HYSPLIT Modeling in Phase II of the EMEP Mercury Modeling Intercomparison Study

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Expert Meeting on
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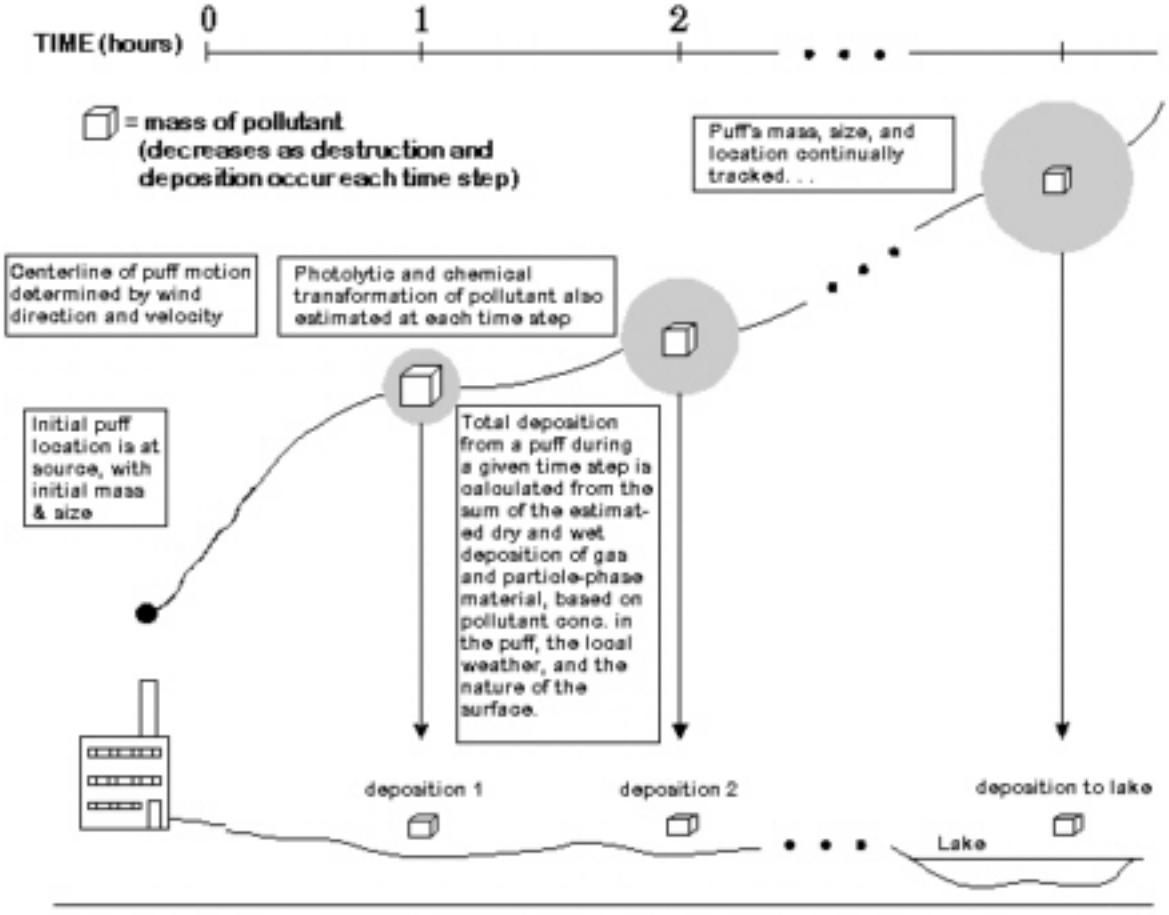
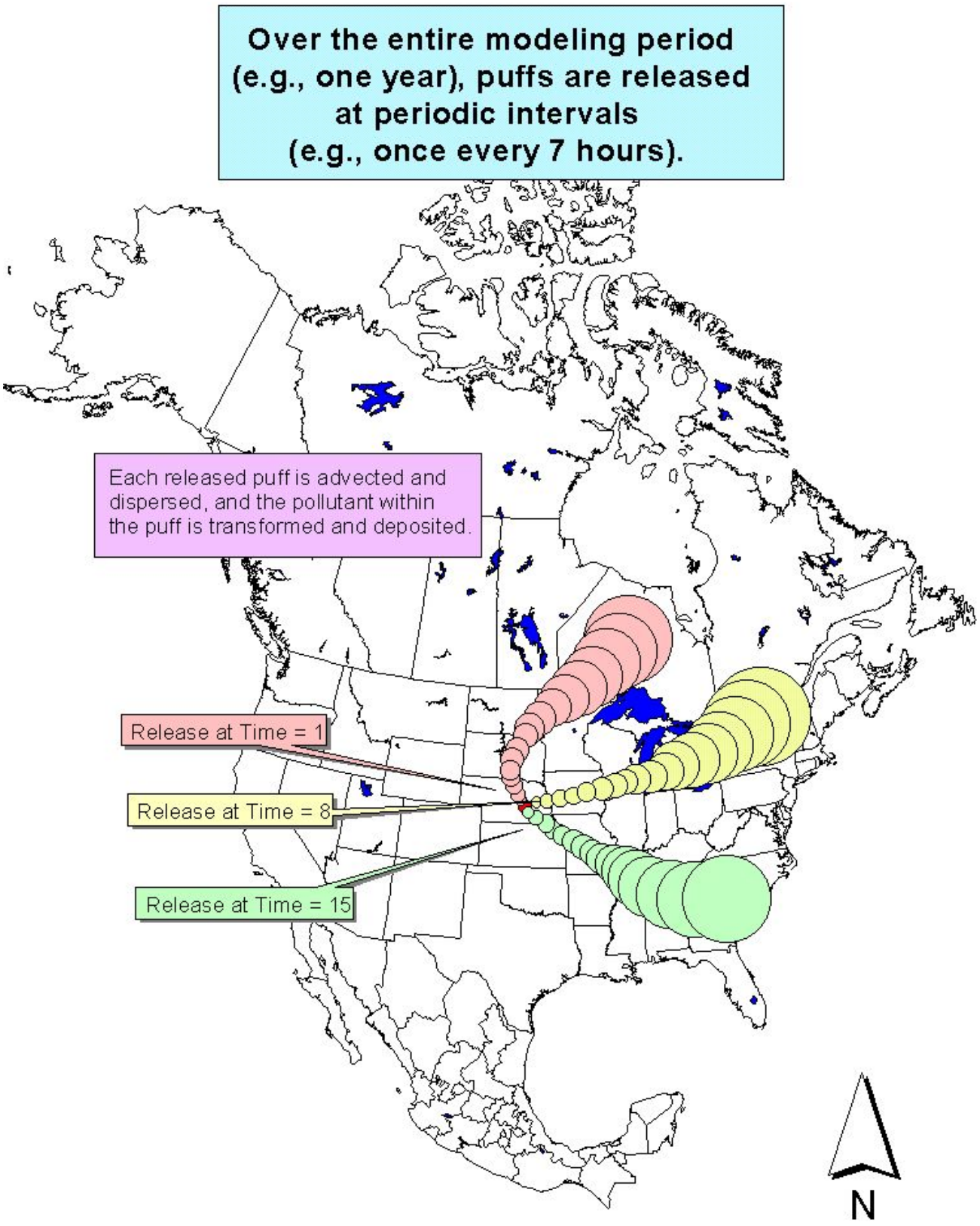
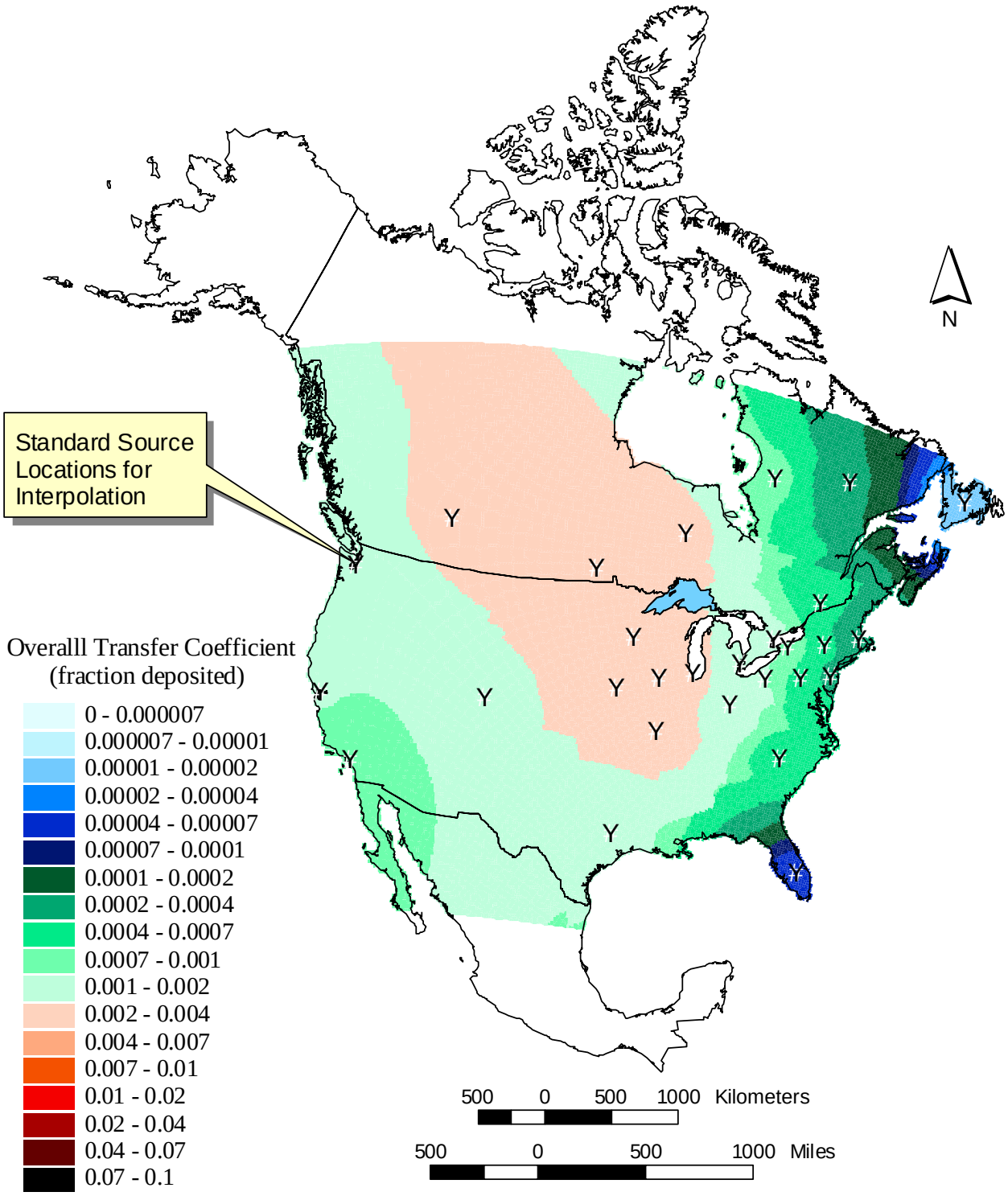
Figure 1. Lagrangian Puff Air Transport and Deposition Model

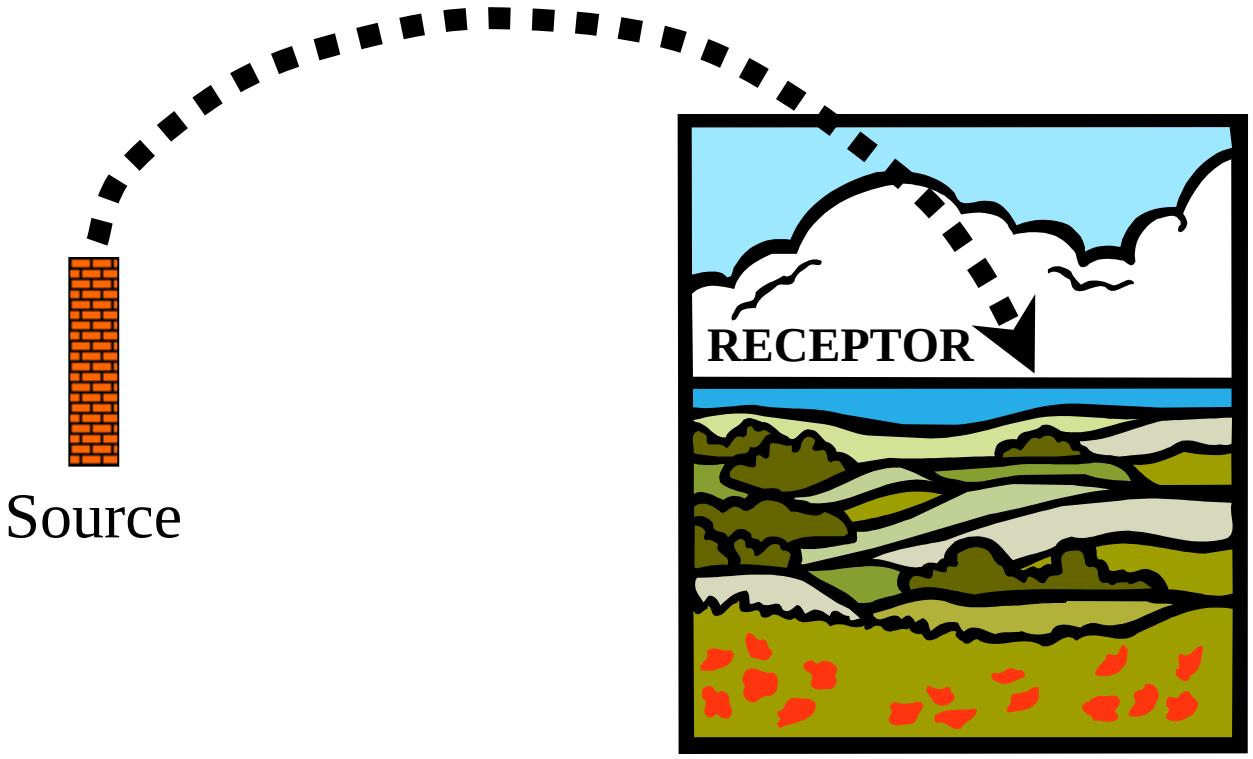



Over the entire modeling period (e.g., one year), puffs are released at periodic intervals (e.g., once every 7 hours).
Each released puff is advected and dispersed, and the pollutant within the puff is transformed and deposited.
Release at Time = 1
Release at Time = 8
Release at Time = 15
N

