Estimating Mercury Emissions from Forest Fires, Lakes, Regional and Local Sources Using Measurements from Milwaukee, WI

LADCO Meeting: "Mercury in the Midwest"
Indianapolis, IN, 20-21 August 2015

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Saint Louis University

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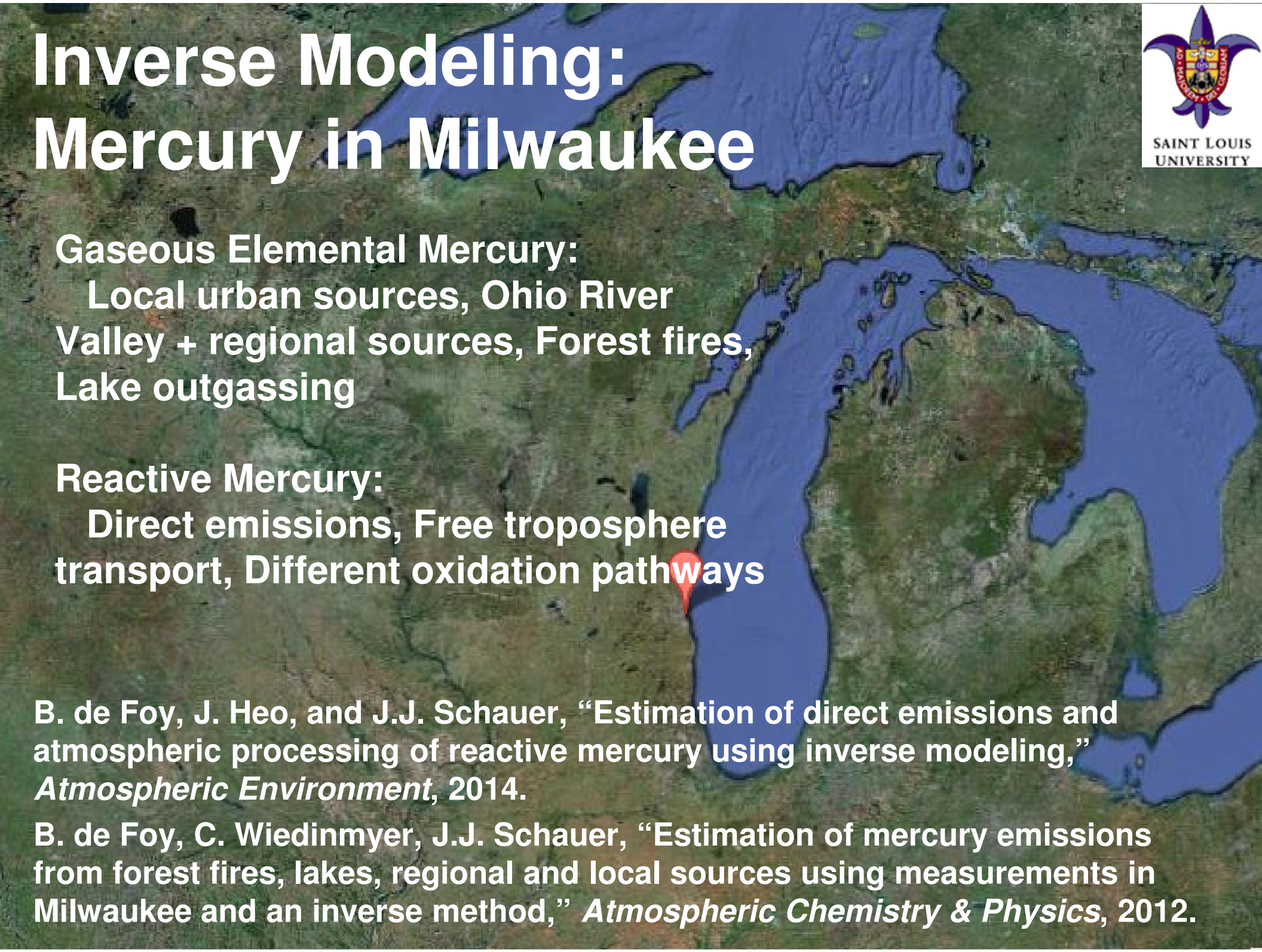
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # RD 83455701

Inverse Modeling: Mercury in Milwaukee



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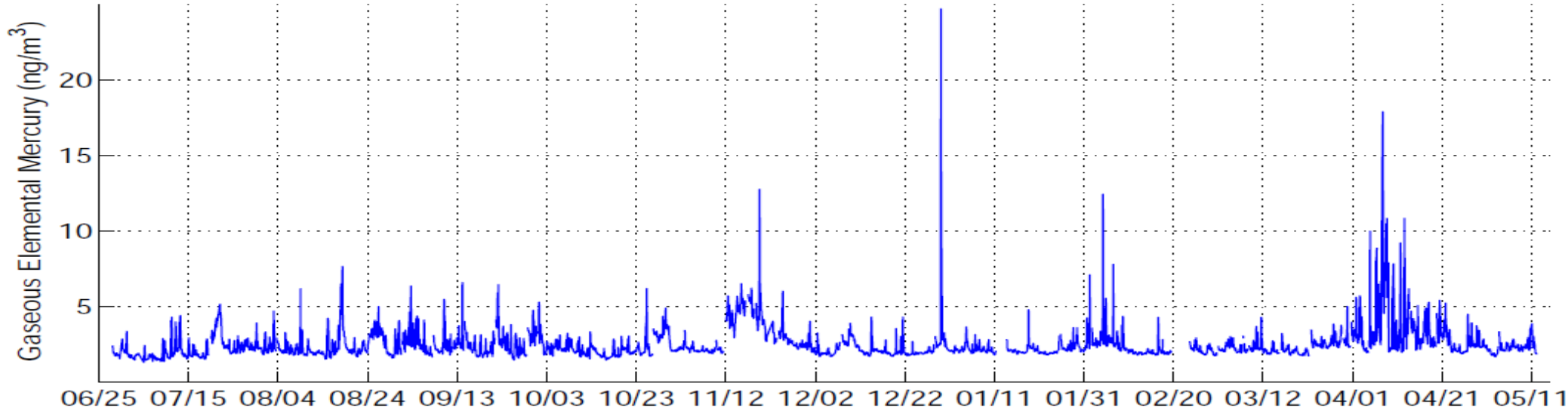
Gaseous Elemental Mercury:
Local urban sources, Ohio River Valley + regional sources, Forest fires, Lake outgassing

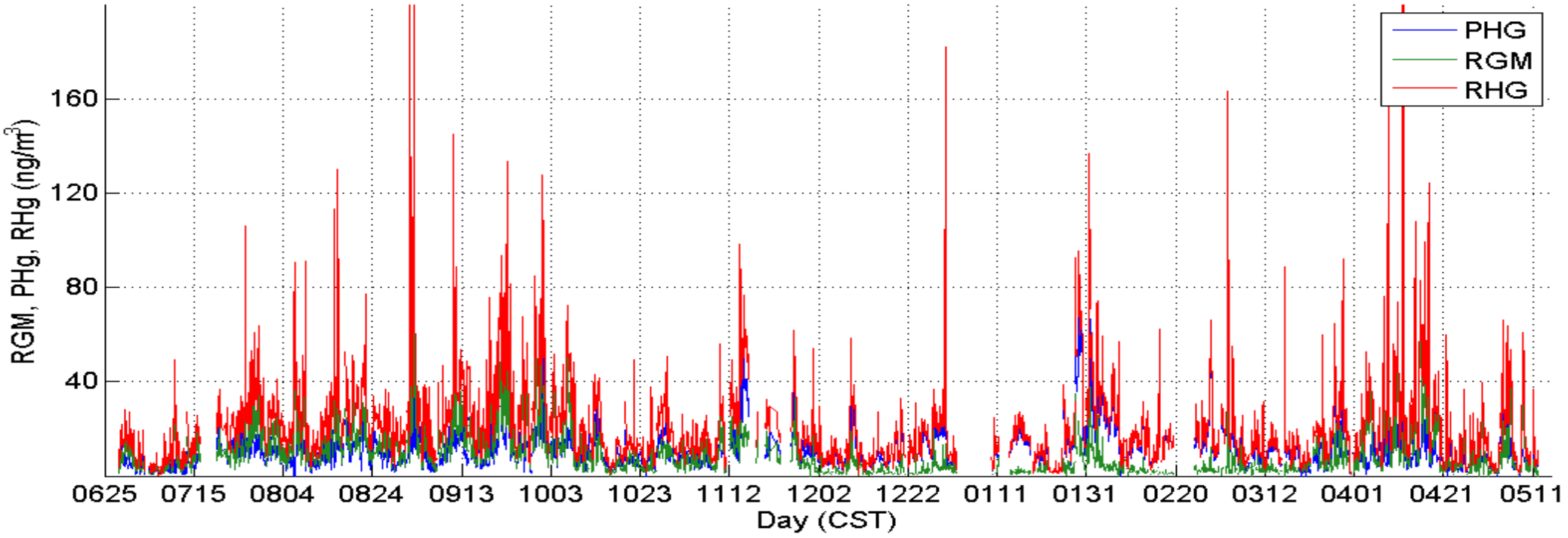
Reactive Mercury:
Direct emissions, Free troposphere transport, Different oxidation pathways

B. de Foy, J. Heo, and J.J. Schauer, "Estimation of direct emissions and atmospheric processing of reactive mercury using inverse modeling," *Atmospheric Environment*, 2014.

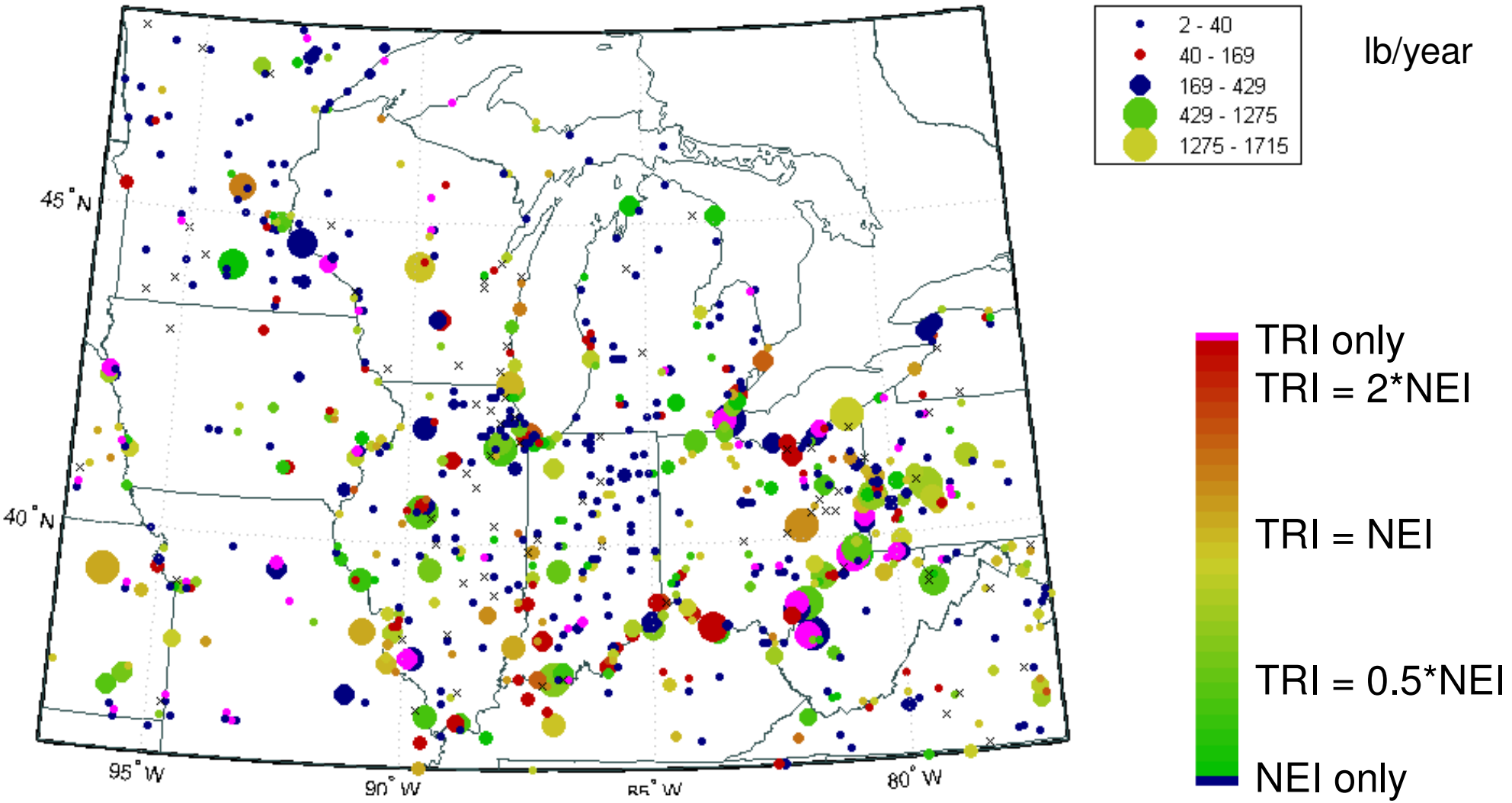
B. de Foy, C. Wiedinmyer, J.J. Schauer, "Estimation of mercury emissions from forest fires, lakes, regional and local sources using measurements in Milwaukee and an inverse method," *Atmospheric Chemistry & Physics*, 2012.

