

Emissions Inventory of PM_{2.5} Trace Elements across the United States

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This paper presents the first National Emissions Inventory (NEI) of fine particulate matter (PM_{2.5}) that includes the full suite of PM_{2.5} trace elements (atomic number > 10) measured at ambient monitoring sites across the U.S. PM_{2.5} emissions in the NEI were organized and aggregated into a set of 84 source categories for which chemical speciation profiles are available (e.g., Unpaved Road Dust, Agricultural Soil, Wildfires). Emission estimates for ten metals classified as Hazardous Air Pollutants (HAP) were refined using data from a recent HAP NEI. All emissions were spatially gridded, and U.S. emissions maps for dozens of trace elements (e.g., Fe, Ti) are presented for the first time. Nationally, the trace elements emitted in the highest quantities are silicon (3.8×10^5 ton/yr), aluminum (1.4×10^5 ton/yr), and calcium (1.3×10^5 ton/yr). Our chemical characterization of the PM_{2.5} inventory shows that most of the previously unspicated emissions are comprised of crustal elements, potassium, sodium, chlorine, and metal-bound oxygen. This work also reveals that the largest PM_{2.5} sources lacking specific speciation data are off-road diesel-powered mobile equipment, road construction dust, marine vessels, gasoline-powered boats, and railroad locomotives.

Introduction

Trace elements constitute only a small fraction of the mass of ambient fine particulate matter (PM_{2.5}), but their concentrations are routinely measured at hundreds of air monitoring sites across the United States (1, 2). These data have proven useful in calculations of visibility degradation (3), receptor-based source-apportionment calculations (4), and for studying the health effects of exposure to metals (5). While the ambient concentrations have been analyzed extensively, emission inventories of PM_{2.5} trace elements have received relatively little attention.

Inventories of particulate emissions contain information spanning as many as five dimensions: spatial, temporal, source-categorical, particle-size, and chemical-composition. A perusal of the literature shows that the resolutions and ranges over which each of these dimensions are spanned varies widely depending on the intended purpose of the inventory. For example, soil-dust and elemental emissions have been inventoried for specific regions of China (6), and metals from the industrial sector have been inventoried in Mumbai, India (7). In southern California, comprehensive inventories of trace elements in PM₁₀ and ultrafine PM have

been developed for select time periods (8, 9). In the U.S., nationwide inventories of lead from all major anthropogenic sources have been assembled since 1970 (10). Nationwide emissions data have been compiled for PM_{2.5} and numerous hazardous air pollutants (HAP), including ten toxic metals, since 1990 (11, 12).

The U.S. National Emission Inventory (NEI) for PM_{2.5} is extremely detailed in the source-categorical and spatial dimensions. Anthropogenic emissions are segregated into more than 3000 distinct source classes. In the spatial dimension, point-source locations are specified by latitude and longitude, while mobile- and area-source emissions are tabulated for each county ($N = 3044$). In the chemical-composition dimension, however, the PM_{2.5} NEI is speciated using “simplified profiles” that include only sulfate (SO₄²⁻), nitrate (NO₃⁻), elemental carbon (EC), organic carbon (OC), and other particulate mass (13). National-scale inventories of selected PM_{2.5} metals have been assembled such as the HAP NEI (<http://www.epa.gov/ttn/chief/net/2002inventory.html>) and the 1985 National Acid Precipitation Assessment Program emissions inventory (14), but a national inventory that contains the full suite of PM_{2.5} species measured routinely at U.S. monitoring sites has yet to be assembled. Without such an inventory, numerical air quality models cannot be used to predict ambient concentrations and deposition patterns of that suite of species across the country.

In this work, we identify a set of source categories for which PM_{2.5} speciation profiles are available and into which all major emission sources in the NEI can be categorized. We survey speciation profiles from the literature that contain the bulk species listed above plus up to 37 trace elements (defined as having atomic number > 10) to develop a comprehensive set of profiles that is representative of emissions from each source category. We demonstrate the utility of these profiles by speciating the PM_{2.5} NEI, thus constructing the first national-scale emissions inventory to contain the full suite of PM_{2.5} species measured across the major air monitoring networks such as the Interagency Monitoring of Protected Visual Environments network (2) and the Chemical Speciation Network (15). The inventory is spatially gridded, and maps of selected species are displayed and analyzed. Similar approaches to emissions inventory development have recently been performed for volatile organic compounds (16) and polycyclic aromatic hydrocarbons (17). This is the first known demonstration of speciating dozens of trace elements in a national PM_{2.5} inventory.