Fraction of Mercury Emissions Deposited in Lake Superior
(grams of total Hg deposited per year / grams of Hg (0) emitted per year)

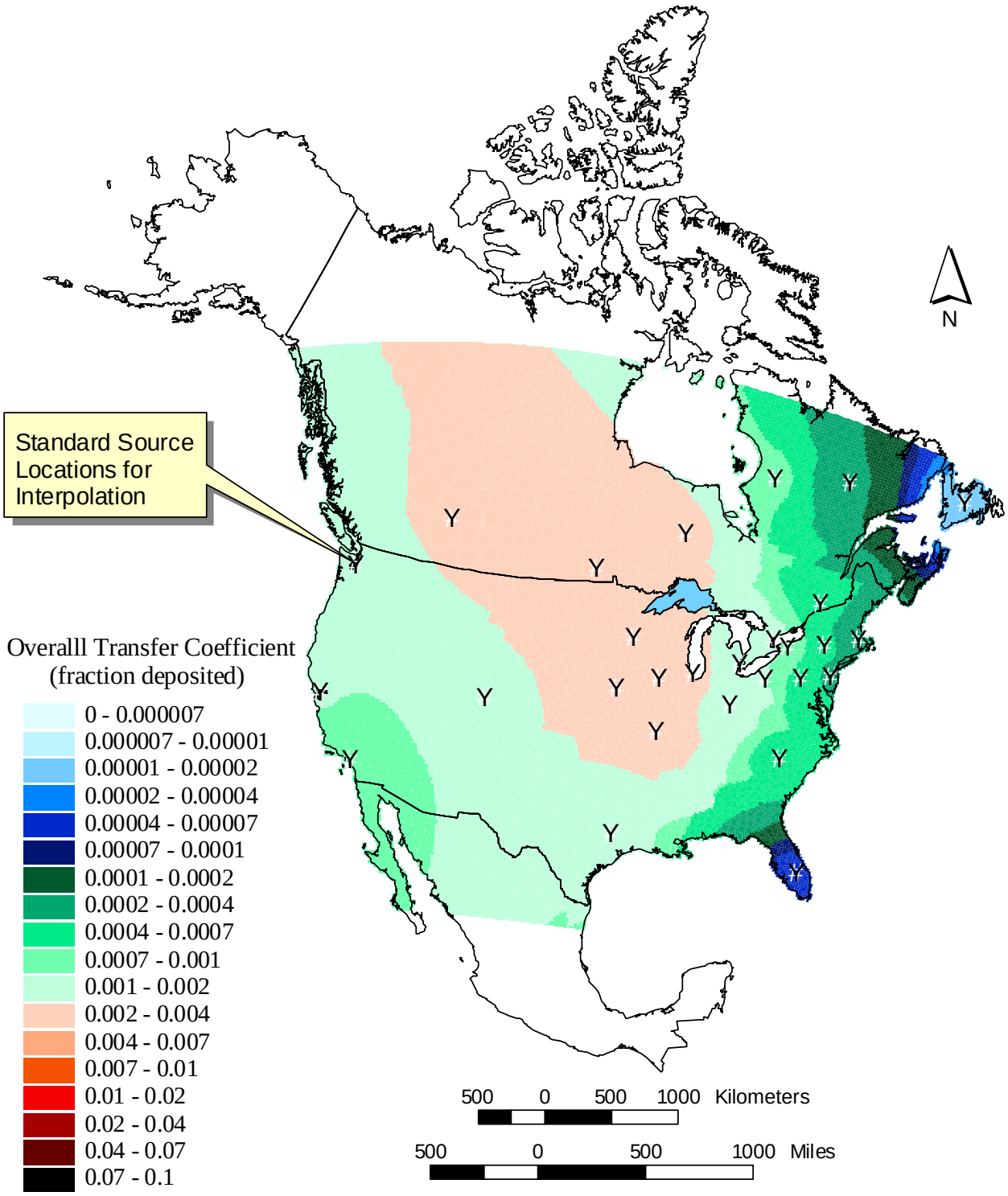


Is the source's impact on any given receptor proportional to its emissions? (for the same emissions speciation)

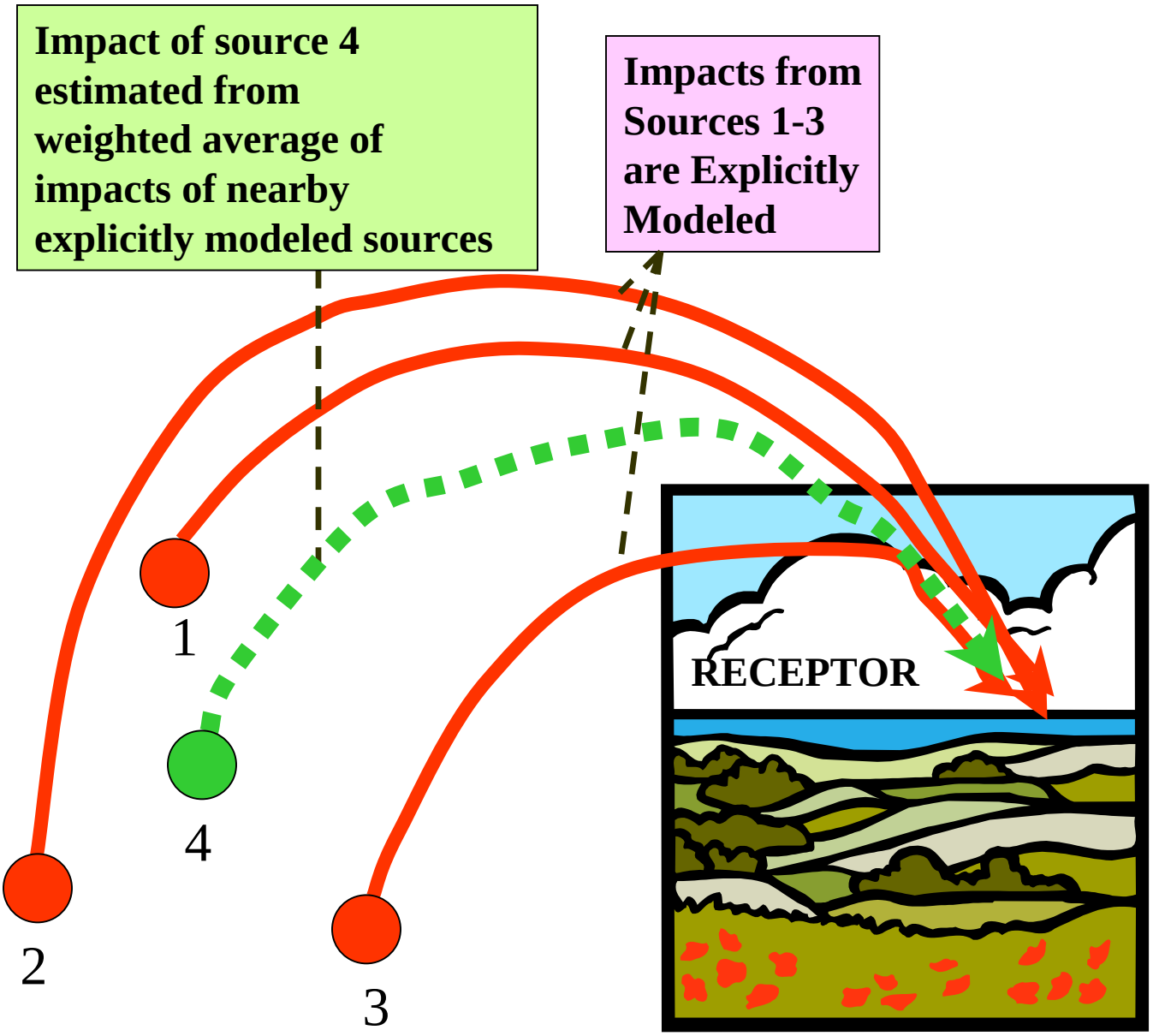


Impact of 5 gram/hr source	? =	5 x	Impact of 1 gram/hr source

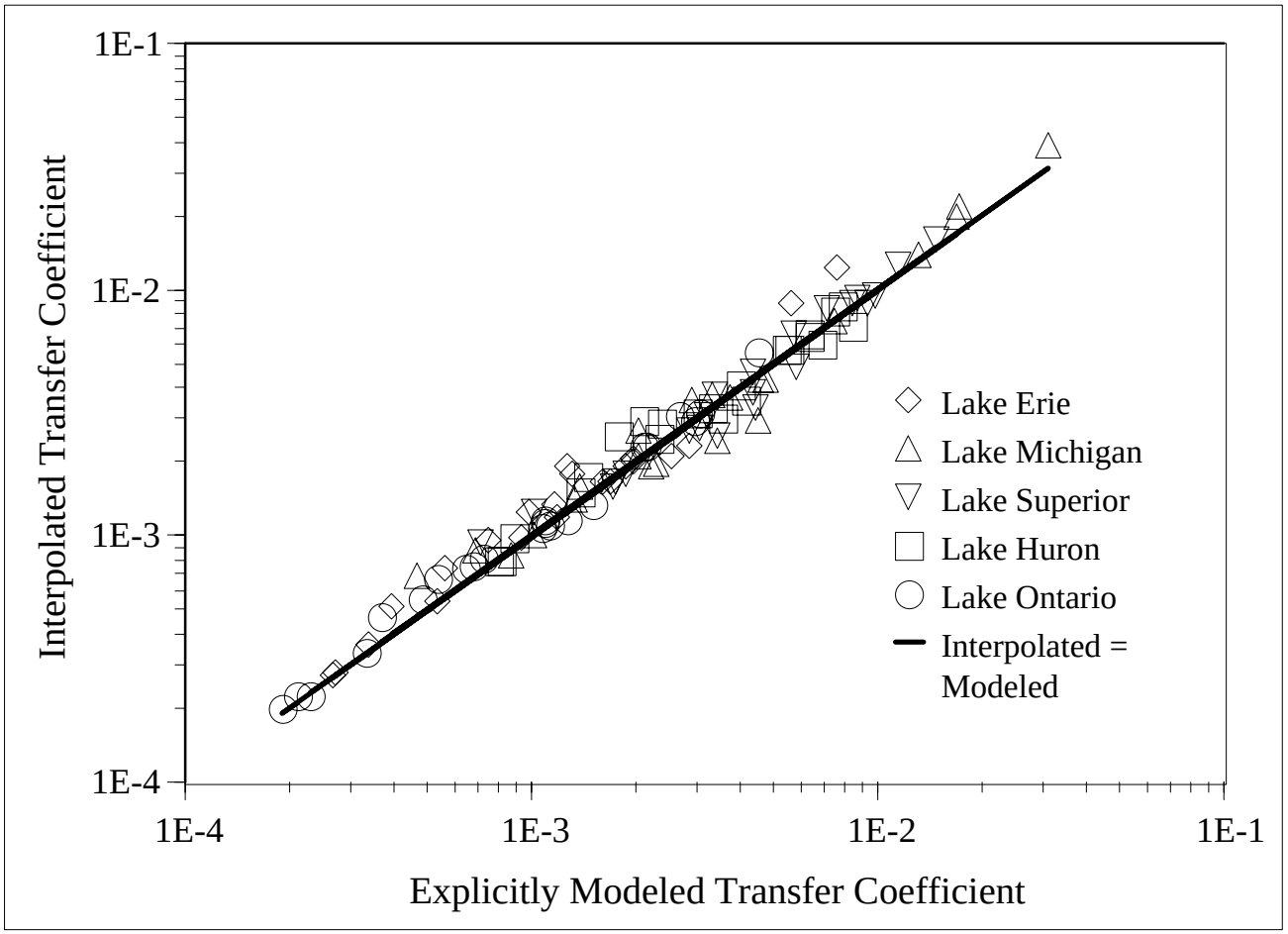
Fraction of Mercury Emissions Deposited in Lake Superior
(grams of total Hg deposited per year / grams of Hg (0) emitted per year)