Speciated Mercury Measurements in Milwaukee

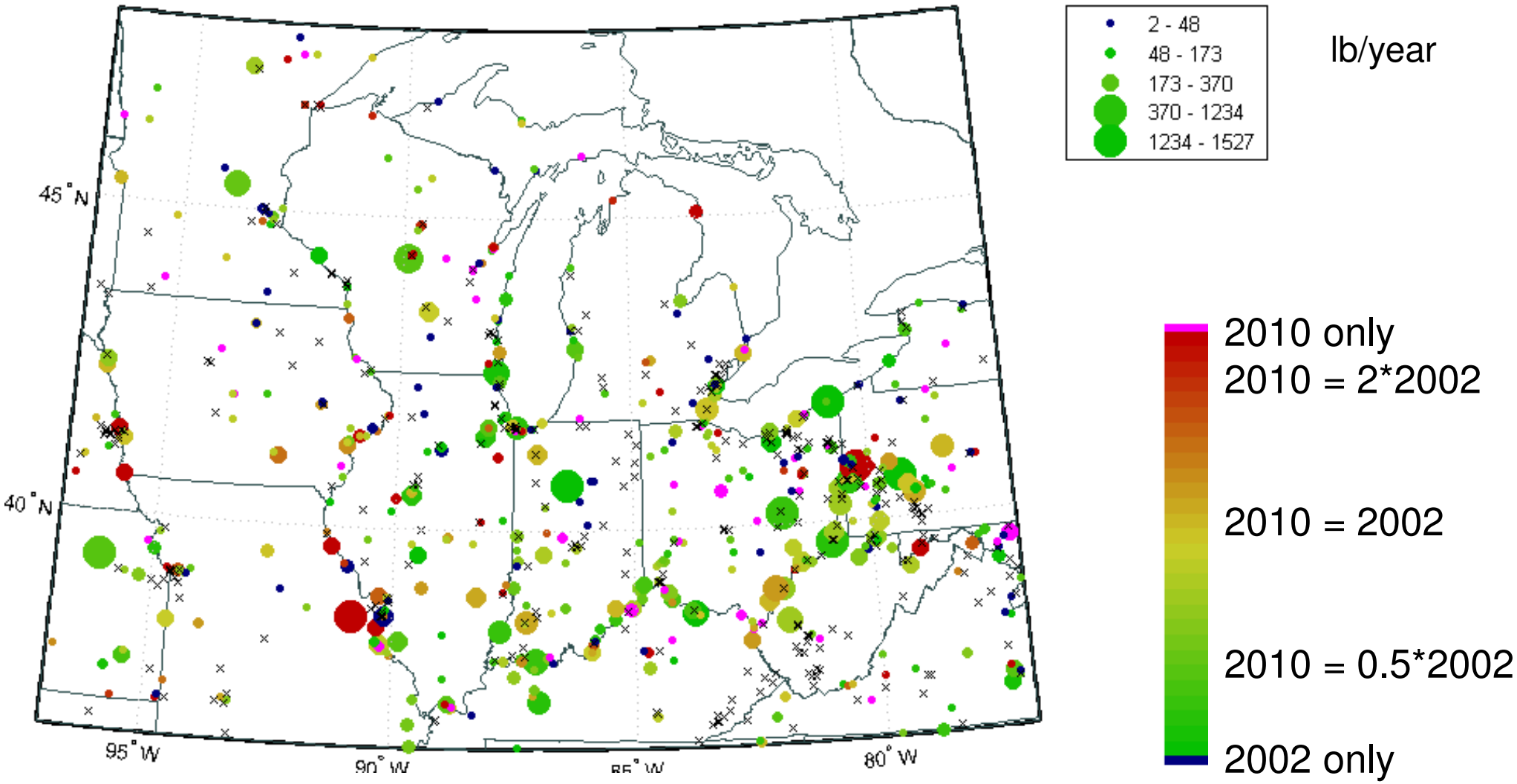




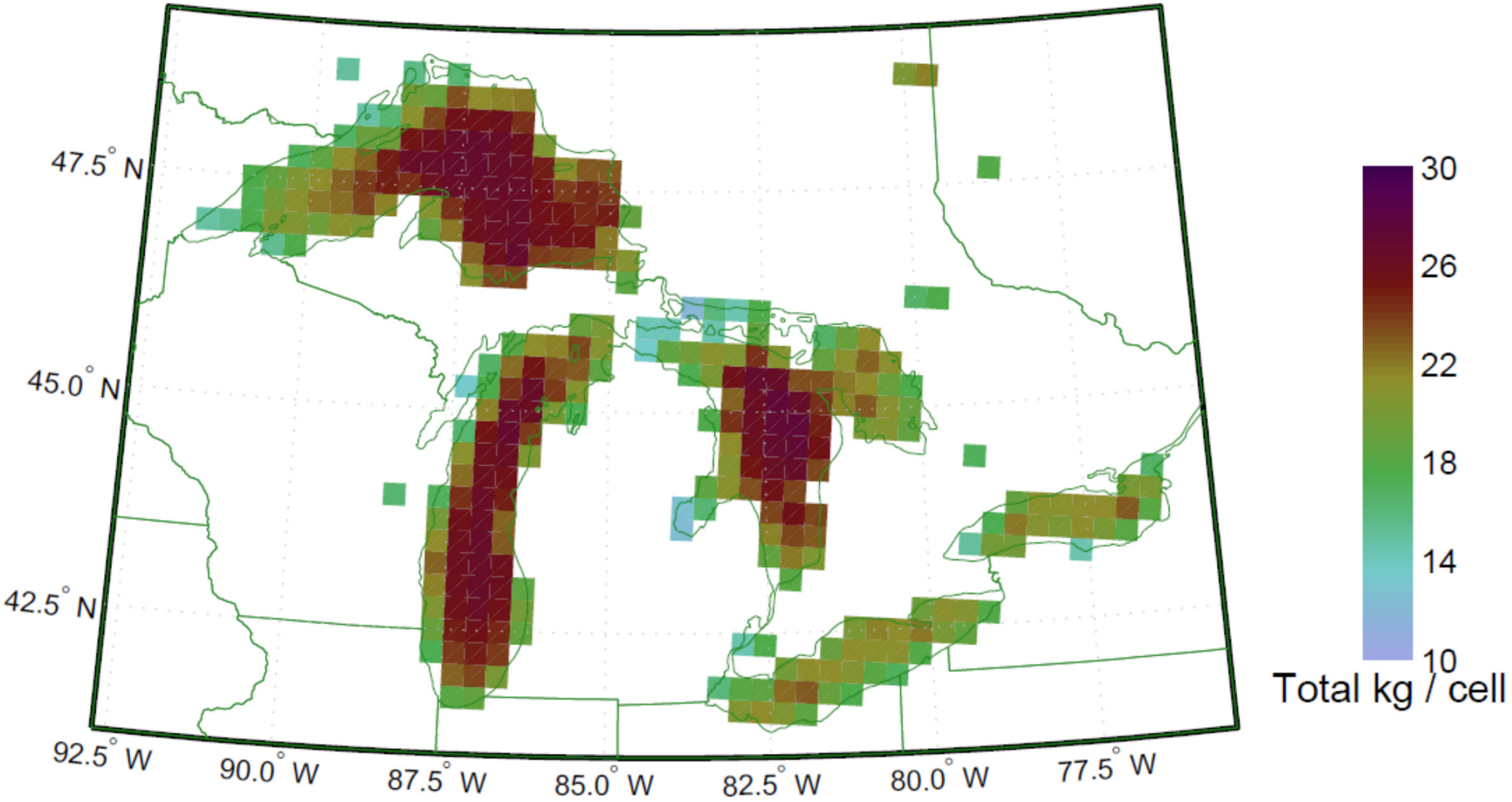
NEI / TRI 2002 Mercury Inventory



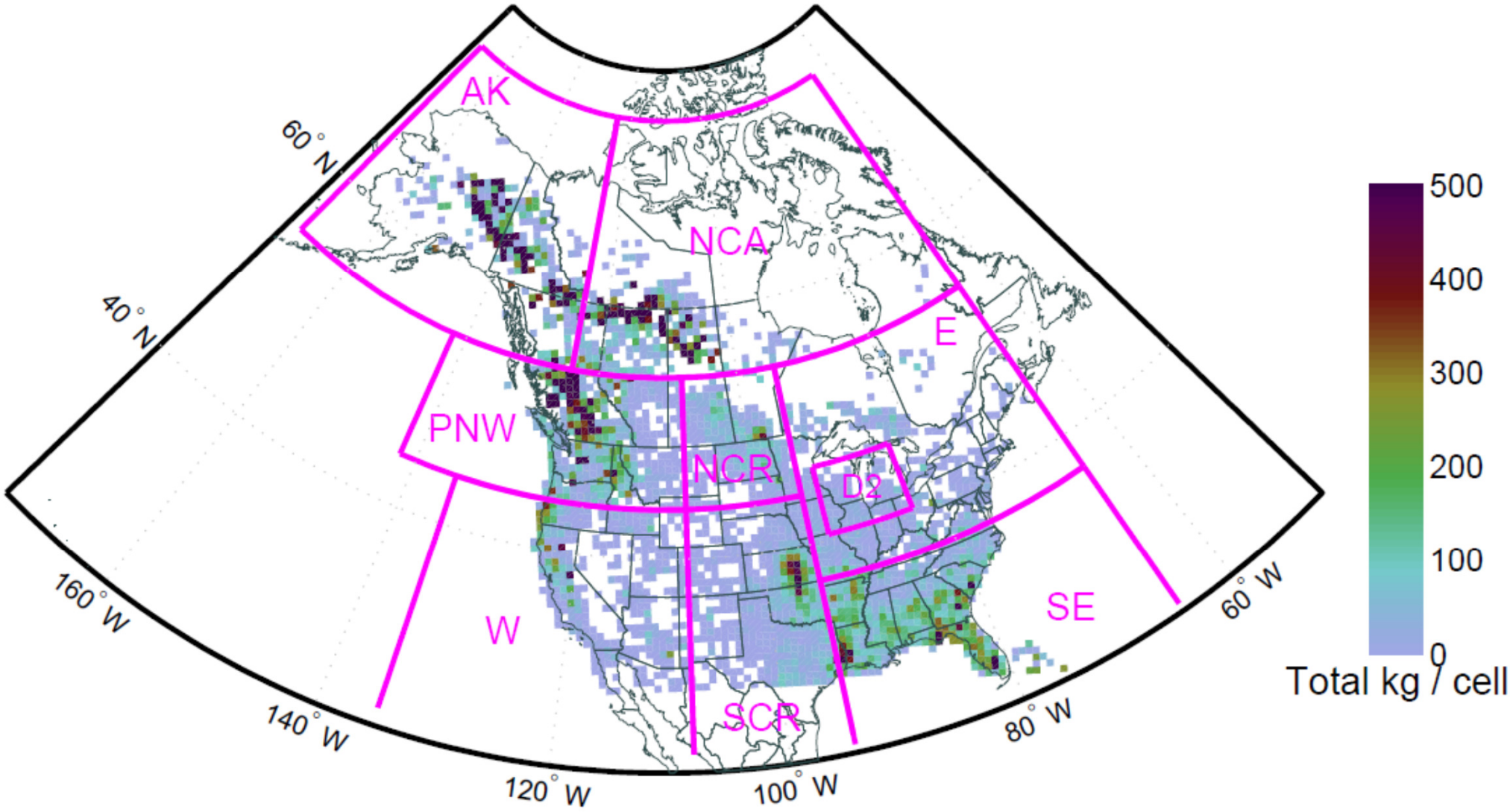
TRI 2010/2002 Mercury Inventory



Lake Surface Emissions of Gaseous Elemental Mercury
28 June 2004 – 11 May 2005

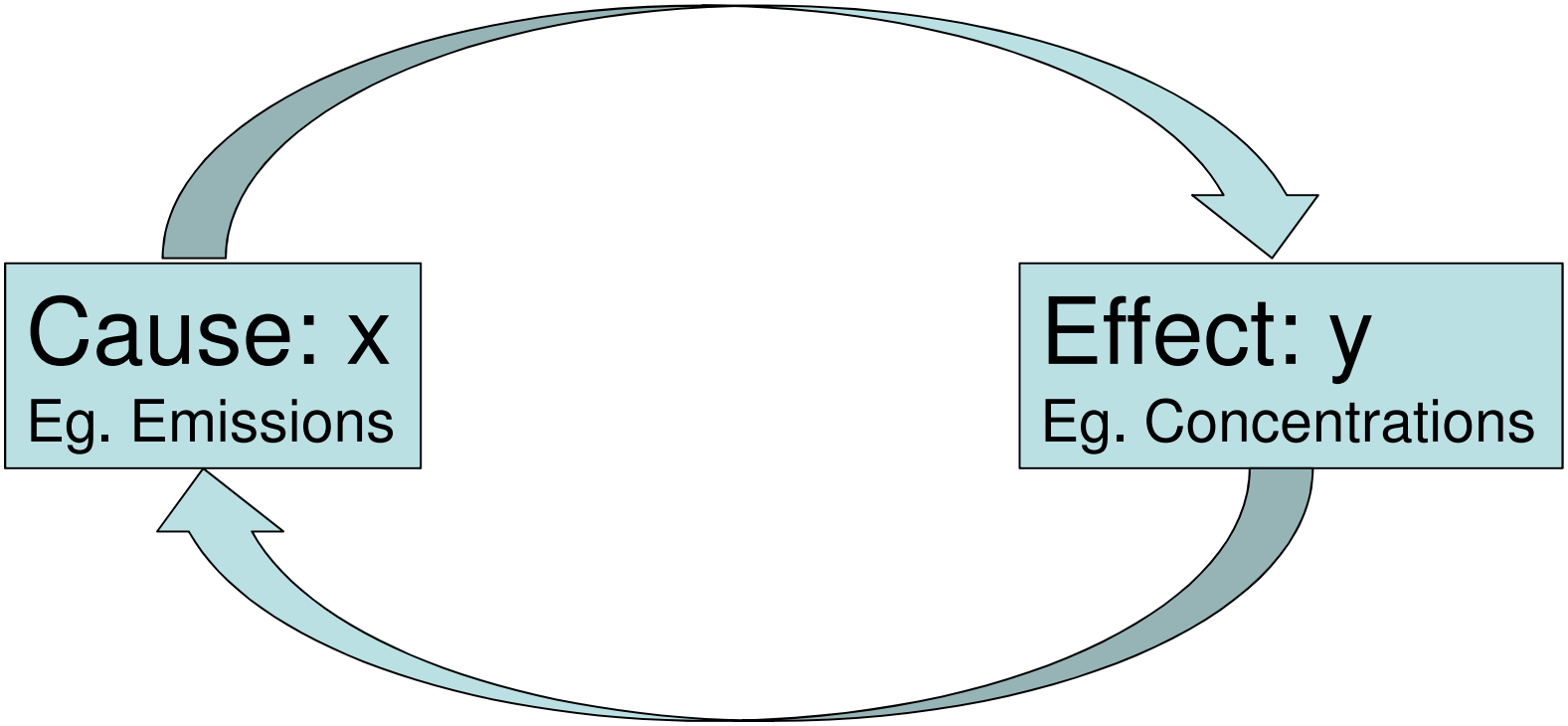


Forest Fire Inventory from FINN (Fire INventory from NCAR)
