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Estimation of Atmospheric Emissions of Six Semivolatile Polycyclic Aromatic Hydrocarbons in Southern Canada and the United States by Use of an Emissions Processing System

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Polycyclic aromatic hydrocarbons (PAHs) are toxic compounds that are ubiquitous in the atmospheric environment. The input for an emissions processing system that was originally configured for the study of criteria air pollutants was updated to calculate emissions of six semivolatile PAHs. The goal of the work was to produce emissions estimates with the spatial and temporal resolution needed to serve as input to a regional air quality model for southern Canada and the U.S. Such modeling is helpful in determining reductions in PAH emissions that may be necessary to protect human and ecosystem health. The total annual emission of the six PAHs ($\Sigma 6\text{PAH}$) for both countries was estimated at 18 273 Mg/year. A total of 90% of these emissions arise from U.S. sources. The top six source types account for 73% of emissions and are related to metal production, open burning, incineration, and forest fires. The emission factors used in this study were derived from published compilations. Although this approach has the advantage of quality control during the compilation process, some compilations include factors from older studies that may overestimate emissions since they do not account for recent improvements in emission control technology. When compared to estimates published in the National Emissions Inventory (NEI) for 2002, the U.S. emissions in this study are higher by a factor of 4 (16 424 vs 4102 Mg/year). The cause of this difference has been investigated, and much of it is likely due to our use of data unavailable in the 2002 NEI but inferred here on the basis of the PAH emissions literature. Augmenting the 2002 NEI with this additional information would bring its reported annual emissions to 8213 Mg/year, which is within a factor of 2 of the estimates herein. The results presented for southern Canada are the first published values for all known PAH sources in that country.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are classified as persistent organic pollutants (POPs) since they are toxic and

subject to long-range transport. As such, they are slated for control through various international agreements (1, 2). PAHs are emitted to the atmosphere from combustion processes and evaporative sources, but unlike other POPs, their atmospheric levels observed in long-term monitoring programs such as the Integrated Atmospheric Deposition Network (IADN) are generally not declining in background areas (3).

Many issues regarding PAH fate in the environment are poorly understood, especially with regard to the relative importance of competing transport and degradation processes. These issues are complicated by the semivolatility of many species and the consequent partitioning they exhibit between the gas and particle phases. For such compounds to be incorporated in regional air quality models, spatially and temporally varying emissions inventories must be used as input.

National emissions information for PAHs exists through Environment Canada's National Pollutant Release Inventory (NPRI) (4) and the U.S. EPA's Toxics Release Inventory (TRI) (5), but these report annual emissions from only a subset of potential sources, generally those above a certain emission mass threshold. The U.S. EPA also produces more complete emissions estimates through its National Emissions Inventory (NEI), although these are partially based on the TRI as well as on inventories from lower levels of government and industry (6).

Model-compatible emissions must ideally incorporate all sources and vary in time and space to interact correctly with the meteorology and chemical processes represented in the model. This study describes the modification of speciation profiles used in an emissions processing system for the calculation of emissions of six appreciably semivolatile PAHs: phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, and chrysene. These species are a subset of the commonly measured 16-PAH parameter. Results are presented for southern Canada and the continental U.S., and for the former, these are the first published spatially and temporally varying emissions estimates that include all known source types. U.S. emissions estimates from this study are compared to those produced through the NEI.

Materials and Methods

The emissions processing system used for this work was the Sparse Matrix Operator Kernel Emissions modeling system, SMOKE v. 2.2 (7). In its existing configuration for Environment Canada's research on air quality, SMOKE's input files were targeted toward the study of criteria air contaminants. Several adaptations were necessary for the inclusion of semivolatile PAHs. A schematic representation of the emission factor determination process is presented in Figure 1, and an overview of the steps in the process is given next. The calculation methods are described in detail in the Supporting Information.

Step 1. Identification of PAH Relevant Source Category Codes (SCCs), TOG Speciation Profiles, and Revisions to Their Mapping Linkages. A basic descriptor for any emitting process is the source category code (SCC), which is an eight- or 10-digit number developed by the U.S. EPA that identifies an emission source. A list of 11 188 SCCs was taken from SMOKE (file SCCDESC) as the starting point for identifying sources likely to emit PAHs.

