

Supplementary Material for

Modeling the Atmospheric Transport and Deposition of Mercury to the Great Lakes

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1. Atmospheric mercury chemistry scheme

In Table 1, we summarize the chemical equilibrium and reaction scheme utilized in this modeling. In Figure 1 we show illustrative rates (expressed as Hg^0 half-lives) of the gas and aqueous phase Hg^0 oxidation reactions. The figure shows the range of rates found in this modeling, using the rate constants chosen and a range of typical model-estimated reactant concentrations (see below).

Note that for these *illustrative* values shown in this figure, the values plotted for ozone and for the hydroxyl radical have been divided by two, to approximately account for the fact that the highest rates tend only to occur in daylight. The aqueous phase reactions have been adjusted to account for the very limited solubility of Hg^0 ; i.e., they are expressed on the basis of total Hg^0 . However, the aqueous phase reactions have not been adjusted for the fact that this phase does not always exist, and so, these reactions only occur at certain times in certain regions of the atmosphere. Therefore, their overall rates – averaged over the entire atmosphere and lifetime of the pollutant – will likely be significantly lower than that shown.

It can be seen from Figure 1 that of the gas-phase oxidation reactions, the reactions with ozone and hydroxyl radical appear to be the most important (i.e., have the lowest half-lives), with typical maximum rates corresponding to half-lives as small as ~1 month.

It can also be seen from Figure 1 that there is significant dependence on the amount of liquid water in the atmosphere, with cloud rates being in general much faster than deliquesced aerosol droplet rates. For the purposes of these illustrative values, liquid water contents of 0.5 and 0.005 g/m^3 were used for the cloud and deliquesced aerosol cases. The reason for this effect is that a smaller proportion of the total Hg^0 in the system is dissolved in the aqueous phase when there is less liquid water in the system.

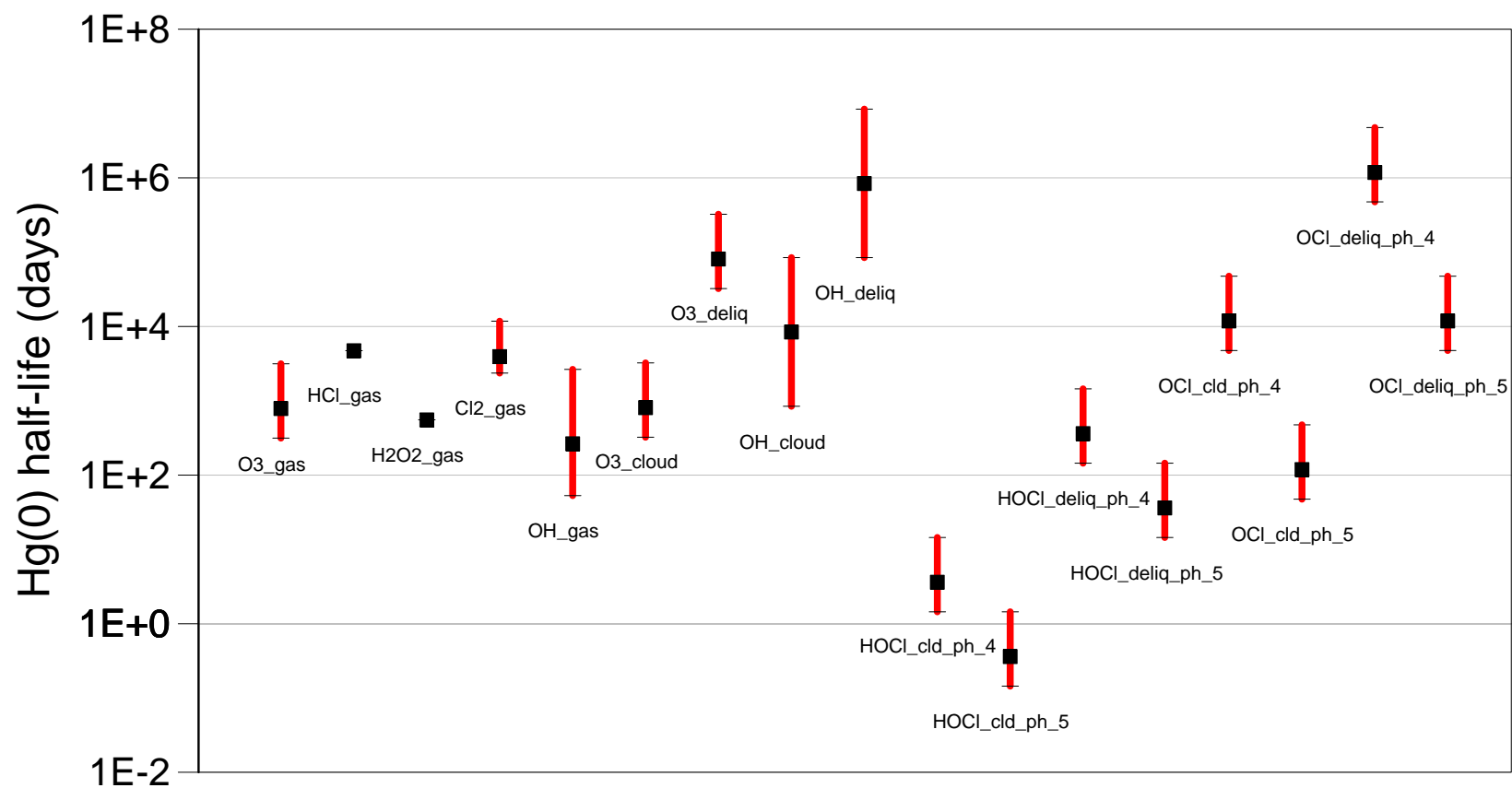
There is also a pH dependence of several of HOCl and OCl^- reactions, and for illustrative purposes, the rates of these reactions have been shown for $\text{pH} = 4$ and $\text{pH} = 5$; the rates are faster at higher pH. The reason for this dependence is that the rates here have been estimated based on an assumed gas-phase concentration of Cl_2 , and, the concentrations of dissolved HOCl and OCl^- in equilibrium with this Cl_2 are pH dependent.