June 04 – May 05



Inverse Modeling

Forward Simulation: $y = Hx$

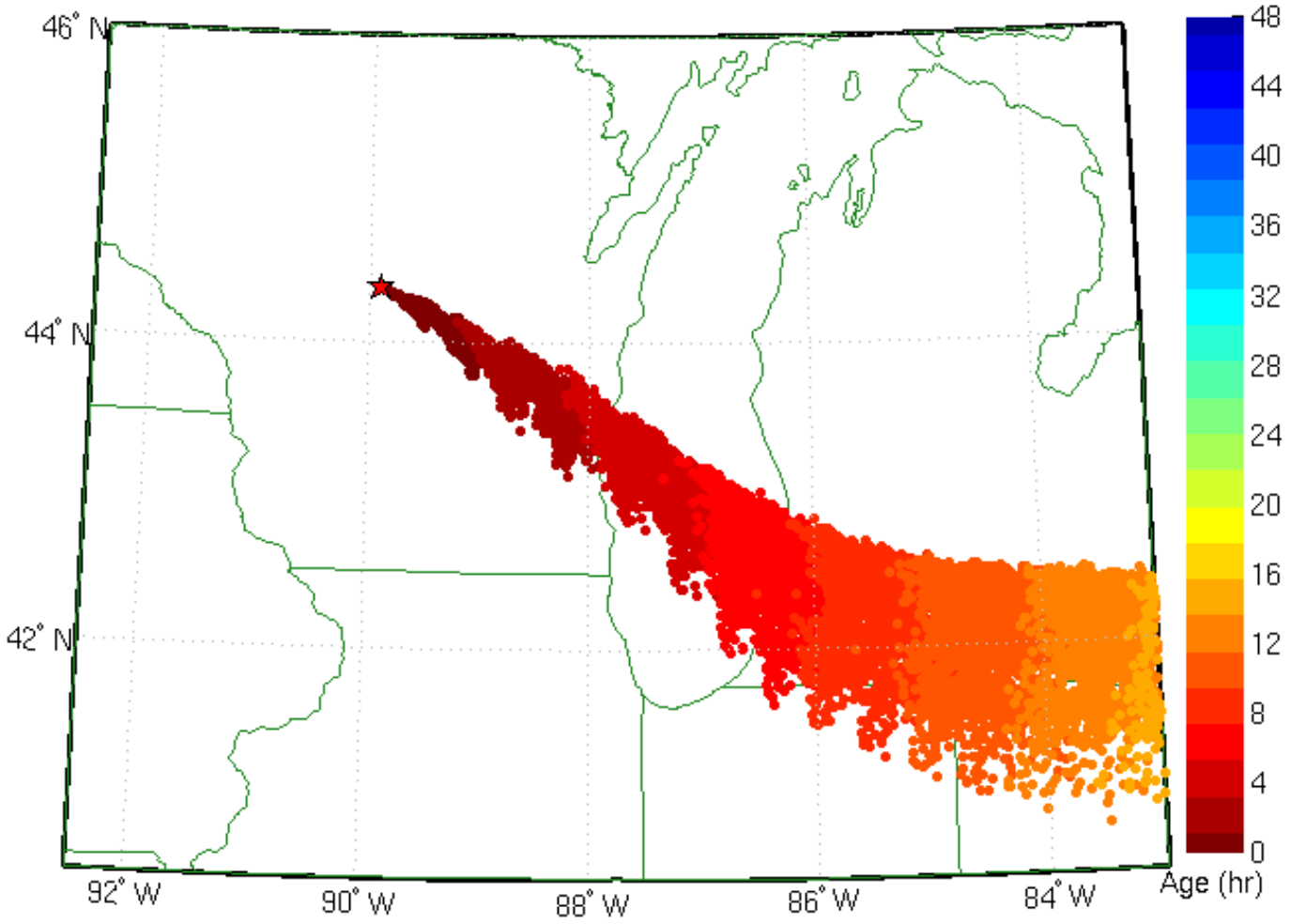


Inverse Problem: $x = H^{-1}y$

Textbook Intro: “Parameter Estimation and Inverse Problems” by Aster, Borchers and Thurber
Graphical Intro: “A Conceptual Introduction to Geophysical Inversion” by Andy Ganse, U. Washington

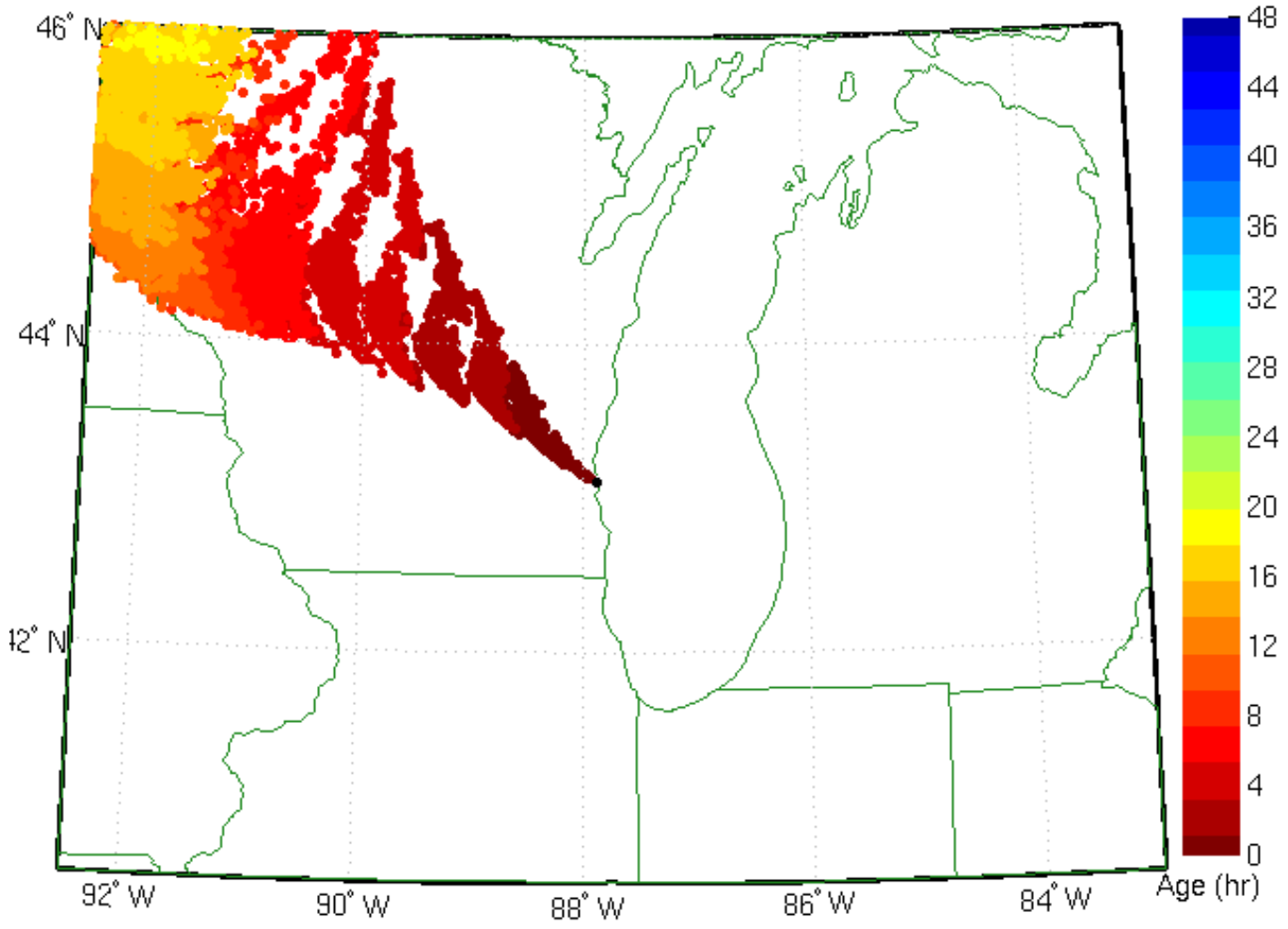
Forward Trajectories, Chlor-Alkali Plant

