Supporting information for: Emissions Inventory of $PM_{2.5}$ Trace Elements across the United States

Adam Reff,* Prakash V. Bhave, George A. Pouliot, Thompson G. Pace, J. David Mobley, and Marc Houyoux

U. S. Environmental Protection Agency, Research Triangle Park, NC 27711

E-mail: reff.adam@epa.gov

1 Introduction

The development of the composite profiles involved deliberating over numerous details regarding the data and meta-data of the SPECIATE profiles, the profile compositing process, the evaluation of the speciated $PM_{2.5}$ inventory against the HAP inventory, and the computation of derived chemical species (i.e. Metallic Oxygen and Organic Material). In addition, the resulting emissions inventory also contains a great amount of spatial-, chemical- and source-specific information that can be subsetted in a large number of possible ways for further study. This Supporting Information is intended to house all of these details that are too numerous to fit in the Methods and Results sections of the main paper, but which could be potentially useful for readers to conduct similar analyses and see a more complete set of results.

2 Unused SPECIATE Profiles

During our survey of the speciation profiles of particulate matter in SPECIATE, numerous profiles were excluded from use in the process of speciating the $PM_{2.5}$ NEI. Over 3000 profiles were found to be derived from measurements of PM_{10} or larger particles, and 88 were from PM_1 or smaller. We also found that 268 of the $PM_{2.5}$ profiles did not appear to be appropriate for matching to any SCCs in the NEI, many of which were collected outside of the U.S.. Many of the raw profiles that we selected were composites of other profiles that were also in SPECIATE, and those non-composite profiles were excluded to prevent double weighting. The database also included roadside and tunnel samples that were excluded due to not being specific to either fuel or vehicle type. Finally, a small number profiles were excluded due to outdated sampling methodologies, obsolete source technologies and erroneous data (i.e. sum of species was > 1).

3 Development of the Source Categorization Scheme

The 66 $PM_{2.5}$ source categories used for speciation of the 2001 CAIR NEI (see Table S1 by Bhave et al. (2007) (*1*)) were used as our starting point because a cross-reference table that maps all 3780 SCCs to one of the 66 source categories had been developed and reviewed extensively prior to our study. The steps below were then taken to develop the set of source categories used in this work.

First, we assessed the underlying speciation data for the original 66 source categories. On this basis, 6 of the categories (liquid waste combustion, jet fuel combustion, carbon black manufacturing, basic oxygen furnace, organic liquid, and nonroad diesel exhaust) were deleted because no source-specific measured profiles were available to speciate their emissions. In addition, 3 of the

original 66 source categories were renamed to reflect better the emission source that their underlying speciation data were collected from: residential heating was renamed as residential natural gas combustion, organic chemical manufacture was renamed as urea fertilizer, and paint manufacture was renamed as surface coating.

Second, we identified source categories that could be subdivided due to the availability of source-specific profiles in SPECIATE v4.0 and the presence of SCCs with comparable specificity. The coal-combustion category was split into industrial-scale combustion of bituminous, subbituminous, and lignite coals, and a fourth category was created for residential coal combustion. The soil-dust category was subdivided into unpaved road dust, agricultural soil, construction dust, dairy soil, limestone dust, crustal material, and industrial soil. The charcoal broiling category was divided into charbroiling and meat frying. By subdividing 3 of the original categories into 13 new categories, 10 additional source categories were added to the list.

Third, we identified SCCs for which source-specific profiles are in SPECIATE 4.0 but the existing source categories were too generic. To improve the speciation of these SCCs, 14 new source categories were created: auto body shredding, boric acid manufacturing, calcium carbide furnace, cast iron cupola, coke calciner, inorganic fertilizer, lime kiln, potato deep-frying, prescribed burning, process gas combustion, slash burning, sludge combustion, steel desulfurization, and tire burning. In the process of adding these source categories, the original petroleum-heater category was rendered obsolete and deleted from the list. In addition, distinct source categories were created for tire dust and brake-lining dust so those emissions can be distinguished easily from onroad vehicle exhaust. Overall, 26 new source categories were added and 7 were deleted from the original list. The final set of 85 source categories is shown in Figure 2 of the main paper and the cross-reference table mentioned above was revised to map each SCC to one of these 85 categories.

4 Motor Vehicle Emissions

The 2001 $PM_{2.5}$ NEI does not distinguish between contributions of brake dust, tire dust, and vehicle exhaust for motor vehicle emissions. Contributions from each of these motor vehicle process were therefore disaggregated by applying emission factors obtained from a base run of the MOBILE 6 model (`http://www.epa.gov/otaq/m6.htm`). The brake/tire/exhaust fractions used are shown in Table 1. These contributions were multiplied against the emissions of the HDDV, LDDV, and Onroad Gasoline SCCs as shown in Table 1. The resulting emissions were then put into the Brake Lining Dust, Tire Dust, and Exhaust (the latter specific to vehicle type) source categories for subsequent speciation. Diesel powered electric generator SCCs were classified into the HDDV source category along with the relevant motor vehicle SCCs, and these are included in the total HDDV Exhaust $PM_{2.5}$ emissions.

SCC Type	Source Category	Brake	Tire	Exhaust
Heavy Duty Diesel Vehicles	HDDV	0.0097	0.0119	0.978
Light Duty Diesel Vehicles	LDDV	0.019	0.0072	0.974
Light Duty Diesel Trucks	LDDV	0.0196	0.0074	0.973
Light Duty Gasoline Vehicles	Onroad Gasoline	0.329	0.124	0.547
Light Duty Gasoline Trucks	Onroad Gasoline	0.256	0.097	0.647
Buses	Onroad Gasoline	0.0097	0.0119	0.978
Motorcycles	Onroad Gasoline	0.245	0.046	0.708

Table 1: Fractions of $PM_{2.5}$ mass attributed Brake Lining Dust, Tire Dust, and Exhaust that were applied to motor vehicle source category emissions

5 Adjustments to raw and composited SPECIATE profiles

5.1 Composite values of carbon species

Different analytical methods can yield very different results for OC and EC in a sample, but total carbon (TC) results are fairly consistent across the methods (*2*). To ensure that (1) the sum of OC and EC in each composite is in agreement with median TC values in the individual profiles and (2) the composite values of OC and EC are reasonably consistent with measurements taken by a thermal-optical reflectance (TOR) method (*3*), the raw OC and EC weight fractions were modified in the following manner prior to compositing. The OC and EC fractions were summed to calculate TC in each source profile. If any SPECIATE profiles in a source category measured carbon using a TOR method, those profiles were used to compute $median(OC)/median(TC)$ and $median(EC)/median(TC)$ ratios. These ratios were multiplied by the TC values from all non-TOR profiles in the same source category to estimate OC and EC values for each profile as would be measured using the TOR method. If no SPECIATE profiles in a category measured carbon by a TOR method, then the $median(OC)/median(TC)$ and $median(EC)/median(TC)$ ratios computed using all profiles in the category were multiplied by TC to calculate an OC and EC value for each profile.

5.2 Sub-composites

During our survey of the SPECIATE data, a number of raw profiles were found to be repeat samples from a single study. To prevent these samples from over-weighting the composite profile for their assigned source category, sub-composites of the similar profiles were created prior to their inclusion in the main composite for each source category. Sub-composites were created in the same manner as the main composites (e.g. median of $PM_{2.5}$ species weight fractions, similar treatment

of OC/EC data). Information about the creation of the sub-composites is shown in Table 2.

Source Category	Sub-composite Description	SPECIATE Profiles
Agricultural Burning	Rice & Straw Burning	4391, 4392
Paved Road Dust	Central CA	3303, 3328, 3348, 3383, 3388, 3423, 3433
	Phoenix	3500, 3503
	Robbins, IL	3971, 3975, 3977
Residential Wood Combustion	N/A (Unknown wood type)	3232, 3233, 3234, 3235, 3236, 3327, 3238, 3239, 3240, 3248, 3273, 3278, 421022.5, 421042.5, 421052.5, 421062.5, 423032.5, 423172.5, 423182.5, 423192.5, 423312.5
	Hardwood	3767, 3768, 3769, 3770, 3920, 3921, 3922, 3923, 3924, 421032.5, 422022.5, 422042.5, 4384, 4385, 4389, 4644
	Softwood	3925, 3926, 3927, 3928, 3929, 3931, 3932, 3933, 3934, 3935, 3936, 3937, 421012.5, 422032.5, 4387, 4645
	HardSoft	Pool of profiles in the Hardwood and Softwood sub-composites
	HardSoftNA	Pool of profiles in the Hardwood, Softwood, and NA sub-composites
	Almond	4386
	Eucalyptus	4388, 4643
	Cedar	4393
	Synthetic	3930, 422052.5
Unpaved Road Dust	Central CA	3323, 3343, 3353, 3368, 3373, 3378, 3438
	Ohio	3532, 3535
	Phoenix	3506, 3509
	Robbins, IL	3967, 3969

Table 2: Sub-composites made during the compositing of SPECIATE profiles. Note that multiple composites were created from overlapping subsets of the raw profiles in the Residential Wood Combustion category, but only the "HardSoft" composite was mapped to the NEI

5.3 Profile-Specific Adjustments

Notes regarding the creation and adjustment of profiles for specific source categories are given in Table 3.

Source Category	SPECIATE Profile #	Notes
Cast Iron Cupola	286012.5	Hybrid created from Heat Treating profile and S value from Cast Iron Cupola profile
Chem Manuf - Avg	900022.5	Only historically based OC/EC/SO_4/NO_3 used - too generic for metals speciation
Coke Calciner	262062.5	Source was only tested for elemental composition, used original ref to calculate SO_4, EC, OC, and NO_3 values.
Copper Production	91008	Pb and As set to 0 due to outdated profiles - these emissions should be controlled by 1990 CAA
Electric Arc Furnace	91011	Cr value in one profile (283052.5) set to 0 to reflect probable updated HAPS controls due to 1990 CAA
Ferromanganese Furnace	91012	Mn value pulled to 0 to reflect probable updated HAPS controls due to 1990 CAA
Heat Treating	286012.5	EC value in SPECIATE 3.2 corrected; values of Ba, Br, Cd, Ca, Cr, Cu, K, Mo, NO3, Pb, and Zn appeared to be imputed numbers below MDL, so they were reduced to 0
Ind Manuf - Avg.	900162.5	Only historically based OC/EC/SO_4/NO_3 used - too generic for metals speciation
InorganicChemicalManufacture	92039	Old 2001 Profile for OC,EC,NO_3, and SO_4
Limestone Dust	91019	CO3 mis-labeled as EC in 43304; EC set to missing, SO_4 calculated from S
Mineral Products - Avg	900132.5	Only historically based OC/EC/SO_4/NO_3 used - too generic for metals speciation
NaturalGasCombustion	91020	Composited by Ron Myers of EPA from profiles 4403 and 4398 informed by data from DOE
Open Hearth Furnace	283022.5	OC value carried over from SPECIATE 3.2 was corrected to match value in the reference
Overall Average-Default	000002.5	Only historically based OC/EC/SO_4/NO_3 used - too generic for metals speciation
Petroleum Ind - Avg	900142.5	Only historically based OC/EC/SO_4/NO_3 used - too generic for metals speciation
Residential Natural Gas Combustion	421072.5	OC and EC were corrected for artifacts explained in profile's reference
ResidualOilCombustion	92072	Hybrid of OC/EC/SO_4/NO_3 profile from Hays et al. (2008) (*4*) and metals from a profile 135012.5
Sandblast	91036	SO_4 and NO_3 from old profile; OC based on TC value in 25702
Secondary Copper	205032.5	Pb set to 0 - Pb would likely be controlled as a CAP
Secondary Lead	204012.5	Pb set to 0 down from 0.5 - Pb would likely be controlled as a CAP
Sintering Furnace	91038	Pb and Cr in 283012.5 set to 0 to account for post-1990 controls; Cd in 283012.5 set to 0 - was $<$ MDL and leading to large differences betwe 2002 Inv.
Slash Burning	91039	SO_4 calculated from S; NO_3 value copied from Wildfires composite profile
Sludge Combustion	171202.5	SO_4 calculated from S; OC, EC, and NO_3 copied from Solid Waste Combustion
Solid Waste Combustion	91040	Hg and Pb were set to 0 due to possibility of battery burning in one profile
Steel Desulfurization	283062.5	Only measured elemental composition; assumed all measured S was SO_4
WoodFiredBoiler	4704	Used old SMOKE profile #NWWAS from 2001 NRML report (*5*); divided the POA measurement by 1.2 to get OC

Table 3: Changes made to specific species' mass fraction values in raw and composite profiles during the compositing process.

5.4 Additional Composite Profiles

In addition to the 85 source categories listed in Figure 2 of the main article, a small number of additional composite source categories were created based on SPECIATE data in anticipation of being useful for future work with emissions inventories. Those profiles and their SPECIATE profile numbers are listed in Table 4.

Source Category	SPECIATE Profile Number
Cast Iron Induction Furnace	282012.5
Cigarette Smoke	91006
Coal Dust	212042.5
Coke Dust	212032.5
Geothermal Background	3724
Metal Welding	257032.5
PMControlledLigniteCombustion	4371
Residential Wood Combustion: Almond	Composite of profiles listed in Table 2
Residential Wood Combustion: Cedar	Composite of profiles listed in Table 2
Residential Wood Combustion: Eucalyptus	Composite of profiles listed in Table 2
Residential Wood Combustion: Hard	Composite of profiles listed in Table 2
Residential Wood Combustion: HardSoftNA	Composite of profiles listed in Table 2
Residential Wood Combustion: N/A	Composite of profiles listed in Table 2
Residential Wood Combustion: Soft	Composite of profiles listed in Table 2
Residential Wood Combustion: Synthetic	Composite of profiles listed in Table 2
Silica Manufacturing	254012.5

Table 4: SPECIATE profile numbers of $PM_{2.5}$ speciation profiles that were created for source categories not present in the 2001 EPA NEI.

6 Differences between current composite speciation profiles and those in SPECIATE v4.0

The composite profiles that are included in the release of SPECIATE v4.0 were composited using a working draft of the database. In addition to the differences due to procedures carried out after publication of the database (previous section) and profile adjustments based on comparison

with the HAP inventory (next section), there are some differences between the profiles in this work and those of the final release of SPECIATE 4.0 due to updates to both the raw data and compositing procedures that were performed after submission of the (draft version) composites for inclusion in the database. These differences are listed below.

1. Erroneous S or SO_4 values: both were available but were inconsistent, and one of these values looked to be erroneous so the other was used to compute a new value. Profiles adjusted in this matter: 254102.5 (Ammonium Sulfate Production), 3999 (Lime Kiln), 4411 (Catalytic Cracking).

2. Missing S or SO_4 values: one of these species was missing, so the other was used to impute a consistent value. This was applied to many of the profiles used in the composites.

3. Br, Cl, Na, K: Naming conventions for these species changed with updates, but these changes were not observed until after the publication of the database. Older versions used the names "Bromine", "Chlorine", "Sodium", and "Potassium", whereas newer versions used "Bromine Atom", "Chlorine Atom", "Sodium Ion" and "Potassium Ion". Later versions also included multiple measurements of the same atom, including the Chloride Ion (Cl^-) typically determined from ion chromatography and XRF-determined "Sodium" and "Potassium". For consistency, all XRF-determined values were used if available, and the ion forms were used if XRF measurements were unavailable.

4. OC and EC: There are differences in OC and EC values between our profiles and those in SPECIATE for a variety of reasons. The post-release profile adjustments done in our work that are described in the previous and next sections are responsible for most of them. Differences specifically due to calculation of the composite OC and EC values include:

- Cigarette smoke: One of the raw profiles (4660) used in the composite had an OC value of 0.625 in the pre-release version of SPECIATE, but a value of 0.46 in the post release version
- Phosphate Manufacturing and Slash Burning: Numerous corrections and updates were made to the compositing method for OC and EC described above; calculations using the latest raw profile data using the above procedure suggest that EC was likely calculated incorrectly for these profiles at the time of the database's release.
- Secondary Aluminum: The OC value in one of the profiles (201012.5) was re-named "Volatile Carbon" in the published version of the database, so that value was dropped from our profile
- Wood Fired Boiler: Prior to the release of SPECIATE, the OC & EC values from the measured profile were being directly used as the emission factors. After SPECIATE's publication, we decided that the source was similar enough to Residential Wood Combustion: HardSoft to group them together when adjusting OC/EC values for the TOR/Non-TOR method described above. It is this adjusted value that was applied to the emissions inventory in this work rather than the value in SPECIATE.