Finally, it can be seen that of the aqueous phase reactions, the reaction with HOCl appears to be the most important, especially for the cloud water situation, with an Hg^0 half-life of ~1 day. As noted above, this rate refers only to situations when the pollutant actually is in a cloud, and thus will not be applicable at all times. Of all the oxidation reactions, this appears to be potentially the most important. These results are consistent with the modeling results of Lin and Pehkonen (1998a), who found that under many ambient conditions, this reaction would likely be more significant than other oxidation reactions.

For the gas-phase oxidation of Hg^0 by molecular chlorine (Cl_2), we used the rate constant reported by Calhoun and Prestbo (2001) of $4.0 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. We note that a similar rate constant of $(2.6 \pm 0.2) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ has recently been reported for this reaction (Ariya et al., 2002).

For the gas-phase ozone reaction (reaction 17 in Table 1), the rate constant utilized in this modeling was $3.0 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, the same constant used in many modeling exercises (Bullock and Brehme, 2002; all models utilizing this reaction in Ryaboshapko et al., 2002). In the original research by Hall (1995), it was found this rate constant appeared to increase significantly above this value in the presence of sunlight. Consistent with this, a range of model values from 3.0×10^{-20} to $42.0 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ was utilized by Lin and Pehkonen (1998b). With the rate constant used in this modeling, the reaction is fairly slow, with a half-life of approximately 1 year, or longer. However, utilizing the Lin and Pehkonen (1998b) range, the Hg^0 half-life might be as low as ~20 days under high ozone conditions (ozone = 100 ppb).

Figure 1. Illustrative, Typical Rates of Gas and Aqueous Phase Hg(0) Oxidation Reactions



Aqueous phase rates have been adjusted for limited solubility of Hg(0) in aqueous phase

"cld" is estimate for cloud water (with liquid water content (LWC) = 0.5 g/m³); "deliq" for deliquesced aerosol (LWC=0.005 g/m³)

Table 1. Atmospheric chemistry scheme for mercury			
#	Chemical Expression	Rate or Equilibrium Constant	Reference
gas liquid equilibrium			
1	$\text{Hg}_{(\text{aq})}^0 \leftrightarrow \text{Hg}_{(\text{gas})}^0$	0.11 molar/atm	Sanemasa (1975).
2	$\text{HgCl}_{2(\text{aq})} \leftrightarrow \text{HgCl}_{2(\text{gas})}$	1.4E+6 molar/atm	Lindqvist and Rodhe (1985)
3	$\text{Hg}(\text{OH})_{2(\text{aq})} \leftrightarrow \text{Hg}(\text{OH})_{2(\text{gas})}$	1.2E+4 molar/atm	Lindqvist and Rodhe (1985)
4	$\text{O}_{3(\text{aq})} \leftrightarrow \text{O}_{3(\text{gas})}$	0.0113 molar/atm	Seinfeld and Pandis (1998)
5	$\text{SO}_{2(\text{aq})} \leftrightarrow \text{SO}_{2(\text{gas})}$	1.23 molar/atm	Seinfeld and Pandis (1998)
6	$\text{Cl}_{2(\text{aq})} \leftrightarrow \text{Cl}_{2(\text{gas})}$	0.076 molar/atm	Lin and Pehkonen (1998a)
7	$\text{H}_2\text{O}_{2(\text{aq})} \leftrightarrow \text{H}_2\text{O}_{2(\text{gas})}$	7.4E+4 molar/atm	Seinfeld and Pandis (1998)
aqueous phase equilibrium (<i>all species in aqueous phase</i>)			
8	$\text{HgCl}_2 \leftrightarrow \text{Hg}^{+2} + 2 \text{Cl}^{-1}$	1.0E-14 molar ²	Sillen and Martell (1964)
9	$\text{Hg}(\text{OH})_2 \leftrightarrow \text{Hg}^{+2} + 2 \text{OH}^{-1}$	1.0E-22 molar ²	Sillen and Martell (1964)
10	$\text{HCl} \leftrightarrow \text{H}^{+} + \text{Cl}^{-1}$	1.7E+6 molar	Marsh and McElroy (1985)
11	$\text{Cl}_2 \leftrightarrow \text{HOCl} + \text{Cl}^{-1} + \text{H}^{+}$	5.0E-4 molar ²	Lin and Pehkonen (1998a)
12	$\text{HOCl} \leftrightarrow \text{OCl}^{-1} + \text{H}^{+}$	3.2E-8 molar	Lin and Pehkonen (1998a)
13	$\text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HSO}_3^{-1} + \text{H}^{+}$	1.23E-2 molar	Seignuer <i>et al.</i> (2000)
14	$\text{HSO}_3^{-1} \leftrightarrow \text{SO}_3^{-2} + \text{H}^{+}$	6.6E-8 molar	Seinfeld and Pandis (1998) citing Smith and Martell (1976)
15	$\text{Hg}^{+2} + \text{SO}_3^{-2} \leftrightarrow \text{HgSO}_3$	5.0E+12 molar ⁻¹	Munthe et al. (1991)
16	$\text{HgSO}_3 + \text{SO}_3^{-2} \leftrightarrow \text{Hg}(\text{SO}_3)_2^{-2}$	2.5E+11 molar ⁻¹	Munthe et al. (1991)
gas phase reactions (<i>all species in gas phase</i>)			
17	$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg}(\text{p})$	3.0E-20 cm ³ /molec-sec	Hall (1995)
18	$\text{Hg}^0 + \text{HCl} \rightarrow \text{HgCl}_2$	1.0E-19 cm ³ /molec-sec	Hall and Bloom (1993)
19	$\text{Hg}^0 + \text{H}_2\text{O}_2 \rightarrow \text{Hg}(\text{p})$	8.5E-19 cm ³ /molec-sec	Tokos et al. (1998) (upper limit for rate constant based on their experiments).
20	$\text{Hg}^0 + \text{Cl}_2 \rightarrow \text{HgCl}_2$	4.0E-18 cm ³ /molec-sec	Calhoun and Prestbo (2001)
21	$\text{Hg}^0 + \text{OH}\bullet \rightarrow \text{Hg}(\text{p})$	8.7E-14 cm ³ /molec-sec	Sommar et al. (2001)

