDF	99.4	0.01	1.5E-014
1,2,3,4,7,8,9-HpCDF	99.4	0.01	1.5E-014
1,2,3,4,6,7,8-HpCDD	99.8	0.01	9.2E-013
OCDF	99.9	0.0001	6.9E-015
OCDD	99.9	0.0001	4.2E-013

[a] Estimated for the following "typical" conditions: ambient temperature = 290 K; aerosol surface area = 3.5×10^{-6} cm^2 per cm^3 of air.

Dynamic Vapor-Particle Partitioning. A dynamic V/P partitioning feature was added to HYSPLIT in which the V/P characteristics for the simulated congener are estimated—at the ambient temperature of a given puff—at each time step. The particle-associated fraction of the puff's congener is allocated to the different particle size ranges segments based on particle surface area (assuming spherical particles). This procedure results in a peak in the dioxin particle size distribution in the range from 0.1 to 0.5 μm diameter,

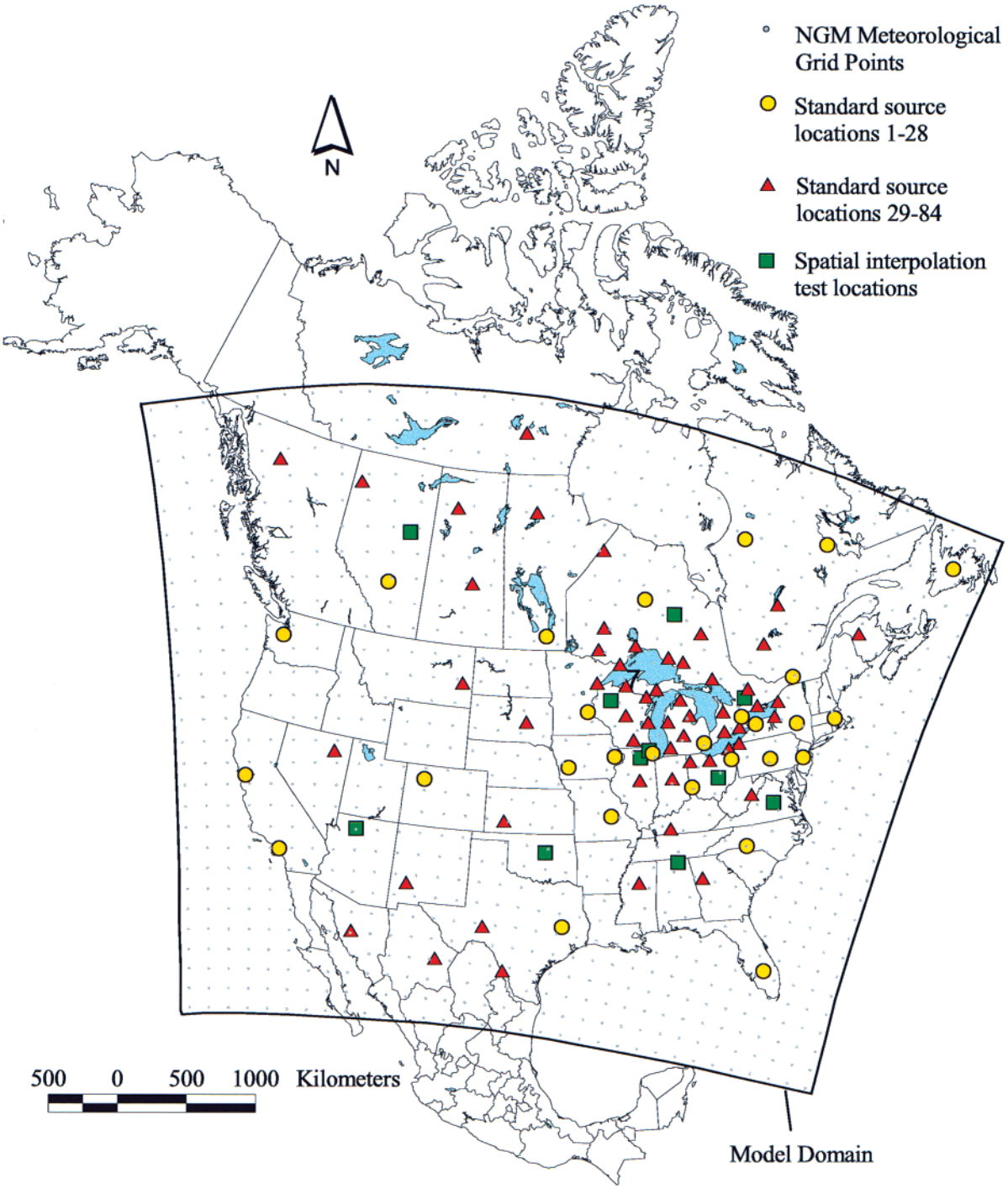

FIGURE 3. Modeling domain, grid for NGM meteorological data, standard source locations, and spatial interpolation test locations.

consistent with ambient measurements (*56*). Fate process pathways that depend on particle size (e.g., dry deposition) are estimated as the mass-weighted sum of the rates for each of the particle size ranges.

Reaction with the Hydroxyl Radical (OH). The most important chemical reaction for atmospheric PCDD/F is believed to be the vapor phase reaction with OH; reactions with ozone, nitrate radical, or HO_2 radical are not expected to be important (*57*, *58*). OH reaction rates have been experimentally determined for simple PCDD/F molecules (e.g., ref *59*), but there have been no measurements for any of the seventeen 2,3,7,8-substituted congeners. Thus, a QSAR-based methodology was used (*60*, *61*) to generate the approximate rate constants shown in Table 3. Using these rates, atmospheric half-lives (relative to this fate process alone) for 2,3,7,8-TCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,3,7,8-PeCDF, and 2,3,4,7,8-PeCDF were estimated to be 5, 65, 6, 144, and 144 days, respectively, using an average hydroxyl radical concentration of 1.5×10^6 molecules cm^{-3}, 12-h days, and the typical fraction of the congener in the vapor phase. In this fate and transport modeling, the hydroxyl radical concentration at any point and time in the modeling domain was estimated using an interpolation procedure based on the results of Lu and Khalil (*62*), who presented modeled concentrations of OH as a function of hour, season, elevation, and latitude.

Photolysis. The photolysis rate of atmospheric PCDD/F congeners is uncertain. In this analysis, approximate maxi-

mum photolysis rates corresponding to a half-lives of 2 and 10 days were used for PCDD/F congeners in the vapor and particle phases, respectively, based on a review of the limited experimental and theoretical evidence available (see SI). The slower particle-phase rate was used based on the relative invulnerability of dioxin in that phase (*63*). The photolysis rate at any given time and location was assumed to be proportional to the surface radiation intensity, with the maximum rate occurring at the maximum surface-level solar flux. Sensitivity analyses showed that the effect of photolysis rate uncertainty on overall model results appears to be relatively small (see below and SI).