WRF-Flexpart, 8 July 2004 00:00

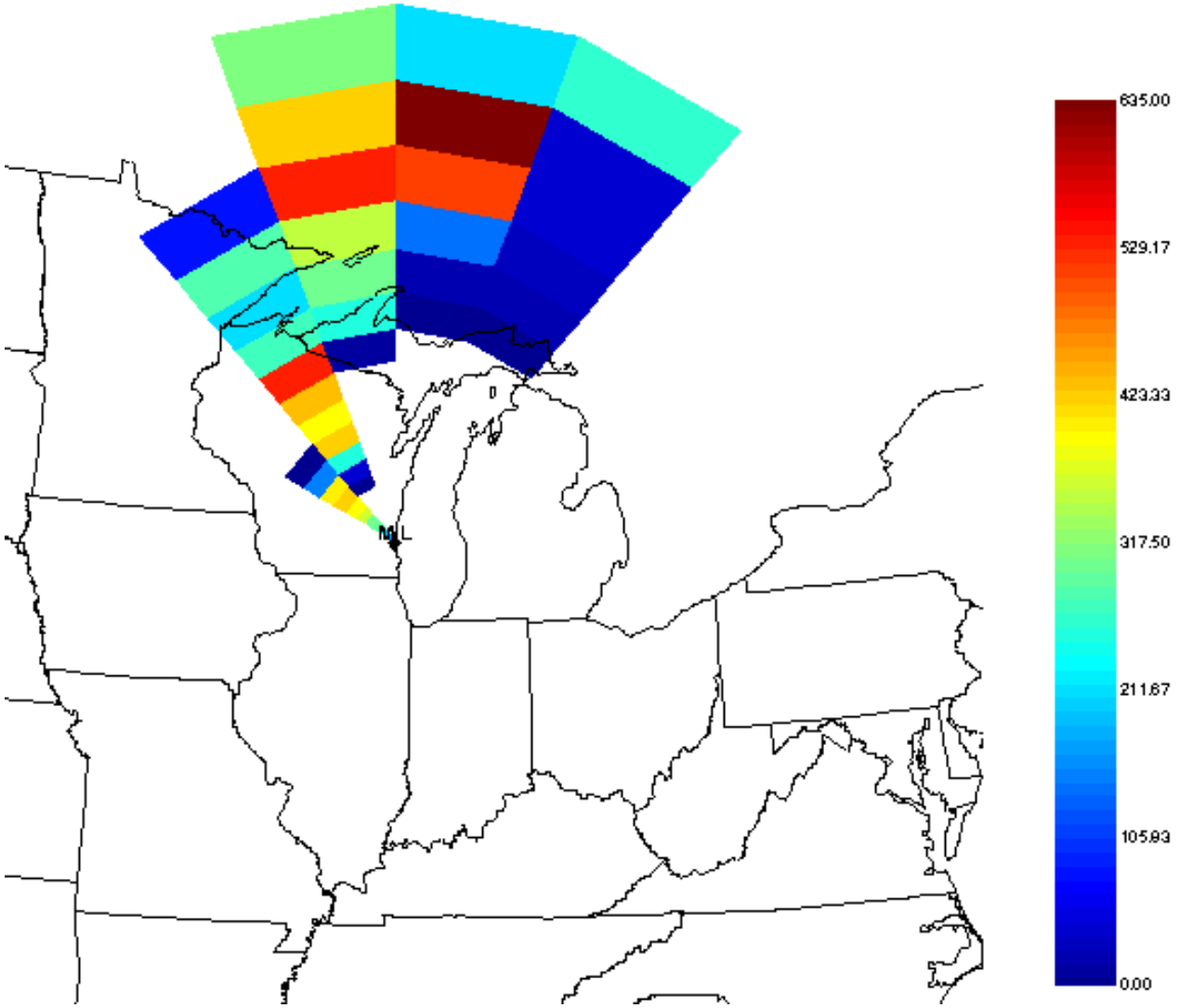


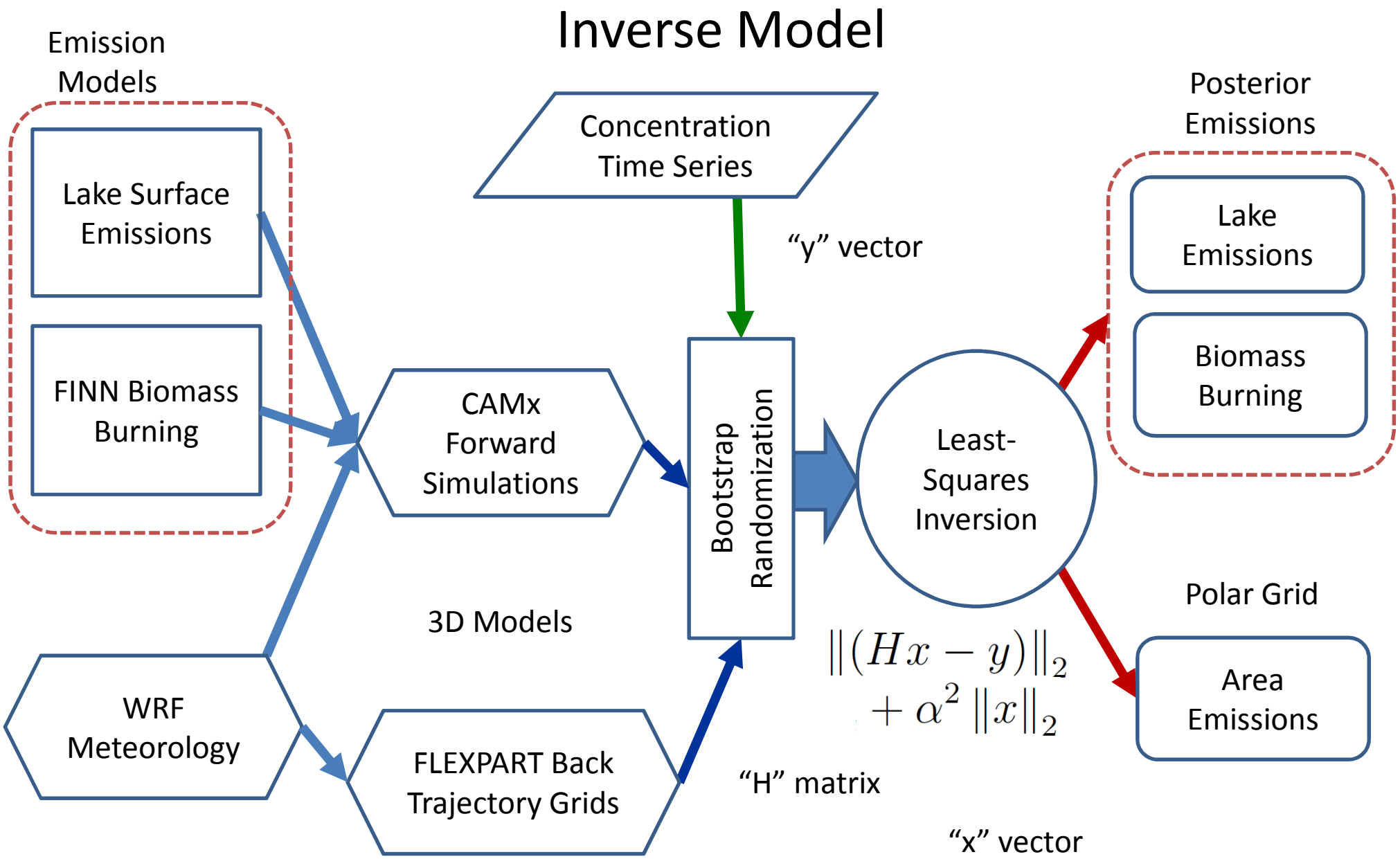
Backward Trajectories, Milwaukee

WRF-Flexpart, 8 July 2004 00:00



Backward Gridded Trajectories on a Polar Grid Residence Time Analysis (Surface layer)




Inverse Model
Emission Models
Lake Surface Emissions
FINN Biomass Burning
Concentration Time Series
"y" vector
CAMx Forward Simulations
3D Models
WRF Meteorology
FLEXPART Back Trajectory Grids
"H" matrix
Bootstrap Randomization
Least-Squares Inversion
$\|(Hx - y)\|_2 + \alpha^2 \|x\|_2$
"x" vector
Posterior Emissions
Lake Emissions
Biomass Burning
Polar Grid
Area Emissions

Inverse Modeling: Bayesian Formulation Simplifies to Least-Squares Inversion when Error Covariances are Diagonal

Bayesian Formulation:

$$J = (\mathbf{H}\boldsymbol{x} - \boldsymbol{y})^T \mathbf{R}_a^{-1} (\mathbf{H}\boldsymbol{x} - \boldsymbol{y}) + \boldsymbol{x}^T \mathbf{R}_b^{-1} \boldsymbol{x}$$

Simplifies to:

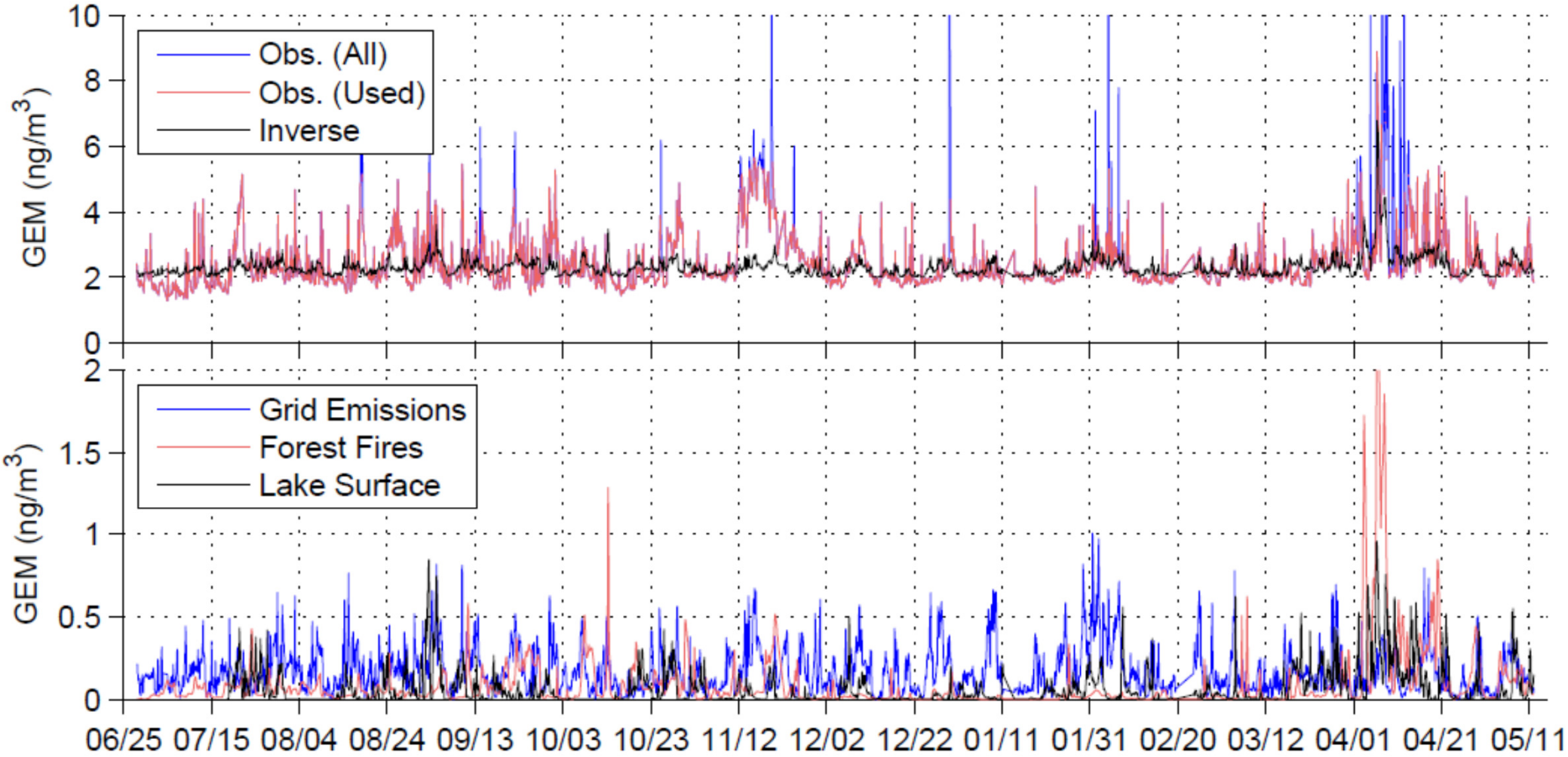
$$J = (\mathbf{H}\boldsymbol{x} - \boldsymbol{y})^T (\mathbf{H}\boldsymbol{x} - \boldsymbol{y}) + \alpha^2 \boldsymbol{x}^T \boldsymbol{x}$$

Solution in a single step of least-squares:

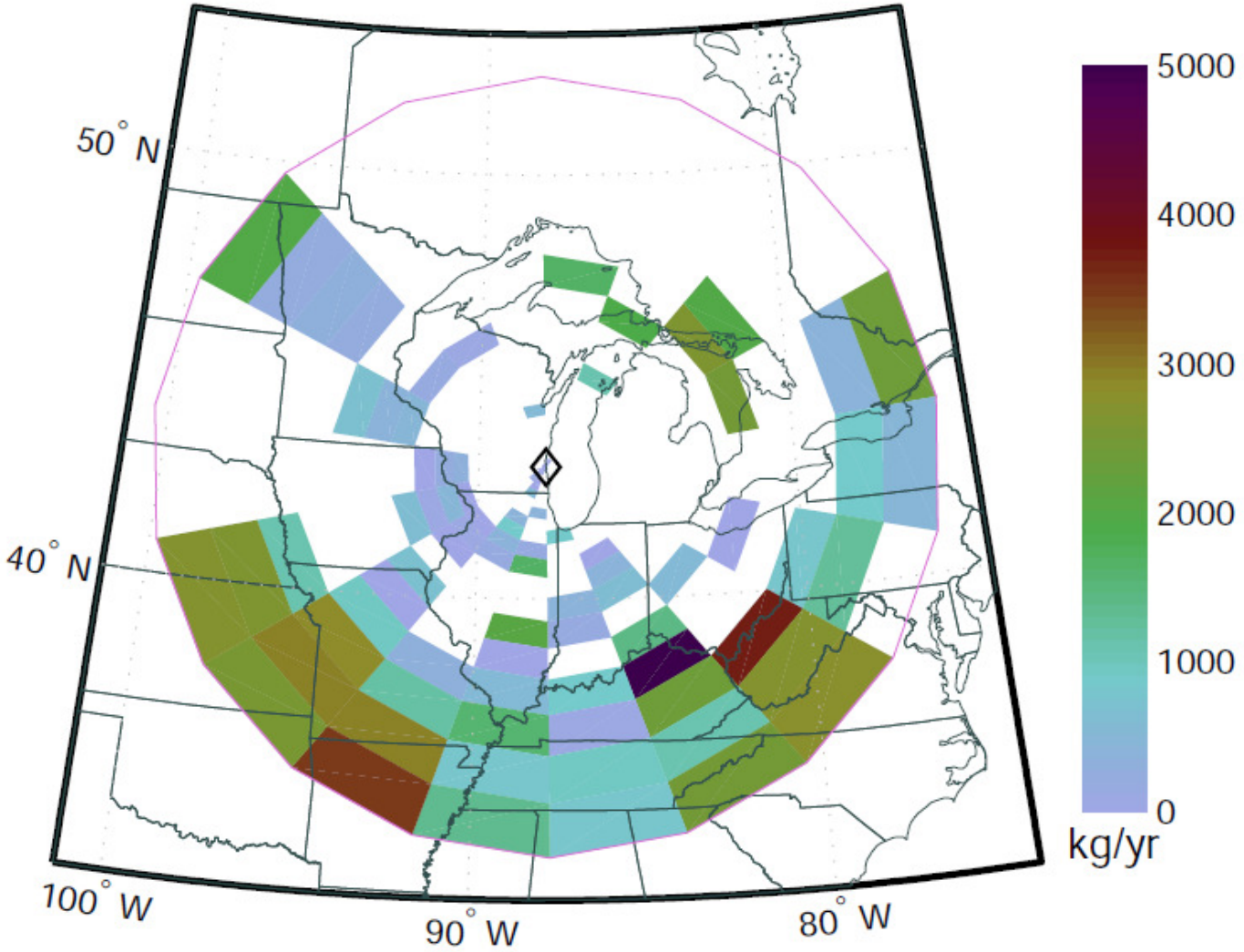
$$J = \left\| \boldsymbol{s} \cdot (\mathbf{H}''\boldsymbol{x} - \boldsymbol{y}'') \right\|_2$$