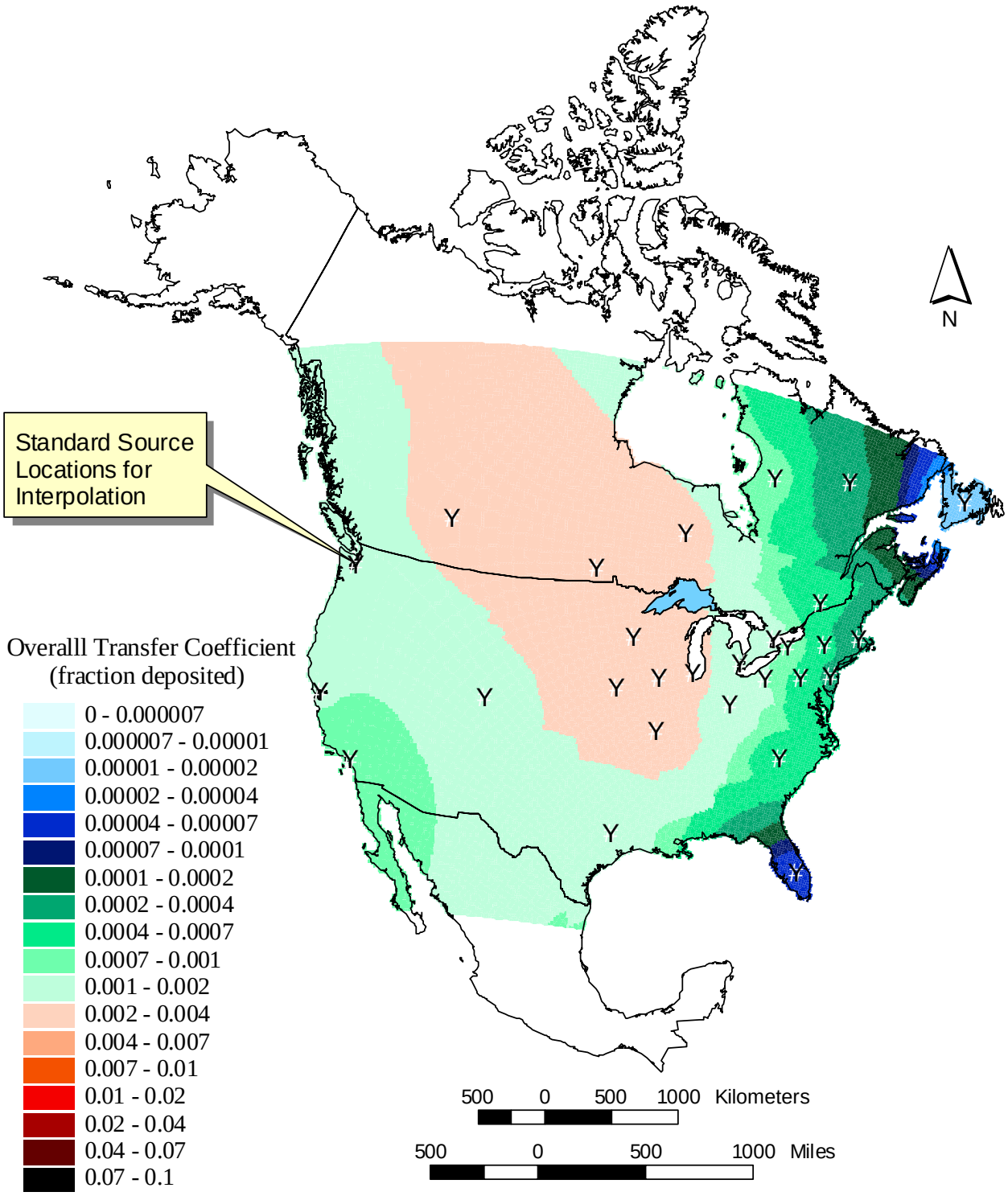
Spatial interpolation



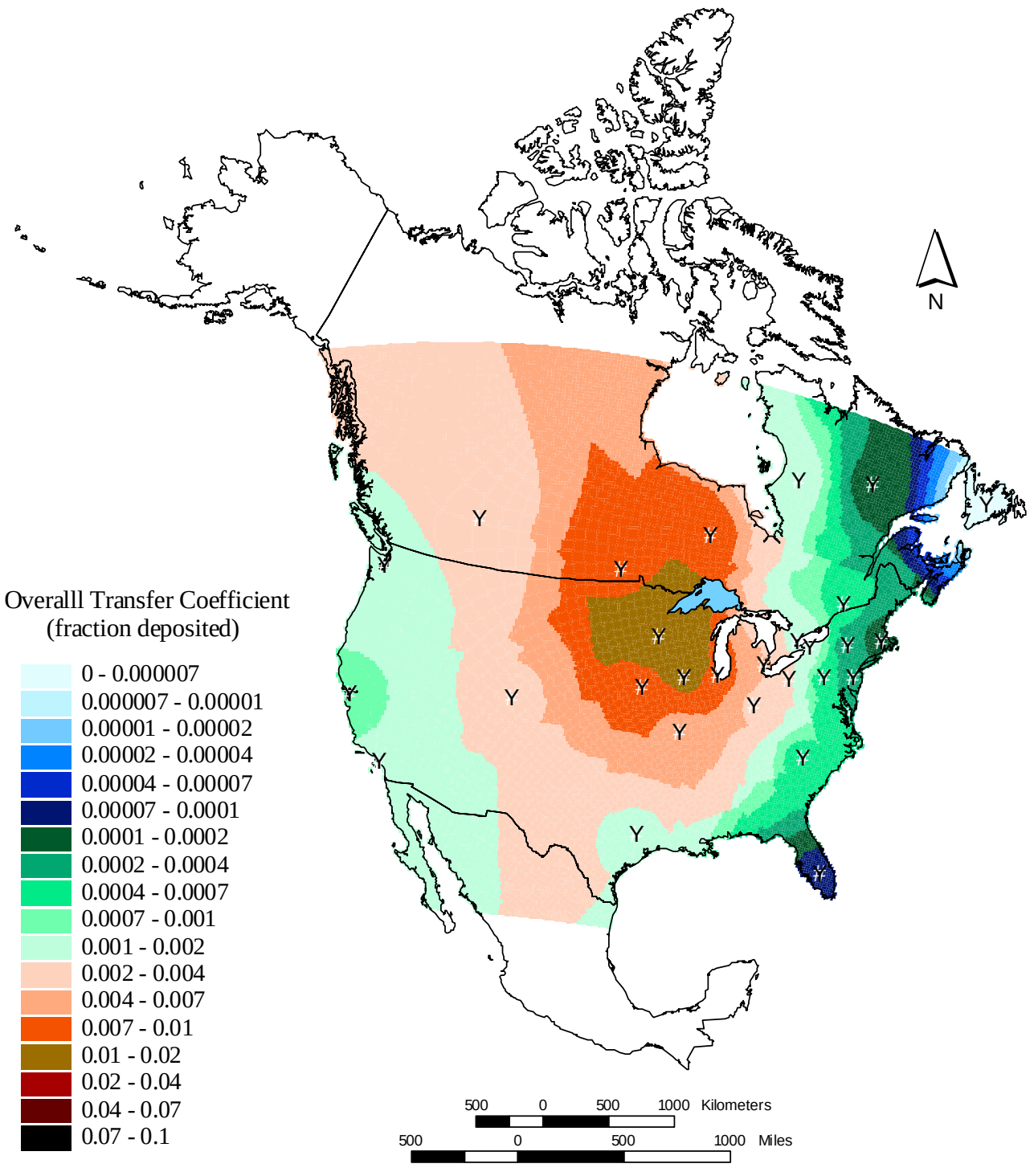
Comparison of interpolated transfer coefficients to the Great Lakes with explicitly modeled transfer coefficients for 2378 TCDD and OCDD

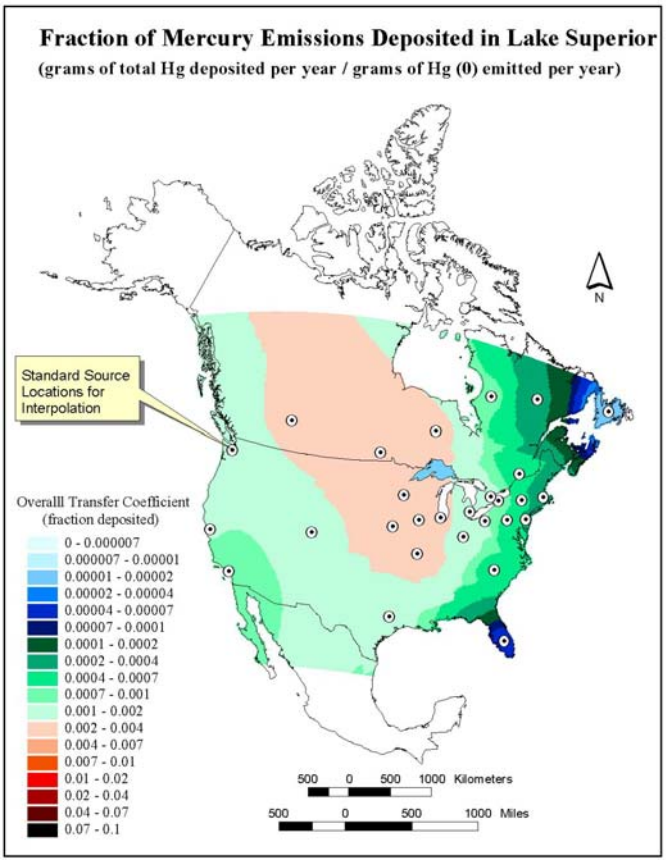


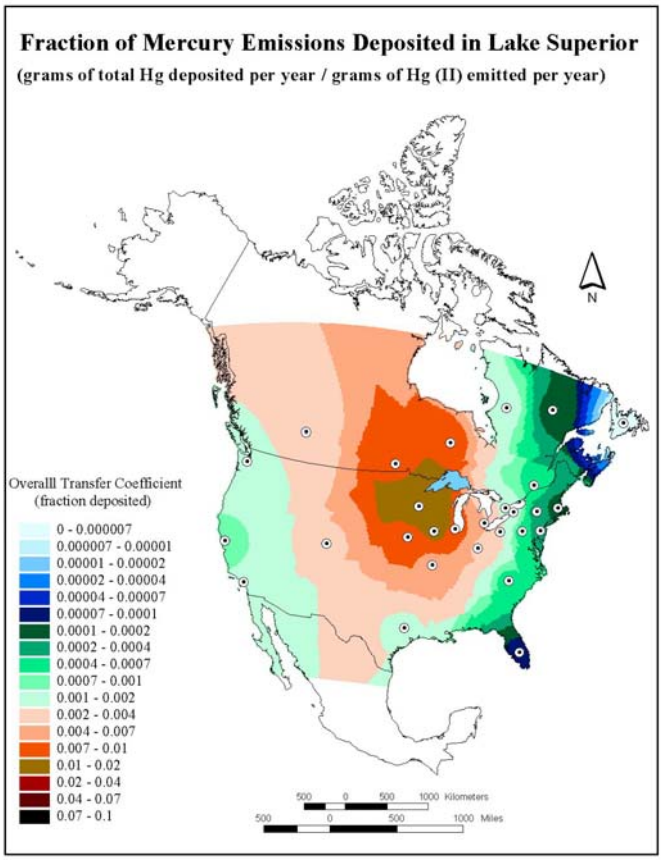
Fraction of Mercury Emissions Deposited in Lake Superior
(grams of total Hg deposited per year / grams of Hg (0) emitted per year)



Fraction of Mercury Emissions Deposited in Lake Superior
(grams of total Hg deposited per year / grams of Hg (II) emitted per year)