5. SubBituminous Coal Combustion: In an early version of the composite profiles, there was no Bituminous category, and the SubBituminous category contained both the bituminous and subbituminous profiles. In a subsequent draft, the SubBituminous composite had the Bituminous profiles removed and put into their own category, but this change was erroneously not made to the SubBituminous profile that was put into SPECIATE.

6. Cigarette Smoke: Some of the weight fractions (In, Mo, NH_4, NO_3) in profile 4660 changed between the March Š06 and August Š06 versions of SPECIATE.

7. Ammonium Sulfate Production (254102.5) and Ammonium Nitrate Production (254092.5): Amounts of NH_4 stoichiometrically equal to S or SO_4 (assuming $(NH_4)_2SO_4$) were added to the profiles.

8. Fiberglass Manufacture: In the initial profile that we analyzed, only the OC, EC, NO_3, and SO_4 fractions from the historical profile were included to make a source category profile. Version 4.0 SPECIATE has weight fractions for a number of additional species (Br, Ca, Cl, Co, Cr, Cu, Fe, K, Ni, Pb, Se, Zn), which all have one of 3 values (0.005, 0.15, 0.0055) that, based on literature of other profiles, look like they are the MDL/2. These newer values were not added to the composite profiles.

9. Food & Ag Ű Drying: Same situation as the Fiberglass manufacture profile.

10. Pulp & Paper -Avg.: A version of SPECIATE that was obtained after submitting the composite profiles had new profiles in this category that were deemed more valid than the single dated profile that was used in the original submission. A composite of these new profiles that excluded the original profile was therefore made for the current work.

11. Onroad Gas Exhaust: New version of SPECIATE added a NO_3 value for profile 4558 (see the REVISION LIST table in SPECIATE) resulting in a difference for that species.

12. Secondary Aluminum: Profile 201012.5 had an Al value added in a version of SPECIATE after the original submission (see REVISION LIST).

13. Sintering Furnace: Cd, Ni, Sb, Sn, and V all appeared to have MDL/2 values inserted where values had previously been missing. Cr, Cd, Pb for one of the profiles (283012.5) were set to 0 during HAPS comparison. Documentation wasnŠt clear on this for Cr and Pb, so this was updated in the paper.

14. Sludge Combustion: OC/EC/SO_4/NO_3 values were imputed to profile #171202.5 from Solid Waste Combustion. However, in SPECIATE, these values were only imputed into the simplified composite (profile # 92081), not into the one raw profile (171202.5).

15. Distillate Oil Combustion: Metals data from Hays et al. (2008) (*4*) was added to the bulk species values that were put into SPECIATE (which were also provided by Hays for the database release).

16. Residual Oil Combustion: Added metals data from Hays et al. (2008) (*4*) to the bulk species values already provided, and also put profiles into the composite that were left out of the SPECIATE composite whose metal values seemed to be fine upon re-examination Ű these profiles were originally left out because bulk species seemed unreasonable (#Šs 135012.5, 135042.5, 3253, 3293).

7 Comparison to 2002 Toxics Inventory

In the HAP inventory, raw emissions of the 9 toxic metals () are estimated in their compound forms (e.g. ammonium dichromate instead of Cr) in total suspended particulate matter; to convert the HAP emissions data to $PM_{2.5}$ elemental emissions for comparison with our speciated inventory, the following formula was applied:

$$E_{El} = \sum_{i}^{n} St_i \cdot F_i \cdot E_i \tag{1}$$

where E_i is the emission of compound i reported in the HAP inventory, St_i is the stoichiometric ratio of the element's mass to the compound's mass, F_i (obtained from the "Toxicity Weighting

Factors" database located at ftp://ftp.epa.gov/EmisInventory/2002finalnei/documentation/point/augmentation_point/tox_wt_factors_2002nei_011007.mdb) is the mass fraction emitted in the $PM_{2.5}$ size range, n is the number of compounds in the HAP inventory that contain element El, and E_{El} is the $PM_{2.5}$ emission of trace element El calculated from the HAP inventory. Equation (1) was applied to calculate emissions of each of the HAP elements in each SCC in the 2002 HAP inventory. F_i values were not available for Hg-containing compounds; instead, fractions of the amount of Hg in the particulate divalent form were applied (*6*) to non-specific Hg emissions, and all particulate Hg was assumed to be present in the fine fraction of PM emissions (*7*). In addition, any ligands on Hg atoms were assumed to have an insignificant mass relative to that of the Hg atom, so that a St_i value of 1 was used for that data.

Data by which to map emissions of metal emissions from the 2002 HAP inventory to the metal emissions of the 2001 speciated $PM_{2.5}$ at both the SCC and county levels were not available. Large differences in source category totals were therefore used to qualitatively flag composite SPECIATE profiles used to create the 2001 NEI. Source-category specific metals emissions that were found to be substantially different (leading to a difference that was at least 20% of the species total emission in the 2002 HAP inventory) between the two inventories are discussed below. The results of making the adjustments discussed below is illustrated in Figure 1. Figure 1 shows that at the national total level, all HAP metal emissions resulting from speciating the 2001 NEI were greater than 2002 HAP inventory emissions; the adjustments described below achieved some reduction of some of the 2001 metal emissions, and in the cases of As, Co, Mn, and Pb, the adjustments below brought the 2001 emissions to a level lower than (but closer to) that of the 2002 inventory.

1. Non-catalyst gasoline exhaust: Pb and Mn emissions are very high in 2001 vs. 2002 for Non-catalyst gasoline exhaust. Solution: profile 311082.5 was removed from Non-catalyst

Gasoline Exhaust category due to originating from a sample of leaded gasoline exhaust (*8*).

2. Secondary Copper: Sb emissions are very high in 2001 vs. 2002 for Secondary Copper Manufacturing. Solution: An antimony roasting profile (205032.5) was historically used for the OC/EC/SO_4 fractions for speciating Secondary Copper Emissions. Those values are continuing to be used, but weight fractions from secondary copper SPECIATE profiles (295012.5 and 295022.5) are being used for speciating the emissions into metals. Pb in this category was also flagged - since all the SPECIATE profiles in this category are from v3.2 and pre-date the 1990 Clean Air Act, the Pb values were set to 0.

3. Prescribed Burning: Cd was found to have a substantial weight fraction in the profile of the Prescribed Burning category. The reference (*9*) for one of the profiles (4467) in the composite says that heavy metals can hyper-accumulate in vegetation. The Cd and other metalsŠ fractions in Prescribed Burning were left as is due to the fact that prescribed burning is spread through areas where anthropogenic combustion sources take place (comparing Prescribed Burning Map to combustion-type and industrial source-type maps), giving a lot of opportunity for the hyper-accumulation process to take place.

4. Bituminous Combustion: Se emissions are much lower in the 2002 inventory than in 2001 (315 vs. 1334 ton/year). The SPECIATE composite value (0.0033) seems reasonably close to the Se value in the selenium factor in Pekney et al. (2006) (*10*). The spatial map suggests that there are many emissions throughout the country, so the SPECIATE value seems likely to be reasonable. As has a value of 0 in SPECIATE profiles and thus in the 2001 emissions, but emits 74 ton/year in 2002, suggesting that analytical methods with lower detection limits (e.g. ICP-MS) need to be used for measuring As emissions from this source category.

5. Copper Production: As value (0.92449) of profile #292022.5 in the Copper Production com-

posite is very high and comes from a 1978 EPA report (EPA-600/2-78-065b (NTIS No. PB286991)). This As weight fraction was set to 0 since the profile is likely outdated Ű As concentrations are limited by the 1990 Clean Air Act, which is likely to limit such a large emission. Pb values were also found to be very high; since all profiles in this category are from SPECIATE 3.2, they likely pre-date controls for lead, so the composite Pb value was set to 0. Sb from this source was also flagged by the screening method because it was not inventoried for 2002.

6. Electric Arc Furnace: Large Cr emissions (128 ton/yr vs. 16 ton/yr in 2002) were being generated in the 2001 inventory due to one profile in this category (28032.5). Large emissions of Cr seem to be unlikely since concentrations are strictly limited by the Clean Air Act.

7. Ferromanganese Furnace: The 2001 emission of Mn from this source category was found to be much higher than the 2002 emission (1664 ton/yr vs. 2.26 ton/yr). One profile (284012.5) is from a 1979 reference, and the other (3993) is from a bad dust sample in South Africa, neither of which is likely to be representative of modern U.S. emissions. There are also very few sources of $PM_{2.5}$ from this source category on the spatial map. To prevent over-prediction of Mn from this source category, the Mn composite weight fraction was forced to be 0.

8. Open Hearth Furnace: Only one SPECIATE profile in this category (283022.5) from a KVB report (No. 5806-783. NTIS No. PB293923) from 1979. The Cr value is 0.02, leading to 297 ton Cr/yr in the 2001 inventory (vs 8.9 in the 2002). The spatial map of Open Hearth Furnace shows a number of points around the country with emissions, so despite the large discrepencies in the national total, the profile will be left as is.

9. Sintering Furnace: Cr, Pb, and Cd emissions were found to be higher in the 2001 inventory

(296, 552, and 54 tons/yr) than in 2002 (1.2, 16.9, and 1.0 tons/yr). One of the profiles (283012.5) is from a 1979 source (KVB Report No. 5806-783. NTIS No. PB293923), and so is expected to be outdated with regards to Cr and Pb weight fractions due to updated control technologies. The Cd value in this profile was an imputed value (0.0055) substituted for a measurement below detection limits. The Cd value was replaced with a 0 due to possible over-calculation of Cd emissions that the profile might lead to, as indicated by the large differences in emissions between the 2001 and 2002 inventory when using the imputed Cd value.

10. Secondary Aluminum: All 3 profiles in this category are from v3.2, one (201012.5) is missing a Sb value, the other two profiles (201022.5 & 201032.5) have similar values of Sb (0.00597 & 0.0057). Spatial map shows numerous emissions, so the 2001 value of 103 ton Sb/year might be more reasonable than the (State reported) 2002 value of 0.29.

11. Secondary Lead: Profile (#204012.5) is from a 1979 source and Pb weight fraction is 0.5. The Secondary Lead spatial map only has a few sources, so the 2002 value (27.5 vs. 682 ton/yr in 2001) seems reasonable. Controls are also likely to have been updated for Pb since it is a criteria pollutant, so the Pb weight fraction in Secondary Lead was changed to 0 to prevent gross over-predictions.

12. Solid Waste Combustion: Pb and Hg were questionable. The composite contains 3 profiles, only one of which (3288) has Hg (0.0135) and also has the highest Pb value (0.0761) from 1989. Other 2 profiles (113012.5 & 171082.5) are from 1987 and have Pb values of 0.00253 & 0.058. Large region of the eastern U.S. has emissions; uncertain state reporting could mean that the large 2001 emissions of Hg and Pb (1391 and 324 ton/yr) are more reasonable than the 2002 values (0 and 86 ton/yr). On the other hand, no information about the sources

sampled for this profile could be found, and batteries might have been getting burned. The amount of mercury in batteries has been in decline and is estimated to no longer be present in solid waste (*6*). Emissions due to recycling of lead-acid batteries are expected to come from recycling facilties rather than general waste disposal facilities (*11*). The Hg and Pb values in the Solid Waste Combustion composite profile were therefore set to 0.

13. Surface Coating: Only one of the 2 profiles (4663) has a non-zero Sb value (0.0142). The reference (Schauer 1998 report to CARB) confirmed the Sb value. A number of metallic compounds (esp TiO2) are in paint, and Sb might be an impurity in extracting or making these compounds. Surface coating operations are widespread, and are state-reported point sources, so the 2001 value of 152 ton/yr might be reasonable vs. the 2002 value of 8.5 ton/yr.

14. Heat Treating: Ni and Cr emissions are much greater in 2001 (541 and 149 ton/year) than in 2002 (6.1 and 7.3 ton/yr). The spatial map of Heat Treating shows abundant emissions, making incomplete reporting from the states a likely possibility. The 2001 emissions therefore seem reasonable, and the profiles were not adjusted.

15. Residual Oil Combustion: The medians of values from 4 SPECIATE profiles were used for element weight fractions; OC, EC, SO_4, and NO_3 values came from recent source tests (*4*). Ni emissions were larger in 2001 (1079 ton/yr) than in 2002 (269 ton/yr). Residual oil combustion $PM_{2.5}$ emissions are widespread, making underestimation by state-reporting of Ni a likely possibility. Se and As were much smaller in the 2001 inventory (5.3 and 10.6 ton/yr) than in 2002 (608 ton/yr and 109 ton/yr), and might be underestimated in the speciated inventory.

16. All metals emissions in the Chem Manuf - Avg, Ind Manuf - Avg., Mineral Products - Avg, Petroleum Ind - Avg, and Pulp & Paper - Avg. profiles were set to 0. These categories and

corresponding profiles were originally developed for speciating $PM_{2.5}$ into OC, EC, SO_4, and NO_3, but are too generic for speciating $PM_{2.5}$ from the many miscellaneous SCCs in these categories into trace elements, as indicated by the large percentage differences of some of the HAPS emissions (ranging as high as 1100%). These SCCs should be classified into more specific categories and updated profiles found or measured for those categories in order to speciate these $PM_{2.5}$ emissions.

8 Calculation of Metallic Oxygen

Metallic oxygen was calculated by applying an oxygen-to-metal ratio to most of the trace element's emissions. These ratios were based on the expected oxidation states of the metals in the atmosphere. Table 5 shows the expected oxide forms of each metal, which are based the most common oxidation states of the metals (*12*). Total Metallic Oxygen was then calculated for each source category using the following equation:

$$Metallic\ Oxygen = \sum_{El}^{n} Ox_{El} \cdot E_{El} \tag{2}$$

where Ox_{El} is the oxygen-to-metal ratio of the expected oxide form of metal El. For metals with more than one common oxidation state, the mean of the oxygen-to-metal ratios was used for the Ox_{El} value. This is an extension of an assumption in Malm et al. (1994) (*13*), where 2 common forms of Fe are assumed to exist in ambient particulate matter in equal quantities. The list of metal oxides in Table 5 is inclusive of metal oxide forms used in some previous studies of particulate matter (*13*, *14*, *15*)

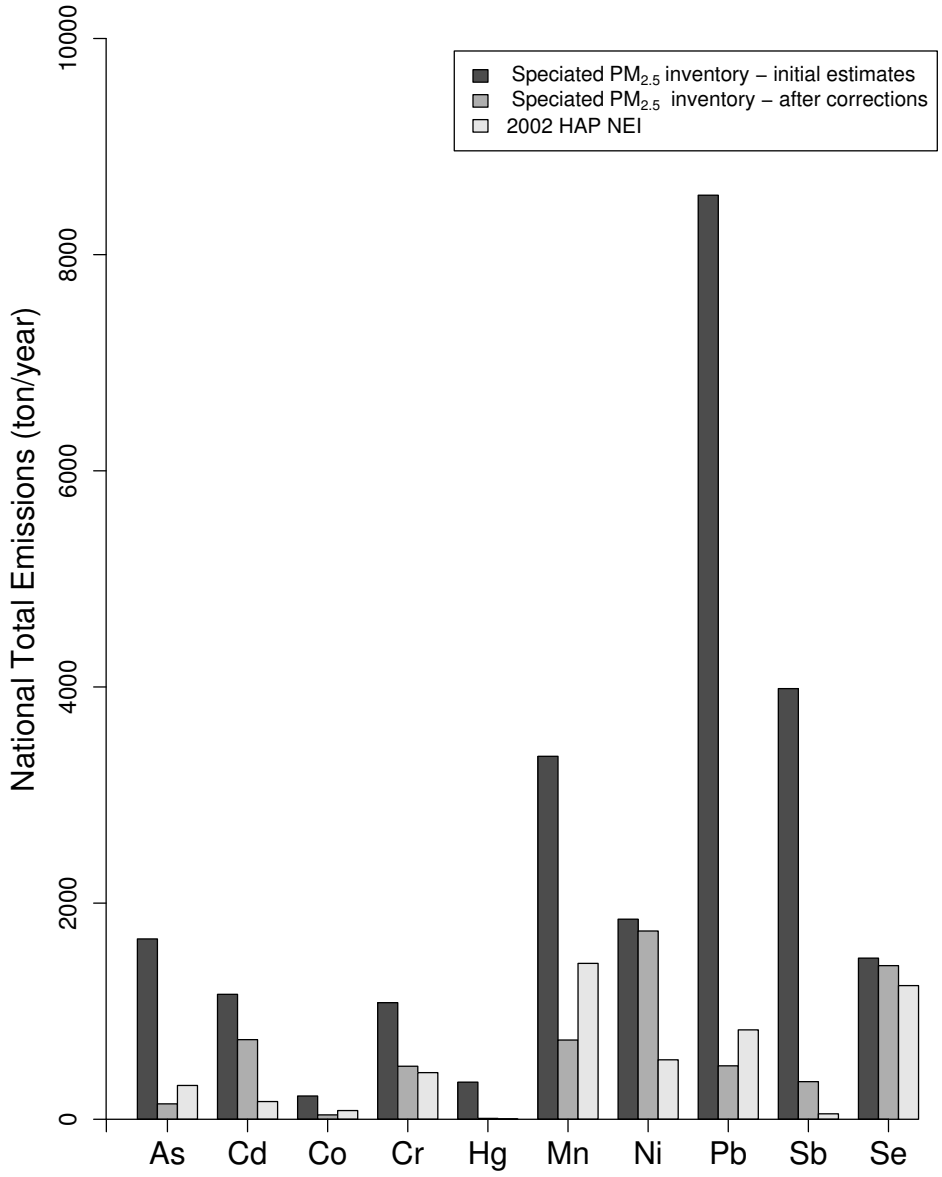


Figure 1: Total emissions of HAPS metals from the 2001 speciated $PM_{2.5}$ inventory and from the 2002 inventory of toxic species. Data aggregated in the white bars was compared to data in the black bars, and SPECIATE composite profiles were updated by through differences highlighted in the comparison. Data in the gray bars is the result of those updates. Note that emissions from Fugitive Dust source categories are not included in these results.