B. de Foy, C. Wiedinmyer, J.J. Schauer, "Estimation of mercury emissions from forest fires, lakes, regional and local sources using measurements in Milwaukee and an inverse method," *Atmospheric Chemistry & Physics*, 2012.

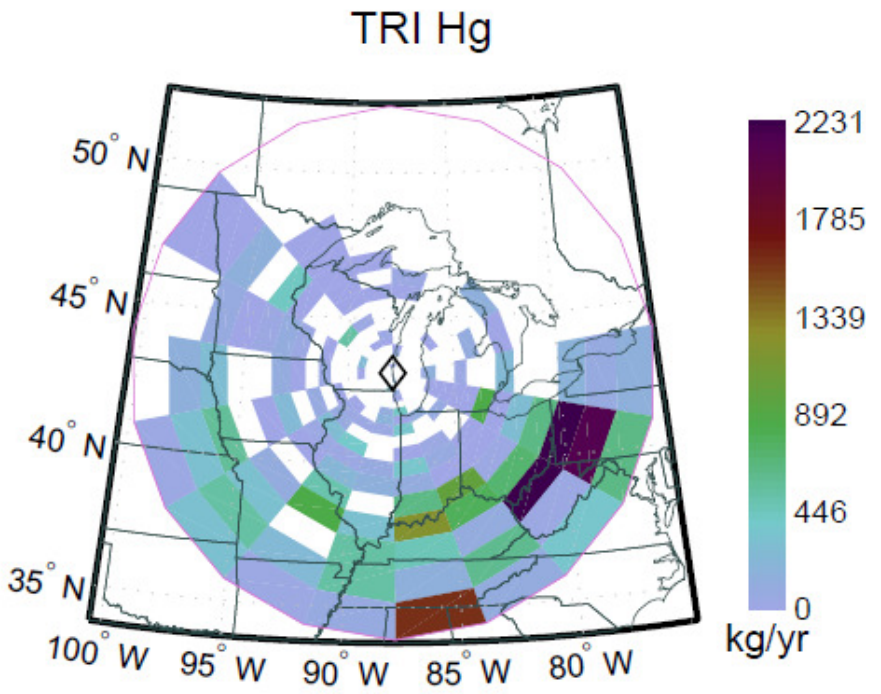
Inverse Model of Gaseous Elemental Mercury in Milwaukee and Contributions from Different Source Groups

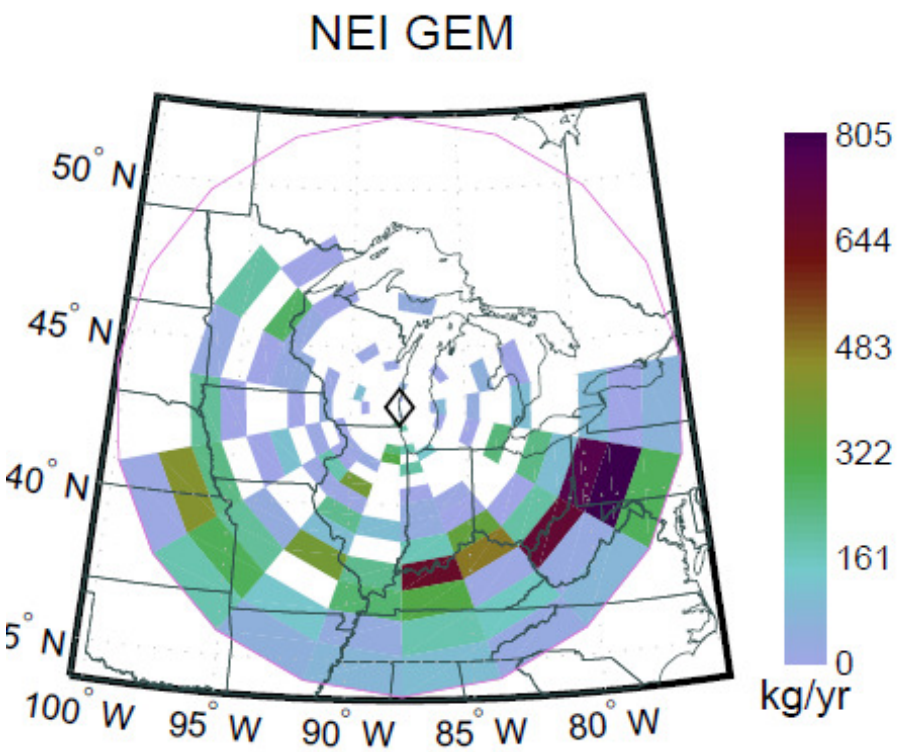


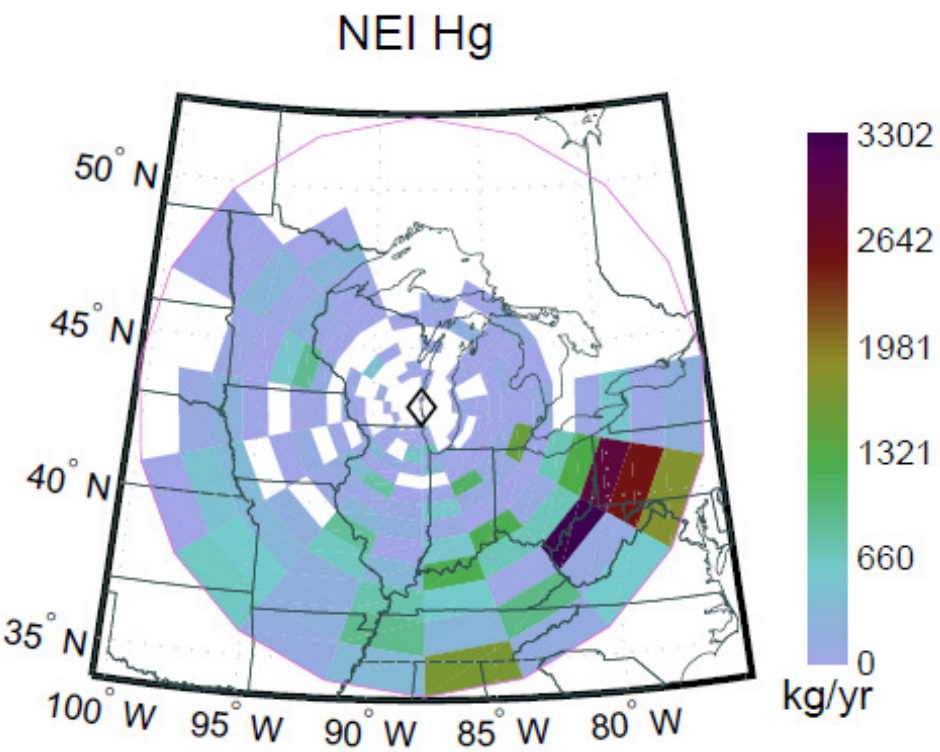
Gridded Emissions of Gaseous Elemental Mercury Estimated from Back-Trajectories



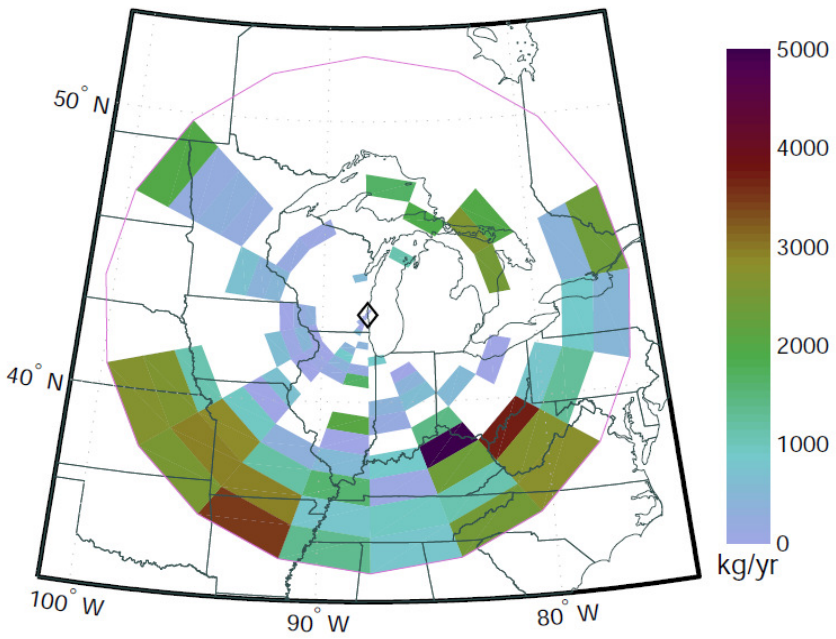
Gridded Emissions of Gaseous Elemental Mercury From Different Inventories