Chemical Transformation Products. The products of atmospheric degradation of PCDD/Fs have not been well characterized. Degradative dechlorination has been observed in the environment (*64*) and this can result in increased toxicity (see Table 3). However, atmospheric concentrations and deposition tend to be much more heavily skewed toward the higher chlorinated congeners than the profiles of most emissions sources (*48, 65*). This suggests that the dechlorination of higher-chlorinated congeners leading to the more toxic tetra- and penta-chlorinated congeners is not a significant process. It has been hypothesized that OCDD and HpCDD may be synthesized from pentachlorophenol in atmospheric droplets, and that this phenomenon may at least partially explain the abundance of these homologue groups in atmospheric deposition (*66*). However, these compounds generally contribute relatively little to the overall toxicity in environmental PCDD/F mixtures, and so, the omission of this phenomenon in the present work is expected to have only a small impact on the *toxicity* of model-estimated deposition.

Dry Deposition. A resistance-based dry deposition algorithm (*32, 67*–*69*) was used for both terrestrial and water surfaces. In formulating the canopy resistance, the value of the surface reactivity parameter was assumed to be 1 (see SI). The methodology was found to be consistent with other commonly used approaches for vapor-phase dry deposition to water surfaces (*70*–*73*). The dry deposition of particles (and hence particle-associated PCDD/F) is more uncertain. Estimates of particle dry deposition to water surfaces were made using a relatively high quasi-laminar sublayer resistance (*74*), consistent with recent measurements (*75*), and with a simple near-surface particle-growth estimation approach (*76*) (assuming 99% humidity in the surface layer).

As a simplifying approximation, the dry deposition of PCDD/F to land and water surfaces has been assumed to be unidirectional, i.e., revolatilization (the so-called *grasshopper* effect) was not considered to be significant. While this process may be significant for lower-chlorinated congeners (*77*), this analysis focused on the more toxicologically significant tetra- to octa-chlorinated PCDD/F congeners. The assumed unidirectional nature of tetra- through octa-chlorinated PCDD/F deposition is consistent with ambient observations. Compounds that revolatilize readily are typically found at significantly higher concentrations in the summer than in the winter, due to the strong temperature dependence of the process (*78*). The few long-term PCDD/F measurement data do not show such an annual trend (e.g., ref *50*); and in fact often show an opposite trend (i.e., higher concentrations in winter). In addition, there does not seem to be any significant diminution of soil concentrations at sites of industrial accidents involving PCDD/F (*79*). Brzuzy and Hites (*80, 81*) have reviewed experimental and theoretical observations on the behavior of soil-deposited PCDD/F and concluded that once deposited, the material is not significantly revolatilized. Similarly, PCDD/F is believed to partition overwhelmingly to particulate matter in water bodies, making it unavailable for revolatilization. Thus, it is generally assumed that essentially all PCDD/F deposited to water bodies ends up in the sediment, and deposition rates to water bodies are frequently estimated by analyzing sediment accumulation rates (e.g., ref *82*).

Wet Deposition. Wet deposition in the HYSPLIT model is simulated as three different phenomena: (a) in-cloud particle washout; (b) below-cloud particle scavenging; and (c) vapor-phase wet deposition. An in-cloud particle washout ratio was estimated from the ambient measurements of Hites and colleagues (*83, 84*).

Indirect Atmospheric Deposition to the Lakes. As a simplifying approximation, we have estimated deposition as only that which falls directly onto the surface of the lakes. No contribution has been estimated for PCDD/F which is deposited onto a lake's watershed, and which may subsequently contribute to the lake's loadings through runoff or other processes. Such indirect deposition is unlikely to be a significant loading process due to the relative immobility of PCDD/F in the soil, as discussed above, and the fact that the watersheds of the Great Lakes are small relative to the water surface area—only on the order of the size of the lakes themselves—compared to that of most water bodies.

Illustrative Examples of Single-Source Modeling Results. 1. Episodic Nature of Source-Receptor Relationships. Even if emissions are constant, the impact of any given source on any given receptor will vary in time due to changing weather patterns. This phenomenon is illustrated in Figure 4 which shows the weekly variations in deposition to Lakes Superior and Ontario arising from a hypothetical continuous emissions source over the course of a 1-year simulation. These results suggest that short-term simulations (or short-term measurements) will be unlikely to provide representative estimates of the long-term average situation. In this analysis, simulations were for an entire year (1996). It is believed that the major features of the source-receptor relationships will be captured in such a lengthy simulation, but additional analysis-years could be examined to evaluate this hypothesis.

2. Deposition and Flux at Different Distances from the Source. The deposition amount and flux at different distances from a hypothetical continuous year-long source of 2,3,7,8-TCDD is shown in Figure 5. While the deposition flux drops off rapidly with distance (lower graph), only about 4% of the emissions are estimated to be deposited within the first 200 km. On this mass basis, there is significant deposition out to 1800 km. Past this distance, the edge of the modeling domain is reached (in the southerly direction). The behavior of other PCDD/F congeners is similar. Thus, a relatively large potential source region must be considered in estimating atmospheric deposition contributions of dioxin to the Great Lakes.

3. Overall Atmospheric Fate of Emitted PCDD/F Congeners. Figure 6 shows the relative importance of different atmospheric fate processes for year-long simulations of 2,3,7,8-TCDF, 2,3,7,8-TCDD, 2,3,4,7,8-PeCDF, and OCDD. The congeners are ordered with regard to their propensity to exist in the vapor phase. The importance of photolysis pathway declines, as would be expected, as the relative fraction in the vapor phase declines. The vapor-phase hydroxyl radical reaction is significant for 2,3,7,8-TCDD, as it has a relatively high propensity to exist in the vapor phase and is relatively reactive with the hydroxyl radical. While higher fractions of 2,3,7,8-TCDF are in the vapor phase, its reactivity with hydroxyl is less than that estimated for 2,3,7,8-TCDD (see Table 3). Wet gas deposition is insignificant for all four congeners, as would be expected given their Henry's Law constants (see SI). Wet below-cloud particle deposition is also insignificant due to the relative inefficiency of below-cloud particle scavenging by precipitation. The remainder of the fate pathways—wet in-cloud particle deposition and vapor and particle dry deposition—show the expected behaviors relative to the tendency of the congeners to exist