Species	Oxide Form 1	Oxide Form 2	Oxide Form 3	Oxygen/Metal Ratio
Ag	Ag_2O			0.074
Al	Al_2O_3			0.889
As	As_2O_3	As_2O_5		0.427
Ba	BaO			0.117
Ca	CaO			0.399
Cd	CdO			0.142
Ce	Ce_2O_3	CeO_2		0.200
Co	CoO	Co_2O_3		0.339
Cr	Cr_2O_3	CrO_3		0.692
Cu	CuO			0.252
Fe	FeO	Fe_2O_3		0.358
Ga	Ga_2O_3			0.344
Hg	Hg_2O	HgO		0.060
In	In_2O_3			0.209
K	K_2O			0.205
La	La_2O_3			0.173
Mg	MgO			0.658
Mn	MnO	MnO_2	Mn_2O_7	0.631
Mo	MoO_2	MoO_3		0.417
Na	Na_2O			0.348
Ni	NiO			0.273
P	P_2O_3	P_2O_5		1.033
Pb	PbO	PbO_2		0.116
Pd	PdO	PdO_2		0.226
Rb	Rb_2O			0.094
Sb	Sb_2O_3	Sb_2O_5		0.263
Se	SeO	SeO_2	SeO_3	0.405
Si	SiO_2			1.139
Sn	SnO	SnO_2		0.202
Sr	SrO			0.183
Ti	TiO_2			0.669
V	V_2O_5			0.785
Zn	ZnO			0.245
Zr	ZrO_2			0.351

Table 5: Assumed oxide forms of each metal and resulting mean oxygen-to-metal ratio used to calculate Metallic Oxides in Equation 2 and Figure 3 of the main paper.

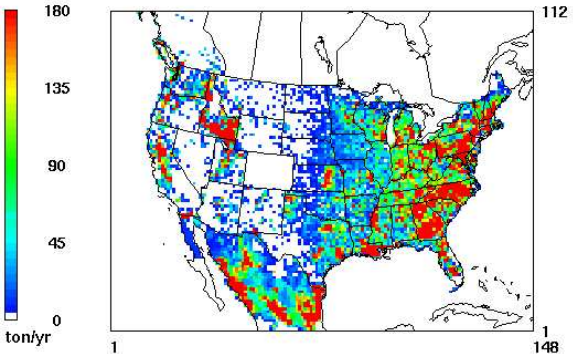
9 Calculation of Organic Material

Organic material was calculated for each source category by multiplying OC emissions by source-category specific OM/OC ratios to calculate an OM emission, and subtracting OC from OM. An OM/OC ratio of 1.25 was used for motor-vehicle exhaust sources, which is a median of the values from Aiken et al. (2008) (*16*) (1.22, 1.25), Lipsky and Robinson (2006) (*17*) with artifact correction (1.4), Russell (2003) (*18*) (1.2, 1.3, 1.1), and Japar et al (1984) (*19*) (1.43). This ratio is also fairly consistent with the value of 1.2 used by Kleeman et al. (2000) (*14*) and Sheesley et al. (2003) (*20*), which was selected based on measurements by Schauer et al. (*21*, *22*). An OM/OC ratio of 1.7 was used for wood combustion sources, which is a median of the values from Aiken et al. (2008) (*16*) (1.55, 1.7), Lipsky and Robinson (2006) (*17*) with artifact correction (1.8), Hays et al (2002) (*9*) (1.2), and Turpin and Lim (2001) (*23*) (1.9) - the 1.9 was computed from the organic-molecular data of Schauer et al. (2001) (*24*). It is in agreement with the mass-closure estimates reported by Sheesley et al. (2003) (*20*) (1.7) and Bae et al. (2006) (*25*) (1.74), and falls in the range of estimates reported by Jimenez et al. (2007) (*26*) (1.5, 1.8, and 2.0). The OM/OC ratio of 1.4 applied to all other source categories' emissions is the long-standing value used applied to numerous studies of atmospheric $PM_{2.5}$ (*23*).

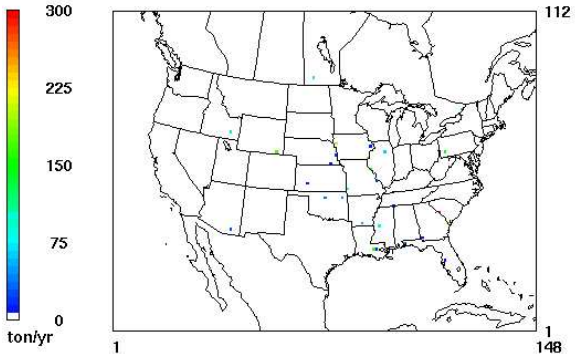
10 Spatial plots of $PM_{2.5}$ Emissions

Figure 2 through Figure 16 show the spatial distributions of $PM_{2.5}$ emissions from each of the 85 source categories; Figure 17 through Figure 22 show the spatial distributions of $PM_{2.5}$ species. Spatial allocation was performed with the Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system (`http://www.smoke-model.org`), and maps were created with the Package for Analysis and Visualization of Environmental data (PAVE) (`http://www.cep.unc.`

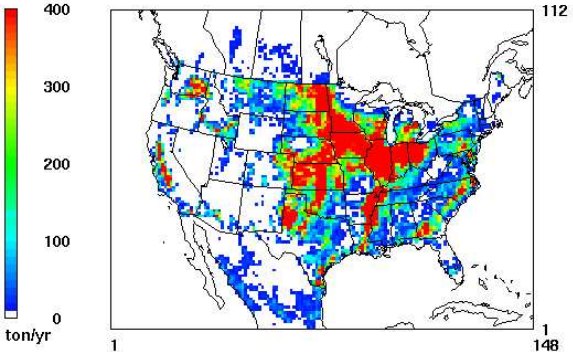
edu/empd/EDSS/pave\protect\T1\textunderscoredoc/).



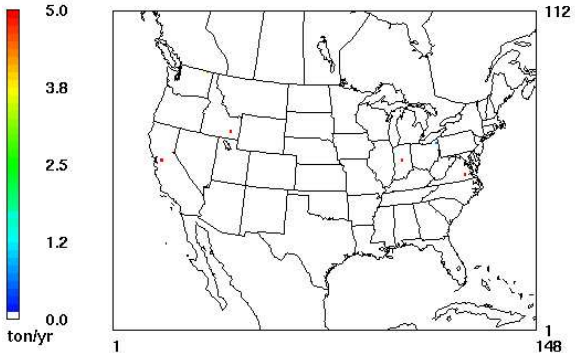
(a) Agricultural Burning



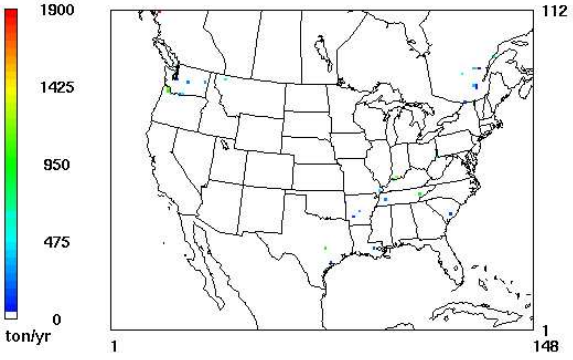
(d) Ammonium Nitrate Production



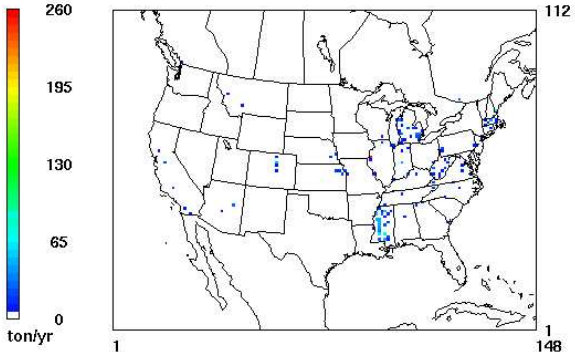
(b) Agricultural Soil



(e) Ammonium Sulfate Production

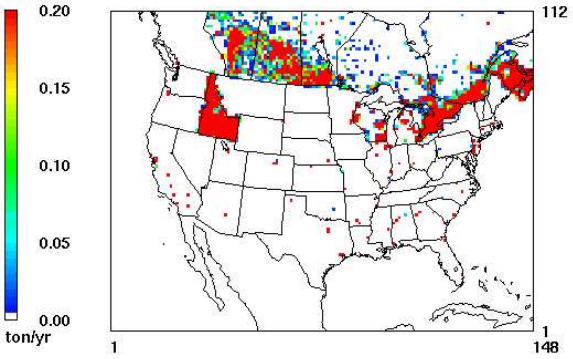


(c) Aluminum Production

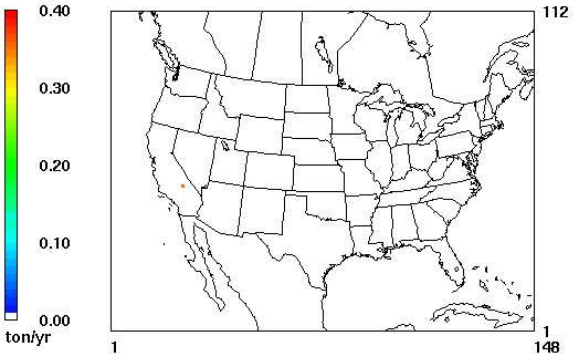


(f) Asphalt Manufacturing

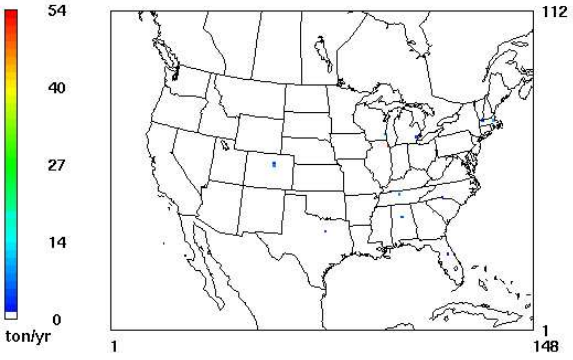
Figure 2: Spatial Plots of $PM_{2.5}$ Emissions by Source Category



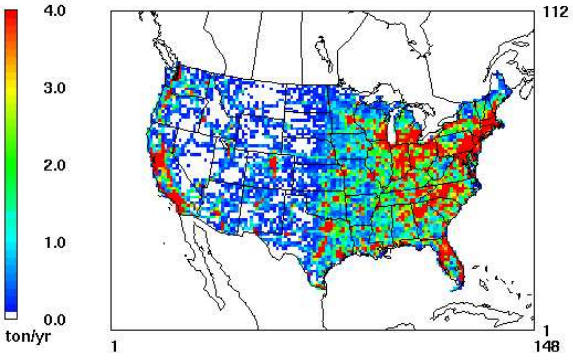
(a) Asphalt Roofing



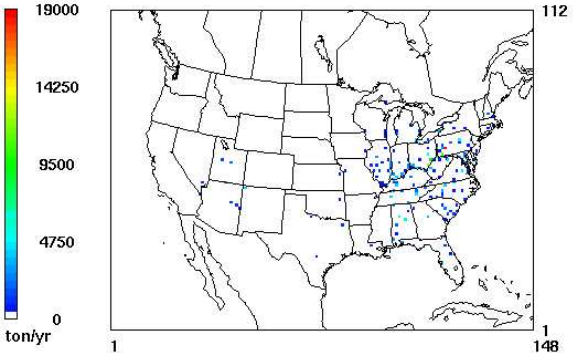
(d) Boric Acid Manuf.



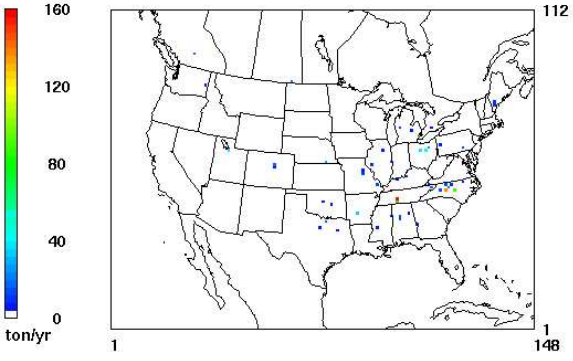
(b) Auto Body Shredding



(e) Brake Lining Dust

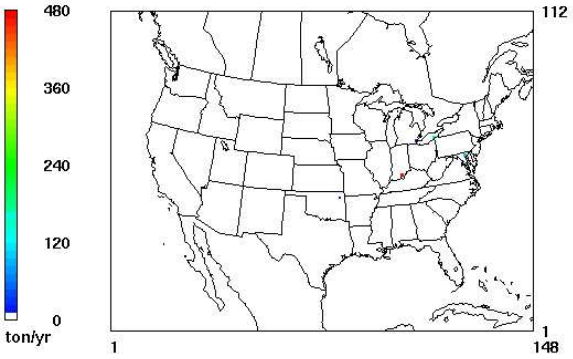


(c) Bituminous Coal Combustion

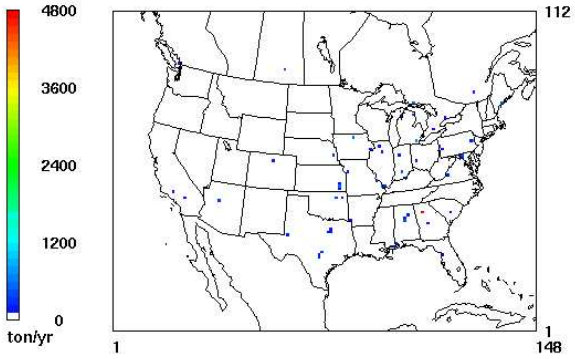


(f) Brick Grinding & Screening

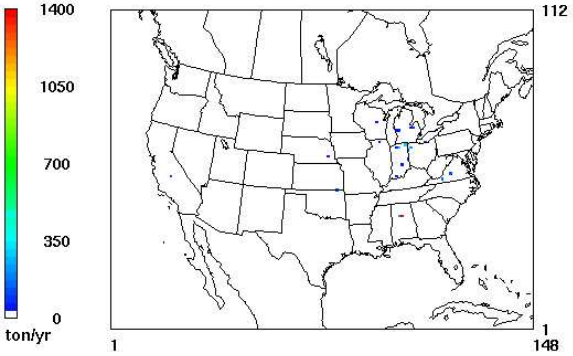
Figure 3: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued



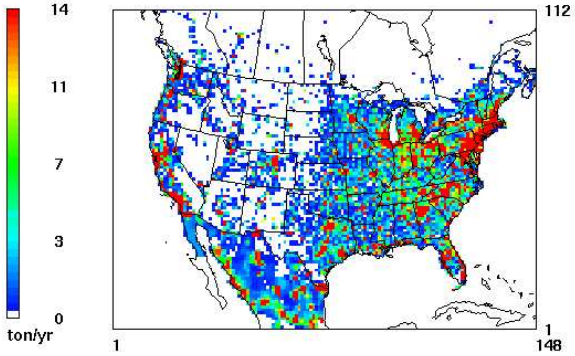
(a) Calcium Carbide Furnace



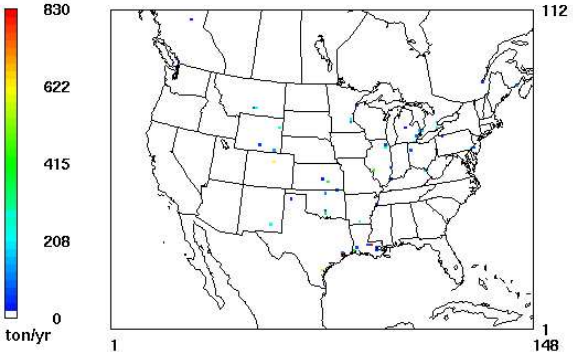
(d) Cement Production



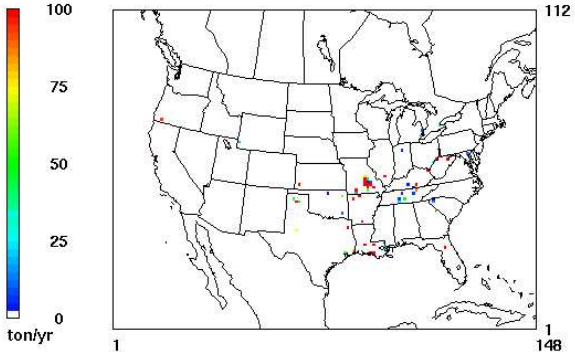
(b) Cast Iron Cupola



(e) Charbroiling

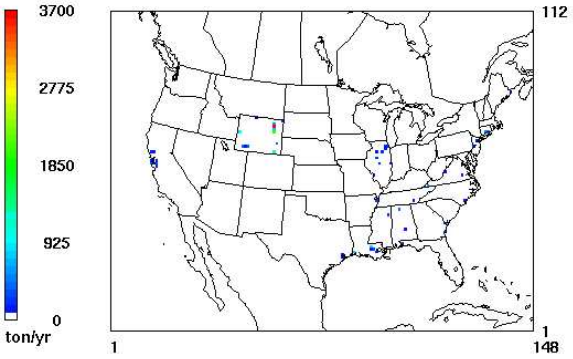


(c) Catalytic Cracking

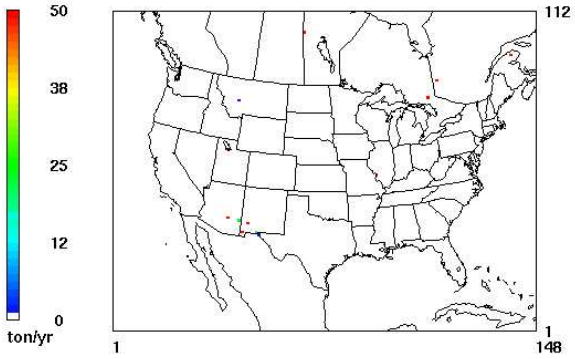


(f) Charcoal Manufacturing

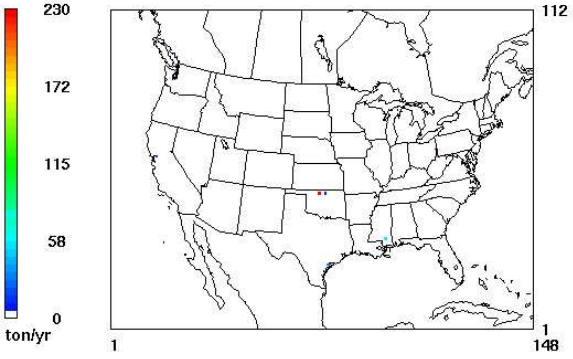
Figure 4: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued



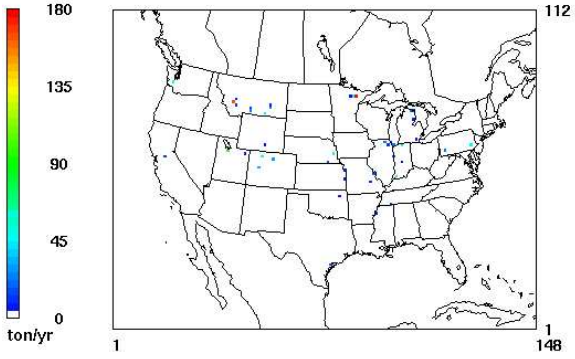
(a) Chem. Manuf. Avg.



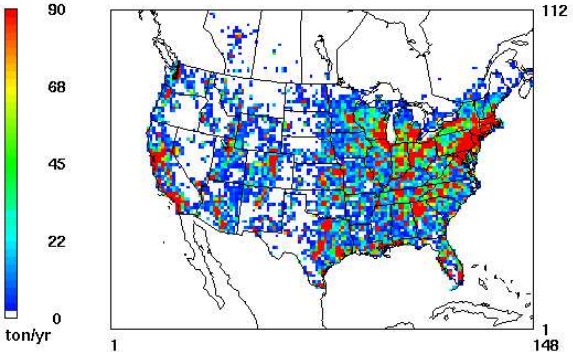
(d) Copper Production



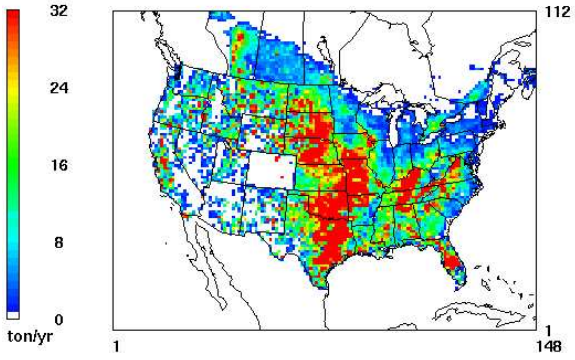
(b) Coke Calciner



(e) Crustal Material

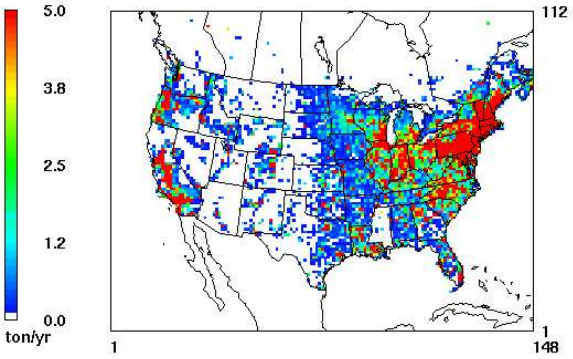


(c) Construction Dust

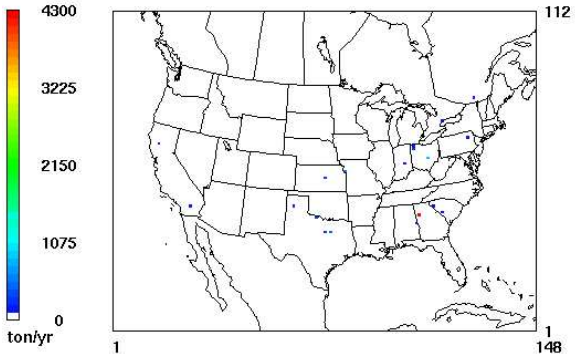


(f) Dairy Soil

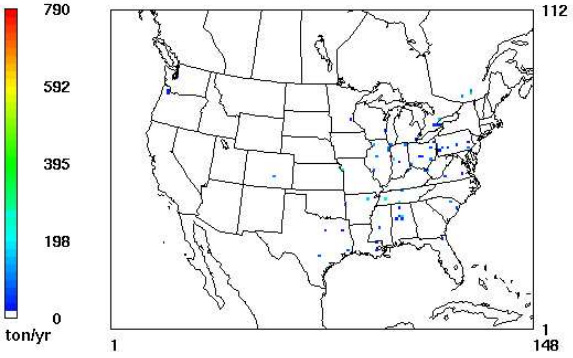
Figure 5: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued



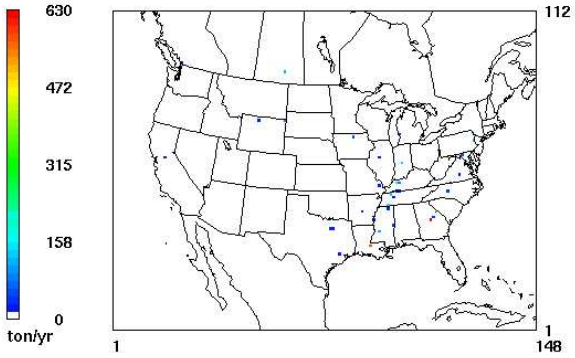
(a) Distillate Oil Combustion



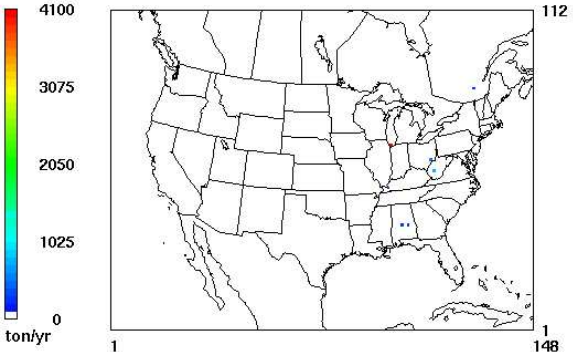
(d) Fiberglass Manuf.



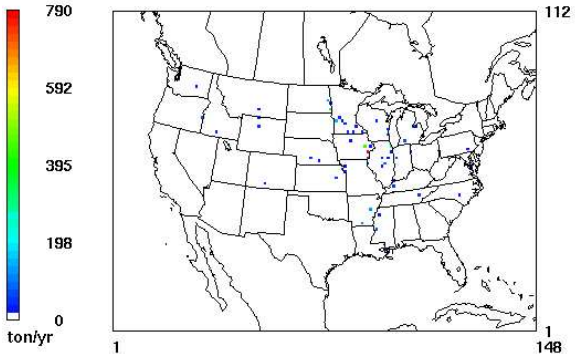
(b) Electric Arc Furnace



(e) Fly Ash

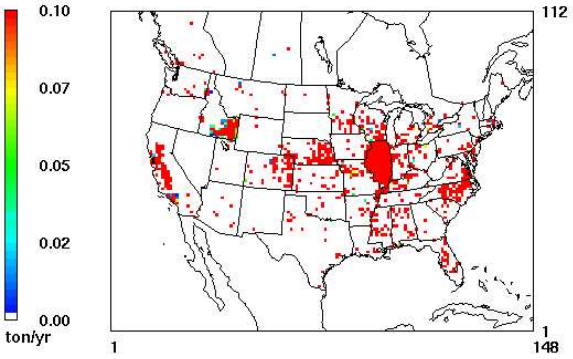


(c) Ferromanganese Furnace

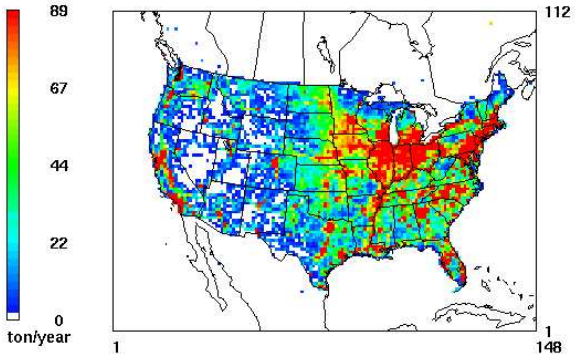


(f) Food & Ag Drying

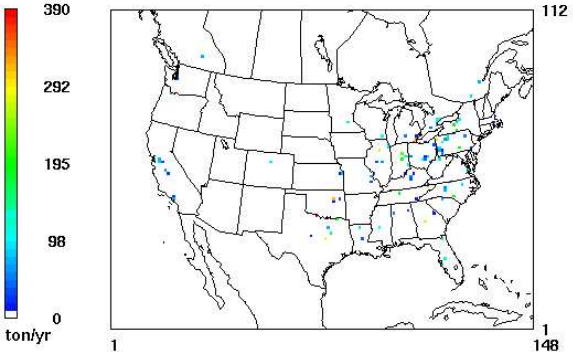
Figure 6: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued



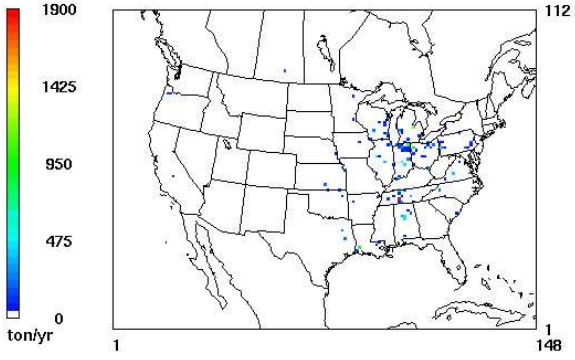
(a) Food & Ag Handling



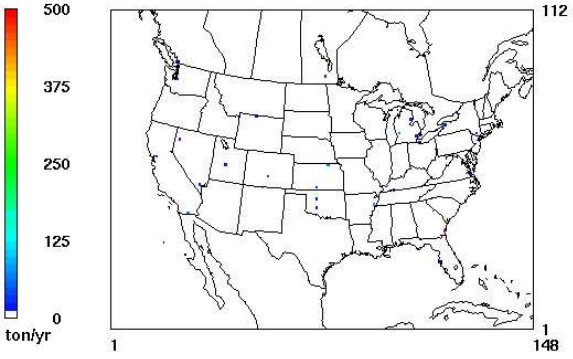
(d) HDDV Exhaust



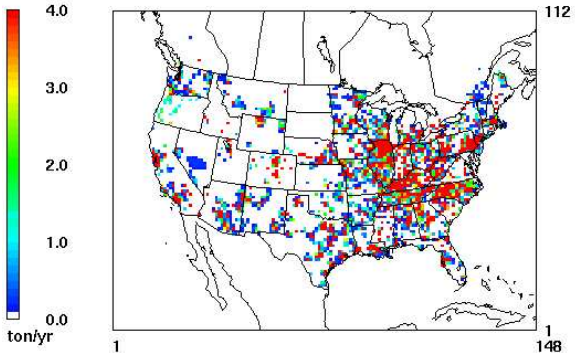
(b) Glass Furnace



(e) Heat Treating

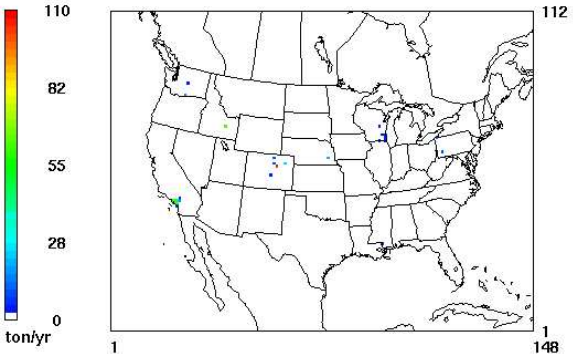


(c) Gypsum Manuf.

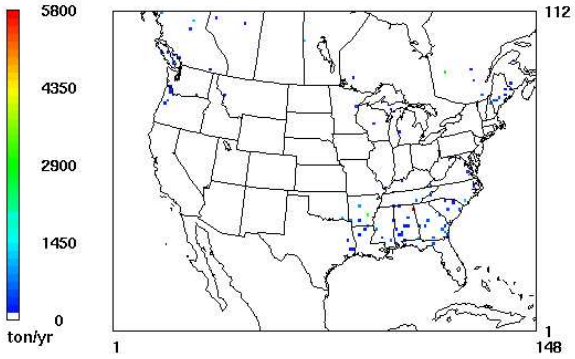


(f) Industrial Manuf. Avg.