Methods

The general strategy for calculating trace elemental emissions is to multiply each source of PM_{2.5} in the NEI by a chemical speciation profile appropriate for that source type. Figure 1 contains a flow diagram of the methods. Specific procedures for generating the speciated PM_{2.5} inventory are summarized below, which includes references to the appropriate section of the Supporting Information where additional details are provided.

U.S. EPA National Emissions Inventory. PM_{2.5} mass emissions were obtained from the 2001 Clean Air Interstate Rule (CAIR) version of the NEI (<http://www.epa.gov/air/interstateairquality/technical.html>). That inventory consists of PM_{2.5} emissions from eight sectors: 1) onroad mobile sources, 2) nonroad mobile sources, 3) fires, 4–5) point and area sources of fugitive dust, 6) electric generating units (EGUs), 7) non-EGU point sources, and 8) other area sources. Point and area-source emissions of fugitive dust are reduced

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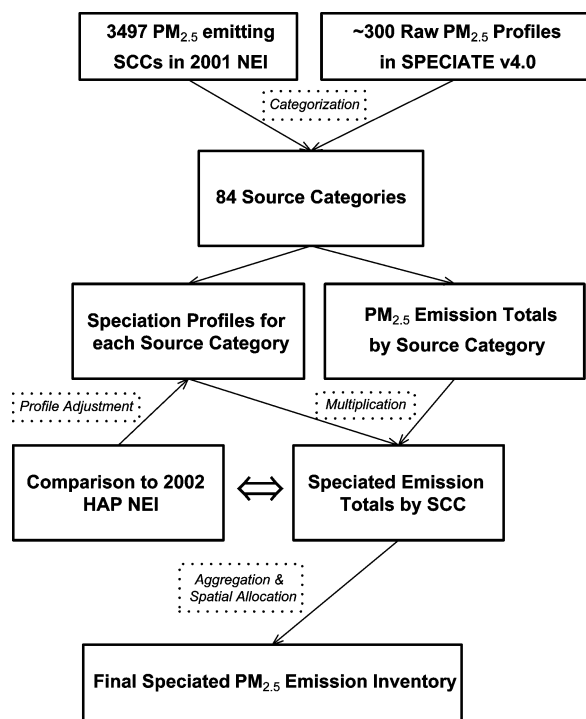


FIGURE 1. Schematic diagram illustrating the procedure followed to create the PM_{2.5} trace-elemental emissions inventory.

by a county-specific factor—ranging from 3% in barren areas to 95% in forested areas—to account for removal processes within several hundred meters of dust sources (18). PM_{2.5} emissions within the inventory are labeled using a set of 3497 source classification codes (SCCs) that are defined based on the emission generating processes and source characteristics.

Source Categories. To compute emissions of each trace element, PM_{2.5} mass emissions from the NEI were multiplied by source-specific speciation profiles. The SPECIATE database (<http://www.epa.gov/ttn/chief/software/speciate/>) is currently the most comprehensive collection of such profiles available, containing over 1000 PM_{2.5} speciation profiles from the literature (13). Most of these profiles consist of trace elements measured by X-ray fluorescence (XRF), OC and EC measured by thermal optical methods, and inorganic ions measured by ion chromatography, each normalized by total PM_{2.5} mass. A detailed analysis of the database revealed that about 300 of the profiles are suitable for speciating PM_{2.5} emission sources in the NEI (see Section S3.1). A 1-to-1 mapping between these profiles and the 3497 SCCs was not feasible due to varying degrees of source specificity between the profile and SCC lists, the absence of appropriate PM_{2.5} profiles for certain SCCs, and the presence of multiple speciation profiles in SPECIATE v4.0 for certain sources. A set of 84 *source categories* was thus developed for grouping SCCs and SPECIATE source profiles on a common basis (see Section S2).