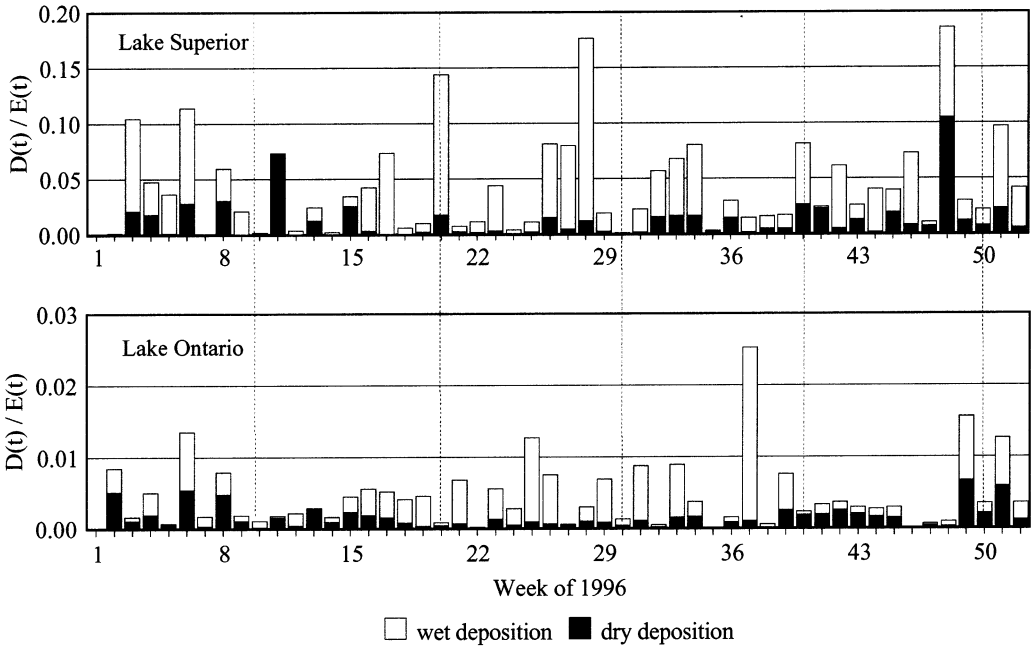

FIGURE 4. Weekly estimates of 1996 wet and dry deposition to Lakes Superior and Ontario arising from a hypothetical, continuous source of 2,3,7,8-TCDD at the center of the modeling domain. The dimensionless values plotted are the ratios between the weekly deposition rate to the given lake [D(t) (g/week)] and the weekly emissions rate [E(t) (g/week)] from the hypothetical source.

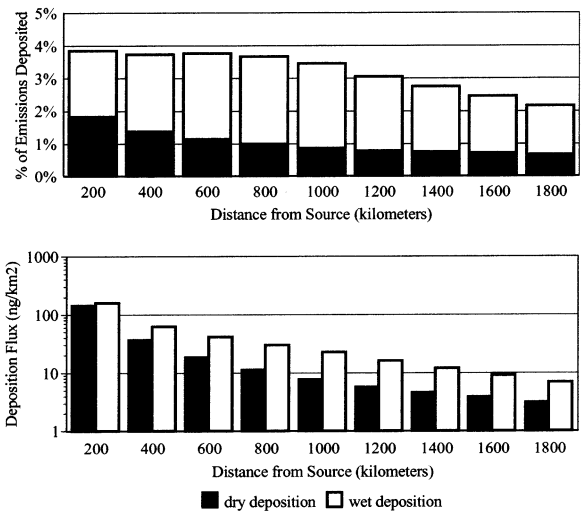

FIGURE 5. Deposition amount and flux of 2,3,7,8-TCDD in successive, concentric, annular 200-km-radius-increment regions away from a hypothetical 1996 year-long continuous source near the center of the modeling domain (latitude = 40° N, longitude = 95° W). The deposition amount has been divided by the total amount emitted in the simulation to give the fraction of the emissions deposited in any given concentric region. The deposition flux for each region has been normalized to correspond to an emissions rate of 1 g/year.

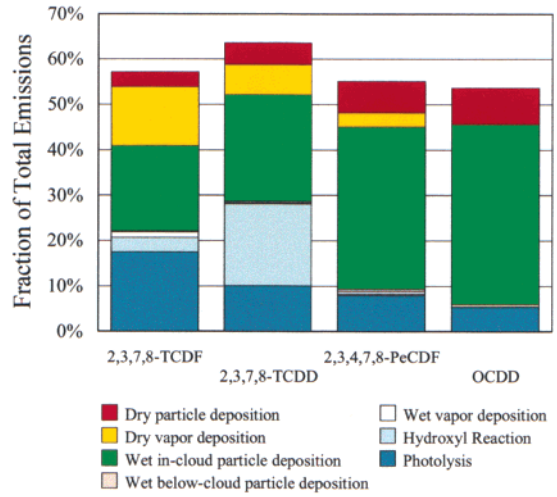

FIGURE 6. Fraction of emissions of four dioxin congeners accounted for in different fate pathways anywhere in the modeling domain for a hypothetical 1996 year-long continuous source near the center of the domain.

in the vapor or particle phase. It can be seen that only about 50−60% of the emissions from this domain-center source location are accounted for by deposition or destruction in the model domain. A small fraction of the remaining material was left in the model-domain atmosphere at the end of the simulation, but the bulk of this additional material left the domain through its sides and top.

Estimating the Fate and Transport of Dioxin Mixtures Emitted from Multiple Sources

A methodology for modeling the atmospheric fate and transport of a given congener emitted from a given source location has been presented above. However, this study used nearly 50 000 discrete sources/source regions in its U.S./Canadian dioxin emissions inventory, each emitting a source-specific mixture of 210 different PCDD/F congeners. It would be impractical to attempt to explicitly model the fate and transport of each congener emitted from each source. At the same time, detailed source-receptor information was sought, because of its obvious policy relevance. Thus, interpolation-based procedures were developed to estimate the impacts of individual sources in a numerically efficient manner. The interpolation procedures employed utilize the concept of a *transfer coefficient*, defined as the fraction of emissions of a given dioxin congener emitted at a given location that is predicted to be deposited in a given receptor over the course of a simulation period.

Spatial Interpolation. To reduce the computational requirements necessary for analysis, explicit HYSPLIT modeling of emissions from a given location were only performed for a limited number of source locations. In cases where

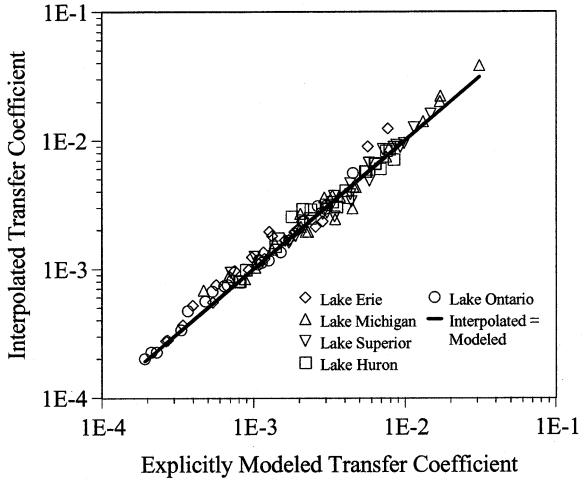

FIGURE 7. Comparison of interpolated transfer coefficients to the Great Lakes with explicitly modeled transfer coefficients for 2,3,7,8-TCDD and OCDD. The transfer coefficient is the dimensionless ratio of the *deposition* (g/yr) to a given lake to the *emissions* from a given interpolation test location (g/yr).