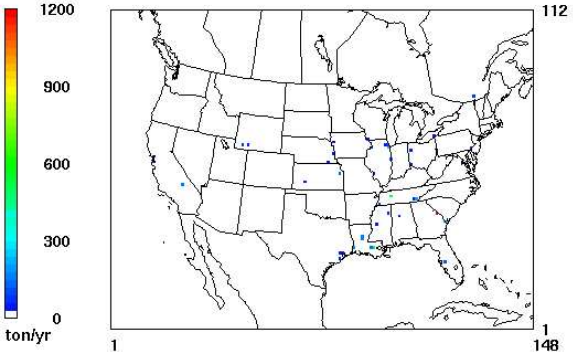
Figure 7: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued



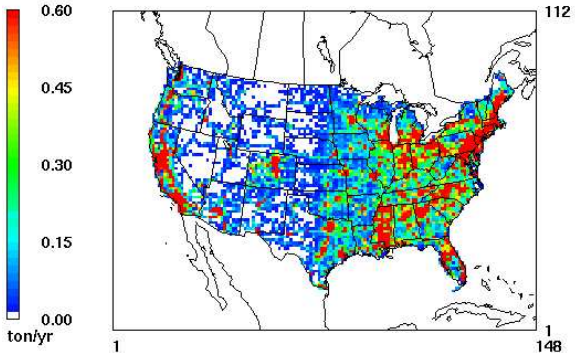
(a) Industrial Soil



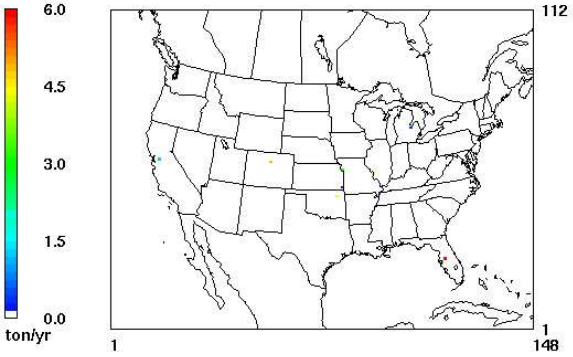
(d) Kraft Recovery Furnace



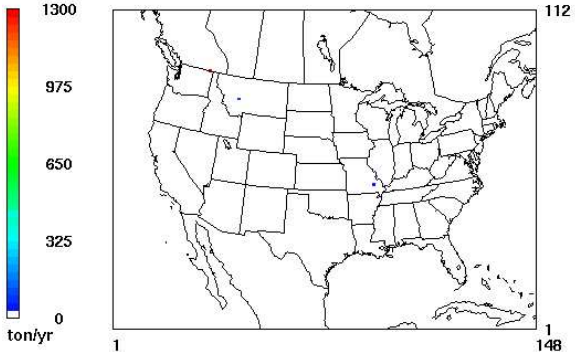
(b) Inorganic Chemical Manuf.



(e) LDDV Exhaust

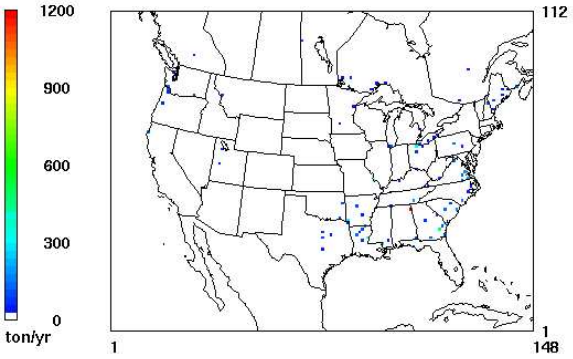


(c) Inorganic Fertilizer

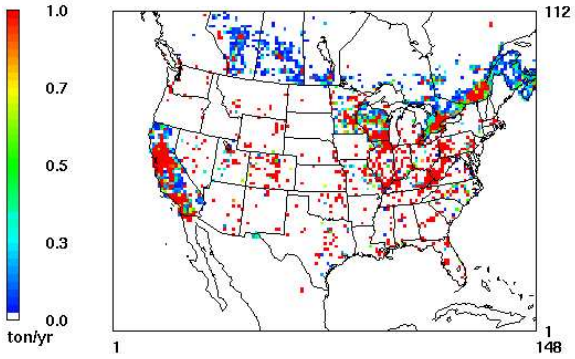


(f) Lead Production

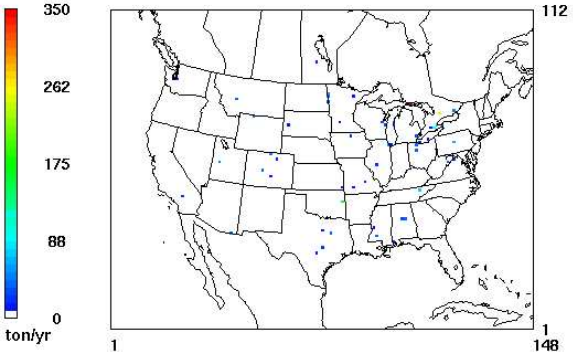
Figure 8: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued



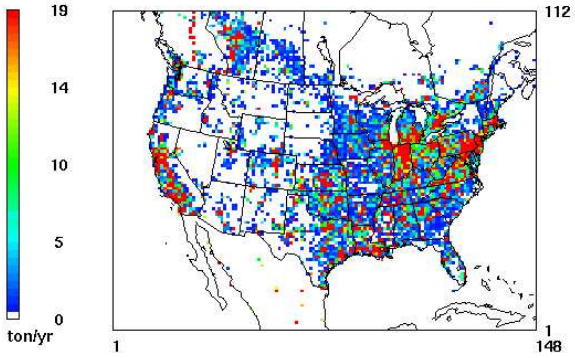
(a) Lime Kiln



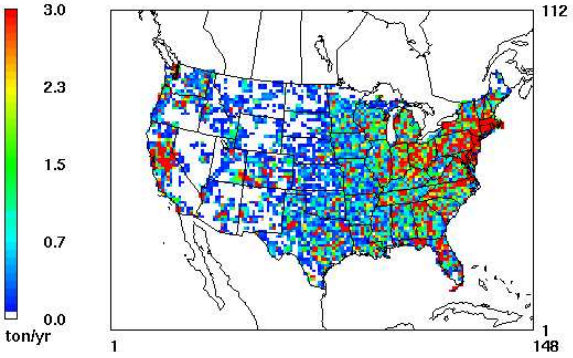
(d) Mineral Products - Avg



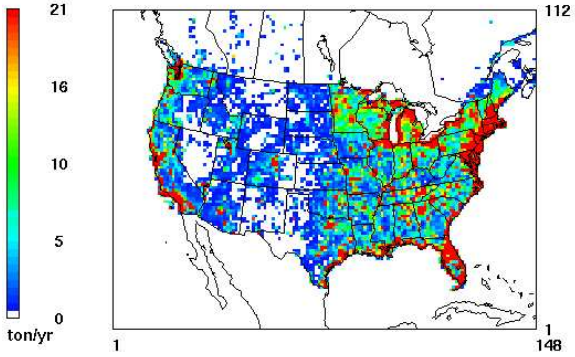
(b) Limestone Dust



(e) Natural Gas Combustion

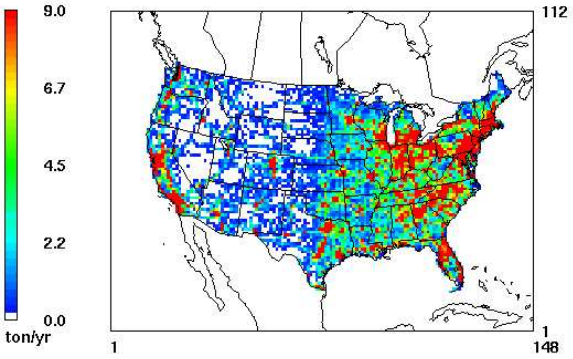


(c) Meat Frying

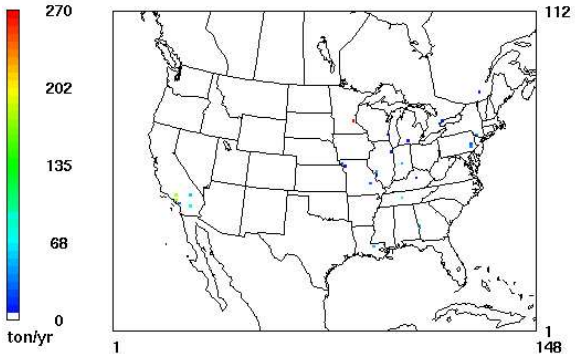


(f) Non-catalyst Gasoline Exhaust

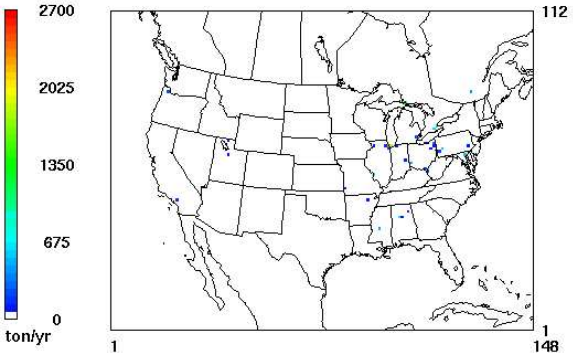
Figure 9: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued



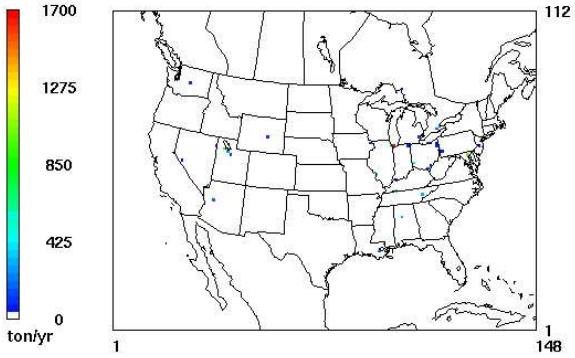
(a) Onroad Gasoline Exhaust



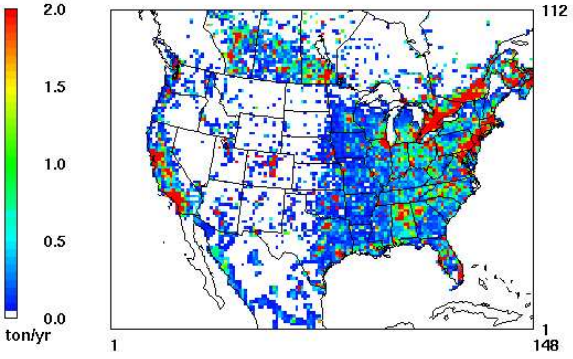
(d) Secondary Lead Production



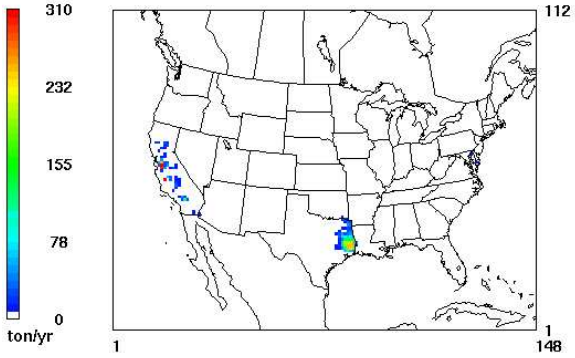
(b) Open Hearth Furnace



(e) Sintering Furnace

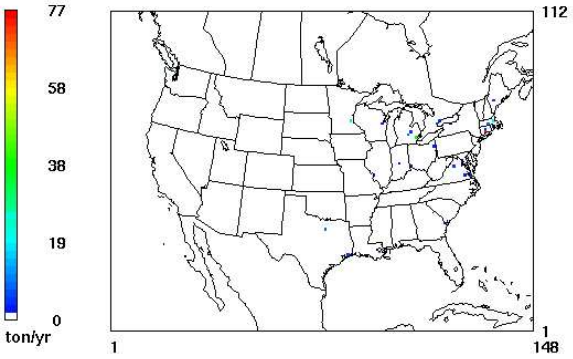


(c) Overall Avg - Default

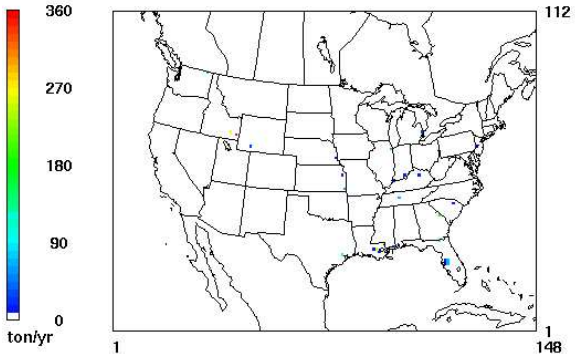


(f) Slash Burning

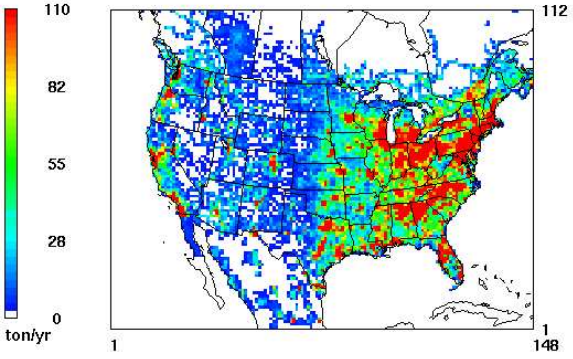
Figure 10: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued



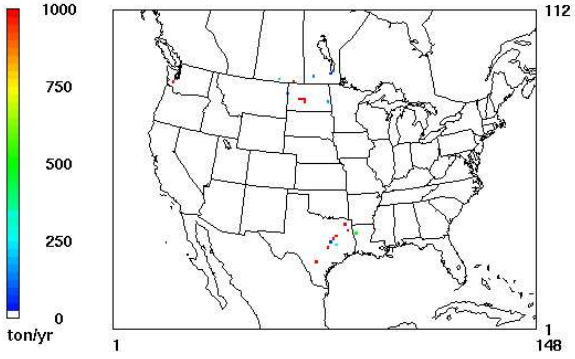
(a) Sludge Combustion



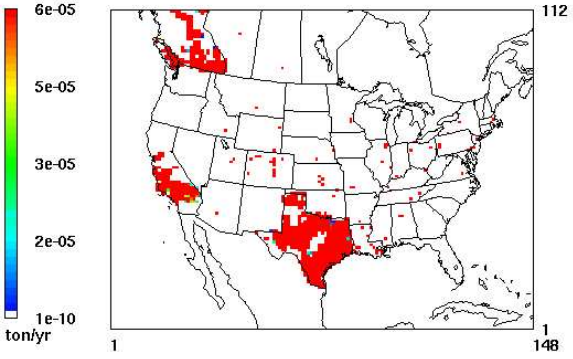
(d) Phosphate Manuf.