Category-Specific Speciation Profiles. After classifying the emissions into source categories, the next step was to create a speciation profile for each category by either identifying an individual profile from SPECIATE v4.0 or constructing one from multiple high-quality profiles in the database. Numerous profile- and source category-specific adjustments were found to be necessary based on data quality, profile notes, and references associated with the individual profiles. Additional species such as particulate water (H₂O), noncarbon organic matter (NCOM), metal-bound oxygen (MO), and other unspicated PM_{2.5} (PMO) were calculated, after which profiles whose sum of species exceeded the total PM_{2.5} mass were adjusted. Section S3

explains these calculation details. The final set of 84 speciation profiles used in this study is in Table S6 and will be included in the next public release of the SPECIATE database.

Emissions Speciation. Next, the NEI was speciated by multiplying the PM_{2.5} emissions from each source category by the corresponding speciation profile in Table S6. This yielded a set of speciated PM_{2.5} emissions for each source category. As indicated in Figure 1, a subset of these results was compared against emissions from an independently derived HAP inventory to evaluate the validity of our speciation profiles. Profiles were adjusted as described below, and emissions were recalculated. This cycle was iterated several times to ensure quality in the resulting inventory.

Profile Updates Using HAP NEI. Many of the profiles in SPECIATE were derived from measurements made during the 1980s and 1990s, so they are outdated for certain HAPs because of control technologies and strategies that have been adopted since that time to meet federally mandated limits on HAP emissions. Data from version 2 of the 2002 NEI for ten HAPs were therefore used to identify outdated mass fractions in the speciation profiles for each source category. Although the year of the HAP inventory (2002) differs from the year of our speciated PM_{2.5} inventory (2001—selected due to having been processed through the Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system at the time of this analysis—see below), the years are sufficiently close for the qualitative evaluation conducted here. The HAP inventory of 10 hazardous elements (As, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, and Se) was aggregated into the same source categories that were used to develop our trace-elemental inventory, of which only 74 are accounted for in the HAP NEI. Differences between the two inventories were then calculated for each combination of 10 elements and 74 source categories. Differences greater than 20% of the HAP inventory's element- and source category-specific emission totals were analyzed to identify speciation profiles needing adjustment. Based on this criterion, profiles for 18 source categories were analyzed, and 10 of them were adjusted in some manner. After the adjustments, all of the HAP metals in our speciated inventory were brought into closer agreement with the HAP inventory (see Section S3.6 and Figure S1 in the Supporting Information).

Spatial Allocation. The SMOKE modeling system (19) was used in this work to process the inventory. Processing steps included distribution of the speciated emissions and the source-segregated emissions to a 36-km grid and use of a SMOKE quality assurance utility (smkreport) to generate text reports of 2001 annual total PM_{2.5} emissions by SCC from the continental U.S. Maps of speciated PM_{2.5} emissions summed over all source categories, and total PM_{2.5} from each source category were created by gridding emissions across the continental U.S. using the utility called smkmerge in the SMOKE modeling system and plotting the resulting output with R statistical software (20).

Results

Speciated PM_{2.5} Emissions. Figure 2 depicts the emissions of all PM_{2.5} species from each of the 84 source categories, summed across the U.S. during 2001. Source categories are sorted based on their total emissions of PM_{2.5} mass, with the highest-emitting categories shown at the top. Those categories are Unpaved Road Dust (6.9×10^5 ton/yr), Agricultural Soil (6.1×10^5 ton/yr), and Wildfires (4.8×10^5 ton/yr). This ranking can differ greatly at individual locations within the U.S. due to the different mixture of sources that dominate urban airsheds as compared to the continental background. The columns of Figure 2 show emissions of PM_{2.5} mass, OC, EC, major ions, NCOM, MO, H₂O, 37 trace elements sorted by atomic number, and PMO. In general, the magnitude of