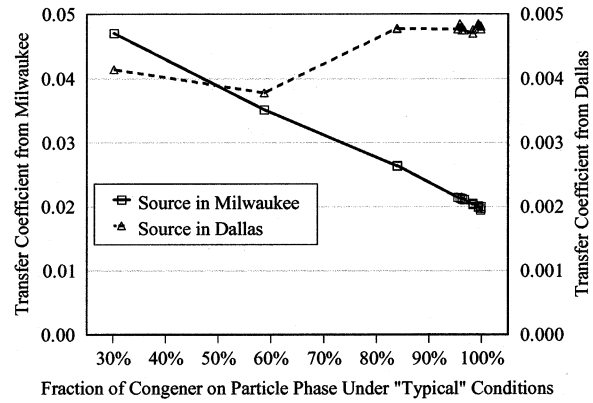

FIGURE 8. Annual (1996) transfer coefficients for the seventeen 2,3,7,8-substituted dioxin congeners to Lake Michigan for a hypothetical, continuous source very near the lake [in Milwaukee, WI (lat. 41.84°, long. 87.69°)], and at a location approximately 800 km southwest of the lake [near Dallas, TX (lat. 33°, long. 97°)]. The abscissa for each congener corresponds to the particle-associated fractions in Table 3.

emissions from a given source were not explicitly simulated, a spatial interpolation method was used to estimate the source's impact on any given receptor based on a weighted average of the nearest explicitly modeled locations. The weighting was done by distance and angular orientation (see SI). The spatial interpolation methodology is based on a series of HYSPLIT single-congener dioxin simulations carried out with a unit-emissions rate (e.g., one gram of pollutant emissions per hour) from one source location at a time, for a number of selected *standard source locations*. For the Great Lakes deposition estimates presented here, 84 standard source locations were used. The standard source locations were chosen to provide satisfactory geographical resolution in areas of strong source emissions, in areas close to each receptor of interest, and in the entire modeling domain. In conducting sensitivity analyses (see below), only 28 such locations were used in some cases. The 84 standard locations (with the 28 point subset marked) are shown in Figure 3.

The interpolation procedure was evaluated by comparing its predictions against explicit simulations for the 11 "test" source locations shown in Figure 3. "Difficult" locations were chosen, to provide a worst-case estimate of the magnitude of errors involved in the interpolation procedure. In actuality, the standard source locations were chosen to represent important source regions contributing dioxin to the Great Lakes, and so the interpolation errors for most significant sources would be somewhat lower than for these test locations. Nevertheless, Figure 7 shows that the interpolation procedure performs reasonably well over the entire range of transfer coefficients encountered. The average absolute value of the percentage difference between the interpolated and simulated transfer coefficients (to the Great Lakes) is 14% for these test locations. The average error is only a 7% overestimation, as positive and negative deviations cancel each other out to some extent. This level of methodological uncertainty is acceptable, given that emissions inventory information (and in some cases, the atmospheric fate simulation methodology) is significantly more uncertain. A directly analogous spatial interpolation procedure was used to estimate the concentration impact arising from a unit emissions source at any arbitrary source location, based on the concentration impacts at the given receptor arising from nearby explicitly simulated standard source locations.

Chemical Interpolation. Only 17 of the 210 congeners—those with chlorine-substitution in the 2,3,7,8 positions (at least)—are considered to be toxic, and so, the simulation was primarily focused on the fate and transport of these 17 congeners. Given the central role that vapor-particle (V/P) partitioning plays in influencing the atmospheric fate of semivolatile compounds (*45*), it was hypothesized that it may be useful to classify the PCDD/F congeners with regard to this phenomenon. Using the typical V/P partitioning characteristics listed in Table 3, the 17 congeners were divided into four V/P partitioning classes: "high" volatility (2,3,7,8-TCDF), "moderate" volatility (2,3,7,8-TCDD), "low" volatility (1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF), and "very low" volatility (the remaining 13 congeners).

Figure 8 plots the overall transfer coefficients to Lake Michigan predicted by a 1-year fate and transport simulation for these 17 PCDD/F congeners for hypothetical emissions from a source close to and a source far away from the lake. While V/P partitioning characteristics were dynamically estimated throughout each simulation for each congener (see above), the annual transfer coefficients are shown as a function of the fraction of the congener estimated to be in the particle phase under the typical conditions described above. Other locations were evaluated as well, and it was found in all cases that while the modeled transfer coefficients varied greatly among different locations, the transfer coefficients fit as expected into the above-defined classes.

Thus, as a simplification, HYSPLIT simulations were conducted for only *four* different congeners at a given source location: 2,3,7,8-TCDF; 2,3,7,8-TCDD; 2,3,4,7,8-PeCDF; and OCDD. Using the transfer coefficients for these four congeners, values for the 13 other 2,3,7,8-substituted congeners were estimated. In the low-volatility group, 1,2,3,7,8-PeCDF was assigned the same transfer coefficient as 2,3,4,7,8-PeCDF. In the "very low" volatility group, the 12 congeners other than OCDD were assigned a transfer coefficient linearly related to their typical-condition particle-phase fraction, using the values for OCDD and 2,3,4,7,8-PeCDF to define the interpolation endpoints. Transfer coefficients for other congeners in each homologue group (e.g., all TCDD congeners except 2,3,7,8-TCDD) were estimated as the average of those for the 2,3,7,8-substituted members in the homologue group. Given the general importance of V/P partitioning, this type of approach could potentially be applied to other pollutant groups comprised of a large number of congeners or closely related species, such as polychlorinated biphenyls, polybrominated diphenyl ethers, polychlorinated camphenes, and possibly even polycyclic aromatic hydrocarbons.