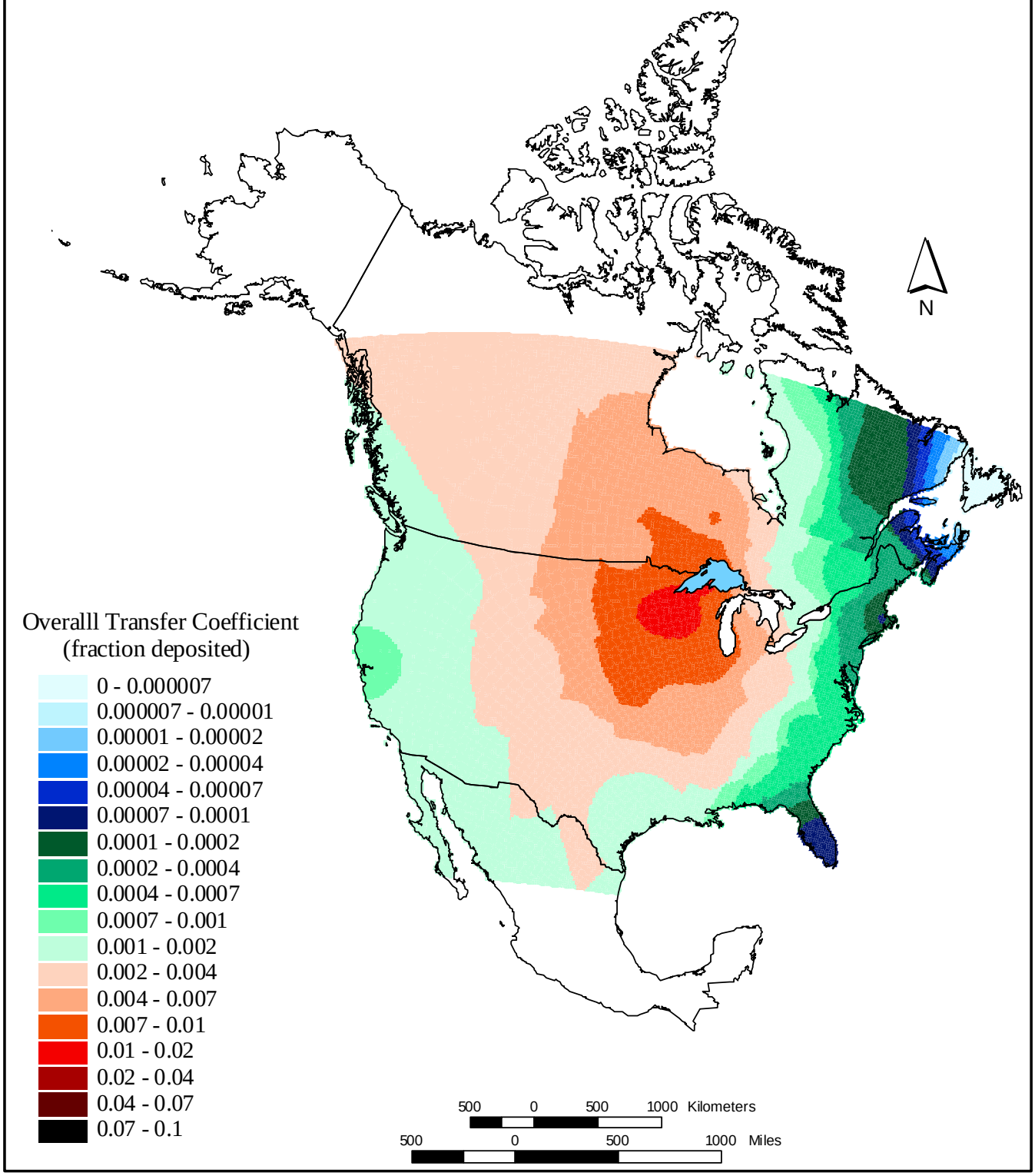


Transfer Coefficients for Hg are strongly influenced by the “type” of Hg emitted

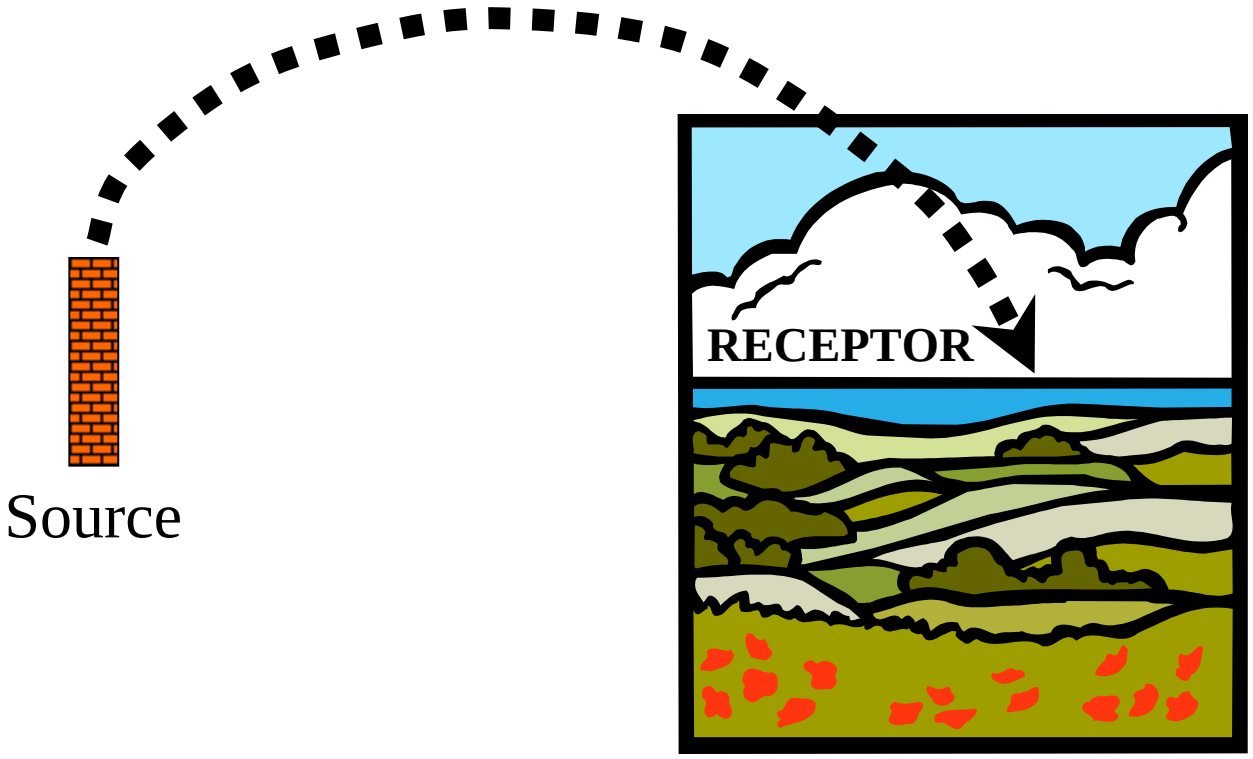
[Hg(II) has much greater local impacts than Hg(0)]

Fraction of Mercury Emissions Deposited in Lake Superior

(grams of total Hg deposited per year / grams of Hg (p) emitted per year)



“Chemical Interpolation”



Impact of Source Emitting 30% Hg(0) 50% Hg(II) 20% Hg(p) =

0.3 x [**Impact of Source Emitting Pure Hg(0)**]

+

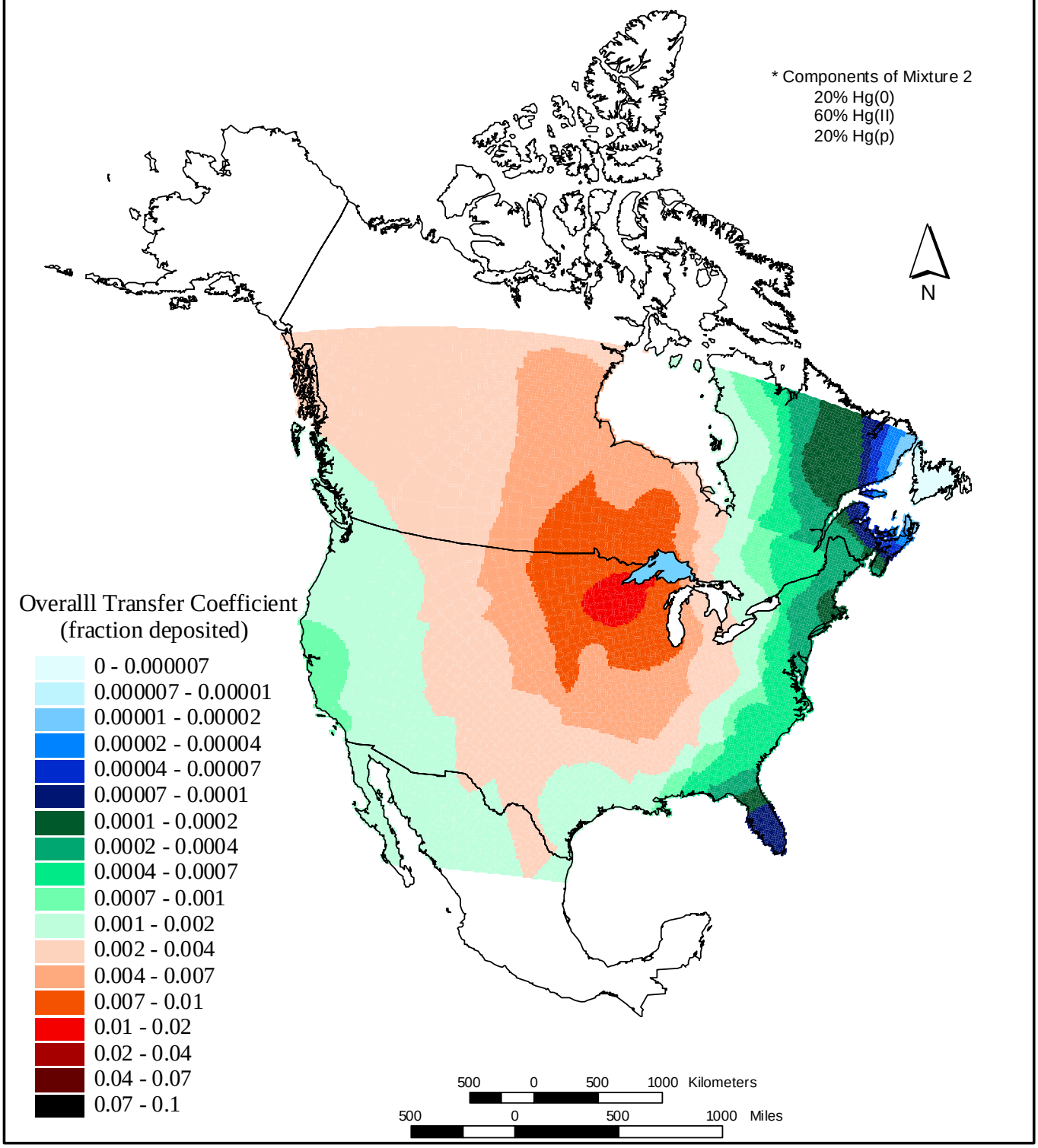
0.5 x [**Impact of Source Emitting Pure Hg(II)**]

+

0.2 x [**Impact of Source Emitting Pure Hg(p)**]

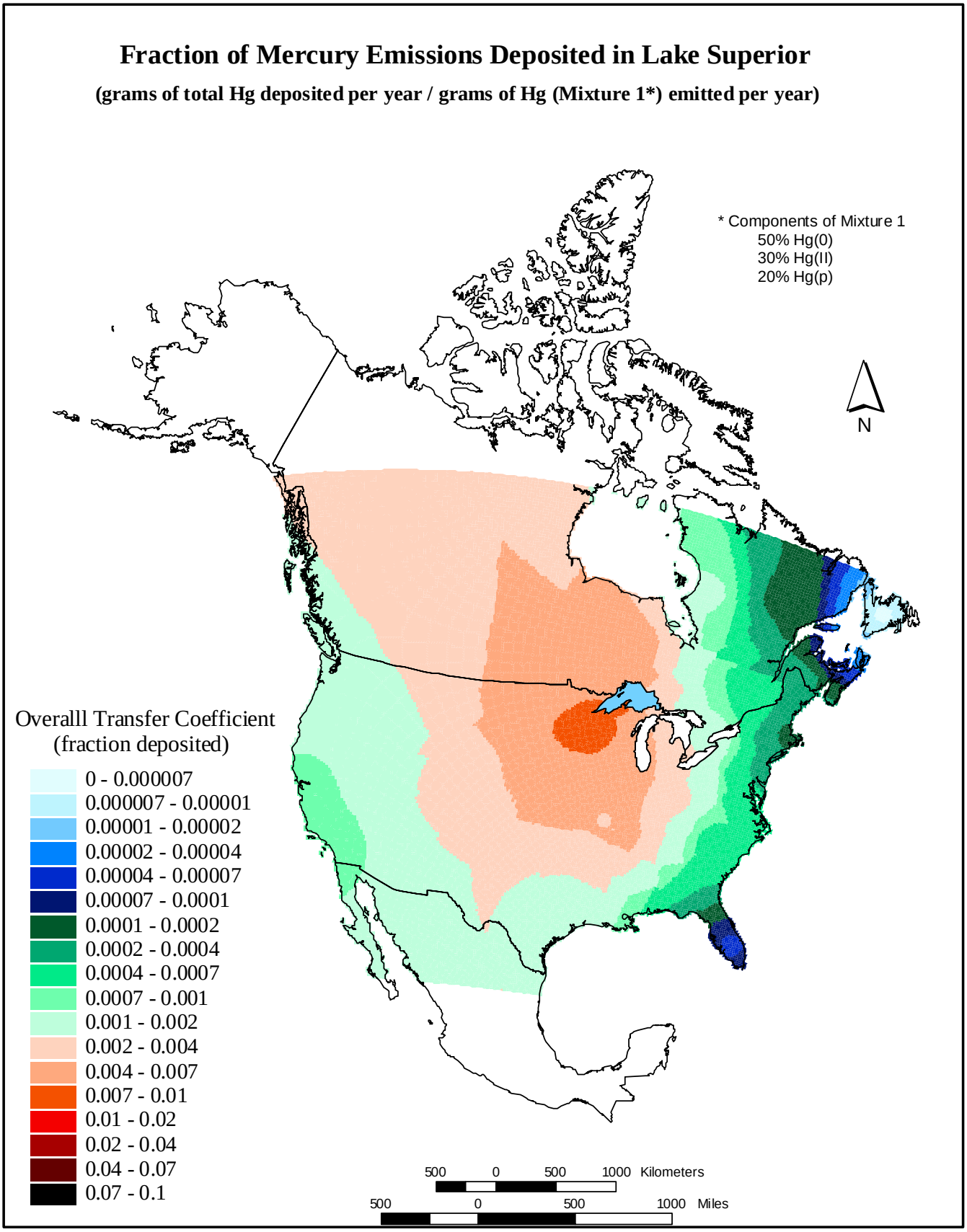
Fraction of Mercury Emissions Deposited in Lake Superior