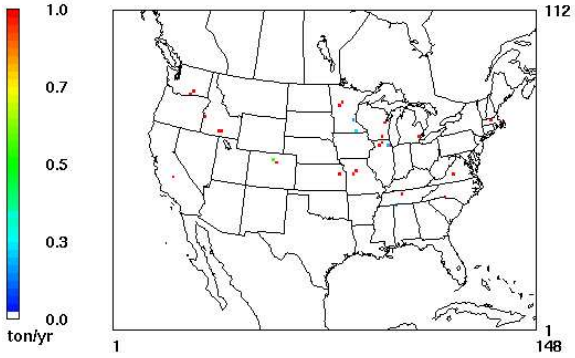
(b) Paved Road Dust



(e) PM & SO_2 Controlled Lignite Combustion

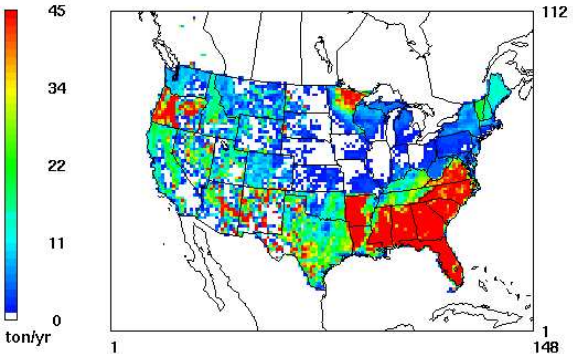


(c) Petroleum Industry - Avg

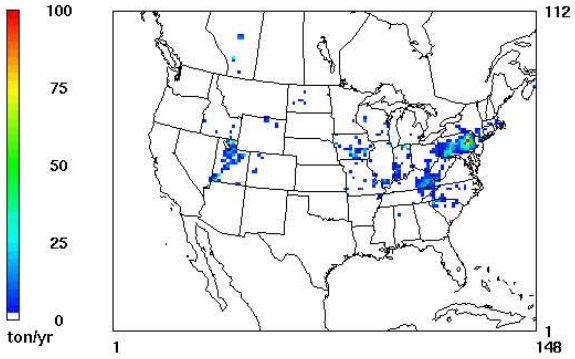


(f) Potato Deep Frying

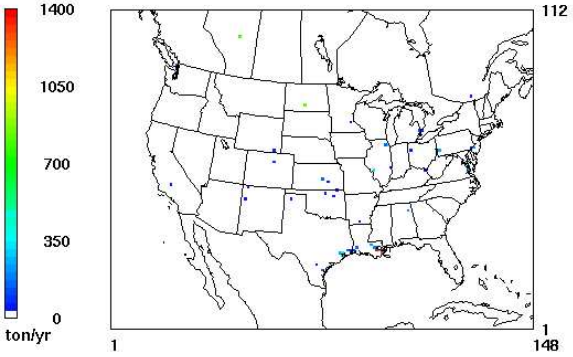
Figure 11: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued



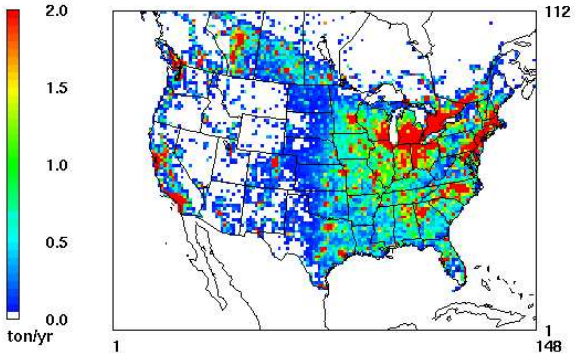
(a) Prescribed Burning



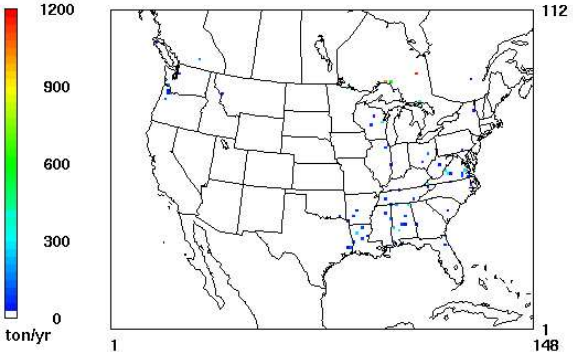
(d) Residential Coal Combustion



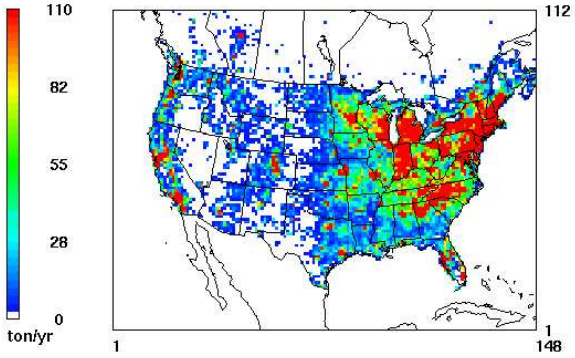
(b) Process Gas Combustion



(e) Residential Natural Gas Combustion

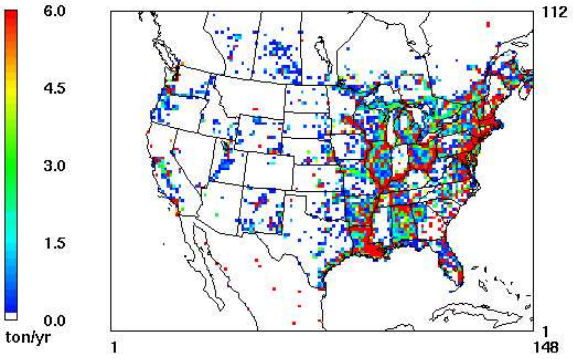


(c) Pulp & Paper - Avg

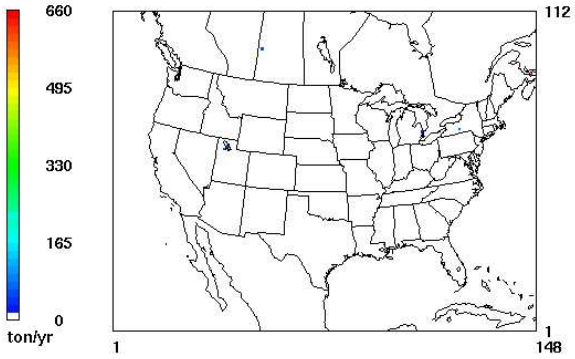


(f) Residential Wood Combustion, Hard & Soft Woods

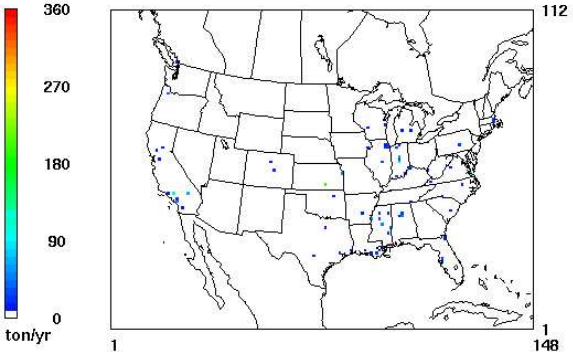
Figure 12: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued



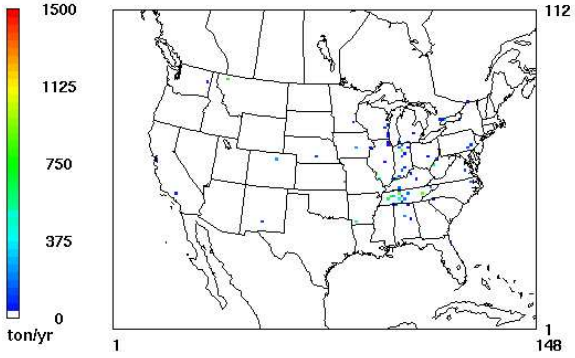
(a) Residual Oil Combustion



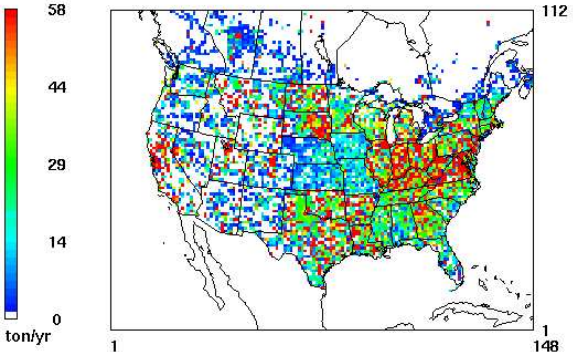
(d) Sea Salt



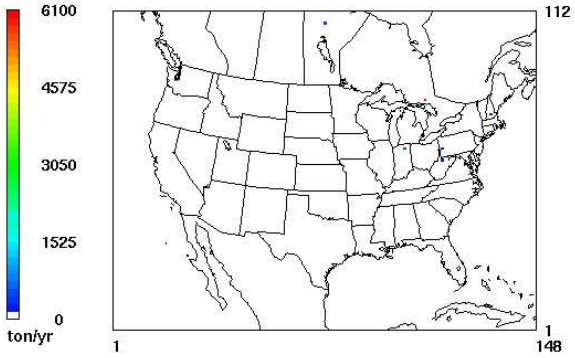
(b) Sandblast



(e) Secondary Aluminum Production

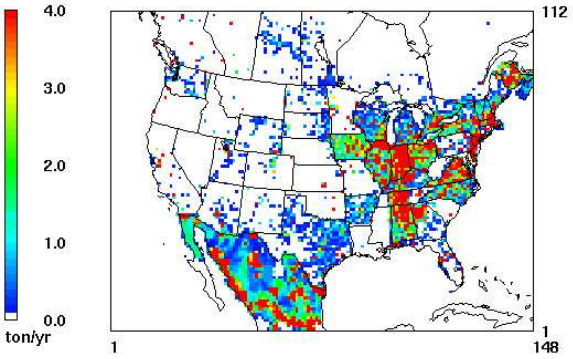


(c) Sand & Gravel

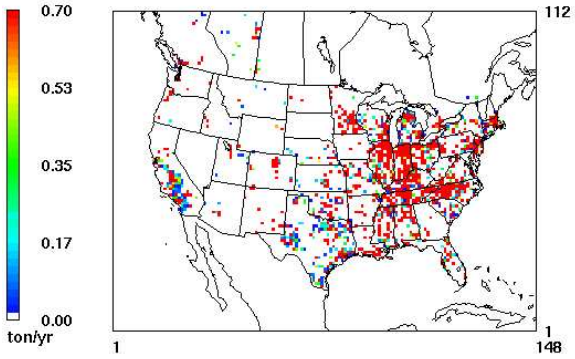


(f) Secondary Copper Production

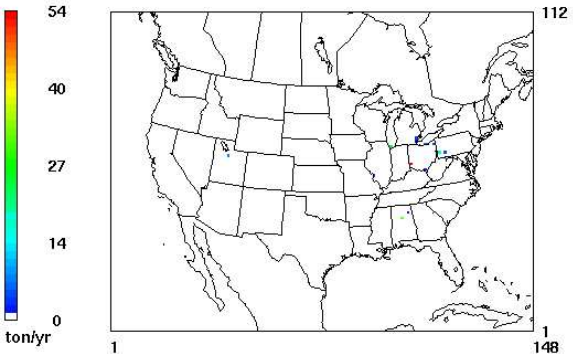
Figure 13: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued



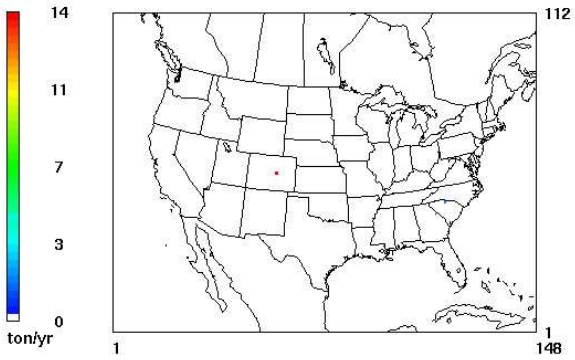
(a) Solid Waste Combustion



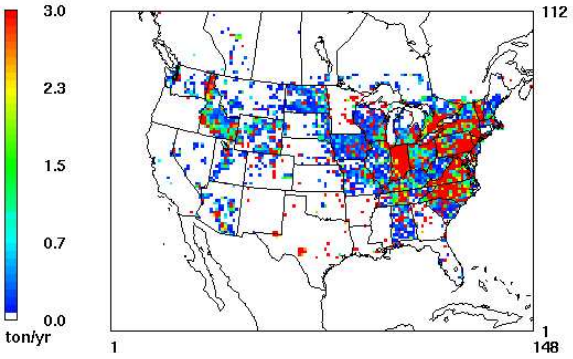
(d) Surface Coating



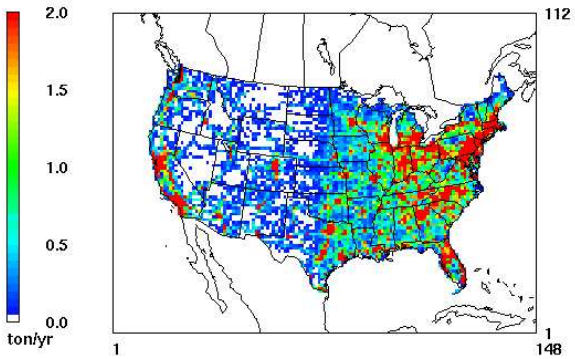
(b) Steel Desulfurization



(e) Tire Burning

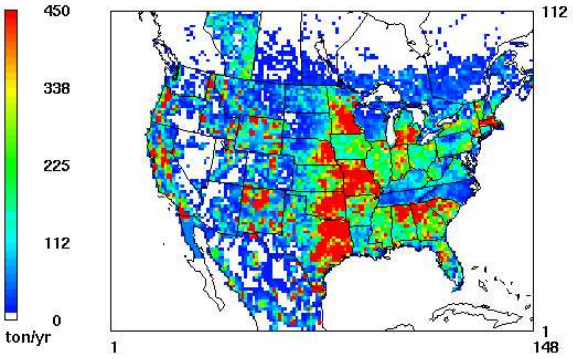


(c) Sub-bituminous Coal Combustion

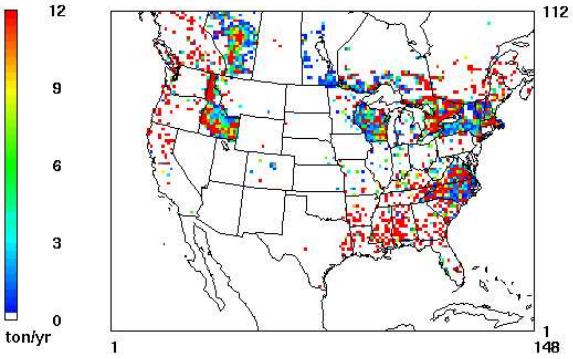


(f) Tire Dust

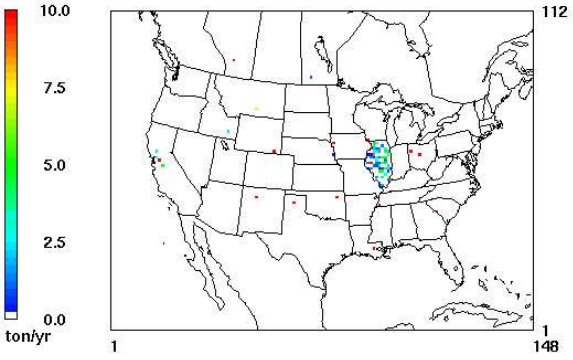
Figure 14: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued



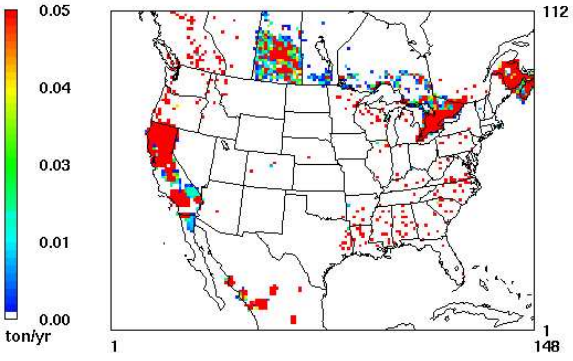
(a) Unpaved Road Dust



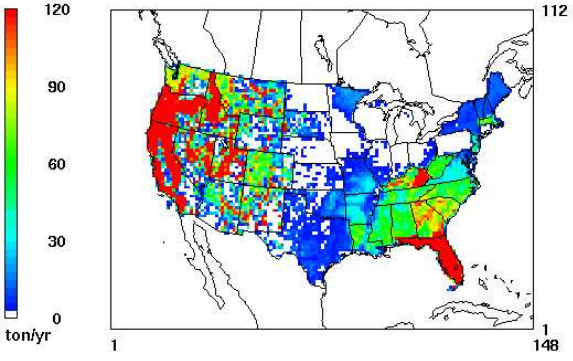
(d) Wood-Fired Boiler



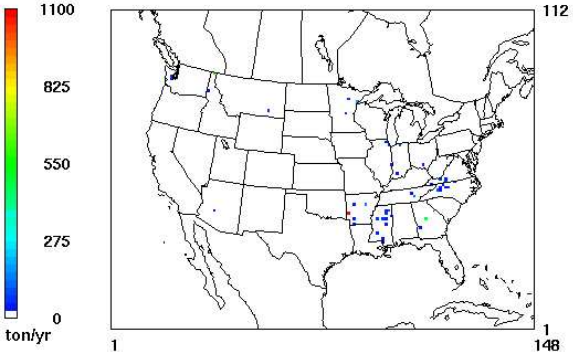
(b) Urea Fertilizer Production



(e) Wood Products - Drying

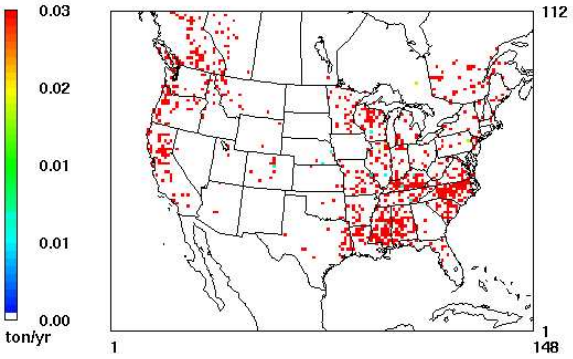


(c) Wildfires



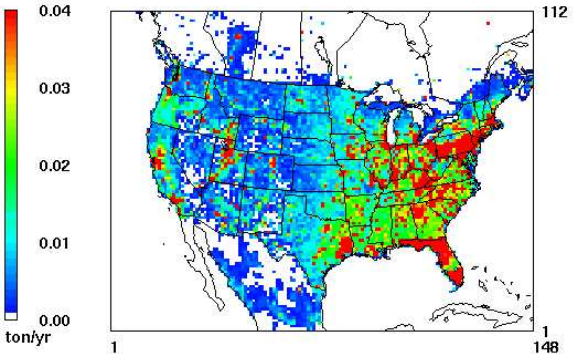
(f) Wood Products - Sanding

Figure 15: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued

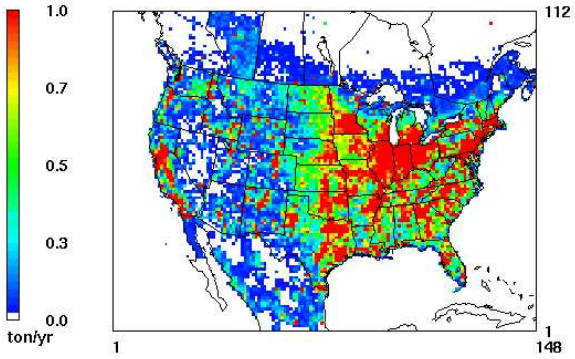


(a) Wood Products - Sawing

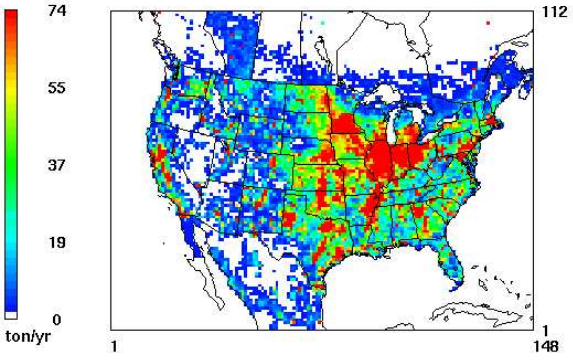
Figure 16: Spatial Plots of $PM_{2.5}$ Emissions by Source Category continued



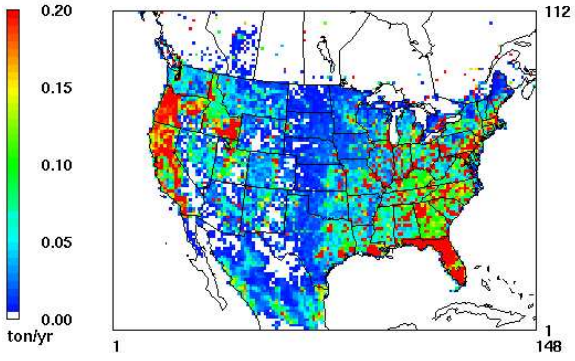
(a) Ag



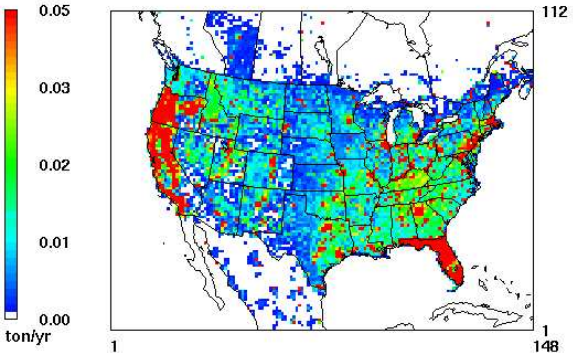
(d) Ba



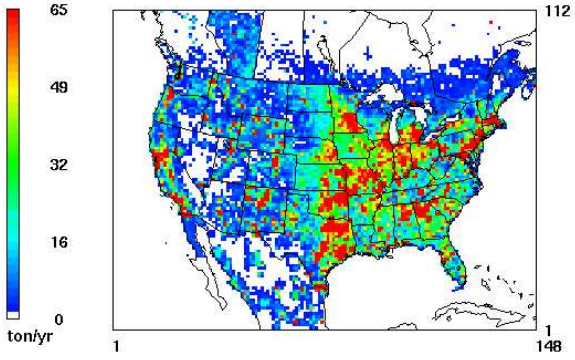
(b) Al



(e) Br

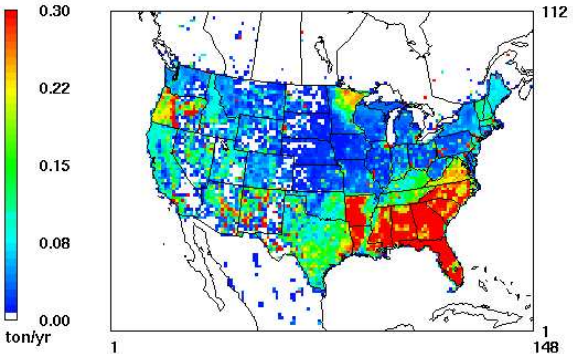


(c) As

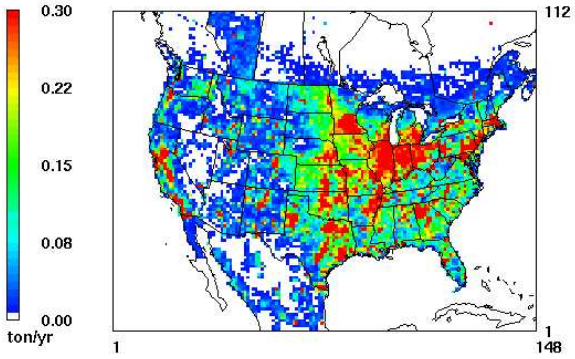


(f) Ca

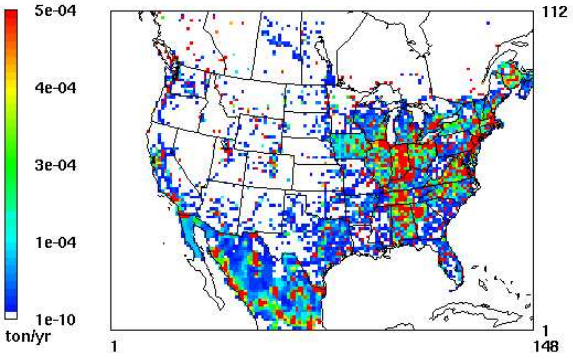
Figure 17: Spatial Plots of $PM_{2.5}$ Species Emissions



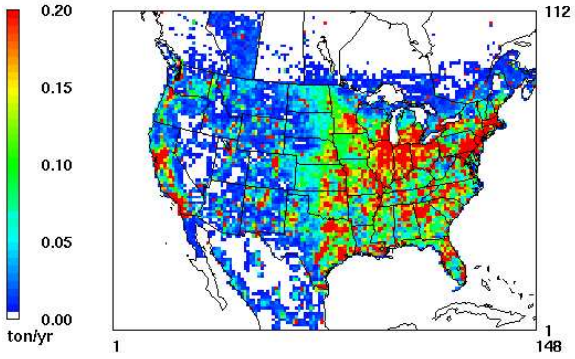
(a) Cd



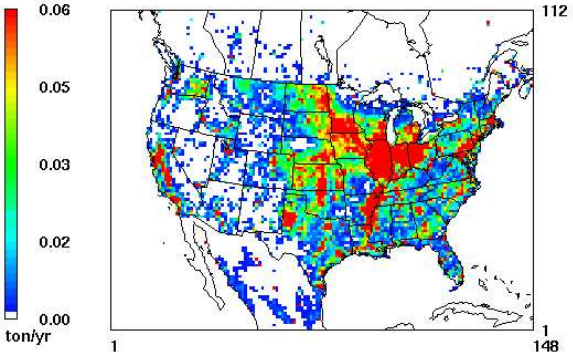
(d) Cr



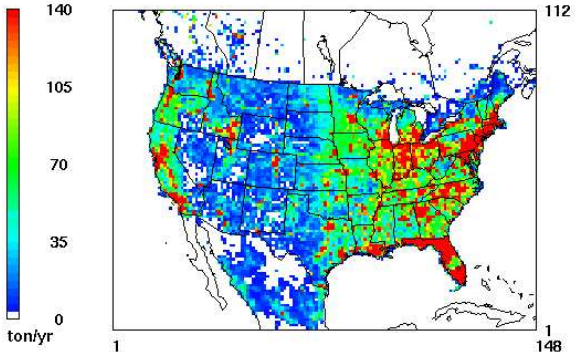
(b) Ce



(e) Cu

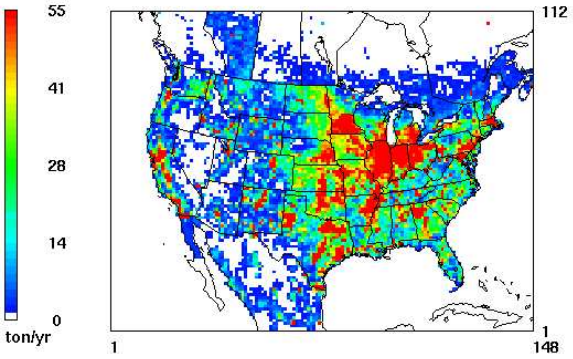


(c) Co

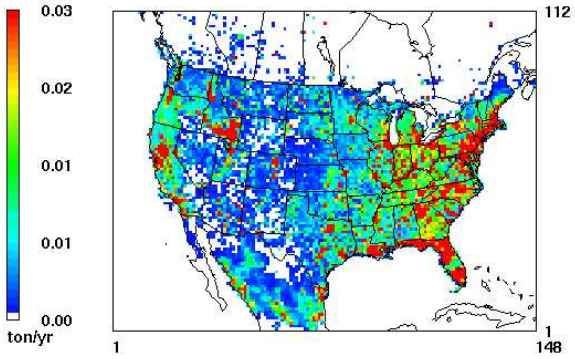


(f) EC

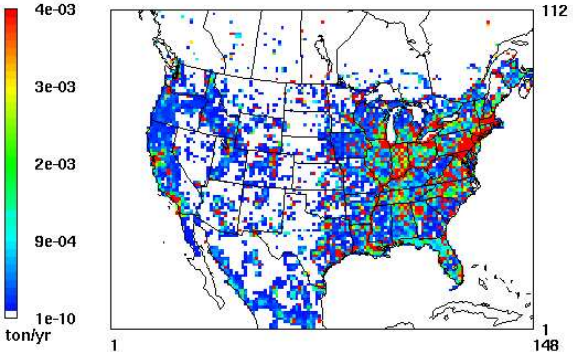
Figure 18: Spatial Plots of $PM_{2.5}$ Species Emissions continued



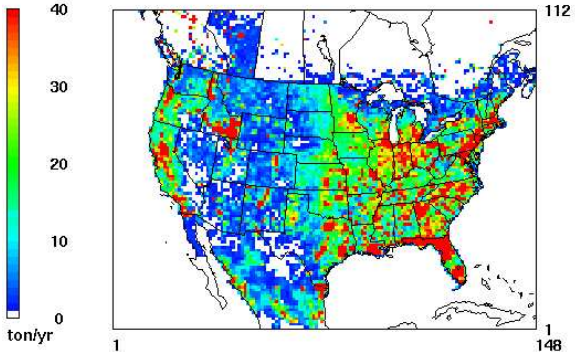
(a) Fe



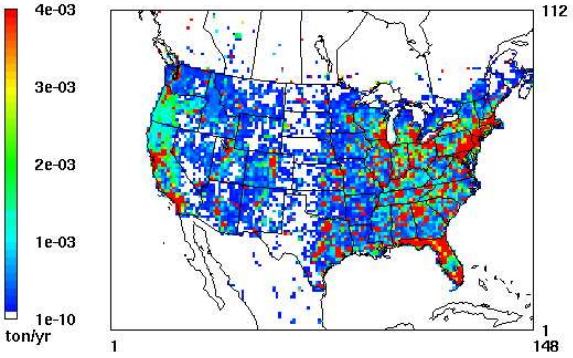
(d) In



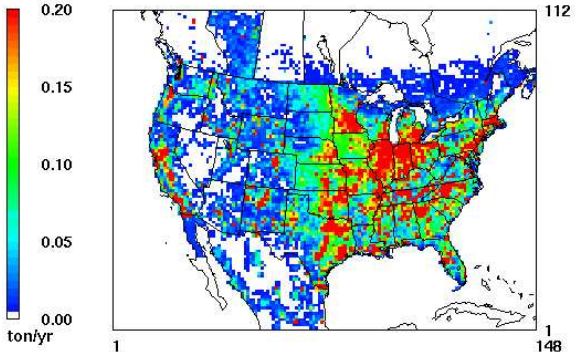
(b) Ga



(e) K

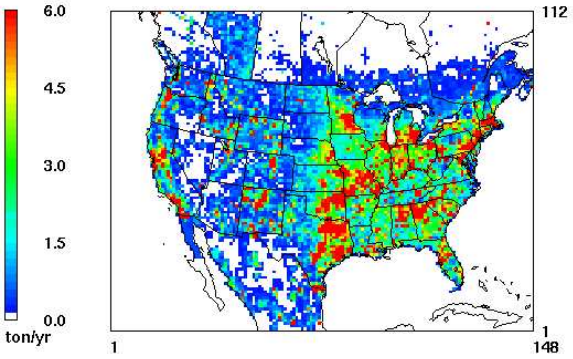


(c) Hg

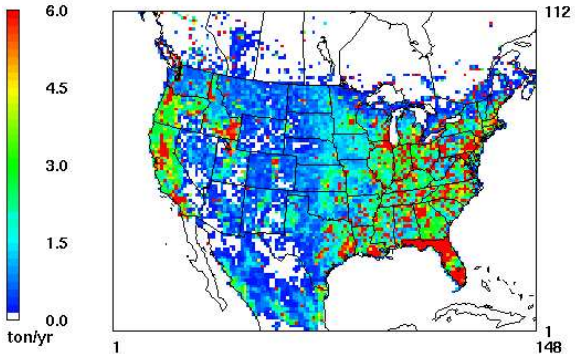


(f) La

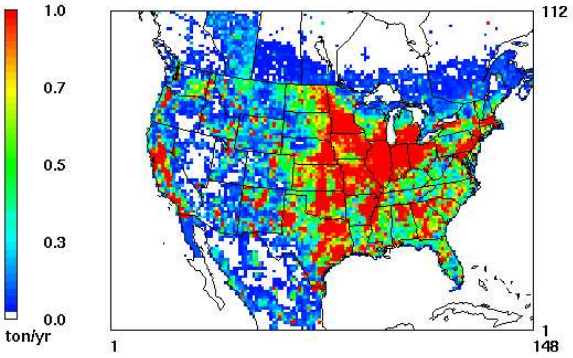
Figure 19: Spatial Plots of $PM_{2.5}$ Species Emissions continued