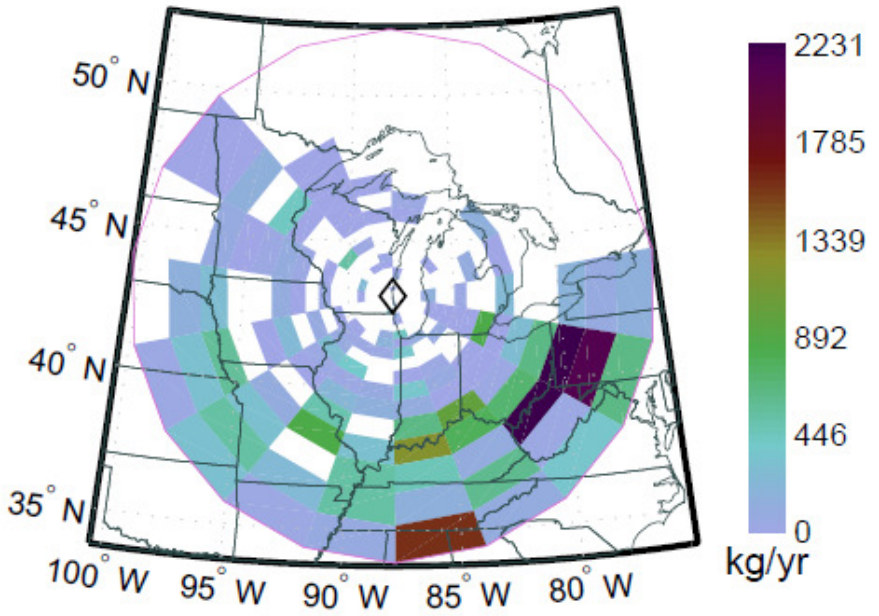




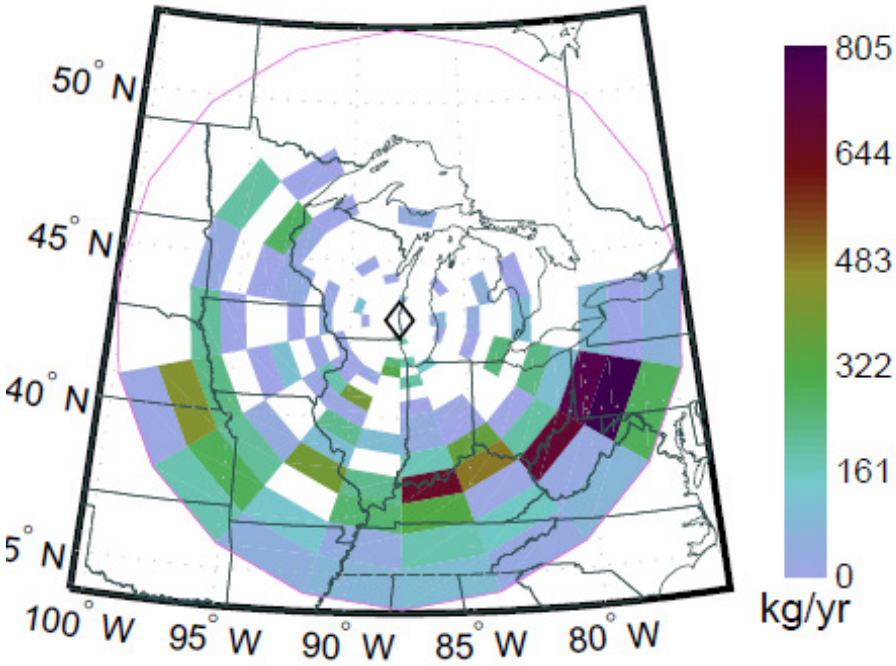
Inverse GEM Emissions



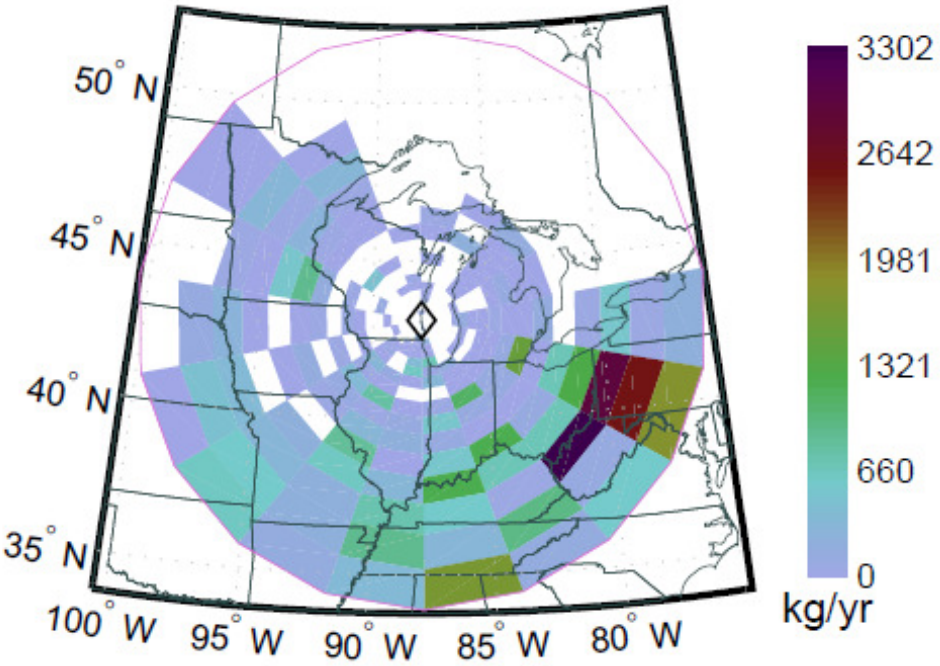
TRI Hg



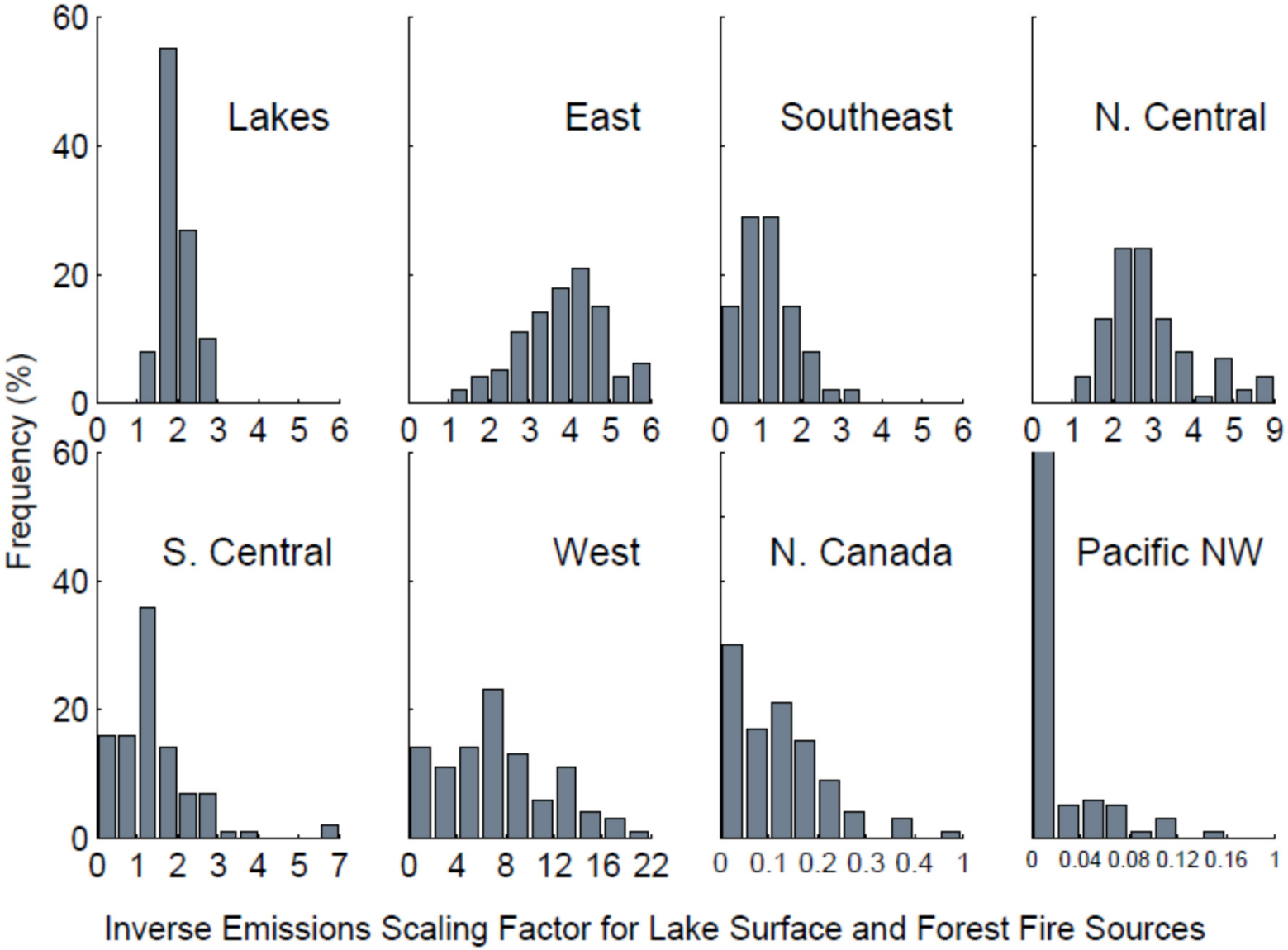
NEI GEM



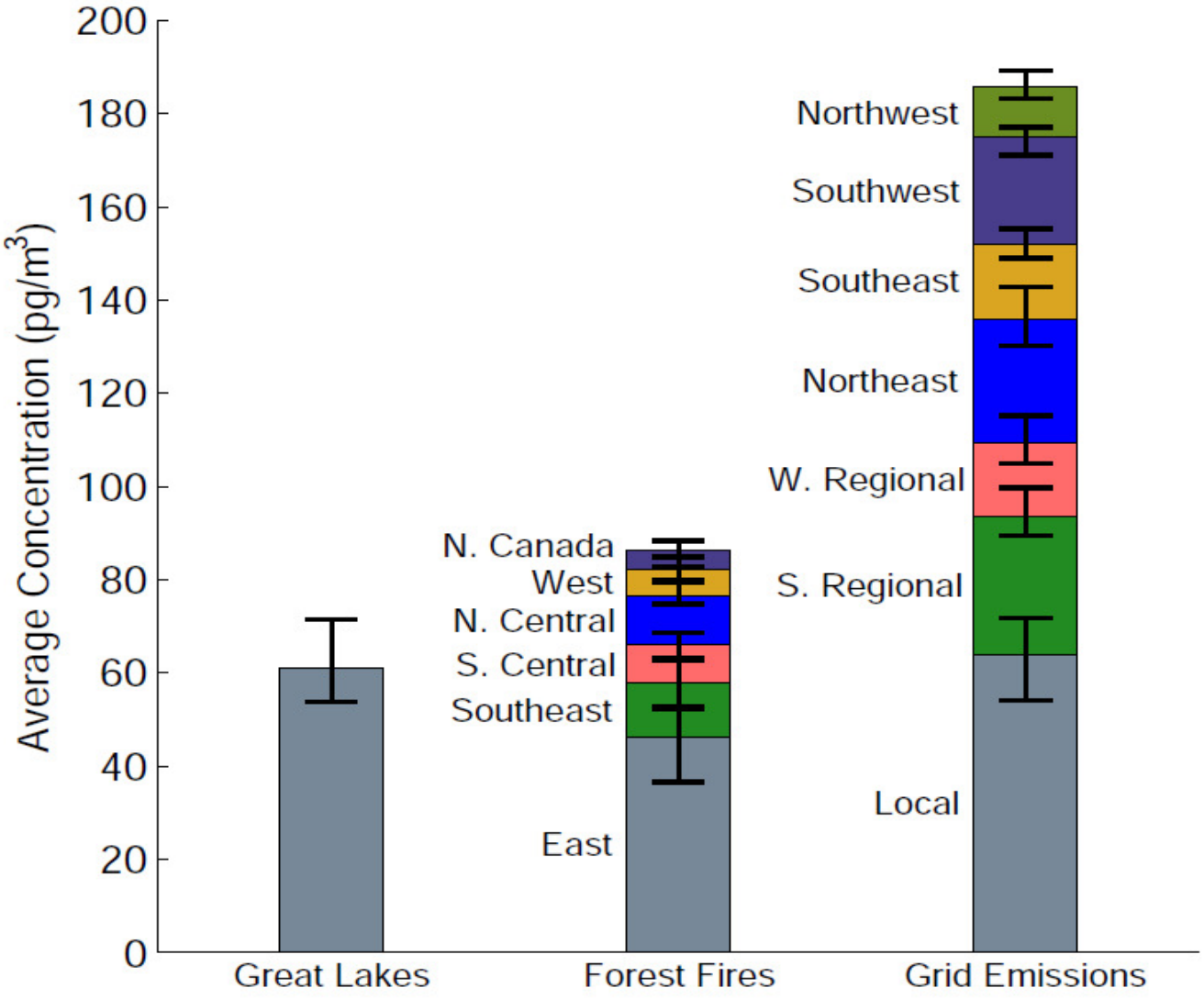
NEI Hg



Scaling Factors on GEM Emissions from Lake Outgassing and Forest Fires by Geographical Sector



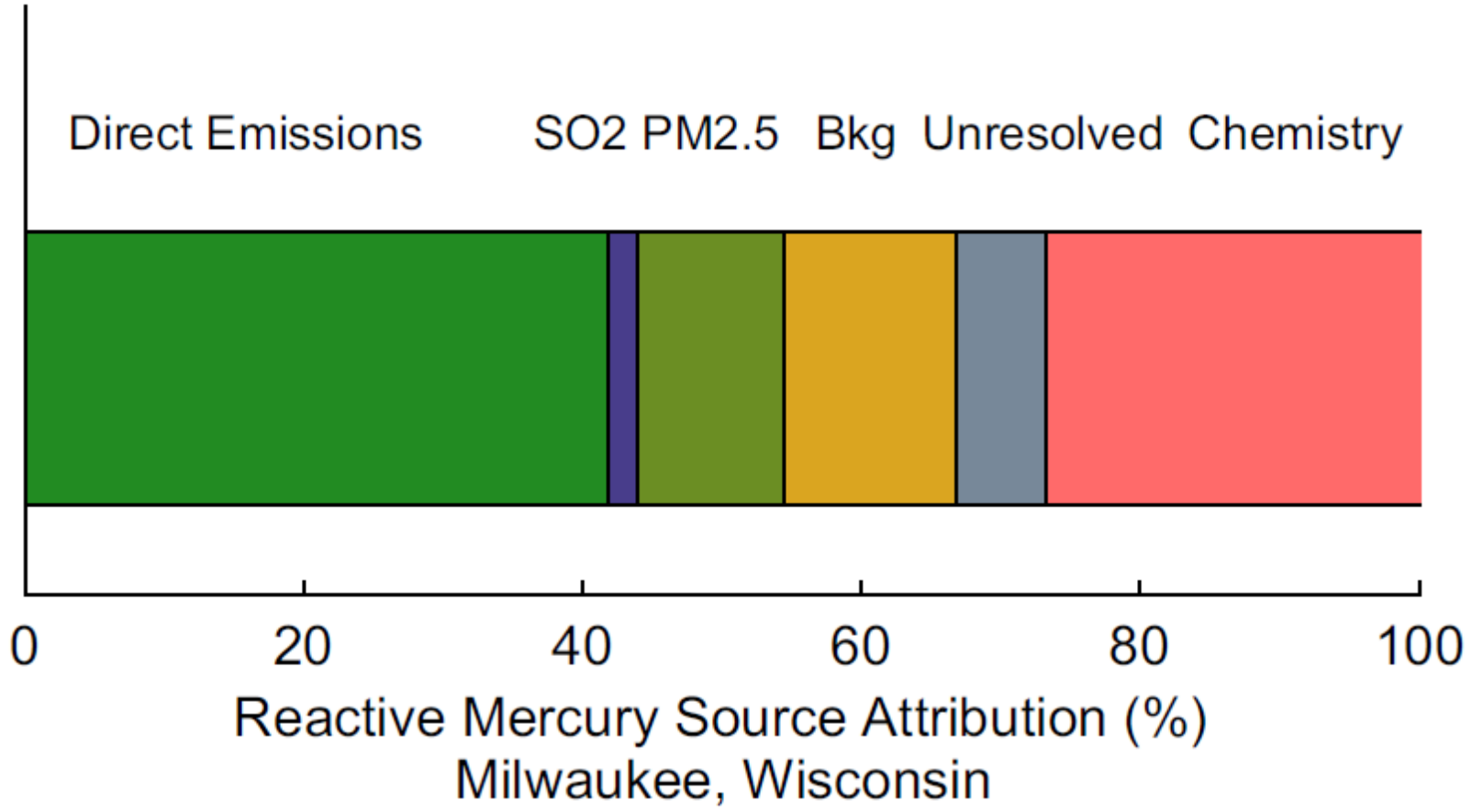
Source Group Impacts on Gaseous Elemental Mercury in Milwaukee Based on CAMx Simulations and Back-Trajectories