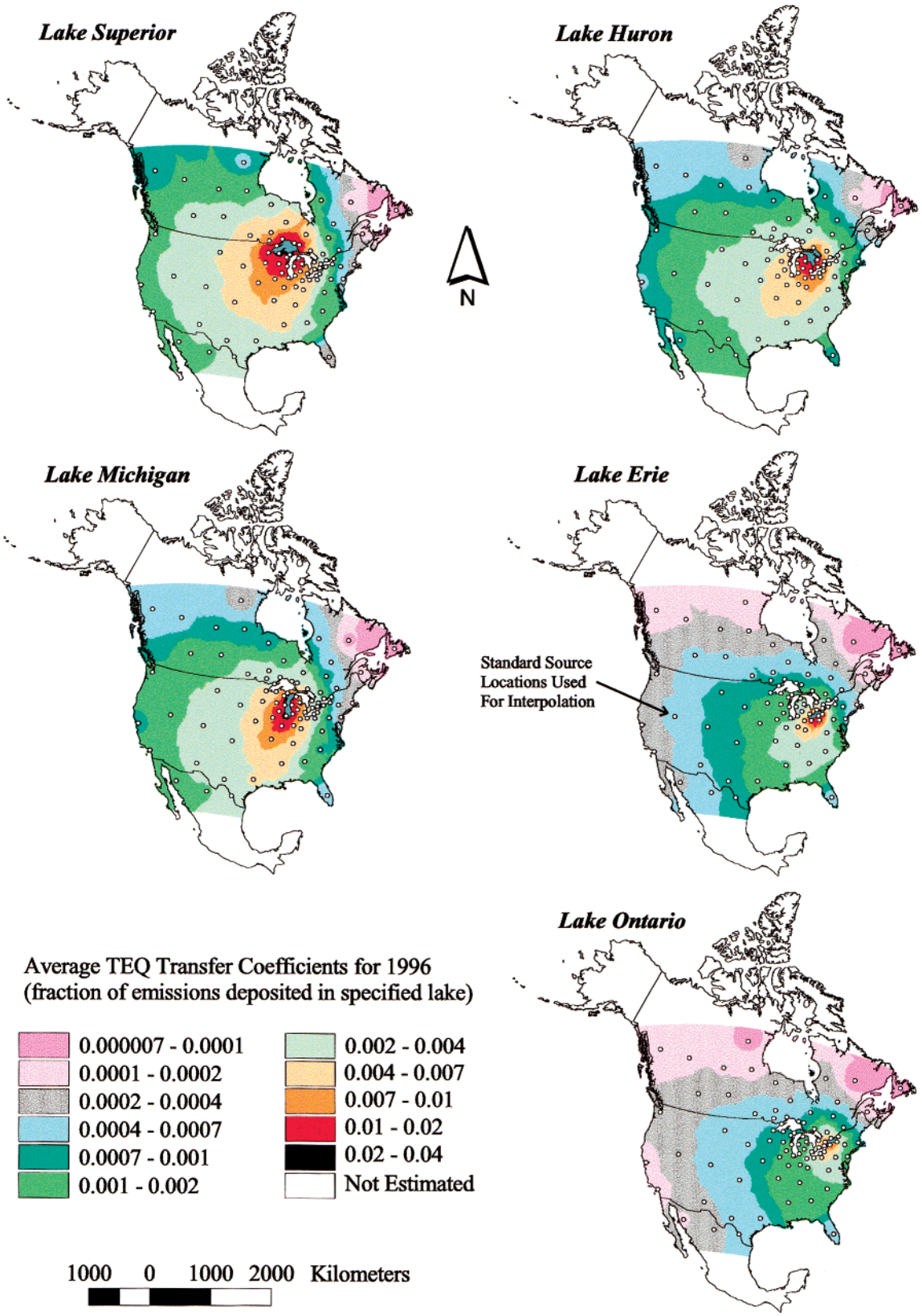

FIGURE 9. Geographical distribution of transfer coefficients to each Great Lake for a typical dioxin congener emissions profile. The mapped values represent the fraction of *hypothetical* 1996 dioxin emissions from a given location that would be deposited in a given lake (e.g, grams TEQ deposited per year/grams TEQ emitted per year). These maps do not contain emissions information; they only indicate the model-estimated propensity for dioxin emitted in any location to be deposited in a given lake, should there be any dioxin emissions at that location.

Transfer Coefficient Maps. A summary of the above interpolation procedures is provided in Figure 9, which shows a series of transfer coefficient maps for overall dioxin TEQ transport and deposition to each of the Great Lakes. These maps are based on calculations using a 25-km grid covering the entire modeling domain, using explicit simulations from 84 standard source locations (shown on the maps and in Figure 3). For the purposes of these examples, an average congener emissions profile was used for each of the grid-squares, representing the average profile for the entire emissions inventory. These figures describe the relative efficiency of transport and deposition between each map location and each of the Great Lakes for hypothetical, continuous emissions throughout the entire year 1996. Note that transfer coefficient maps such as these are unique for a given congener or mix of congeners, for a given receptor, and for a given averaging time period. Figure 9 shows the general importance of transport from the west and southwest of the lakes, relative to other directions. While the transfer coefficients diminish with distance from a given lake, they do not drop so precipitously that contributions from regional and long-range sources are insignificant. In some parts of the maps in Figure 9 (e.g., in some of the northern areas), limitations of the interpolation procedure can be observed, i.e., there are uneven ("blotchy") patterns that appear to be related to the standard source locations. Far from the lakes, the standard source locations are relatively sparse, and the spatial interpolation procedure is therefore less accurate. In addition, for some locations, there may be very few periods throughout the year when emitted material is transported to a given lake, and this adds additional uncertainty to the transfer coefficient estimates. However, since these regions generally have few emissions and/or are far from the lakes, these limitations have little effect on the model-estimated deposition to the Great Lakes.

Overall Modeling System. Conceptually, the overall modeling analysis entailed multiplying the emissions inventory map (Figure 2) with the transfer coefficient map for a given lake (Figure 9). The analysis was performed numerically on a congener- and source-specific basis, rather than relying on the overall TEQ transfer coefficients shown in Figure 9 (which are only "valid" for the average congener profile used to make them) or the aggregated emissions shown on the aforementioned emissions map. This technique allowed estimates of the atmospheric deposition contribution of *each* source in the emissions inventory to be made for each lake. The actual impact of a given source on a given lake was scaled up proportionally from the unit-source simulation results to the actual emissions.

This methodology assumes that atmospheric fate and transport of dioxin from any given source is not influenced by the emissions from any other source, based on the following arguments. First, in the model used here, each of the fate processes affecting PCDD/F congeners in the atmosphere is algorithmically described by a first-order rate expression (i.e., $rate = kc$, where c is the concentration of dioxin and k is a dynamically estimated rate parameter that does not depend on c). Second, because of its trace concentration in the atmosphere, dioxin is highly unlikely to have any significant effect on concentrations of fate-relevant compounds (e.g., hydroxyl radical) or processes (e.g., precipitation). Finally, the V/P partitioning methodology used here results in an estimate of the *fraction* of a given congener expected to be associated with the gas and particle phases in the atmosphere (at any given location and time). It is implicit in this methodology that any particular dioxin congener emitted from any given source would be governed by this same V/P partitioning fraction, and that all of the PCDD/F in the atmosphere is exchangeable. With this set of assumptions, the presence of dioxin from one source in the atmosphere does not affect the V/P partitioning characteristics of any other source. Thus, in the case of atmospheric dioxin, we believe it is valid to consider dioxin sources to be linearly independent of one another. This is likely to be true for many other trace pollutants in the atmosphere, but is certainly not true, for example, for emissions of VOCs and NO_x.

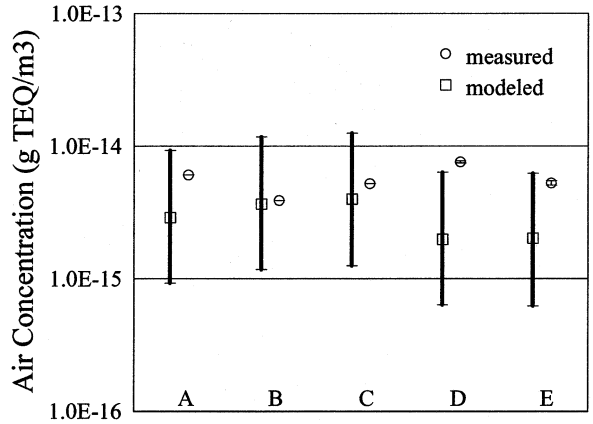

FIGURE 10. Comparison of model predictions with month-long ambient concentration measurements. Sample locations and dates (all dates 1996): A. Mohawk Mtn CT (5/14–6/13); B. Mohawk Mtn CT (8/14–9/13); C. Mohawk Mtn CT (10/22–11/22) D. Northern VT (8/1–8/28); E. Central VT (8/1–8/28).

While each source was not explicitly modeled, the interpolation process allows each source's contribution to each receptor to be estimated (on a congener by congener basis). Development of such detailed source-receptor information in comprehensive modeling analyses is computationally difficult. While "tagged-species" and other approaches have been used, most studies have only developed individual estimates for a few sources or source regions. Thus, the source-receptor accounting of ~50 000 sources in this work is somewhat unusual. This methodology does not require the use of a Lagrangian model as the single-source, single-congener "engine" such as that used here; an Eulerian model could be used as well.