aqueous phase reactions (<i>all species in aqueous phase unless noted</i>)			
22	$\text{Hg}^0 + \text{O}_3 \rightarrow \text{Hg}^{+2}$	$4.7\text{E}+7 \text{ (molar-sec)}^{-1}$	Munthe (1992)
23	$\text{Hg}^0 + \text{OH}\bullet \rightarrow \text{Hg}^{+2}$	$2.0\text{E}+9 \text{ (molar-sec)}^{-1}$	Lin and Pehkonen (1997)
24	$\text{HgSO}_3 \rightarrow \text{Hg}^0$	$T^*e^{((31.971*T)-12595.0)/T} \text{ sec}^{-1}$ [T = temperature (K)]	Van Loon et al. (2002)
25	$\text{Hg(II)} + \text{HO}_2\bullet \rightarrow \text{Hg}^0$	$\sim 0 \text{ (molar-sec)}^{-1}$	Gardfeldt and Jonnson (2003)
26	$\text{Hg}^0 + \text{HOCl} \rightarrow \text{Hg}^{+2}$	$2.09\text{E}+6 \text{ (molar-sec)}^{-1}$	Lin and Pehkonen (1998a)
27	$\text{Hg}^0 + \text{OCl}^{-1} \rightarrow \text{Hg}^{+2}$	$1.99\text{E}+6 \text{ (molar-sec)}^{-1}$	Lin and Pehkonen (1998a)
28	$\text{Hg(II)} \leftrightarrow \text{Hg(II)}_{(\text{soot})}$	$9.0\text{E}+2 \text{ liters/gram;}$ $t = 1/\text{hour}$	<i>eqbrm</i> : Seigneur et al. (1998); <i>rate</i> : Bullock and Brehme (2002).
29	$\text{Hg}^{+2} + h\nu \rightarrow \text{Hg}^0$	$(\text{sec})^{-1}$ $6.0\text{E}-7 \text{ (maximum)}$	Xiao et al. (1994); Bullock and Brehme (2002)

2. Methodology used to estimate concentrations of reactants and other necessary parameters in the atmospheric chemistry scheme

Mercury interacts with a number of compounds in the atmosphere, and estimates of the concentration of all relevant species must be accomplished in the simulation. In this modeling, a number of techniques were used to estimate the concentrations of such species, as summarized in Table 2.

Ambient data were used, as described below, to estimate SO₂, O₃, and soot concentrations, and the pH and Cl⁻ concentration of aqueous droplets in the atmosphere. The data were linearly “filled-in” for any missing values. For example, if the measured value was 10 ppb at a particular time period, the next two time periods were missing, and the following time period had a measured value of 40 ppb, then the value for the two missing time periods were estimated to be 20 ppb and 30 ppb, respectively. The data were then fit to a 1x1 degree lat/long grid using a weighted averaging procedure, based on distance from each grid point. This allowed the convenient estimation of the necessary values at any location in the modeling domain at any time during the 1996 modeling period.

For SO₂ and O₃, ambient monitoring data from the U.S. EPA CASTNET network were used. The online CASTNET database contained weekly SO₂ concentrations at 68 sites for some or all of 1996 (only 6 of those sites had data available for at least 90% of the year). Annual averages at these sites ranged from 0.2 - 8.8 µg/m³. For O₃, hourly concentrations were available at 65 sites during 1996. On average, data were available for 71% of the hours in 1996 for these 65 sites, and annual averages ranged from approximately 20-50 ppb.

SO₂ and O₃ data from the U.S. EPA AIRS database and from Canada were not used because a number of the sites were located in heavily polluted areas and it was not possible to determine how to develop reasonable gridded averages from these data. The CASTNET monitoring data network is designed to be regionally representative and thus was deemed most appropriate for this modeling exercise.