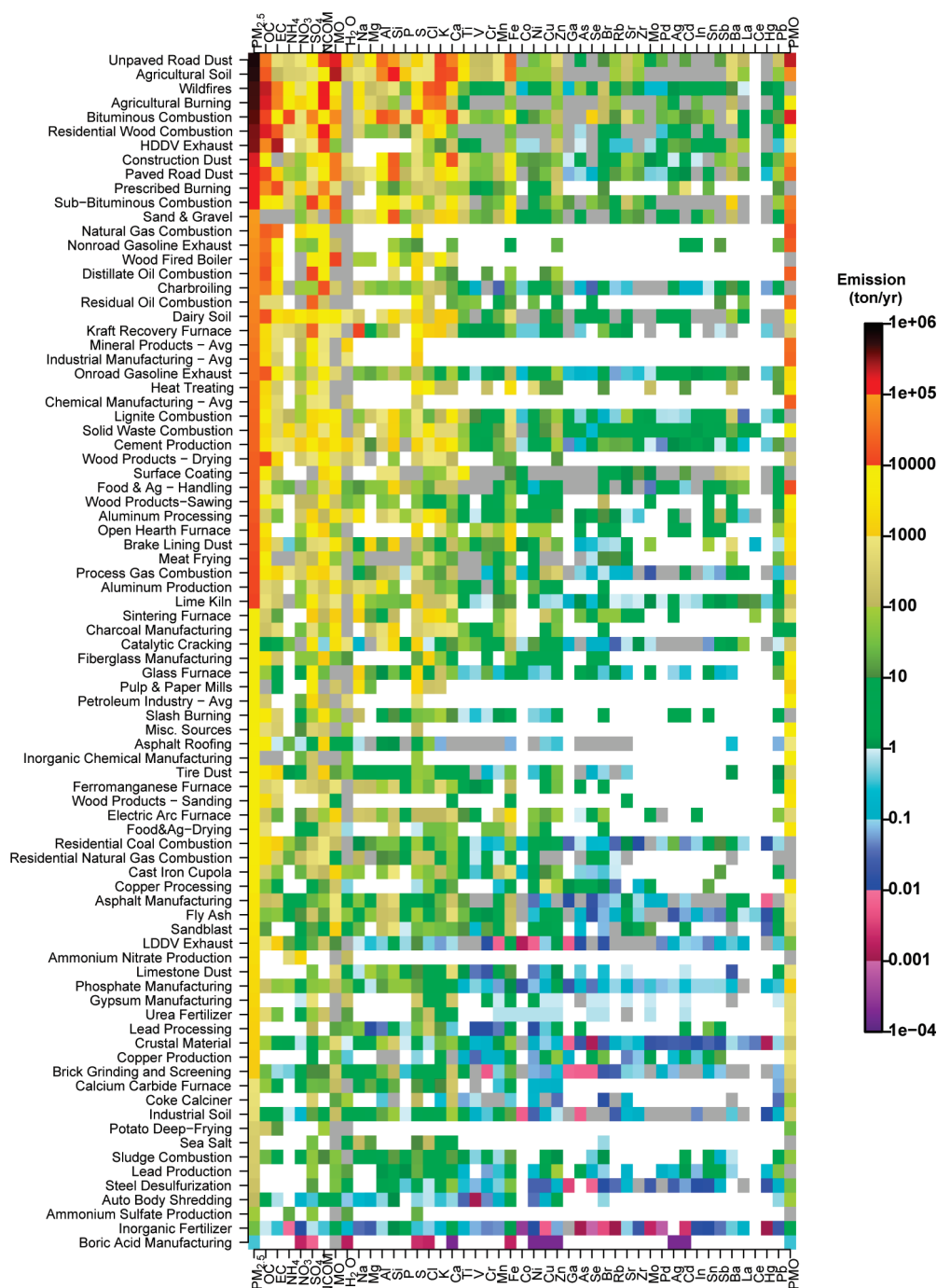


FIGURE 2. Continental U.S. total emissions of $PM_{2.5}$, bulk species, and trace elements (x-axis) in each source category (y-axis), calculated by applying our final speciation profiles (Table S6) to the 2001 NEI. Grey tiles indicate cases where the mass fractions in a given speciation profile were reported as zero. White spaces indicate species that were not reported in the speciation profiles or measurements that were deemed obsolete due to recent changes in emission control programs (see Section S3.6).

trace-elemental emissions tends to decrease with increasing atomic mass.

Unlike source apportionment analyses, in which the $PM_{2.5}$ contributions from five to ten different source categories are typically resolved, the source specificity of the NEI and the speciation profiles allows one to compute emission contributions from a much larger number of sources. When similar source categories are aggregated together, a number of features in Figure 2 are found to be consistent with results commonly reported in the $PM_{2.5}$ source apportionment literature. For example,

(1) The dominant source of crustal elements such as Mg, Al, Si, Ca, and Fe is fugitive dust. As shown in Figure 2, the major sources of fugitive dust in the NEI are unpaved and

paved roads, agricultural tilling, construction dust, and sand/gravel from mining and quarrying operations. Natural windblown dust from arid land is likely to be a major source of crustal elements as well but is not currently included in the NEI.