Model Evaluation

The model was evaluated by comparing model-predicted concentrations with ambient air concentration measurements and sediment-derived deposition flux measurements. Of the available PCDD/F ambient air monitoring data for 1996, there were only five appropriate *month-long* sampling events in rural locations: one sample each at two different sites in Vermont (*23*) and three samples at a remote site in Connecticut (*85*). A few additionally available 1996 month-long samples (*23*) were not used because they were collected at sites where short-range transport from local sources—at scales much smaller than the resolution of the meteorological data used—exerted a dominant influence on the measured dioxin concentrations.

Figure 10 provides a summary (in terms of overall TEQ) of the comparison between the model predictions and the month-long ambient air concentration measurements. The uncertainty ranges shown for the modeling predictions are those due only to the estimated uncertainties in the emissions. Other modeling uncertainties were generally less significant—e.g., see Figure 16 below—and so their inclusion here would only slightly expand the uncertainty range. While the modeling predictions are generally consistent with the ambient measurements within the estimated uncertainty ranges, there may be a tendency for the *midrange* emissions to underpredict the measured concentrations. The extent of underprediction of the different congeners and homologue

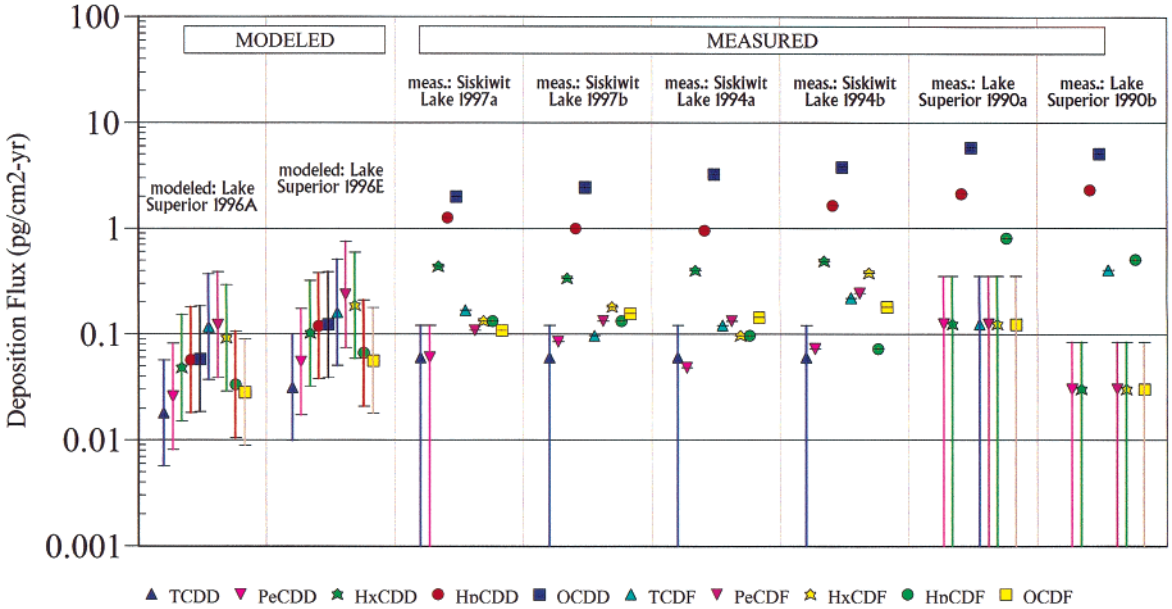

FIGURE 11. Modeled 1996 fluxes to Lake Superior compared to 1994 and 1997 fluxes to Siskiwit Lake on Isle Royale (*88*) and 1990 fluxes to Lake Superior (*5*, *87*) estimated from sediment core measurements. Two sets of model-estimated flux data are shown, corresponding to two different dry deposition methodologies (*A* and *E*; see SI). Nondetects in the measurements are plotted with a midpoint value at 1/2 the detection limit (DL), with a range of 0 to the DL. The Siskiwit Lake sediment DL was taken to be 10 pg/g (of dry sediment) for each homologue group (*89*). Measurements in Isle Royale and Lake Superior were each reported at two sediment sampling sites (*a* and *b*).

groups was generally similar, although the underpredictions for HpCDD and OCDD were somewhat greater than that for other homologue groups (see SI). A potential explanation for the underprediction of HpCDD and OCDD is discussed below.

This analysis used relatively coarse meteorological data fields and assumed that emissions were continuous for most sources. These factors can lead to large simulation errors for estimating concentrations at a given location, especially for short periods of time. Thus, while there were a number of shorter-duration (2 day) ambient PCDD/F measurements made at rural and semirural locations in Canada during 1996 (*86*), these measurements were not used for model evaluation purposes. A preliminary comparison of the modeling predictions with these measurements found that the model was able to satisfactorily predict the approximate value for only about half of these measurements. However, for these and the remaining measurements, it was found that the model (with midrange emissions estimates) tended to underestimate the ambient concentrations. Additional work, including detailed back-trajectory analyses, utilization of more highly resolved meteorological data, and more precise temporal resolution of regional emissions will be necessary to pinpoint potential causes of these underestimates.

As atmospheric deposition is believed to be the predominant dioxin loading pathway for Lake Superior, model-estimated deposition fluxes can be compared against those estimated from sediment cores. Pearson and colleagues (*5*, *87*) estimated historical fluxes through 1990 based on cores collected in the southwestern portion of Lake Superior and two nearby lakes. Baker and Hites (*88*) reported sediment-based flux measurements from 1888 to 1998 for Siskiwit Lake on Isle Royale in Lake Superior. Figure 11 presents a comparison of these sediment-based data with model estimates using two diverse dry deposition methodologies. It is important to note that available inventory information indicates that there may have been significant decreases in PCDD/F emissions during the 1990−1996 period. Thus, the fluxes measured in 1990 and 1994 would be expected to be higher than the 1996 modeled fluxes. Second, the model-estimated fluxes are for Lake Superior as a whole, while the sediment-based measured fluxes are for specific locations in Lake Superior. Thus, to the extent that there are spatial gradients in the deposition flux, the measurements may not represent the average flux for the whole lake. Indeed, the data from Pearson and co-workers (*5*, *87*) suggest that deposition gradients in the Lake Superior region may be significant, as sediment-based flux estimates varied between Lake Superior and the two other lakes in the region that were measured.

Nevertheless, for most of the homologue groups, the model estimated 1996 deposition fluxes for Lake Superior are consistent with the 1997 Siskiwit Lake measured fluxes, within the uncertainties in each. However, the model significantly underestimates the fluxes of OCDD and HpCDD. This discrepancy may be due to the hypothesized formation of OCDD and HpCDD in atmospheric droplets from pentachlorophenol (*66*), which, as noted above, was not included in this analysis. However, HpCDD and OCDD are estimated to contribute only about 2% of the total TEQ deposition due to their relatively low toxicities, and thus the effect of their underestimation is not particularly significant from a toxicological perspective.

The above evaluation exercises suggest that the model results are generally consistent with ambient measurements, but that there may be a tendency toward underestimation if the midrange emissions estimates are used. Keeping the emissions inventory constant, the degree of underestimation was found to be similar over a range of different modeling methodologies. Thus, underestimation errors in the emissions inventory may be the most likely cause of this tendency. This is not unexpected, given the omission from the inventory of several potentially important source categories and the large uncertainties present in the emissions estimates from the source categories that were included.