For soot, data from the IMPROVE monitoring network were used. Daily average values were reported twice per week at 55 sites for some or all of 1996. Annual site averages ranged from 0.1 - 1 µg/m³.

For the pH and chloride ion concentration of aqueous droplets in the atmosphere, data from the National Atmospheric Deposition Program (NADP) and from a comparable program in Canada were utilized. Weekly precipitation data for 187 NADP and 74 Canadian sites were available for 1996. Annual pH averages ranged from 4.2 to 5.9. Annual average chloride ion concentrations ranged from less than 0.1 mg/liter to 1.4 mg/liter. As would be expected, higher concentrations of chloride ion were found in coastal locations, due to the influence of the sea salt aerosol.

Compared to the above species and parameters, relatively little is known about the concentrations of inorganic reactive chlorine species in the atmosphere (Graedel and Keene, 1995). Evidence of inorganic chlorine gases other than HCl was only recently reported (Pszenny *et al.*, 1993), who measured concentrations of Cl₂ ranging from <13 to 127 pptv. Consistent with these data, Spicer *et al.* (1998) reported measurements of Cl₂ concentrations in coastal air, ranging from <10 to 150 ppt. The processes influencing Cl₂ concentrations in the atmosphere are complex (Knipping and Dabdub, 2002), and there are few measurements available to support accurate estimates for modeling, analogous to the procedure followed above for SO₂ and other more “conventional” species.

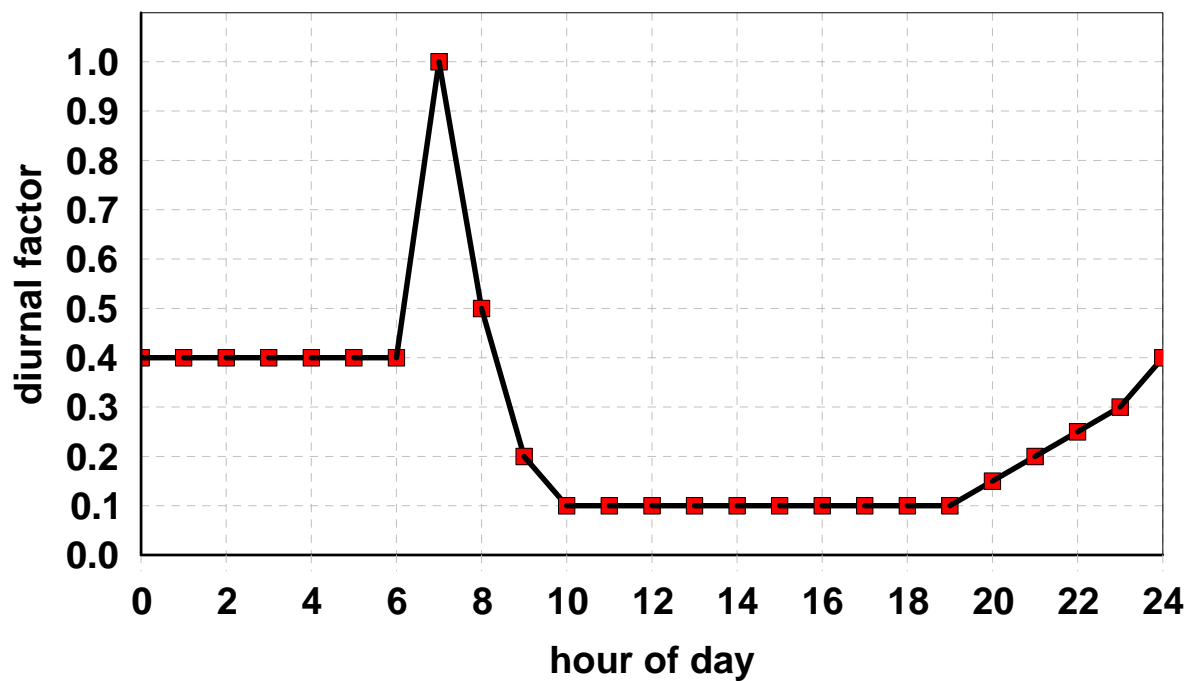
It is known that concentrations of Cl₂ tend to be smaller during the day because it is subject to photolysis. As an approximation, we used the following procedure to estimate the gas-phase Cl₂ concentration. First, an approximate diurnal variation factor (see Figure 2), ranging from 0 - 1 was estimated based on available theoretical and experimental data. This factor was then multiplied by the Cl₂ (gas, maximum) concentrations – in the manner shown below – to get an estimate of the Cl₂_gas concentration.

- (a) for $[\text{Cl}^{-1}] < 0.1 \text{ mg/liter}$, Cl₂ (gas, maximum) = 20 ppt;
- (b) for $0.1 < [\text{Cl}^{-1}] < 0.5 \text{ mg/liter}$, Cl₂ (gas, maximum) (ppt) = 200 x $[\text{Cl}^{-1}](\text{mg/liter})$;
- (c) for $[\text{Cl}^{-1}] > 0.5 \text{ mg/liter}$, Cl₂ (gas, maximum) = 100 ppt.

This procedure is admittedly somewhat simplistic, but, it is hoped that reasonably representative average concentrations and the broad features of the spatial variation of atmospheric Cl₂ were estimated. Sensitivity analysis showed that the results were not strongly influenced when the Cl₂ estimation procedure was varied, e.g., omission of the diurnal variation.