SMOKE can process emissions for compounds explicitly or as speciated components of an aggregate compound such as total organic gases (TOG) or particulate matter (PM). In the latter case, the aggregate is split according to a speciation

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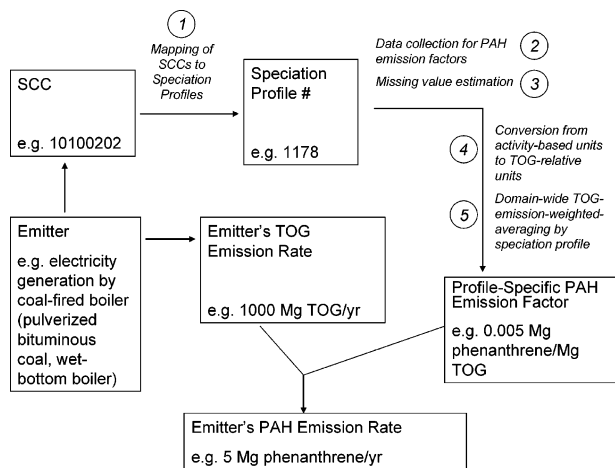


FIGURE 1. Schematic representation of the PAH emission factor determination process.

profile that disaggregates it into component compounds at fixed fractions on a mass or molar basis. Because of the paucity of available emission factors and inventory data relative to the potential number of atmospheric PAH sources, speciated PAH emissions were estimated relative to an existing inventory of an aggregate parameter in this work. TOG was chosen as that aggregate parameter, although no assumption was made as to the phase (gas or particle) of the emitted PAHs. Emission factors were developed for total PAH emissions, and the partitioning between particle and gas was left to the downstream user of the information (e.g., air quality model).

Step 2. Compilation of PAH Emission Factors from the Literature. PAH emission factors were taken from available compilations (8, 9) as well as being derived from an existing inventory for mobile sources (10).

Step 3. Procedures for Inferring Missing Emission Factors from Available Data. Emission factors were available for only some of the six target PAHs for many SCCs, and in some cases, isomer pair data were represented by a single number (e.g., phenanthrene and anthracene reported as a single factor). Estimates of missing PAH emission factors were based on average species ratios within the speciation profile to which they were mapped (viz. those SCCs within a given profile with more emissions factor data were used to infer the factors for those SCCs lacking this information).

Step 4. Conversion of Emission Factors to TOG Units. SMOKE was set up to calculate compound specific emissions relative to aggregate emissions parameters such as TOG. To convert the activity values collected previously to mass emissions of PAHs, the PAH emission factors had to be converted from activity units (stationary sources, e.g., mass PAH emitted/mass coal burned) or a PM₁₀ basis (mobile sources) to TOG units (e.g., mass PAH emitted/mass TOG emitted).

Step 5. Weighting the Emissions Factors within a Speciation Profile by Binational Total TOG Emissions. The first four steps led to a list of emission factors for the six target PAHs for 197 SCCs associated with 33 TOG speciation profiles. SMOKE, however, requires a single set of factors for each profile, so a mass-weighting step had to be performed. This is described in the Supporting Information and is based on VOC emissions inventories for Canada and the U.S. for 2000 and 2001, respectively (11, 12).

PAH Emission Calculations. The information derived in steps 1–5 was assembled, and in combination with the annual TOG emissions, the total annual PAH emissions were calculated for each PAH in each speciation profile. The

emission factors and related information were also compiled in the speciation profile format required by SMOKE, and the emissions processing system was run separately for all profiles within each category of point, nonpoint, and mobile sources. The runs were conducted for two 24 h periods on Tuesdays in January and July. The SMOKE domain was a 42 km × 42 km grid covering the continental U.S. and southern Canada, and the time step was 1 h. As part of its processing, SMOKE makes use of temporal disaggregation factors to determine mass emissions as a function of time. In a manner similar to the speciation profiles, a relatively small number of temporal disaggregation profiles is linked to the sources on an SCC basis. These temporal profiles allow for the calculation of time-dependent PAH emissions on an hourly basis by the day of the week and month.

The retention of the emission data by the speciation profile is not typically part of SMOKE processing, in which aggregate emissions output into broader source categories (e.g., all mobile emissions, all point source emissions, etc.) for model-ready estimates. The input files for SMOKE in this study were created to retain this information by giving a different variable name to each PAH profile combination. This allowed for the calculation of the relative contributions of different profiles toward total PAH emissions as described next.

Results and Discussion

Annual Σ6PAH Emissions. The total estimated annual emissions of the six target PAHs and total organic gases (TOG) associated with those emissions for southern Canada and the U.S. are presented in Table 1 and Table S3 of the Supporting Information. Table 1 lists the largest 16 sources that represent 98% of the estimated emissions, and each contributes at least 100 Mg/year. The total annual estimate for the entire domain is also presented in Table 1. Table S4 contains a complete listing of all estimated sources. The estimated Σ6PAH emission for both countries is 18 273 Mg/year. Six speciation profiles contribute more than 1000 Mg/year each. Three of these relate to primary and secondary metal production, and the other three are open burning, incineration, and forest fires, and all are known to be major sources of PAHs (13). In total, these six sources contribute 13 408 Mg/year or 73.4% of the total estimated Σ6PAH.