Model-Estimated Deposition to the Great Lakes

An example of the detailed source-receptor results of this analysis is presented in Figure 12, in which the aggregated contribution from sources within each U.S. county and

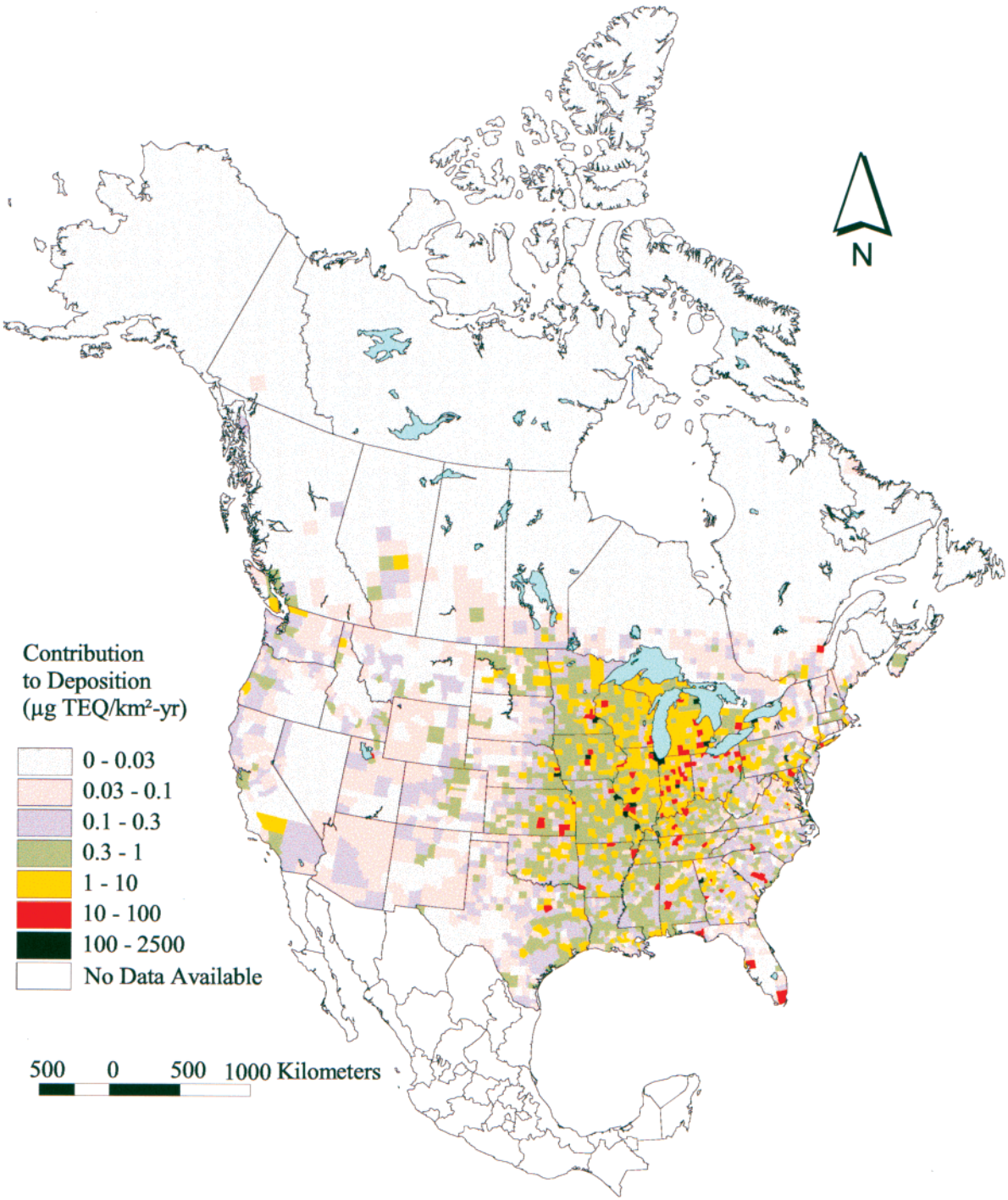

FIGURE 12. Geographical distribution of the estimated contributions to the 1996 atmospheric deposition of dioxin to Lake Superior.

Canadian grid square to dioxin deposition to Lake Superior is represented (see SI for maps for the other Great Lakes). Figure 13 shows the fraction of the model-predicted deposition to Lake Superior (13.4 g TEQ/yr) arising from each major source category in the emissions inventory. In this figure, the range of contributions shown for each source category is that arising from the estimated uncertainty in emissions for that class, and the midrange estimate is indicated.

The emissions and deposition contributions arising from different distance ranges from Lakes Superior and Michigan are presented in Figure 14. A substantial contribution of atmospheric deposition of dioxin (on a TEQ basis) occurs from relatively distant sources for Lake Superior, while a more significant fraction (~40%) of the deposition arises from emissions within 100 km of Lake Michigan. This difference is primarily due to greater emissions nearby Lake Michigan than nearby Lake Superior. Comparable analyses for the other Great Lakes show that the distance pattern for Lake Huron is comparable to Lake Superior, while Lakes Erie and Ontario have patterns similar to Lake Michigan. Sources in Mexico have not been included in this analysis; thus, the contribution to each of the lakes from the largest distances in Figures 14 is slightly underestimated. Given the distances involved, it is expected that the contribution of dioxin from Mexico to the Great Lakes will be relatively insignificant, but this hypothesis could be evaluated by extending this analysis to include an emissions inventory (and associated transfer coefficients) for sources for Mexico. An inventory for Mexico

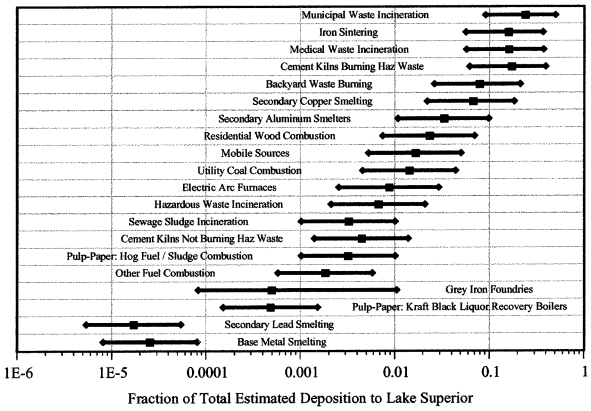

FIGURE 13. Fraction of the estimated 1996 dioxin atmospheric deposition contributions to Lake Superior arising from different categories of U.S. and Canadian emission sources.

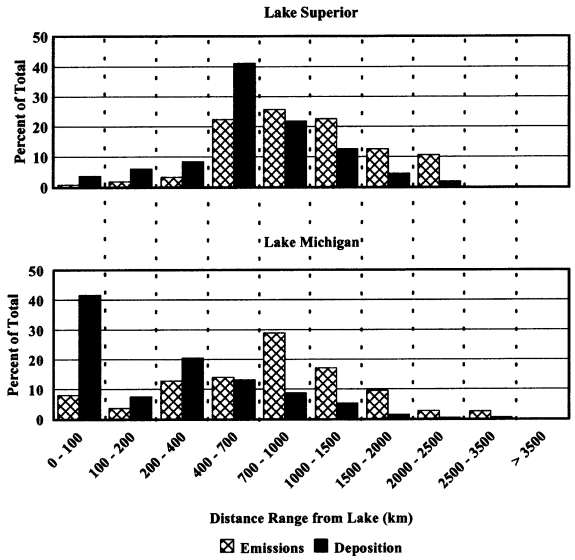

FIGURE 14. Fraction of total estimated 1996 emissions and deposition of dioxin to Lakes Superior and Michigan contributed from different distance ranges away from each lake.