There is another potentially important uncertainty in estimating the rates of the aqueous-phase and gas-phase chlorine-mediated reactions. In one method, the gas phase concentration of Cl₂ is regarded as a constant, and the corresponding equilibrium concentrations of HOCl and OCl⁻¹ are estimated. In an alternative method, the *total* atmospheric concentration of Cl_{2(gas)}, Cl_{2(aq)}, HOCl_(aq) and OCl⁻¹_(aq) is regarded as a constant, and the equilibrium relationships are used to estimate the relative amounts of each species. There is very limited available data, but the data do not appear to indicate a dependence of Cl_{2(gas)} on atmospheric liquid water content. Spicer *et al.* (1998) found similar concentrations of Cl_{2(gas)} with and without heavy fog conditions. In the measurements by Pszenny *et al.* (1993), higher Cl_{2(gas)} concentrations tended to occur at higher humidities. Both data sets suggest that the first method [constant Cl_{2(gas)}] may be more realistic. Moreover, the mechanisms for Cl₂ generation appear to be droplet-related (Vogt *et al.* 1996; Oum *et al.*, 1998), and so this may explain why the gas-phase concentration can be sustained when droplets are present even though a fraction of the Cl₂-related suite of species is dissolved in the droplets. Therefore this approach was used in the present analysis. A sensitivity analysis was carried out using each of the alternative methodologies above and it was found that the simulation results were not strongly affected by this uncertainty.

Figure 2. Assumed Diurnal Pattern for Gas-Phase Cl₂



We note that another source of uncertainty is that there may be other chlorine-containing species prevalent during the day (e.g., atomic chlorine, formed from the photolysis of Cl_2) that may oxidize Hg^0 . Bromine-containing compounds may also be important. These other reactants were not included in the chemical reaction scheme used in this modeling, as data regarding their concentrations and reaction rates with atmospheric mercury species are not sufficient to allow their inclusion in the simulation.

Data for HCl is similarly very scarce. Graedel and Keene (1995) summarized available ambient measurements and found values on the order of 1 ppb. Coastal regions did not appear to have systematically higher concentrations of HCl. For the purposes of this modeling, a value of 1 ppb was assumed throughout the modeling domain. Based on available data, this compound is relatively inefficient at oxidizing Hg^0 (see Figure 1), and so, this very approximate estimation methodology was deemed adequate for these simulations.

Atmospheric hydrogen peroxide H_2O_2 is an important atmospheric reactant (Sakugawa *et al.*, 1990), but is relatively inefficient at oxidizing Hg^0 (see Figure 1). Measurements of atmospheric H_2O_2 concentrations show typical concentrations on the order of 1 ppb (Sakugawa *et al.*, 1990; Boatman *et al.* 1990; Daum *et al.*, 1990; Van Valin *et al.*, 1990). For the purposes of this modeling, a value of 1 ppb was assumed throughout the modeling domain. While admittedly crude, this estimate was deemed adequate for these simulations due to the relative insignificance of this reaction in oxidizing Hg^0 .

Finally, atmospheric concentrations of the hydroxyl radical were estimated using data presented by Lu and Khalil (1991), who presented model-estimated values of $\text{OH}\bullet$ concentration as function of time of day, season, elevation, and latitude.

Table 2. Estimation methodologies for compounds important in the atmospheric chemistry of mercury		
Compound	Method of Estimation	Source of Data or Estimate
SO ₂	1996 ambient measurements	CASTNET monitoring data (U.S. EPA) [http://www.epa.gov/castnet]
O ₃	1996 ambient measurements	CASTNET monitoring data (U.S. EPA) [http://www.epa.gov/castnet]
soot	1996 ambient measurements	IMPROVE monitoring data (U.S. National Park Service) [http://vista.cira.colostate.edu/improve]
pH	1996 ambient measurements	NADP monitoring data [http://nadp.sws.uiuc.edu ; Larson 2003]
		NatChem monitoring data (Environment Canada) [Ro and Vet, 2002].
Cl ⁻¹ _(aq)	1996 ambient measurements	NADP monitoring data [http://nadp.sws.uiuc.edu ; Larson 2003]
		NatChem monitoring data (Environment Canada) [Ro and Vet, 2002].
Cl ₂	parameter-ization based on Cl ⁻¹ _(aq)	gas-phase maximum concentration assumed to be proportional to measurement-based estimates of aqueous phase chloride ion concentrations; and an additional diurnal factor was included that was multiplied by this gas-phase maximum concentration.
OH•	parameter-ization based on model	Parameterization involving elevation, latitude, season, and time of day, based on results presented by Lu and Khalil (1991).
H ₂ O ₂	assumed value	Total atmospheric concentration assumed equivalent to a gas-phase concentration of 1 ppbv.
HCl	assumed value	Total atmospheric concentration assumed equivalent to a gas-phase concentration of 1 ppbv.

3. Geographical distribution of mercury contributions to the Great Lakes

Maps showing the geographical distribution of mercury contributions to Lakes Huron, Michigan, Erie, and Ontario are shown below – Figures 3 through 6 – analogous to the map shown for Lake Superior in the main body of the paper.

Figure 3. Geographic distribution of contributions to atmospheric deposition of mercury to Lake Huron ($\mu\text{g}/\text{km}^2\text{-yr}$).