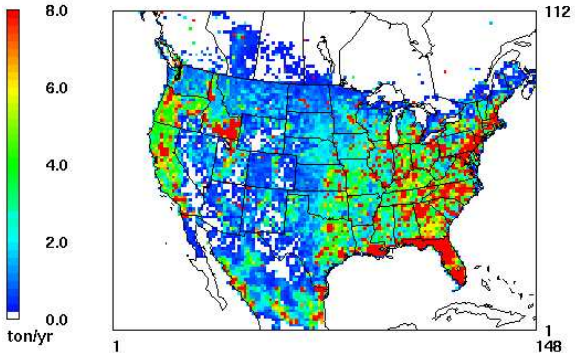
(a) Mg



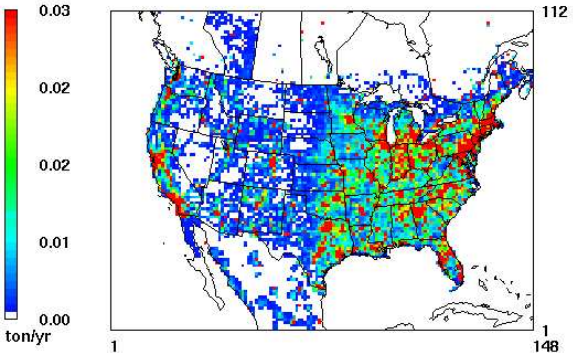
(d) Na



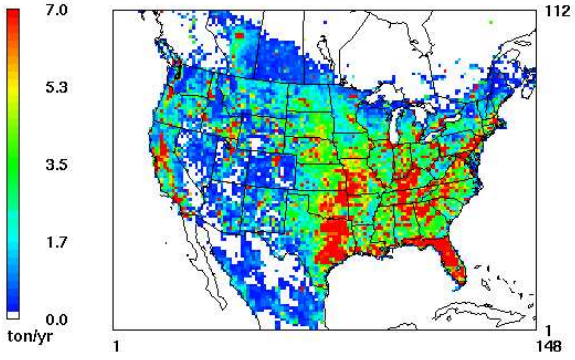
(b) Mn



(e) NH_4

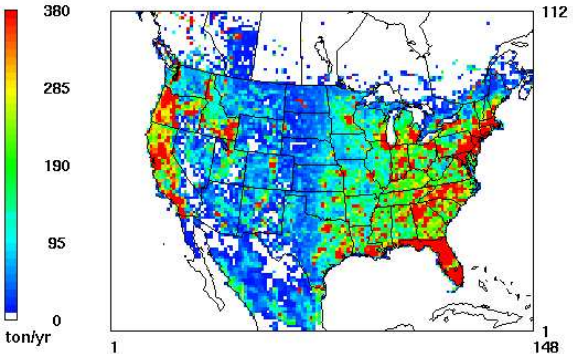


(c) Mo

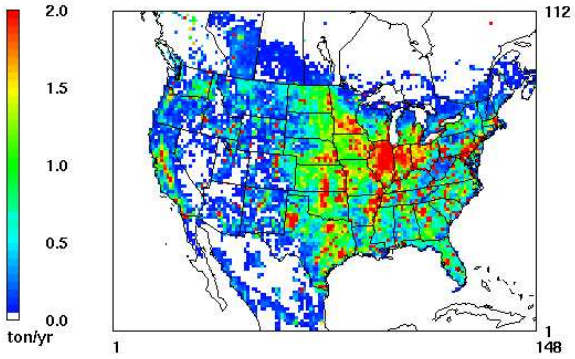


(f) NO3

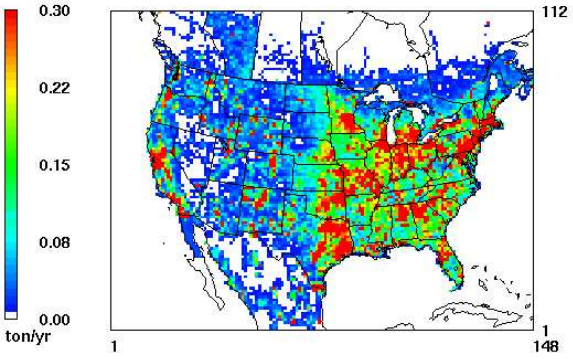
Figure 20: Spatial Plots of $PM_{2.5}$ Species Emissions continued



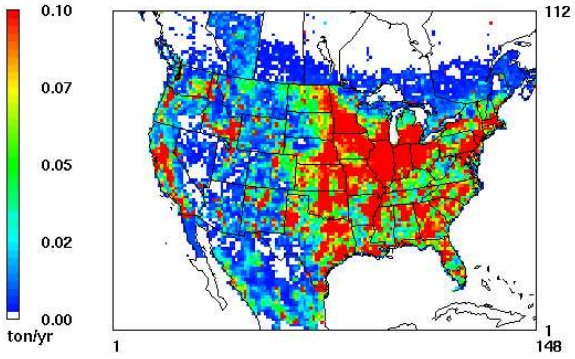
(a) OC



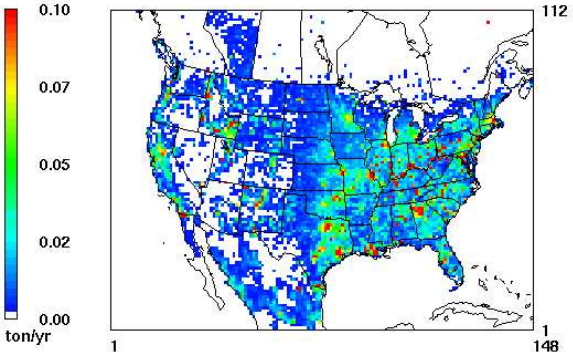
(d) P



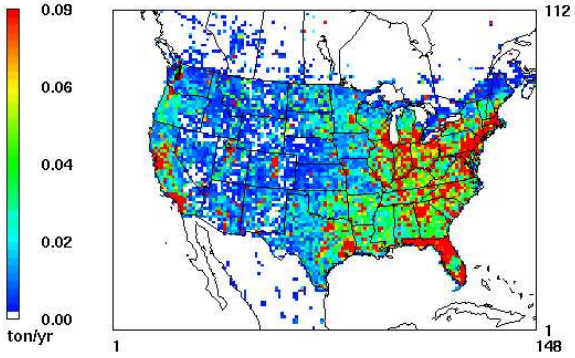
(b) Pb



(e) Rb

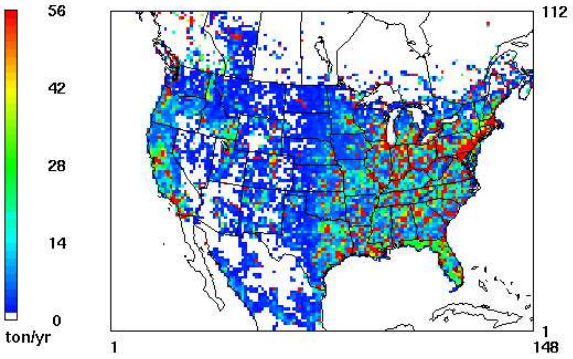


(c) Pd

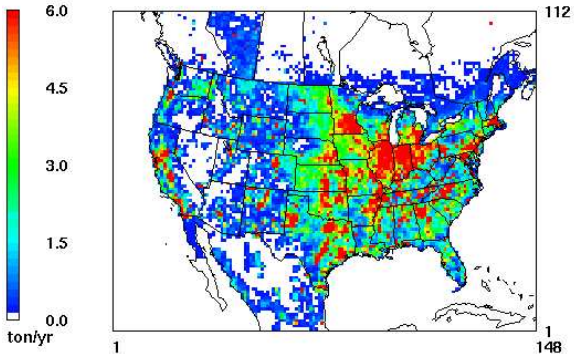


(f) Sn

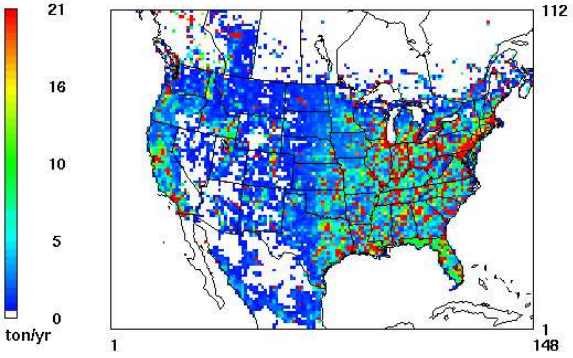
Figure 21: Spatial Plots of $PM_{2.5}$ Species Emissions continued



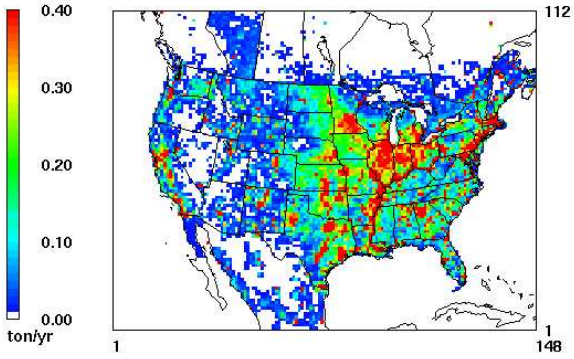
(a) SO4



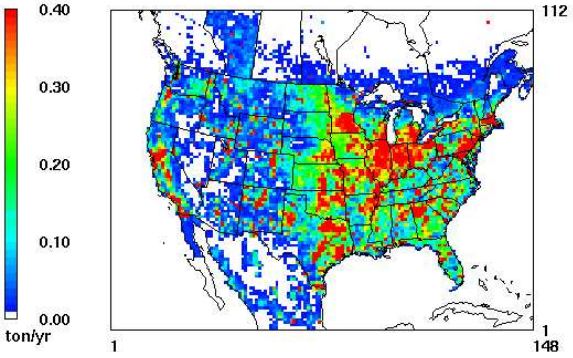
(d) Ti



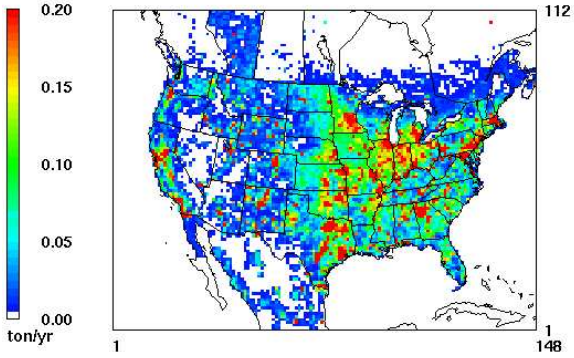
(b) S



(e) V



(c) Sr



(f) Zr

Figure 22: Spatial Plots of $PM_{2.5}$ Species Emissions continued

References

(1) Bhave, P.; Pouliot, G. A.; Zheng, M. Diagnostic model evaluation for carbonaceous $PM_{2.5}$ using organic markers measured in the Southeastern U.S. *Environmental Science and Technology* **2007**, *41*, 1577–1583.

(2) Chow, J.; Watson, J.; Crow, D.; Lowenthal, D.; Merrifield, T. Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Science and Technology* **2001**, *34*, 23–34.

(3) Chow, J.; Watson, J.; Pritchett, L.; Pierson, W.; Frazier, C.; Purcell, R. The DRI thermal/optical reflectance carbon analysis system: description, evaluation and application in US air quality studies. *Atmospheric Environment* **1993**, *27A*, 1185–1201.

(4) Hays, M.; Beck, L.; Barfield, P.; Lavrich, R.; Dong, Y.; Wal, R. V. Physical and chemical characterization of residential oil boiler emissions. *Environmental Science and Technology* **2008**, *42*, 2496–2502.

(5) EPA, *Source Sampling - Fine Particulate Matter: Wood-Fired Industrial Boiler*; Technical Report EPA-600/R-01-106, 2001.

(6) EPA, *Mercury Study Report to Congress*; Technical Report, 1997.

(7) Seigneur, C.; Abeck, H.; Chia, G.; Reinhard, M.; Bloom, N. S.; Prestbo, E.; Saxena, P. Mercury adsorption to elemental carbon (soot) particles and atmospheric particulate matter. *Atmospheric Environment* **1998**, *32*, 2649–2657.

(8) Hildemann, L.; Markowski, G.; Cass, G. Chemical composition of emissions from urban sources of fine organic aerosol. *Environmental Science and Technology* **1991**, 744–759.

(9) Hays, M.; Geron, C.; Linna, K.; Smith, N. Speciation of gas-phase and fine particle emissions from burning of foliar fuels. *Environmental Science and Technology* **2002**, *36*, 2281–2295.

(10) Pekney, N.; Davidson, C.; Robinson, A.; Zhou, L.; Hopke, P.; Eatough, D.; Rogge, W. Major source categories for $PM_{2.5}$ in Pittsburgh using PMF and UNMIX. *Aerosol Science and Technology* **2006**, *40*, 910–924.

(11) EPA, *Air Quality Criteria for Lead (Final)*; Technical Report EPA/600/R-05/144aF-bF, 2006.

(12) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Oxford:Butterworth-Heinemann: Oxford, 1997.

(13) Malm, W.; Sisler, J. F.; Huffman, D.; Eldred, R. A.; Cahill, T. A. Spatial and seasonal trends in particle concentration and optical extinction in the United States. *Journal of Geophysical Research* **1994**, *99*, 1347–1370.

(14) Kleeman, M. J.; Schauer, J. J.; Cass, G. R. Size and composition of fine particulate matter emitted from motor vehicles. *Environmental Science and Technology* **2000**, *34*, 1132–1142.

(15) Stelson, A. W.; Seinfeld, J. H. Chemical mass accounting of urban aerosol. *Environmental Science and Technology* **1981**, *15*, 671–679.

(16) Aiken, A. C.; Decarlo, P. F.; Kroll, J. H.; Worsnop, D. R.; Huffman, J. A.; Docherty, K. S.; Ulbrich, I. M.; Mohr, C.; Kimmel, J. R.; Sueper, D.; Sun, Y.; Zhang, Q.; Trimborn, A.; Northway, M.; Ziemann, P. J.; Canagaratna, M. R.; Onasch, T. B.; Alfarra, M. R.; Prevot, A. S.; Dommen, J.; Duplissy, J.; Metzger, A.; Baltensperger, U.; Jimenez, J. L. O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry. *Environmental Science and Technology* **2008**, *42*, 4478–4485.

(17) Lipsky, E. M.; Robinson, A. L. Effects of dilution on fine particle mass and partitioning of semivolatile organics in diesel exhaust and wood smoke. *Environmental Science and Technology* **2006**, *40*, 155–162.

(18) Russell, L. M. Aerosol Organic-Mass-to-Organic-Carbon Ratio Measurements. *Environmental Science and Technology* **2003**, *37*, 2982–2987.

(19) Japar, S. M.; Szkarlat, A. C.; Gorse Jr., R. A.; Heyerdahl, E. K.; Johnson, R. L.; Rau, J. A.; Huntzicker, J. J. Comparison of solvent extraction and thermal-optical carbon analysis methods: Application to diesel vehicle exhaust aerosol. *Environmental Science and Technology* **1984**, *18*, 231–234.

(20) Sheesley, R. J.; Schauer, J. J.; Chowdhury, Z.; Cass, G. R.; Simoneit, B. R. Characterization of organic aerosols emitted from the combustion of biomass indigenous to South Asia. *Journal of Geophysical Research* **2003**, *108*, Article number 4285.

(21) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. Measurement of Emissions from Air Pollution Sources 2. C1 through C30 Organic Compounds from Medium Duty Diesel Trucks. *Environmental Science and Technology* **1999b**, *33*, 1578–1587.

(22) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. Measurement of Emissions from Air Pollution Sources 5. C1 through C32 Organic Compounds from Gasoline-Powered Motor Vehicles. *Environmental Science and Technology* **2002**, *36*, 1169–1180.

(23) Turpin, B.; Lim, H. Species contributions to $PM_{2.5}$ mass concentrations: Revisiting common assumptions for estimating organic mass. *Aerosol Science and Technology* **2001**, *35*, 602–610.

(24) Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. Measurement of Emissions from Air Pollution Sources 3. C1 through C29 Organic Compounds from Fireplace Combustion of Wood. *Environmental Science and Technology* **2001**, *35*, 1716–1728.

(25) Bae, M.; Schauer, J.; Turner, J. Estimation of the monthly average ratios of organic mass to organic carbon for fine particulate matter at an urban site. *Aerosol Science and Technology* **2006**, 1123–1139.

(26) Jimenez, J. R.; Claiborn, C. S.; Dhammapala, R. S.; Simpson, C. D. Methoxyphenols and levoglucosan ratios in $PM_{2.5}$ from wheat and Kentucky bluegrass stubble burning in eastern Washington and northern Idaho. *Environmental Science and Technology* **2007**, *41*, 7824–7829.