(grams of total Hg deposited per year / grams of Hg (Mixture 2*) emitted per year)

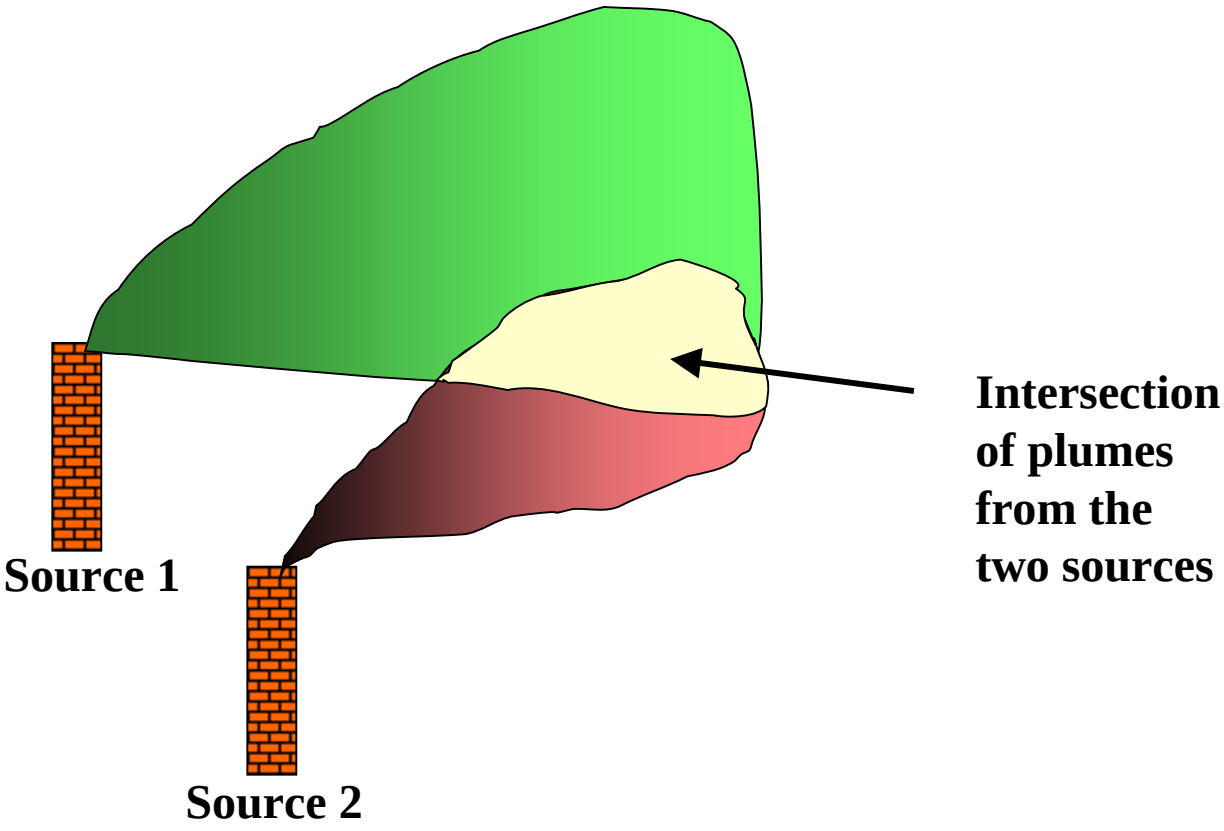


Fraction of Mercury Emissions Deposited in Lake Superior

(grams of total Hg deposited per year / grams of Hg (Mixture 1*) emitted per year)



Do the emissions from one source affect the fate and transport of emissions from another source?



***If* interaction is important,**
then sources not independent,
and Eulerian approach is needed

Why might the atmospheric fate of mercury emissions be essentially linearly independent?

- **Hg is present at extremely trace levels in the atmosphere**

- **Hg won't affect meteorology (can simulate meteorology independently, and provide results to drive model)**

- **Most species that complex or react with Hg are generally present at *much* higher concentrations than Hg**

- **Other species (e.g. OH) generally react with many other compounds than Hg, so while present in trace quantities, their concentrations cannot be strongly influenced by Hg**

- **Wet and dry deposition processes are generally 1st order with respect to Hg**

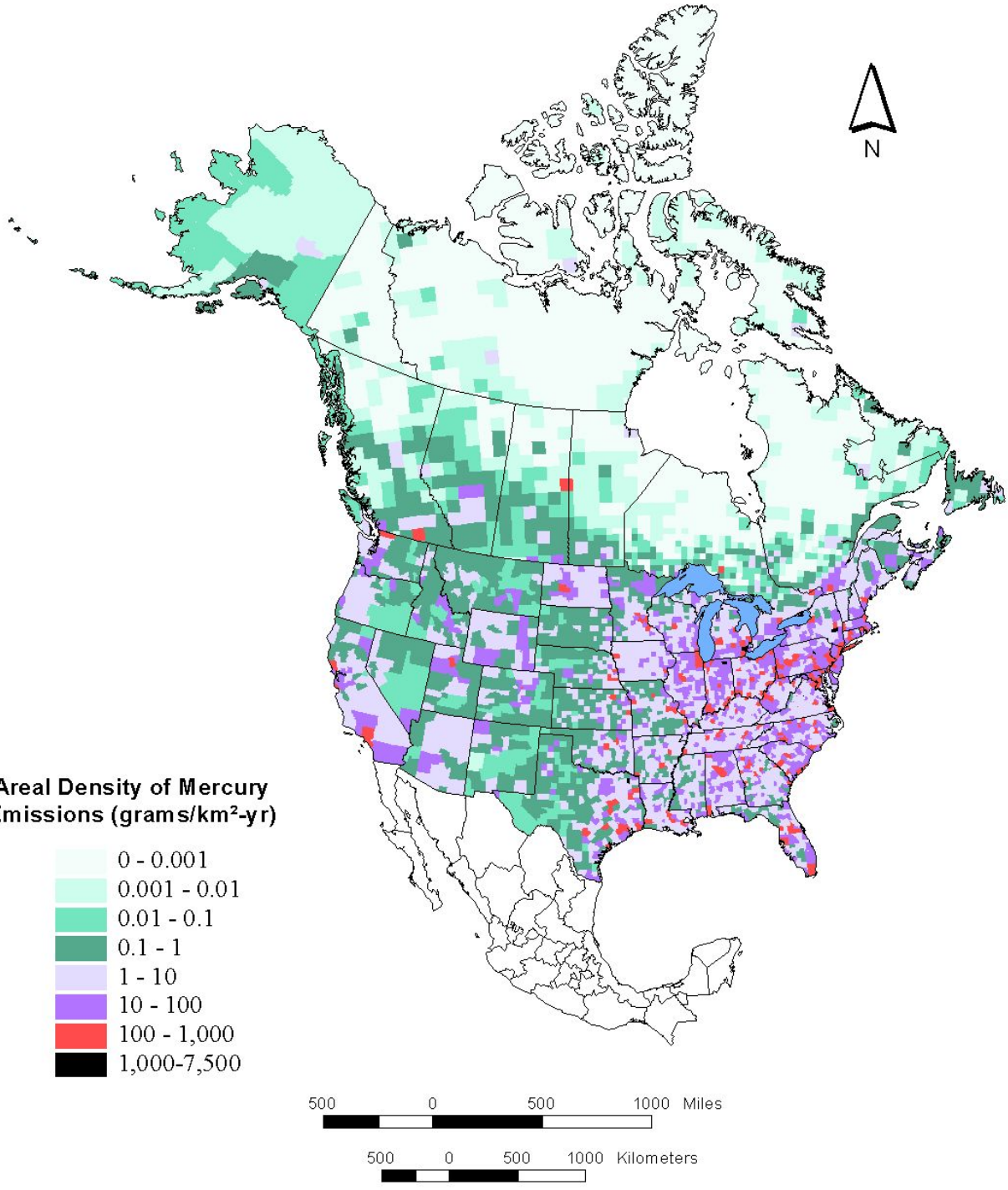
- **The current "consensus" chemical mechanism (equilibrium + reactions) does not contain any equations that are not 1st order in Hg**

Chemical Equilibrium and Reaction Scheme for Atmospheric Mercury

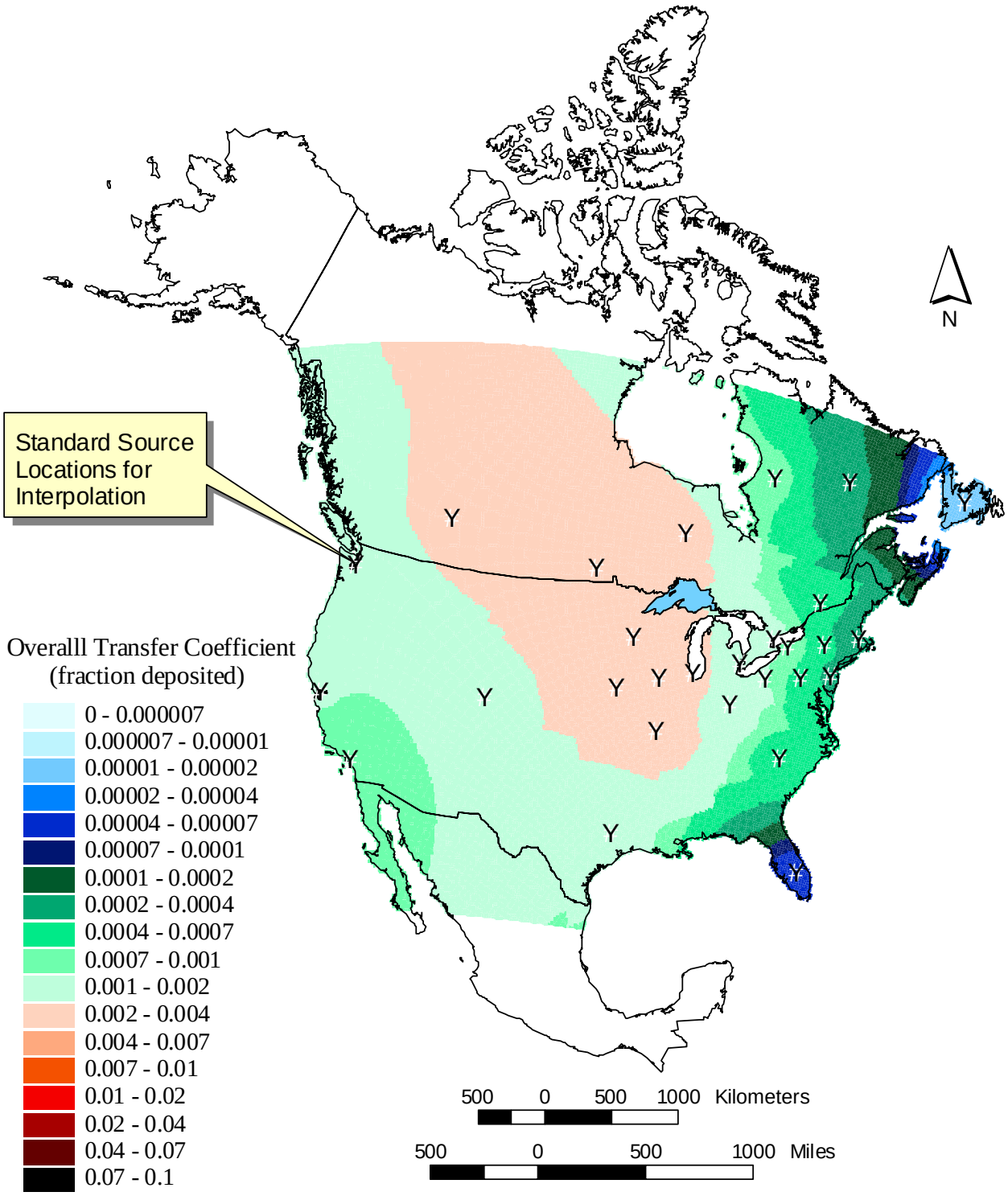
gas-liquid eqlbrm	Hg(0)(aq) = K1 * Hg(0)(gas)	K1 =	1.1E-01	molar/atm
gas-liquid eqlbrm	HgCl2(aq) = K2 * HgCl2(gas)	K2 =	1.4E+06	molar/atm
gas-liquid eqlbrm	Hg(OH)2(aq) = K3 * Hg(OH)2(gas)	K3 =	1.2E+04	molar/atm
gas-liquid eqlbrm	O3(aq) = K4 * O3(gas)	K4 =	1.1E-02	molar/atm
gas-liquid eqlbrm	SO2(aq) = K5 * SO2(gas)	K5 =	1.2E+00	molar/atm
gas-liquid eqlbrm	HCl(aq) = K6 * HCl(gas)	K6 =	1.1E+00	molar/atm
gas-liquid eqlbrm	Cl2(aq) = K7 * Cl2(gas)	K7 =	7.6E-02	molar/atm
gas-liquid eqlbrm	H2O2(aq) = K8 * H2O2(gas)	K8 =	7.4E+04	molar/atm
aq phase eqlbrm	HgCl2 (aq) <--> Hg2+ + 2 Cl-1	K9 =	1.0E-14	molar*molar
aq phase eqlbrm	Hg(OH)2 (aq) <--> Hg2+ + 2 OH-1	K10 =	1.0E-22	molar*molar
aq phase eqlbrm	HCl(aq) <--> H+ + Cl-1	K11 =	1.7E+06	molar
aq phase eqlbrm	Cl2 (aq) <--> HOCl + Cl-1 + H+	K12 =	5.0E-04	molar*molar
aq phase eqlbrm	HOCl <--> OCl-1 + H+	K13 =	3.2E-08	molar
aq phase eqlbrm	SO2 (aq) + H2O2 (aq) <--> SO4-2 + 2 H+	K14 =	very fast titration	
aq phase eqlbrm	SO2 (aq) + H2O <--> HSO3-1 + H+	K15 =	1.2E-02	molar
aq phase eqlbrm	HSO3-1 <--> SO3-2 + H+	K16 =	6.6E-08	molar
aq phase eqlbrm	Hg+2 + SO3-2 <--> HgSO3	K17 =	5.0E+12	1/molar
aq phase eqlbrm	HgSO3 + SO3-2 <--> Hg(SO3)2-2	K18 =	2.5E+11	1/molar
gas phase rxn	Hg(0) (g) + O3 (g) --> Hg(II) (g)	R01 =	3.0E-20	cm3 / molec - sec
gas phase rxn	Hg(0) (g) + HCl (g) --> HgCl2 (g)	R02 =	1.0E-19	cm3 / molec - sec
gas phase rxn	Hg(0) (g) + H2O2 (g) --> Hg(OH)2 (g)	R03 =	8.5E-19	cm3 / molec - sec
gas phase rxn	Hg(0) (g) + Cl2 (g) --> HgCl2 (g)	R04 =	4.0E-18	cm3 / molec - sec
aq phase rxn	Hg(0) (aq) + O3 (aq) --> Hg+2	R05 =	4.7E+07	1/molar-sec
aq phase rxn	Hg(0) (aq) + OH-1 (aq) --> Hg+2	R06 =	2.0E+09	1/molar-sec
aq phase rxn	HgSO3 (aq) --> Hg(0) (aq)	R07 =	1.1E-02	1/sec
aq phase rxn	Hg(II) (aq) + HO2 (aq) --> Hg(0) (aq)	R08 =	1.7E+04	1/molar-sec
aq phase rxn	Hg(0) (aq) + HOCl (aq) --> Hg+2	R09 =	2.1E+06	1/molar-sec
aq phase rxn	Hg(0) (aq) + OCl-1 --> Hg+2	R10 =	2.0E+06	1/molar-sec
aq phase rxn	Hg(II) (aq) <--> Hg(II) (soot)	R11 =	9.0E+02	liters/gram; t = 1/hour