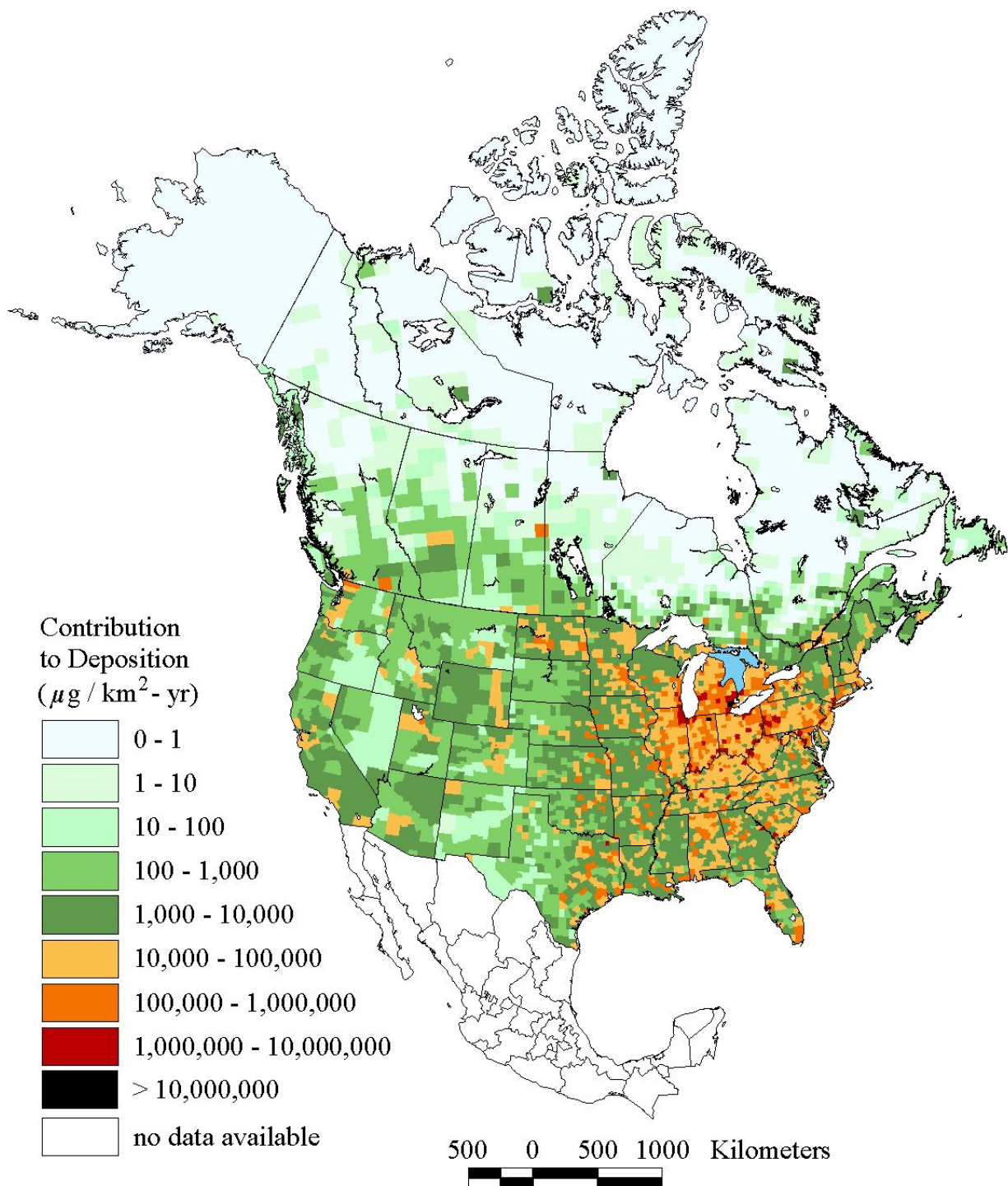


Figure 4. Geographic distribution of contributions to atmospheric deposition of mercury to Michigan ($\mu\text{g}/\text{km}^2\text{-yr}$).