(2) Biomass burning makes a dominant contribution of particulate Cl, K, and primary OC. Figure 2 shows that major categories within biomass burning are wildfires, agricultural burning, residential wood combustion, prescribed burning for land management, and wood-fired boilers. During select time periods, the relative contributions from each of these categories may differ from the annual totals shown here (e.g., wildfire activity peaks in Summer, prescribed burning in Spring, and residential wood combustion in Winter), but a

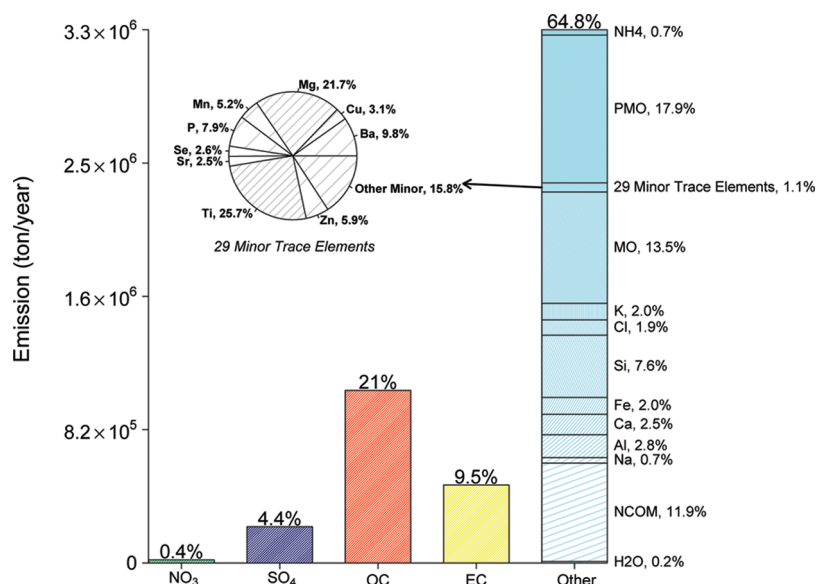


FIGURE 3. Chemical composition of the speciated PM_{2.5} NEI. The species listed along the x-axis represent those in the NEI prior to this work, with percentages atop each bar showing their net contributions to the annual total PM_{2.5} inventory. The stacked layers within the right-most bar show a breakdown of the species previously grouped as "Other". The pie chart shows the breakdown of the minor trace elements too numerous to fit into the "Other" bar; in the pie, the "Other Minor" slice contains 20 trace elements that each contribute less than 2% of the minor elements' emissions (e.g., V, Cr, Co).

more detailed discussion of temporal trends is beyond the scope of this work.

(3) Coal combustion is the largest source of S, Se, Sr, Hg, and primary SO₄²⁻. In our speciated inventory, these emissions are further segregated based on coal type, with bituminous coal producing the largest PM_{2.5} emissions (4.1×10^5 ton/yr), followed by subbituminous (1.1×10^5 ton/yr), and lignite coal (25,000 ton/yr). Residential coal combustion makes a small contribution to the PM_{2.5} inventory (5200 ton/yr) on a national scale.

(4) It is well-known that diesel engines are the largest source of EC. Figure 2 shows that they also emit large quantities of primary OC and Zn. Due to the dearth of speciation data from different types of diesel engines, the "HDDV Exhaust" source category used in this work includes contributions from nonroad vehicles such as construction and mining equipment, agricultural equipment, marine vessels, railroad locomotives, and aircraft as well as onroad diesel vehicles and diesel-powered electricity generators.

(5) Barium has often been used as a tracer for dust from brake linings (21). While this is clearly a major source of Ba, our analysis reveals that coal combustion emits much larger quantities of Ba on a national basis.

(6) Industrial processing of copper is the largest source of Cu.

In addition to the features listed above, Figure 2 displays some aspects of trace-elemental emissions that are not commonly reported in the literature. For example, surface coating operations emit the largest quantities of Ti, Sb, and La. While coal combustion is shown to be the largest source of Hg nationwide, wildfires also make a significant contribution (22) due to re-emission of Hg that accumulated on the ground via atmospheric deposition. Unpaved road dust is the largest source of Pb on a national basis, which is due to the sheer magnitude of dust emissions coupled with the small mass fraction of Pb in the speciation profile (0.03%). Fugitive dust emissions also make the greatest contributions to V, Co, Mn, Rb, and Zr.