Atmospheric Mercury Emissions

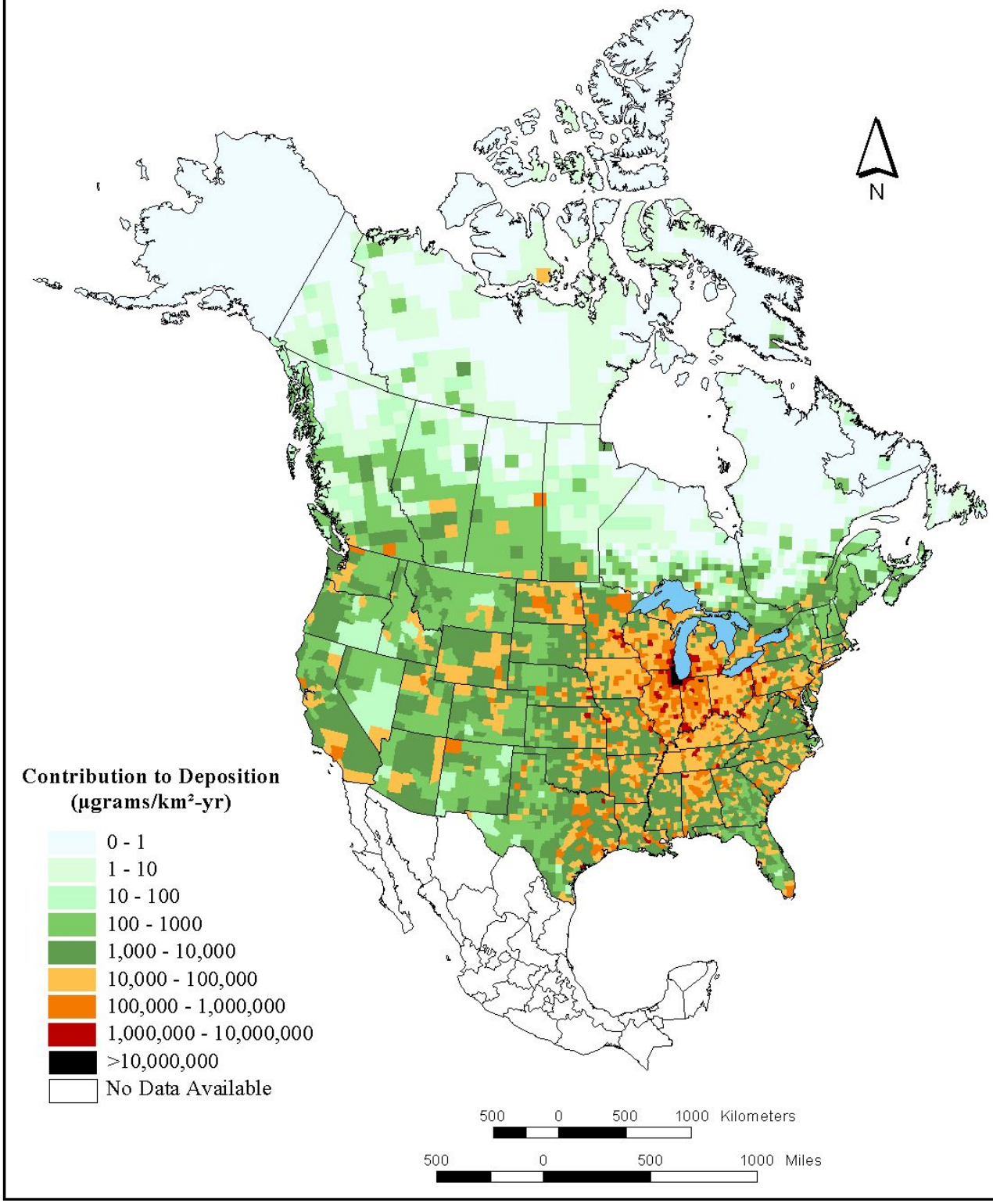
(Canada: 1995; U.S. 1996, 1999)

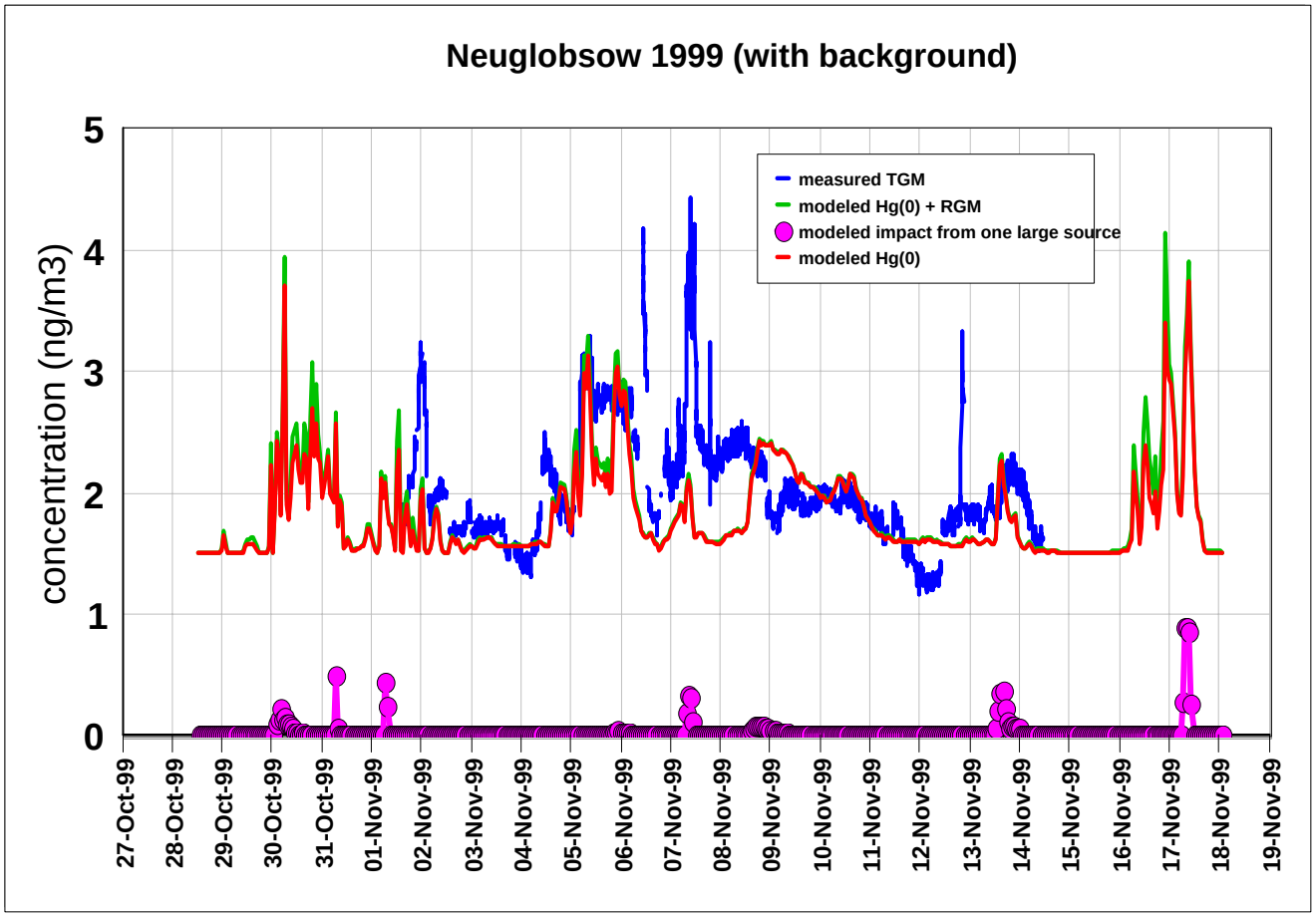


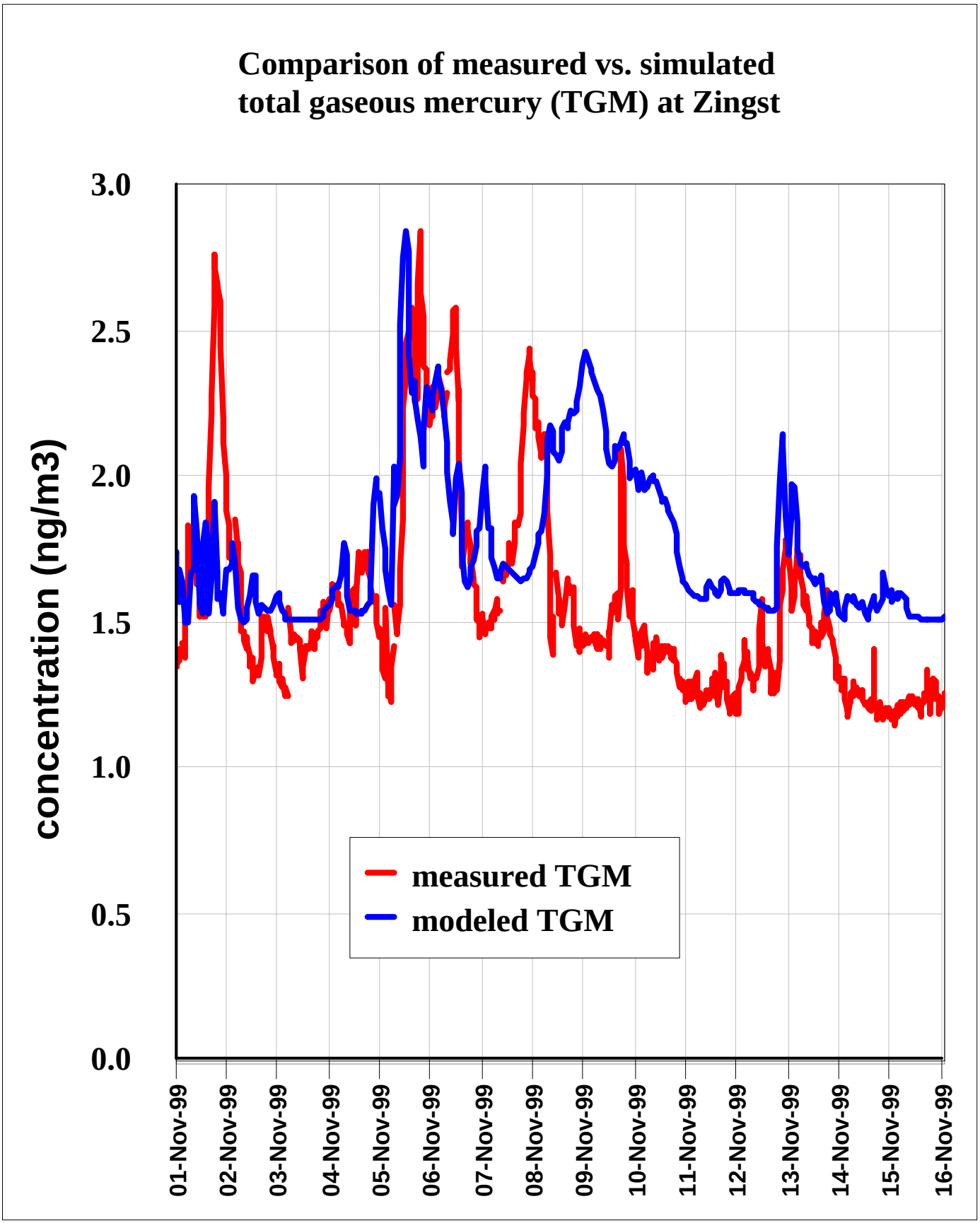
Fraction of Mercury Emissions Deposited in Lake Superior
(grams of total Hg deposited per year / grams of Hg (0) emitted per year)