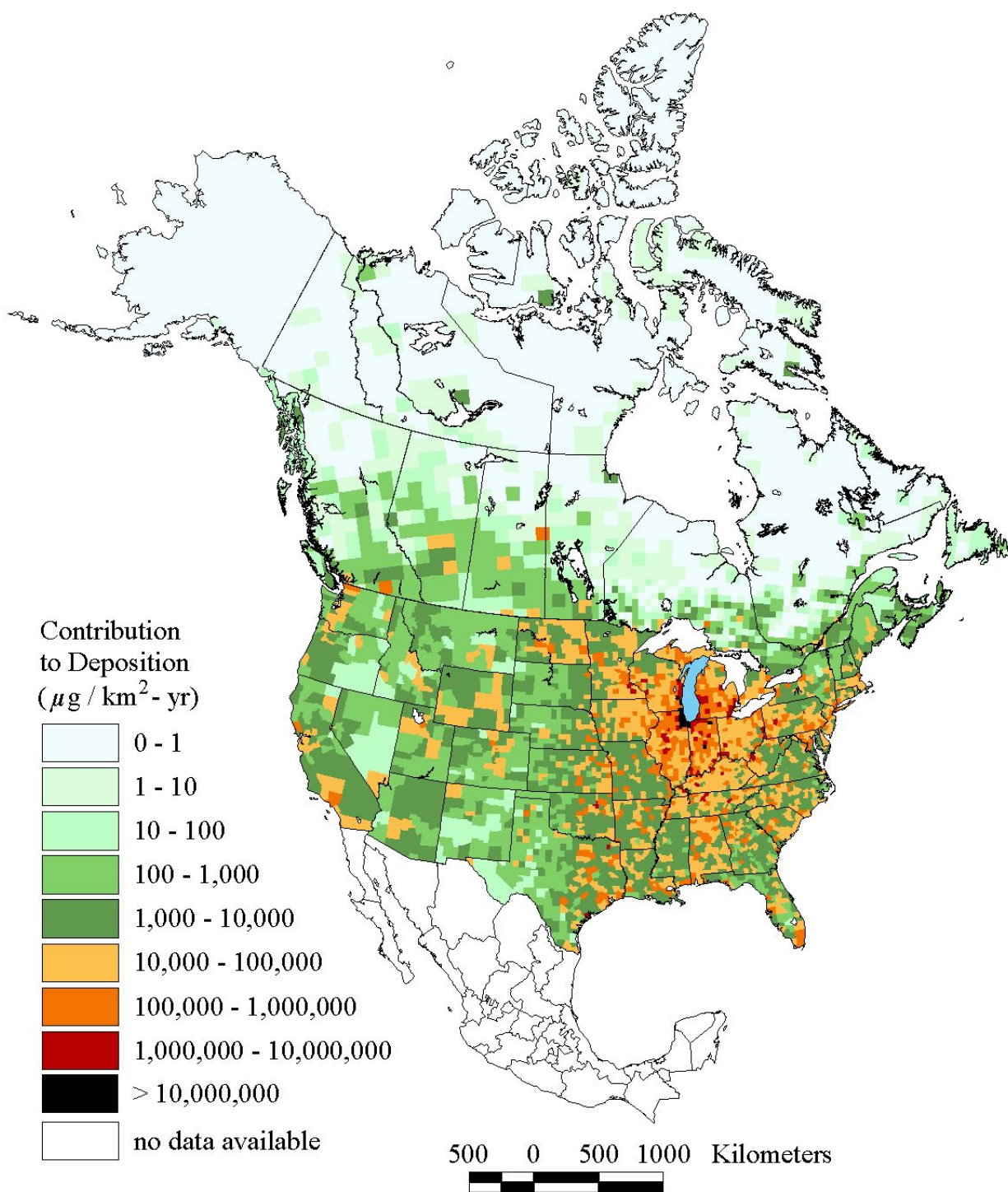


Figure 5. Geographic distribution of contributions to atmospheric deposition of mercury to Lake Erie ($\mu\text{g}/\text{km}^2\text{-yr}$).