The colorless portions of Figure 2 provide a visual indication of data incompleteness in the final speciation profiles. Most of the source categories contain nonzero values for at least 21 out of the 37 elements considered here. Elements found most commonly in the profiles are S, K, Ca,

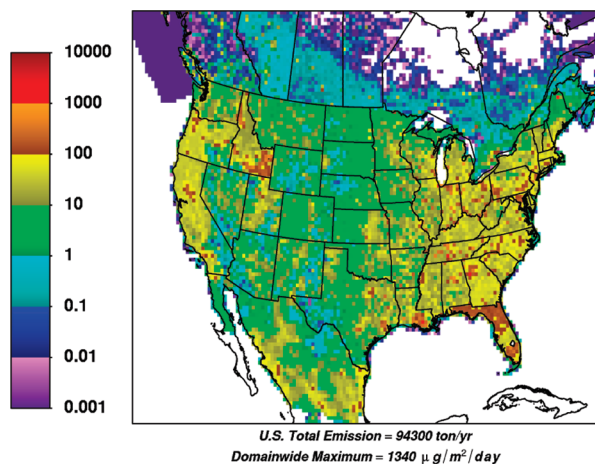
and Fe, whereas the least common are Ga, Ce, and Hg. Some of the most notable data gaps illuminated by Figure 2 are in the source categories which contain "Avg" in their names (e.g., "Mineral Products—Avg"; see Section S3.5). The major PM_{2.5} sources falling within these source categories are cooling towers, wastewater treatment, mineral production, petroleum production, and production of various chemicals such as plastics, chlorine and derivatives, rubber, inks, and olefins. Future source characterization efforts could target emissions from these specific sources to fill in the data gaps.

Of course, the mere availability of trace-elemental data does not guarantee high quality. XRF analyses are known to have relatively high detection limits which may introduce error to the speciated PM_{2.5} inventory. In our comparisons with the HAP NEI, for example, we found the As mass fractions in the coal and residual oil combustion profiles to be inadequate (see Section S3.6). New source profiles collected using analytical techniques with lower detection limits (e.g., ICP-MS) are likely to improve the quality of the inventory presented here (23).

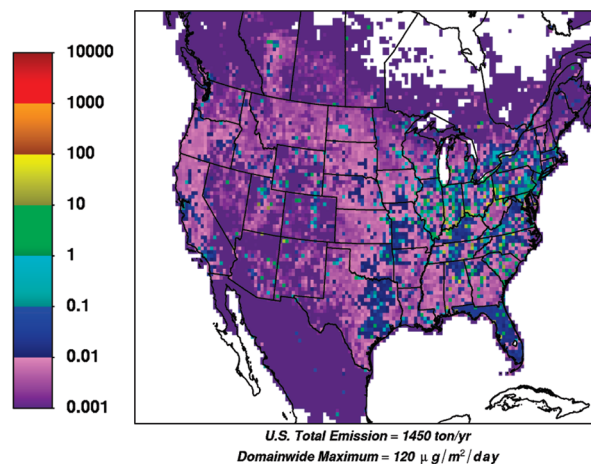
The speciated breakdown of national total PM_{2.5} emissions is shown in Figure 3. The first four bars on the left of Figure 3 show how the NEI was speciated using simplified profiles prior to the present study. Those profiles include only SO₄²⁻, NO₃⁻, OC, and EC, with all other species collected into the fifth bar of Figure 3. Application of our speciation profiles led to more detailed speciation of the "other" material, as indicated by the stacked layers inside the right-most bar and the accompanying pie chart in Figure 3. Major components of the previously unspicated mass include Si, Al, Ca, Fe, K, and Cl as well as NCOM and MO. The total unspicated mass is greatly reduced, from 64.8% in the original PM_{2.5} NEI to only 17.9% in our final inventory. Most of this remaining mass originates from three source categories: Unpaved Road Dust (PMO = 32%), Bituminous Combustion (PMO = 44%), and Construction Dust (PMO = 40%). Thus, an efficient approach for improving mass closure in the PM_{2.5} NEI would be to enhance the speciation profiles for these source categories.