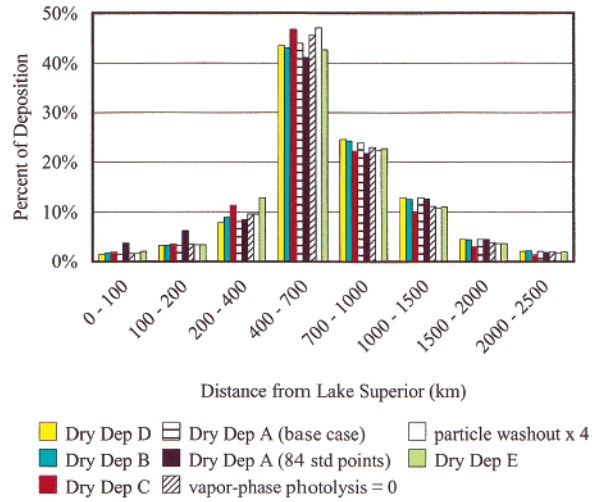

FIGURE 15. Effect of fate simulation variations on the geographical pattern of deposition contributions to Lake Superior. See SI for details regarding the different dry deposition algorithms and other fate estimation variations.

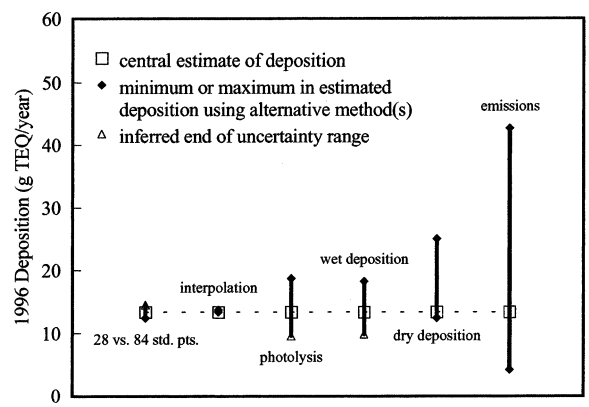

FIGURE 16. Uncertainties in model estimates of total 1996 dioxin deposition to Lake Superior. When variations in only one direction were evaluated, the other endpoint of the uncertainty range was inferred by assuming that the influence of the variation was approximately the same on either side of the central estimate.

has recently been prepared (*90*), allowing such an analysis to be carried out. Further extension of the analysis to include sources in additional countries might also be useful but would also be expected to add relatively little to the analysis of the dioxin input to the Great Lakes; in any event, this hypothesis could also be tested in future work.

Sensitivity Analyses and Uncertainties. A number of sensitivity analyses conducted for single-source, single-congener simulations were discussed above. Analogous analyses for multiple source simulations were conducted and will be briefly summarized here (see SI for details). First, the effect of different spatial interpolation methodologies was found to be minimal; there was at most a 5% variation in the predicted deposition to any Great Lake in the use of a wide range of interpolation methodologies. Second, the effect of the most important uncertainties in the fate estimation methodologies—algorithms for dry deposition, wet deposition, and photolysis—was evaluated. The relative contributions from sources within different distance ranges from Lake Superior are presented in Figure 15, as an example of these results. The same general pattern exists for all the variations, and this same consistency was found for the other Great Lakes. As a summary of the sensitivity analyses, Figure 16 shows uncertainties in the model-estimated deposition of dioxin to Lake Superior. The influence of six different aspects of the simulation are shown, including the number of standard source locations used (84 vs 28), the interpolation methodology, the photolysis rate, the characterization of wet and dry deposition, and the emissions themselves. Results for the other Great Lakes were similar. Thus, while uncertainties in the fate simulation methodology result in uncertainties in the magnitude of the model-predicted deposition to the Great Lakes, the estimates of the relative importance of different sources or source regions are not strongly affected. However, emissions uncertainties may have a pronounced effect on the overall predicted deposition, estimates of the relative importance of different sources and source regions, and the ability of the model to successfully reproduce ambient measurements.

Inherent variability in emissions and the inability to precisely model environmental fate and transport will always create uncertainty in estimates such as those attempted in this analysis. However, the *exact* contributions of individual sources to a given receptor do not need to be known for most purposes. Indeed, it may be enough to understand a few key issues: (1) the relative importance of the atmospheric deposition pathway relative to other loading pathways; (2) the geographical extent of the problem, i.e., the extent to which deposition arises from local, regional, continental, and global scales; and (3) the relative contribution of different

source categories. While every effort should be made to develop the most accurate possible answer to these questions, approximations can still be useful. Regarding the relative importance of the atmospheric pathway, there are two factors involved: (a) the amount of atmospheric deposition and (b) the amount of loading due to other pathways. As discussed above, the largest uncertainty in estimating the deposition amount is likely the emissions—resulting in an uncertainty of approximately a factor of 3 on either side of the central estimate. However, the loadings due to other pathways are also very uncertain (*4*), and this leads to large uncertainties in answering the first question. With regard to the second and third issues, the sensitivity analyses discussed above have shown that the overall patterns of contributions as a function of distance and the relative contributions of different source classes are not influenced significantly by methodological variations of the simulation. It may not particularly matter whether 70% or 50% of the contributing air sources arise from within 100 km of the lake—the policy response will likely be similar in either case. Only if the estimates are grossly incorrect will policy deliberations be seriously affected.

Moreover, while there are uncertainties in the assessment of atmospheric deposition presented here, there are substantial uncertainties in other aspects of the overall problem of dioxin contamination in the Great Lakes, e.g., the effects of such loading and the economic aspects of amelioration. The source-receptor results presented here appear to be relatively robust and, within the estimated uncertainty, are generally consistent with ambient measurements. To the extent that additional accuracy is desired, there are several actions that can be taken to reduce uncertainties, including the following: (a) increased ambient dioxin monitoring in the Great Lakes region, to allow more detailed model evaluation and to provide data for independent semiempirical estimates of atmospheric deposition; (b) additional efforts to improve the accuracy of emissions inventories—including timely updates; (c) collection of additional information on non-atmospheric loading pathways so that atmospheric contributions can be placed in their proper context; and (d) additional research on important fate processes for atmospheric dioxin, such as photolysis, hydroxyl radical reactions, vapor/particle partitioning, and wet and dry deposition.

Acknowledgments

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Supporting Information Available

Additional details regarding the PCDD/F emissions inventory, modeling single congeners from single sources, interpolation methods for estimating source—receptor relationships for multiple congeners emitted from multiple sources, model evaluation, sensitivity analyses of the spatial interpolation methodology, effect of variations in PCDD/F atmospheric fate estimation methodologies, and deposition to the Great Lakes for 1996. This material is available free of charge via the Internet at http://pubs.acs.org.

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