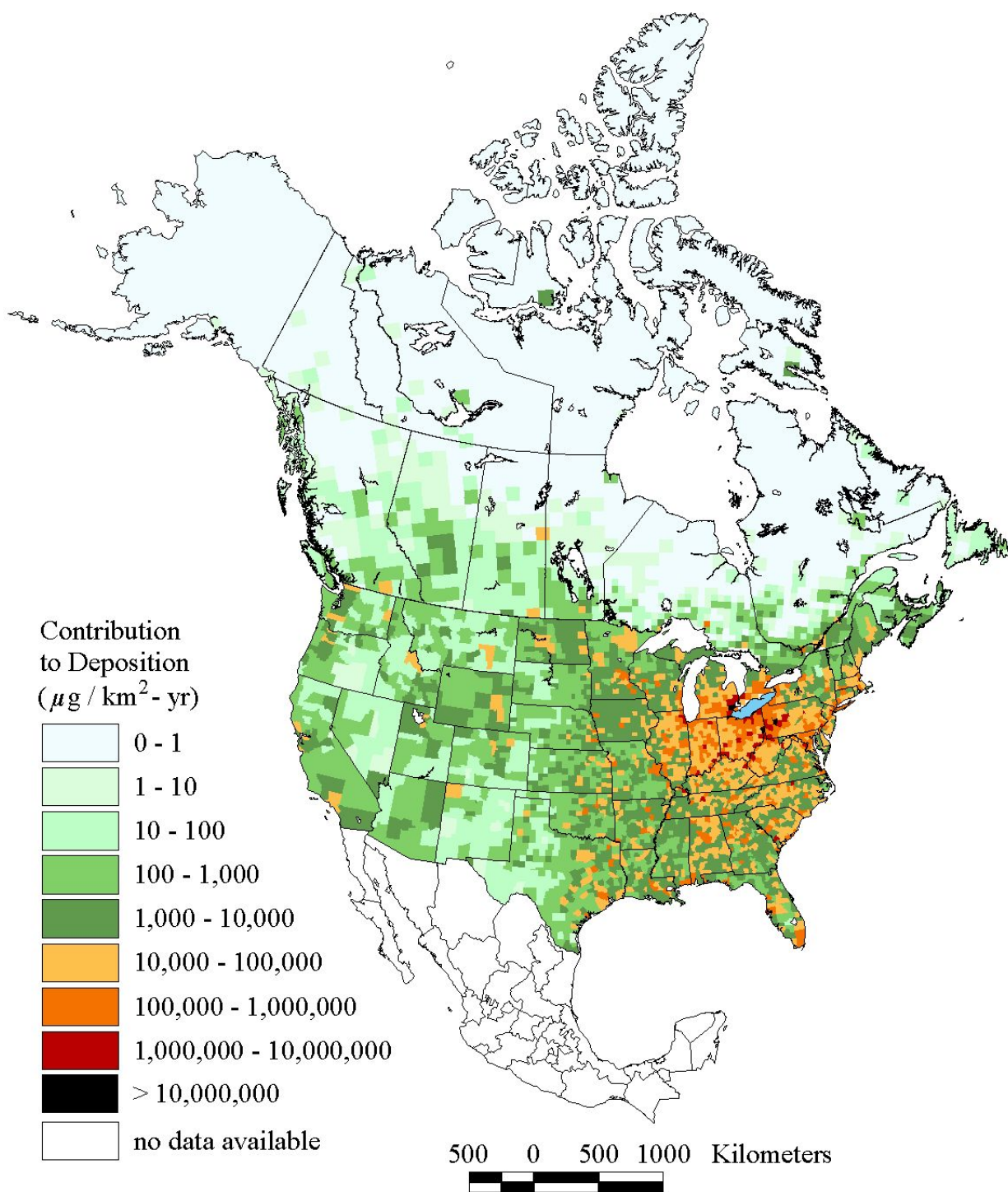
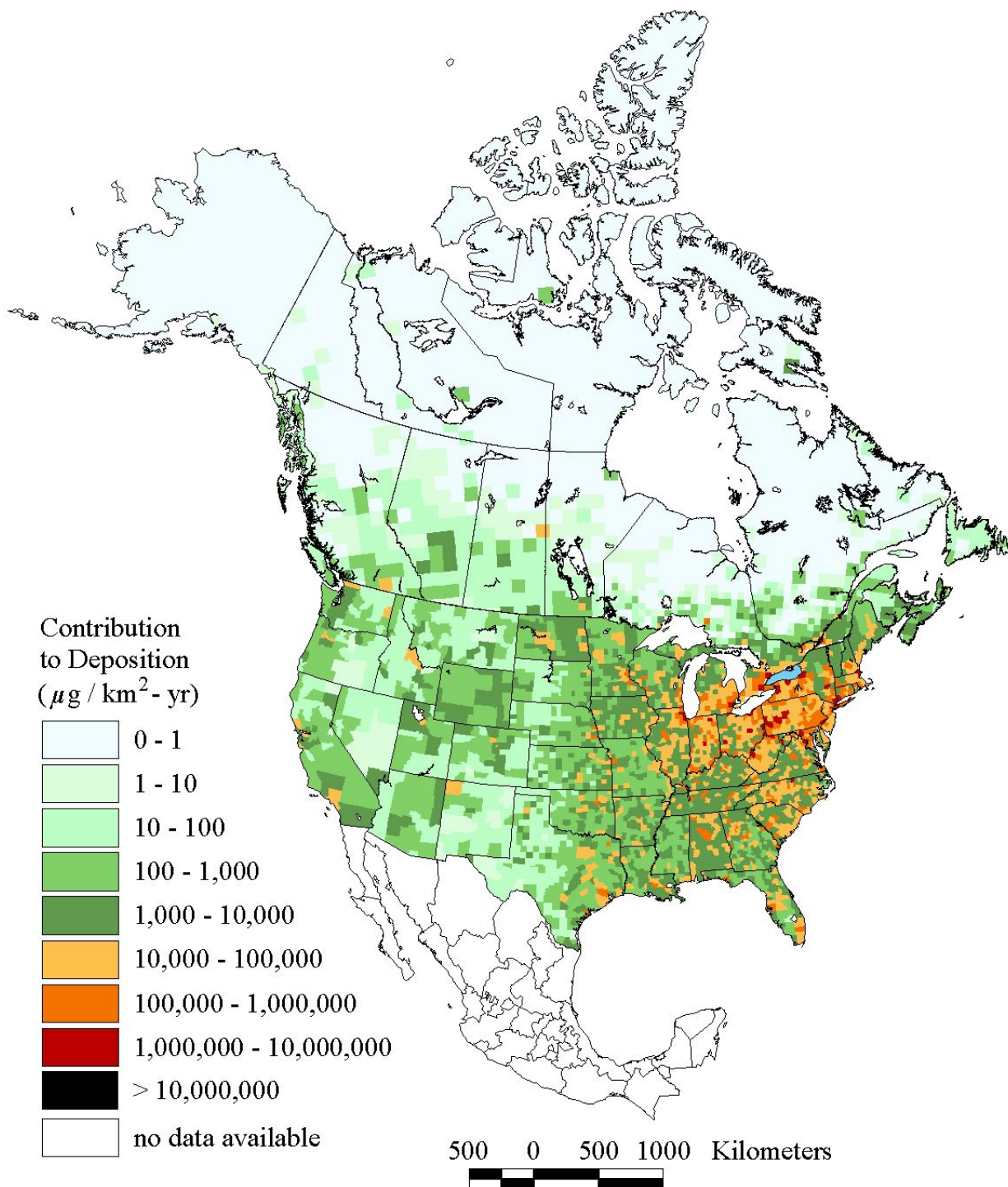


Figure 6. Geographic distribution of contributions to atmospheric deposition of mercury to Lake Ontario ($\mu\text{g}/\text{km}^2\text{-yr}$).



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