Spatial Patterns of PM_{2.5} Trace Element Emissions.

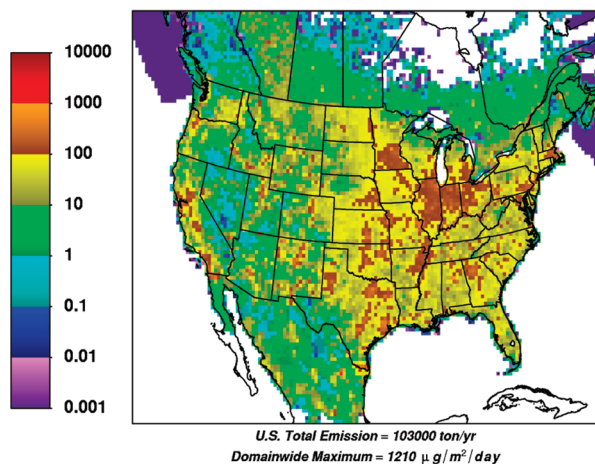
Figure 4 shows maps of four elements whose emissions exhibit some representative spatial characteristics. Emissions maps of the remaining species as well as PM_{2.5} totals from



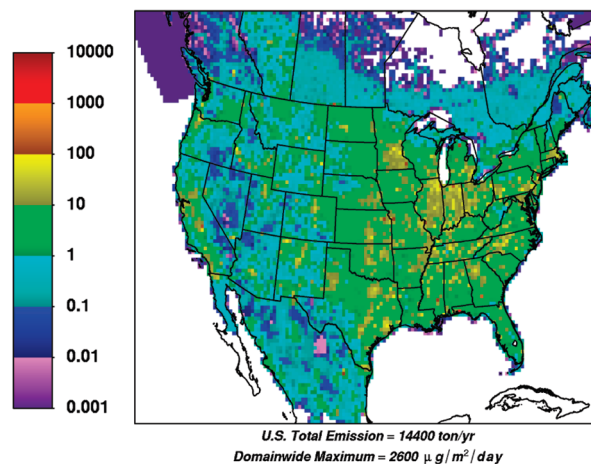
(a) Cl



(c) Se



(b) Fe



(d) Ti

FIGURE 4. Spatial distributions of 2001 NEI PM_{2.5} emissions ($\mu\text{g}/\text{m}^2/\text{yr}$) of select trace elements. Grid cells where the emissions flux is zero are indicated by white space. Cells where the flux is nonzero and less than $10^{-3} \mu\text{g}/\text{m}^2/\text{yr}$ are shown in dark purple.

each of the 84 source categories are in Section S4. Emissions from Canada and Mexico in the 2001 CAIR inventory can be seen in many of these maps; however, those emissions are not counted in the U.S. national totals discussed throughout this work.

Species such as Cl and K are emitted primarily from biomass burning. As shown in Figure 4(a), Cl emissions are largest in Florida. This is due to some large wild fire events in 2001 (24) which should not be considered representative of the emissions during other years. Cl emissions along the west coast are also primarily from Wildfires; in the Northeast and other urban areas, they are predominantly from Residential Wood Combustion. Agricultural Burning is responsible for the large Cl emissions in the southeast regions of Idaho and Louisiana. A pattern similar to Figure 4(a) can be seen in the spatial distributions of K (which also has large contributions from fugitive dust) and Br (see Figures S4(e) and S7(a)).

Emissions of crustal elements are exemplified by the map of Fe emissions in Figure 4(b). The high emissions of Fe across Indiana, Illinois, southern Minnesota, northwestern Texas, and eastern Arkansas are due to the influence of PM_{2.5} emissions from the Agricultural Soil category (see Figure S10(b)). Unpaved Road Dust emissions (Figure S10(a)) are responsible for the strong Fe emissions in eastern Texas, northern California, and the “hotspots” in the southeastern

states (e.g., Atlanta, GA). Low Fe emissions can be seen in Nevada, Arizona, and Utah, where Agricultural Soil emissions are absent. The spatial pattern of fugitive dust sources can also be seen in the map of Al emissions (Figure S3(f)) as well as those of Si and Ca (Figures S4(a) and S4(f)) which additionally show some influence of coal combustion.