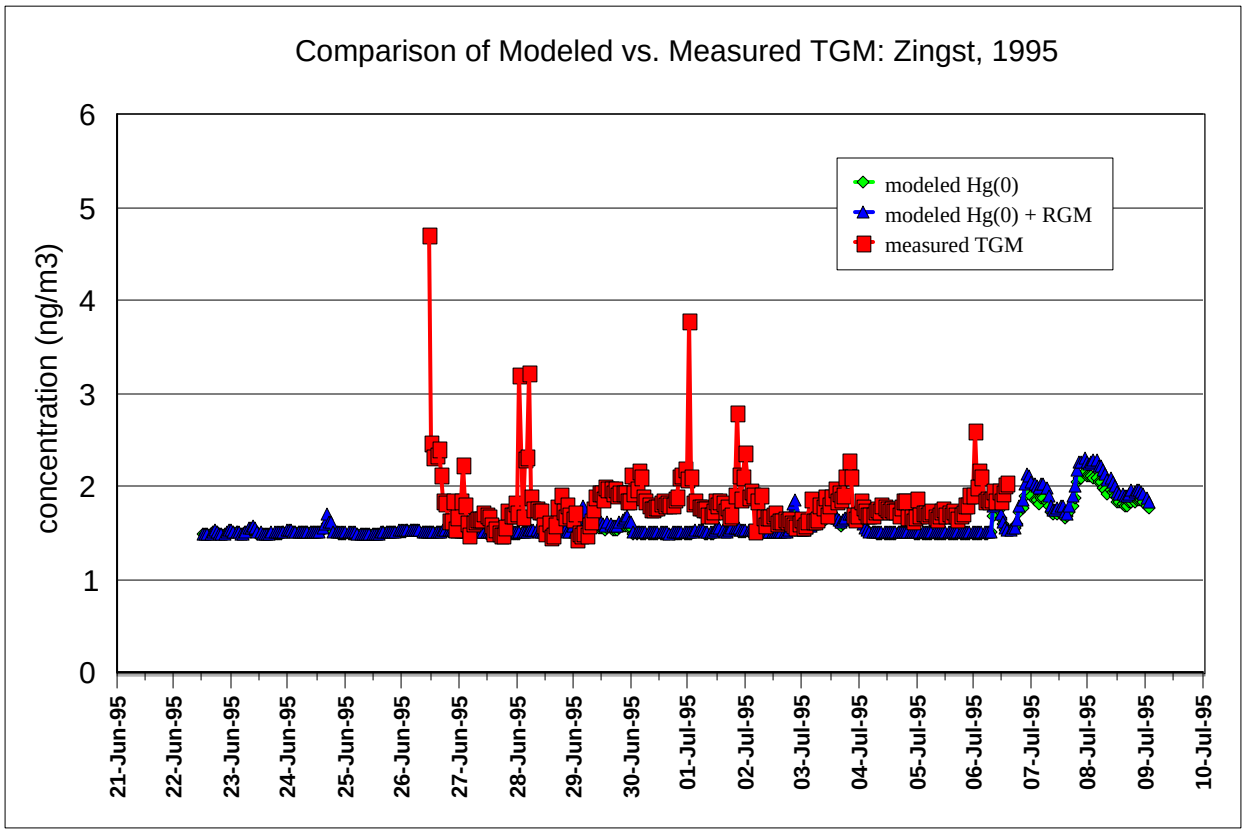
Estimated Contributions to the Atmospheric Deposition of Mercury to Lake Michigan (µgrams/km²-yr)



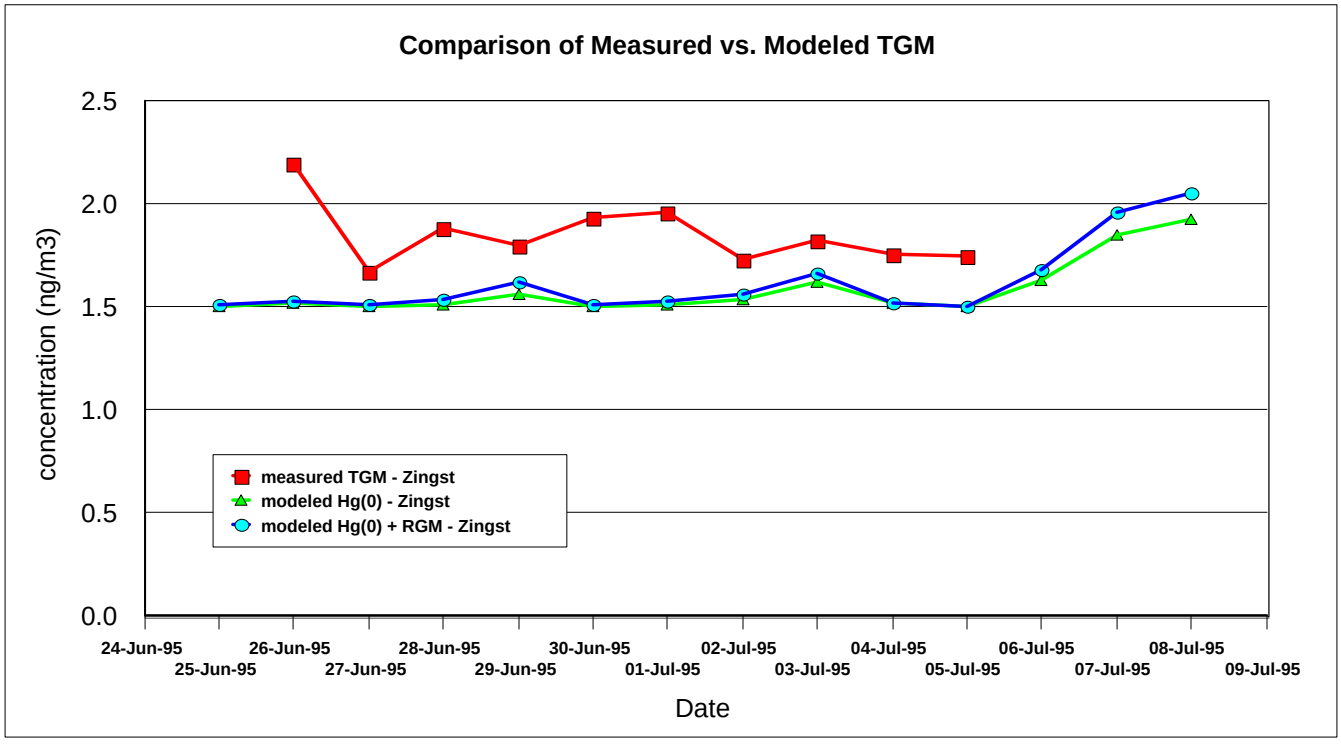

Neuglobsow 1999 (with background)
concentration (ng/m3)
0
1
2
3
4
5
measured TGM
modeled Hg(0) + RGM
modeled impact from one large source
modeled Hg(0)
27-Oct-99
28-Oct-99
29-Oct-99
30-Oct-99
31-Oct-99
01-Nov-99
02-Nov-99
03-Nov-99
04-Nov-99
05-Nov-99
06-Nov-99
07-Nov-99
08-Nov-99
09-Nov-99
10-Nov-99
11-Nov-99
12-Nov-99
13-Nov-99
14-Nov-99
15-Nov-99
16-Nov-99
17-Nov-99
18-Nov-99
19-Nov-99


Comparison of measured vs. simulated
total gaseous mercury (TGM) at Zingst
concentration (ng/m3)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
measured TGM
modeled TGM
01-Nov-99
02-Nov-99
03-Nov-99
04-Nov-99
05-Nov-99
06-Nov-99
07-Nov-99
08-Nov-99
09-Nov-99
10-Nov-99
11-Nov-99
12-Nov-99
13-Nov-99
14-Nov-99
15-Nov-99
16-Nov-99