Source Group Impacts on GEM in Milwaukee Based on CAMx Simulations and Back-Trajectories (pg/m^3)

Source group		Median	Lower-quartile	Upper-quartile
Grids	Local (50 km radius)	63.8	54.1	71.7
	South regional	29.7	25.8	35.9
	Northeast	26.6	21.0	33.6
	Southeast	16.2	13.1	19.4
	West regional	15.8	11.5	21.7
	Southwest	22.9	19.0	25.0
	Northwest	10.6	8.2	14.2
Total Grid		187.9	177.3	202.2
Fires	WRF d2	0.0	0.0	0.0
	East	46.2	36.6	52.8
	Southeast	11.6	6.2	16.5
	South central	8.2	5.6	10.7
	North central	10.6	8.8	13.4
	West	5.5	3.2	8.3
	Pacific northwest	0.0	0.0	0.4
	Northern Canada	4.2	0.7	6.3
	Alaska	0.0	0.0	0.0
Total Fires		86.2	61.0	108.3
Lake surface		61.2	53.8	71.5
Local and regional background		490.0	480.0	510.0
Global background		1500.0	1500.0	1500.0
Unaccounted for in model		149.2	144.3	150.4
Inverted time series		2330.3	2323.9	2341.1
Measurements		2479.5	2468.2	2491.4

Reactive Mercury: Need to Include Time Series to Represent Oxidation Pathways



CAMx Chemical Mechanism for Mercury Oxidation

CAMx Mercury Reactions with O_3, H_2O_2, OH:

$$\mathrm{Hg(0)\,(g) + O_3\,(g) \rightarrow Hg(II)\,(g),} \quad k = 3\times10^{-20}\ \mathrm{cm^3\ molec^{-1}s^{-1}}$$

$$\mathrm{Hg(0)\,(g) + H_2O_2\,(g) \rightarrow Hg(OH)_2\,(g),} \quad k = 8.5\times10^{-19}\ \mathrm{cm^3\ molec^{-1}s^{-1}}$$

$$\mathrm{Hg(0)\,(g) + OH\,(g) \rightarrow Hg(OH)_2\,(g),} \quad k = 8\times10^{-14}\ \mathrm{cm^3\ molec^{-1}s^{-1}},$$

CAMx Mercury Reactions with Bromine:

$$\mathrm{Hg(0)\,(g) + Br\,(g) \rightarrow HgBr\,(g),} \quad k_1 = 3.6\times10^{-13}\,P\left(\frac{T}{298}\right)^{-1.86}\ \mathrm{cm^3\ molec^{-1}s^{-1}}$$

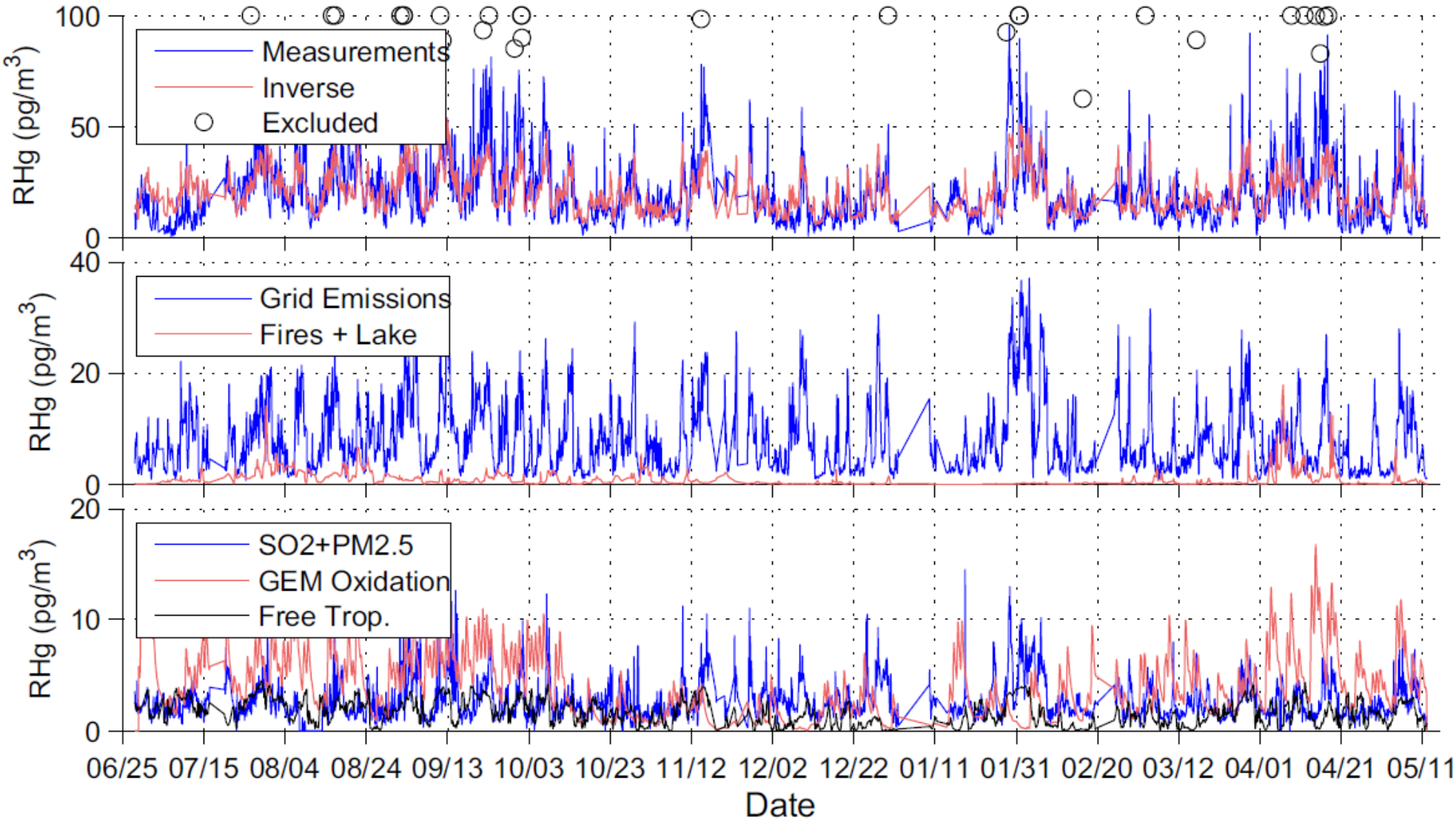
$$\mathrm{HgBr\,(g) \rightarrow Hg(0)\,(g),} \quad k_2 = 3.9\times10^{9}\exp\left(\frac{-8537}{T}\right)\ \mathrm{s^{-1}}$$

$$\mathrm{HgBr\,(g) + Br\,(g) \rightarrow HgBr_2\,(g),} \quad k_3 = 2.5\times10^{-10}\left(\frac{T}{298}\right)^{-0.57}\ \mathrm{cm^3\ molec^{-1}s^{-1}}$$

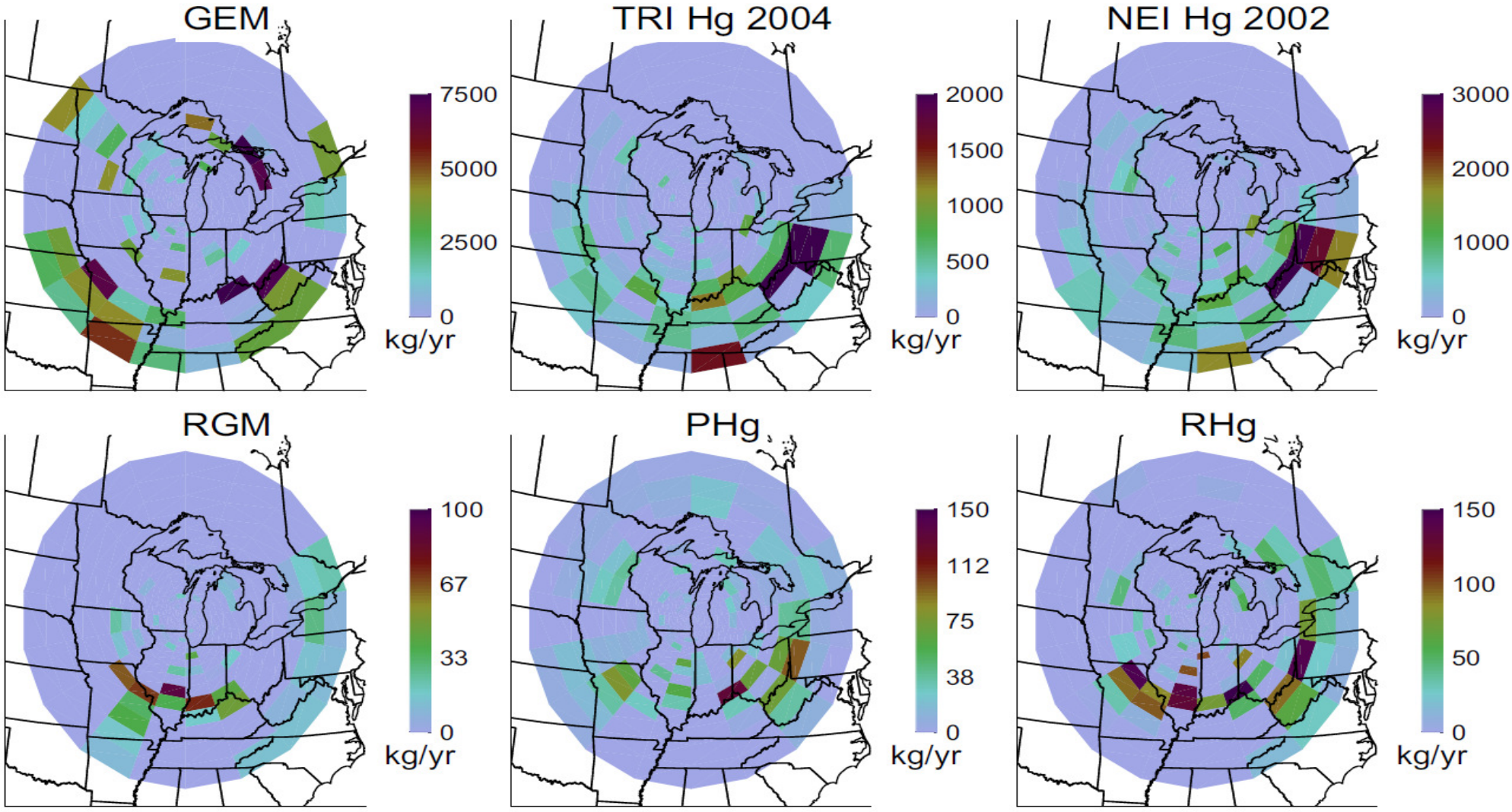
$$\mathrm{HgBr\,(g) + OH\,(g) \rightarrow HgBrOH\,(g),} \quad k_4 = 2.5\times10^{-10}\left(\frac{T}{298}\right)^{-0.57}\ \mathrm{cm^3\ molec^{-1}s^{-1}}$$

$$\mathrm{Hg(0)\,(g) + BrO\,(g) \rightarrow Hg(II)\,(g),} \quad k_5 = 1\times10^{-15}\ \mathrm{cm^3\ molec^{-1}s^{-1}}$$