Coal-fired power plants emit over 96% of Se on a national basis. In Figure 4(c), these large point sources can be seen throughout the Ohio River valley and some of the western states. Due to the logarithmic color scale used in all of our maps, minor area sources of Se appear as large swaths of dark blue (e.g., Wildfires in Florida, Oregon, and California; Dairy Soil in eastern Texas and western Missouri) even though those sources contribute a minuscule fraction of the national Se emissions.

Figure 4(d) shows the emissions map for Ti, in which the grid cells with maximum fluxes correspond with the spatial distribution of Surface Coating emissions sources (see Figure S14(f)). This is due to the abundance of TiO₂ in paint and coating products, consistent with our finding from Figure 2. However, this finding contrasts with the common assumption that Ti is dominated by soil oxides (2, 3). In locations where Surface Coating emissions are significant (e.g., Chicago, southeastern Minnesota, western North Carolina, central California), that assumption may be invalid.

Discussion

As a result of this work, the PM_{2.5} NEI has been greatly enhanced in the compositional dimension. Whereas the previous NEI resolved only 35% of the U.S. emissions into four chemical species, our new set of profiles resolve 82% of the NEI into 44 species. In the process, nationwide emissions of 10 HAP metals from fugitive dust sources and wildfires have been estimated for the first time. The enhanced inventory will enable the use of regional-scale models for detailed investigations of atmospheric chemistry issues. For example, speciated emissions of Mn and Fe could improve the accuracy of aqueous-phase chemistry mechanisms which use those metals to catalyze sulfur oxidation (25). Emission estimates of Cl and Br can assist studies that probe the effects of halogen radicals on O₃ photochemistry (26). In addition, emissions of Mg, K, and Ca can be used in new thermodynamic equilibrium modules to predict the inorganic gas/particle partitioning behavior (27). Also, speciation of the PM_{2.5} inventory may prove to be a cost-effective aid in the source apportionment of trace elements by providing confirmatory data for receptor modeling studies (28).

Through the process of speciating the 2001 PM_{2.5} NEI, some critical gaps in the SPECIATE database were revealed. Separate chemical profiles are not available for road construction dust (102,000 ton/yr) and heavy construction dust (72,300 ton/yr), so all of those emissions were mapped to a single Construction Dust profile. Similarly, no speciation profiles were found for the off-road diesel engines used in construction and mining equipment (68,500 ton/yr), agricultural equipment (67,800 ton/yr), and railroad locomotives (24,600 ton/yr), so those emissions were all mapped to the HDDV category. No profiles are available for marine vessels (39,500 ton/yr), so their emissions were mapped to the HDDV and Residual Oil Combustion categories depending on the type of fuel consumed. Emissions from gasoline-powered boats (34,700 ton/yr) were mapped to a profile from a noncatalyst-equipped automobile. Emissions from bagasse boilers (15,200 ton/yr) were mapped to a Wood Fired Boiler profile. Emissions from waste incinerators (14,800 ton/yr) and solid waste boilers (9000 ton/yr) were mapped to a Solid Waste Combustion profile. Emissions from coal mining, cleaning, and material handling (12,600 ton/yr) were mapped to the Mineral Product - Avg profile. Collection of profiles from these specific sources may be the most important manner by which to enhance the inventory presented in this study.

A careful examination of the emission maps also revealed reporting inconsistencies in the PM_{2.5} NEI that should be targeted in future inventory updates (see Section S4). Major PM_{2.5} sources that are not considered in the NEI include natural wind-blown dust, vegetative detritus, pollen fragments, sea salt (the "Sea Salt" source category in our inventory contains only salt mining SCCs), and cigarette smoke. Most source category profiles were composited from fewer than 10 source profiles which, in many cases, did not originate from spatially disparate source tests. The maps in Figure 4 and Section S4 can be used as a guide for prioritizing sources to sample in the future. Compositing a more spatially disparate collection of profiles will result in a more statistically robust set of source category profiles and will provide data for region-specific emissions speciation. Future work is planned for evaluating our speciated emissions against ambient concentrations of the full suite of species measured routinely across the U.S., which will guide new improvements to the inventory. Ultimately, air quality models that use this inventory can be used to assess the effectiveness of future emission control programs that target specific trace elements.

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Supporting Information Available

Complete procedural details, the final set of 84 speciation profiles, and the full set of emissions maps. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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