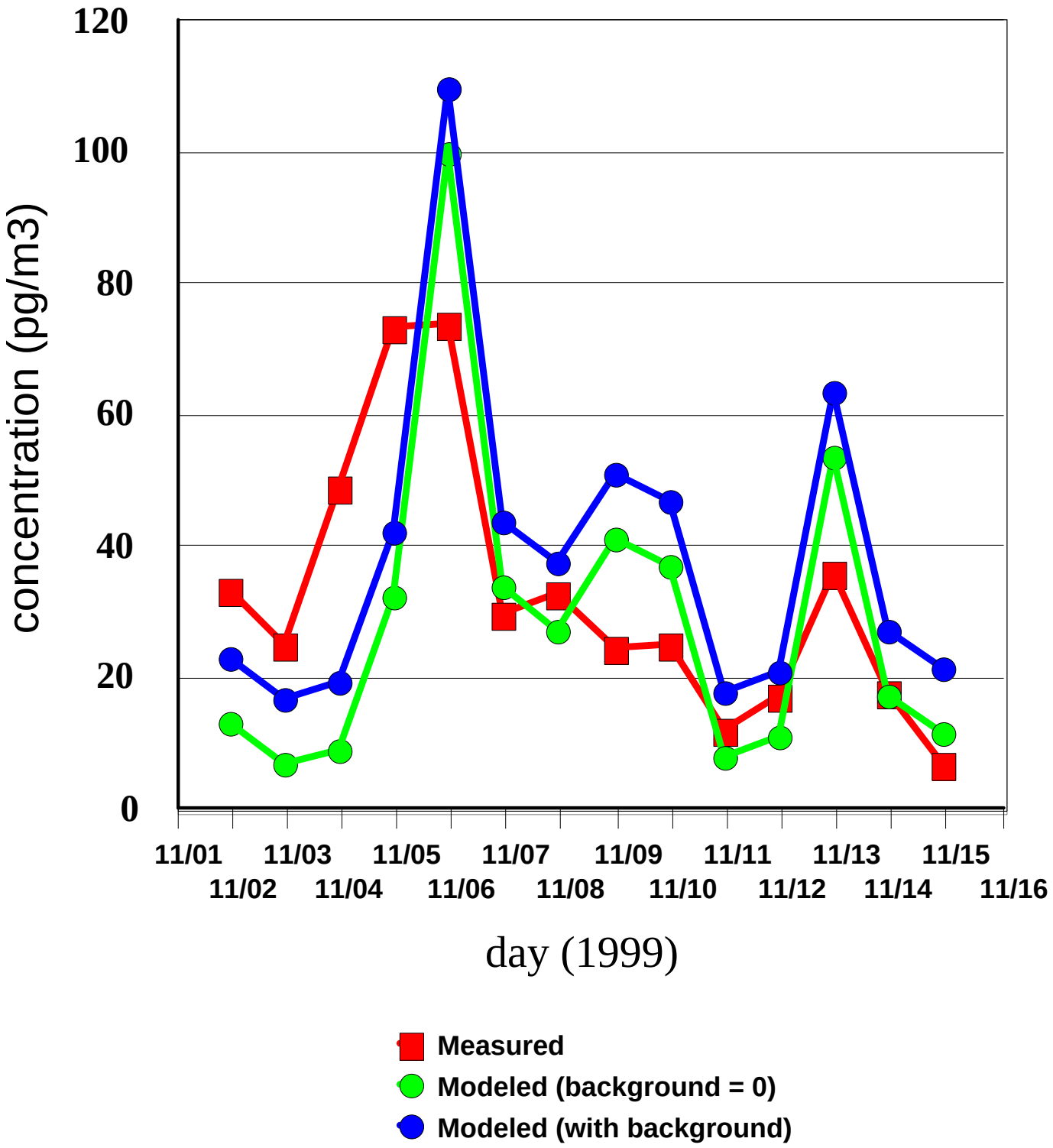
Correlation Coefficient = - 0.03

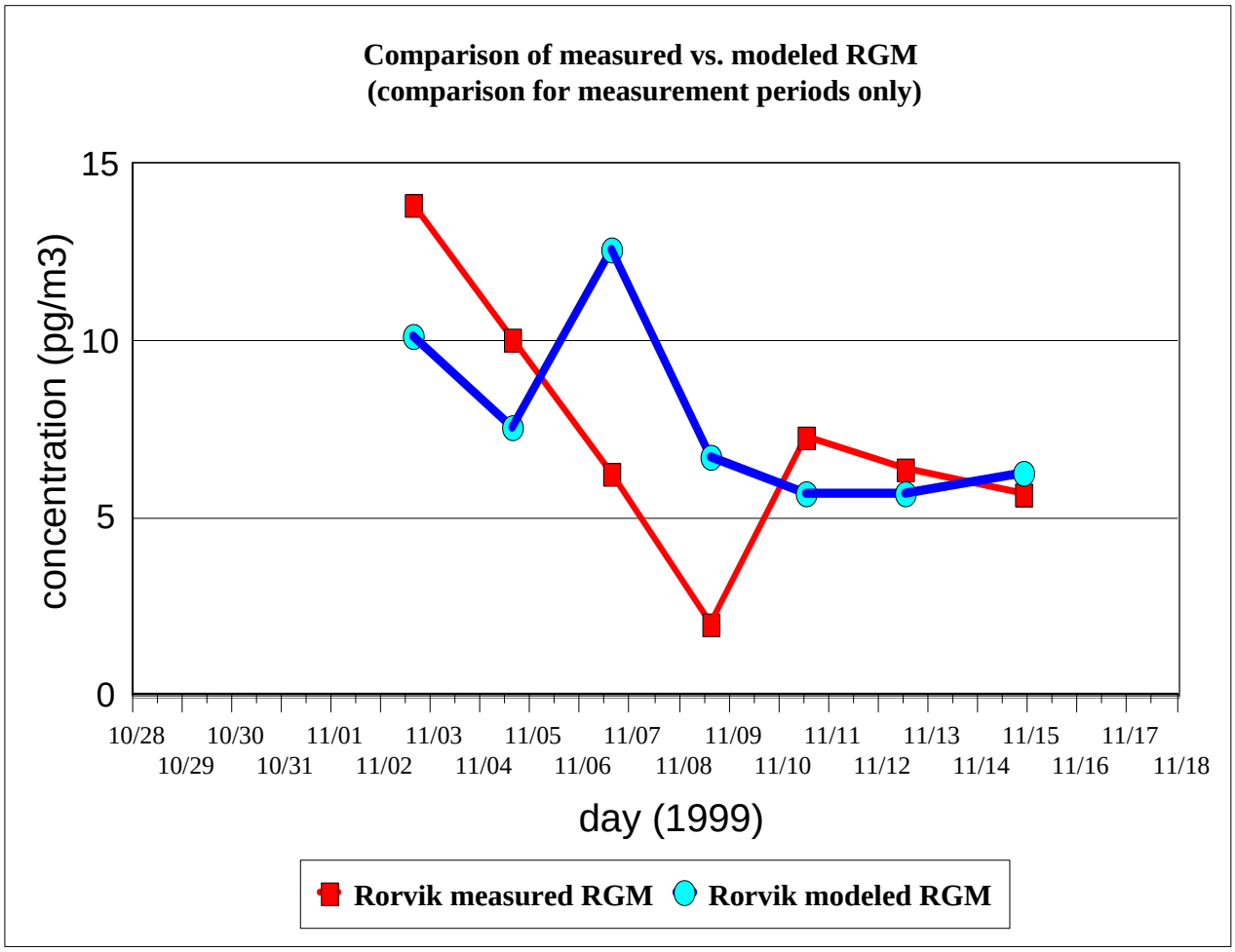


But daily avg conc not too far off…



Comparison of measured vs. simulated total particulate mercury at Zingst



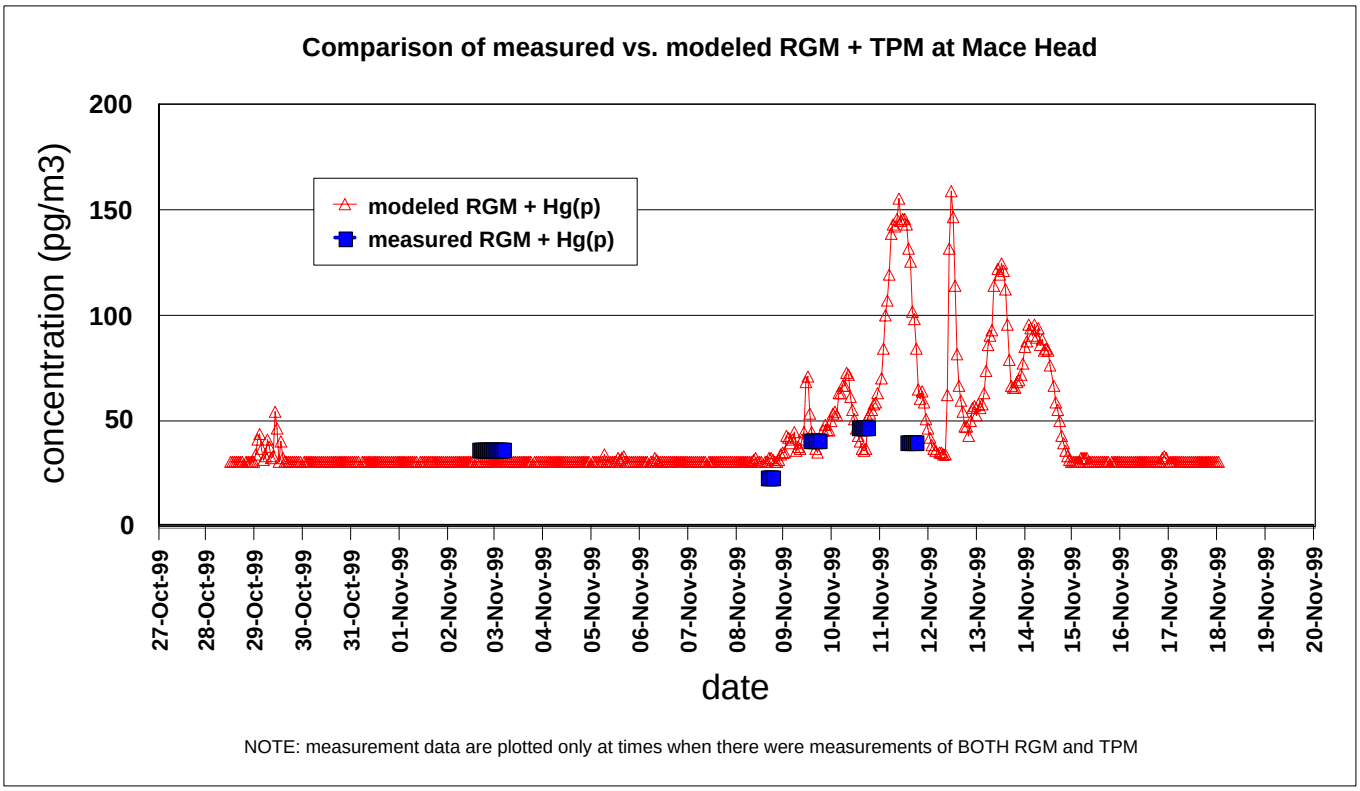

Comparison of measured vs. modeled RGM
(comparison for measurement periods only)
15
10
5
0
concentration (pg/m3)
10/28
10/29
10/30
10/31
11/01
11/02
11/03
11/04
11/05
11/06
11/07
11/08
11/09
11/10
11/11
11/12
11/13
11/14
11/15
11/16
11/17
11/18
day (1999)
Rorvik measured RGM
Rorvik modeled RGM

- **In the *first* version of the HYSPLIT-Hg model used in this intercomparison, Hg(p) was assumed to be completely converted to dissolved Hg(II) whenever a particle becomes a droplet (e.g., above approximately 80% relative humidity); and dissolved Hg(II) assumed to become Hg(p) whenever the droplet dries out**

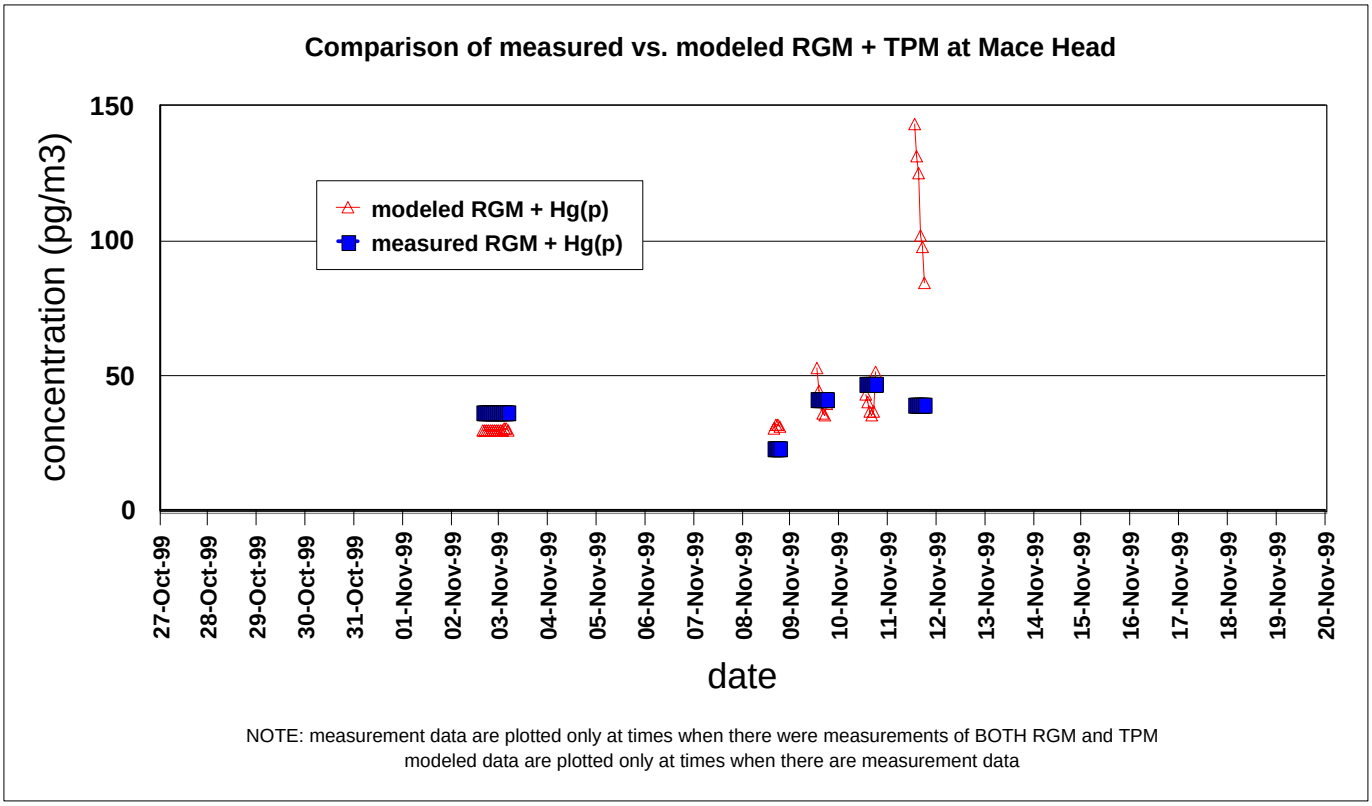
- **Hg(p) and Hg(II) were thus somewhat "equivalent" in the model**

- **With this assumption, the model tended to *under*predict Hg(p) and *over*predict Hg(II), suggesting that the assumption of *complete* conversion was not valid.**

- **However, it was encouraging to note that the model was getting approximately the right answer for the sum of the two forms of mercury (Hg(p) + Hg(II), representing the total pool of oxidized Hg in the atmosphere [*see the following graphs*]**



NOTE: measurement data are plotted only at times when there were measurements of BOTH RGM and TPM



NOTE: measurement data are plotted only at times when there were measurements of BOTH RGM and TPM
modeled data are plotted only at times when there are measurement data

As a result of this observation, the model was re-run with the assumption that Hg(p) was *not* soluble.

With this assumption, the results for Hg(p) and RGM were dramatically better. [These new results are what have been shown in this presentation, except for the immediately preceding RGM+Hg(p) graphs]

The affect of changing this assumption had a negligible impact on Hg(0), as might be expected, given the generally very low concentrations of Hg(II) and Hg(p) relative to Hg(0).

Some Concluding Notes

The version of HYSPLIT-Hg used for these calculations represented a very early stage of development of the model.

The model has been changed significantly since these runs… (hopefully improved!)

Methodology assumes linear independence of sources; potential advantage that detailed source-receptor relationships can be estimated

Hg(p) solubility?

It may be useful to reconsider some of the model evaluation metrics