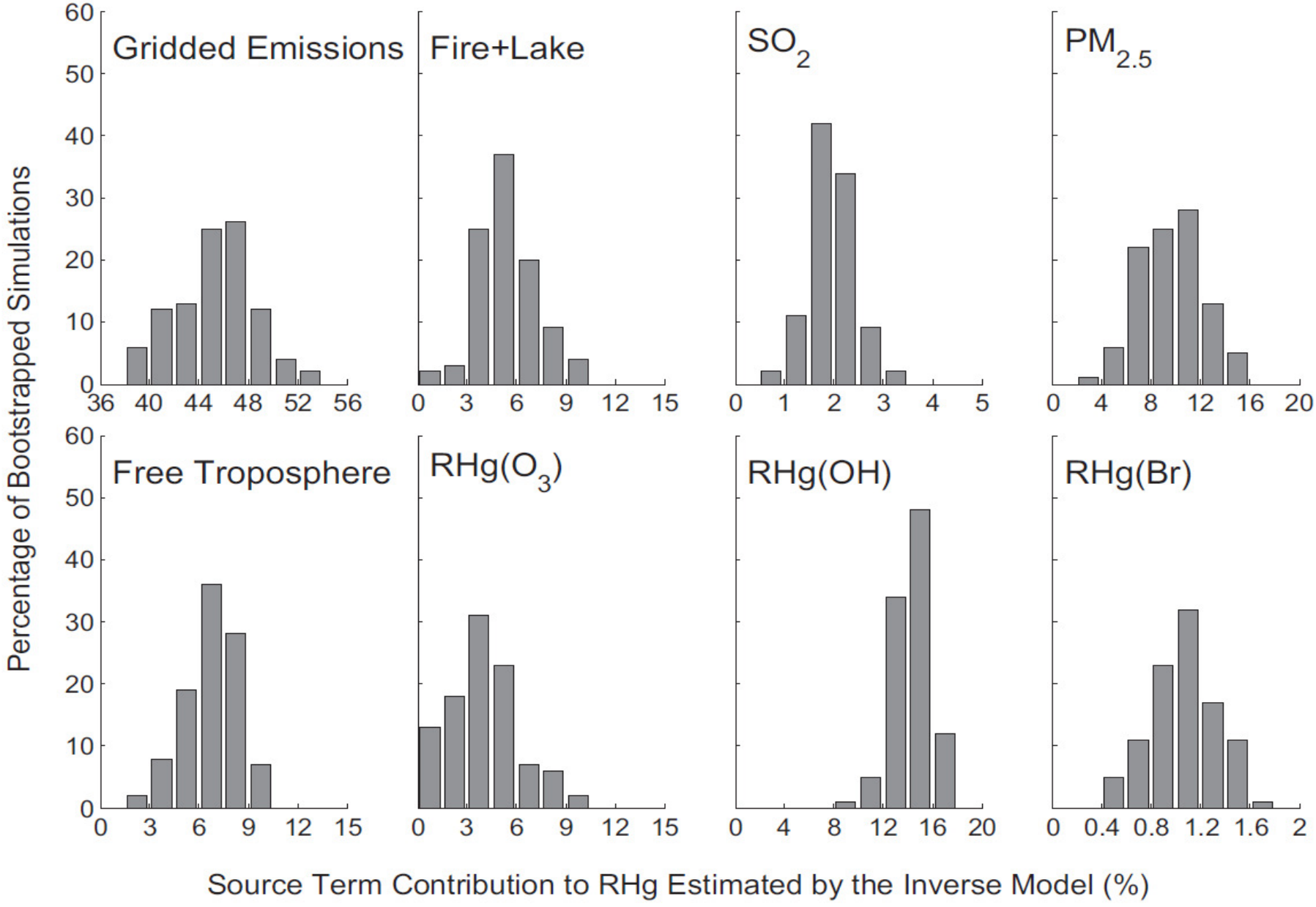
Time Series of Measured and Inverse Reactive Mercury



Gridded Emissions of Speciated Mercury Compared with TRI and NEI



Contributions to Reactive Mercury in Milwaukee Uncertainty Analysis using Bootstrapping

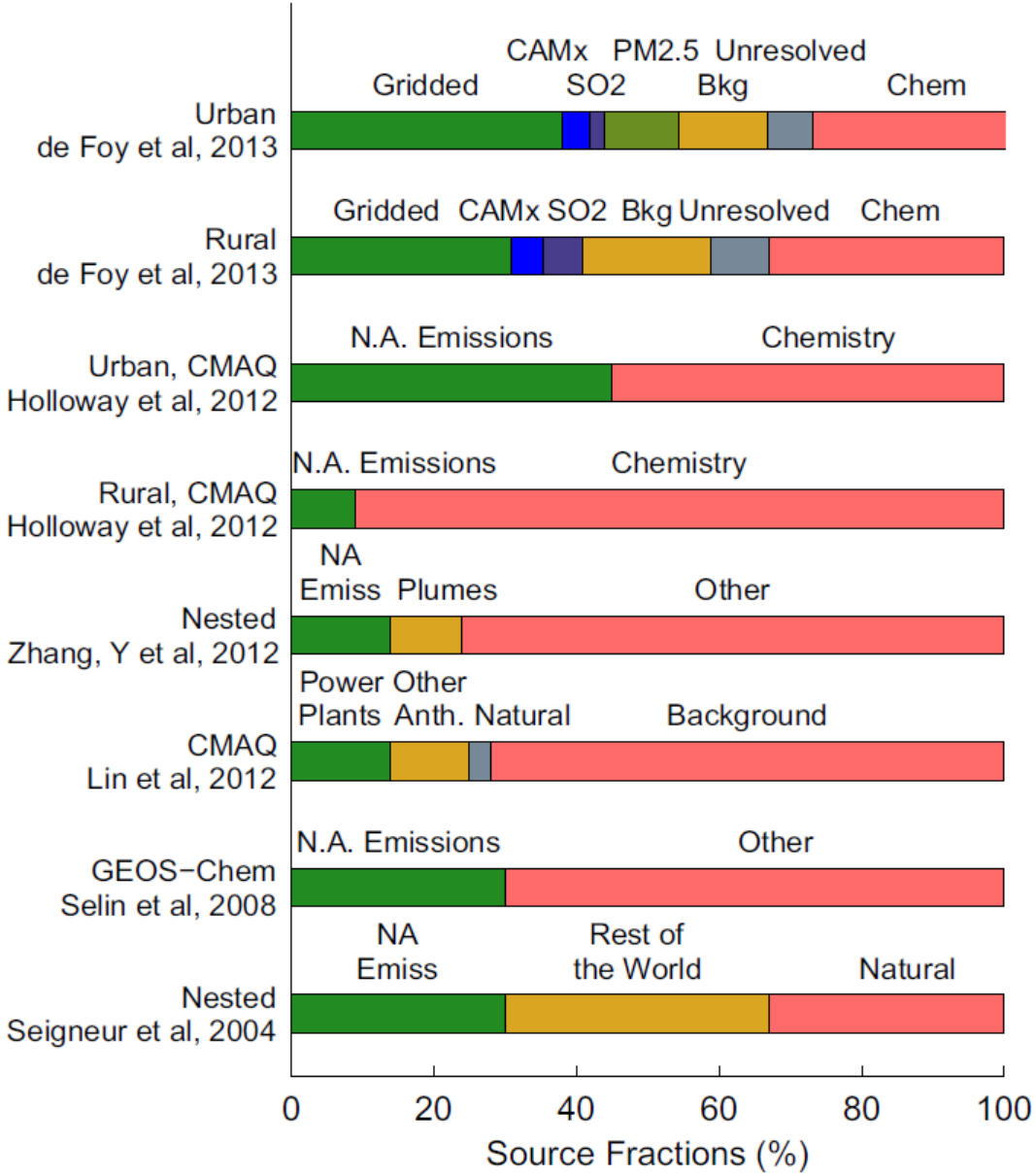


Mercury Associated with Different Source Groups and Oxidation Pathways (%)

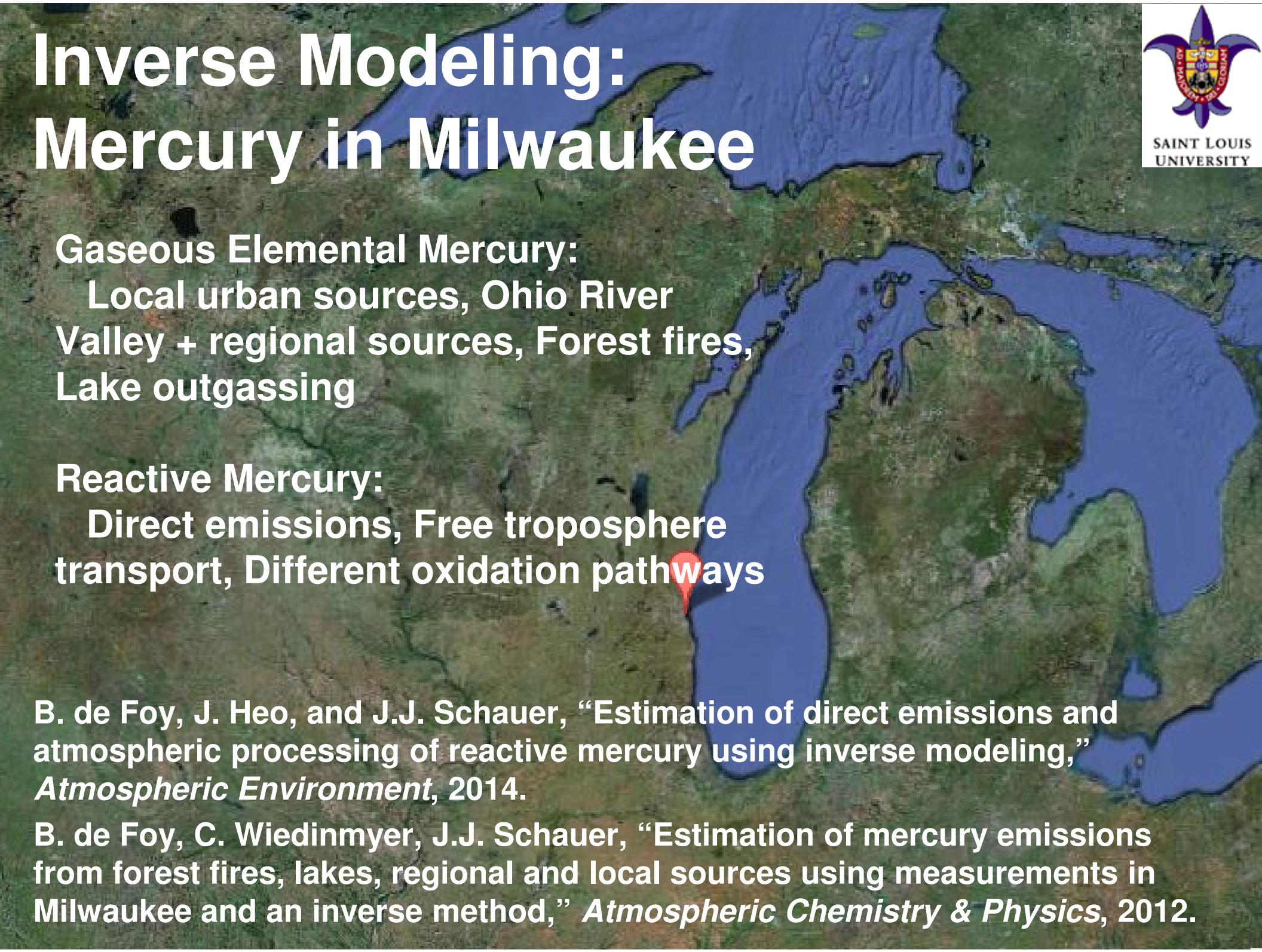
Hg form	Gridded	CAMx	SO_2	$PM_{2.5}$
GEM	13.9 ± 1.9	7.2 ± 1.4	0.7 ± 0.2	5.6 ± 1.2
RGM	32.2 ± 3.5	8.4 ± 3.2	2.4 ± 0.6	0.0 ± 0.0
PHg	50.0 ± 3.5	0.4 ± 0.7	2.1 ± 0.6	24.0 ± 2.6
RHg	40.6 ± 3.0	4.1 ± 1.8	2.3 ± 0.5	11.2 ± 2.6

Hg form	Free trop.	RGM(O_3)	RGM(OH)	RGM(Br)
GEM	0.0 ± 0.7	0.2 ± 1.2	0.3 ± 0.5	0.0 ± 0.1
RGM	14.8 ± 2.7	11.7 ± 3.1	24.9 ± 2.0	0.0 ± 0.0
PHg	4.0 ± 1.8	0.0 ± 0.2	2.1 ± 1.9	5.7 ± 0.6
RHg	8.1 ± 1.6	3.9 ± 2.1	15.5 ± 1.6	1.2 ± 0.3

Source Attribution of Reactive Mercury: Current Inverse model suggests that a greater fraction is directly emitted compared to previous modeling studies



Inverse Modeling: Mercury in Milwaukee



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