A further 10 speciation profiles were estimated to emit between 100 and 1000 Mg/year of Σ6PAH, and together, they contribute a further 4503 Mg/year or 24.6% of the total estimate. Included in these are gasoline and diesel motor vehicles, which are often cited as major contributors to urban atmospheric PAH levels (e.g., ref 14). However, activities with SCCs mapped to these profiles (some of which are stationary engines, not motor vehicles) are estimated to contribute 996 Mg/year, just 5.45% of total emissions.

The remaining 2% of Σ6PAH emissions arise from 40 speciation profiles, each contributing less than 100 Mg/year. Eight speciation profiles contribute no Σ6PAH to these estimates as a result of their negligible TOG emissions.

This study estimates a total annual emission of Σ6PAH of 1849 Mg/year from southern Canada or 10% of the total for Canada and the U.S. This is in line with the difference in population of the two countries and their similar levels of industrialization.

The results in Table 1 are listed in descending order of Σ6PAH emissions by speciation profile, and the names of the profiles generally suggest whether the source is a point, nonpoint, or mobile one. However, in reality, some profiles have component SCCs that belong to more than one source type. For example, speciation profile 0001b (external combustion boiler—residual oil) is mapped from SCCs that are point sources (e.g., SCC 31390002, residual oil process heaters in the electrical equipment industry), nonpoint sources (e.g., SCC2101005000, all area source residual oil boilers for electric

TABLE 1. Annual Estimated Emissions (Mg/Year) of Six PAHs from the Largest 16 Sources and TOG Associated with Those PAH Emissions for Southern Canada and the U.S.^a

| speciation profile no. | name | PHEN | ANTH | FLRT | PYR | BaA | CHRY | 6PAH | TOG ^b |
|---------------------------|--|------|------|------|------|------|------|-------|------------------|
| 1036b | secondary aluminum – pouring and casting | 821 | 821 | 1224 | 1276 | 469 | 359 | 4971 | 9425 |
| 9010b | secondary metal production – average | 349 | 349 | 521 | 543 | 200 | 153 | 2116 | 4012 |
| 1202b | primary aluminum production | 881 | 126 | 412 | 249 | 95 | 171 | 1934 | 2701 |
| 0121b | open burning dump – landscape/pruning | 352 | 103 | 524 | 499 | 97 | 241 | 1815 | 774147 |
| 0307b | miscellaneous burning – forest fires | 235 | 81 | 375 | 391 | 149 | 249 | 1479 | 597899 |
| 0122b | bar screen waste incinerator | 30 | 21 | 45 | 477 | 35 | 81 | 1094 | 995937 |
| 1185b | coal-fired boiler – industrial | 380 | 127 | 92 | 161 | 41 | 48 | 850 | 24367 |
| 0016b | basic oxygen furnace | 281 | 97 | 43 | 21 | 55 | 109 | 607 | 4767 |
| 1167b | residential wood combustion | 264 | 55 | 57 | 102 | 49 | 57 | 584 | 1752066 |
| 0013b | iron sintering | 253 | 87 | 39 | 19 | 50 | 98 | 546 | 4286 |
| 1101b | light duty gasoline vehicles – 46 car study | 204 | 68 | 73 | 100 | 8 | 8 | 461 | 6088513 |
| 9001b | external combustion boilers – industrial average | 180 | 42 | 53 | 58 | 14 | 26 | 373 | 20721 |
| 1201b | light-duty diesel vehicles | 143 | 28 | 72 | 94 | 12 | 8 | 356 | 572453 |
| 0014b | open hearth furnace with oxygen lance | 159 | 55 | 25 | 12 | 31 | 62 | 344 | 2699 |
| 9009b | primary metal production – average | 93 | 13 | 43 | 26 | 10 | 18 | 204 | 285 |
| 1186b | heavy duty gasoline trucks | 79 | 26 | 28 | 39 | 3 | 3 | 179 | 275361 |
| | Total | 4870 | 2139 | 4084 | 4122 | 1338 | 1720 | 18273 | 12296369 |

^a All entries have been rounded to the nearest whole number. PHEN = phenanthrene, ANTH = anthracene, FLRT = fluoranthene, PYR = pyrene, BAA = benz[a]anthracene, and CHRY = chrysene. All profile names include the suffix PAH-emitting, which has been omitted here for the sake of brevity. ^b Source: refs 11 and 12.

TABLE 2. Comparison of Σ 6PAH Emission Estimates to the 2002 U.S. NEI (Mg/Year)^a

| estimate | U.S. NEI 2002 | this study U.S. only | this study Canada + U.S. |
|--|---------------|----------------------|--------------------------|
| Point Sources | | | |
| reported as individual species | 181 | | |
| estimated missing species | 327 | | |
| reported as POM or 16-PAH ^b | 193 | | |
| missing SCCs ^c within PAH-emitting profiles | 3705 | | |
| sub-total: point sources | 4405 | 10832 | 12115 |
| Nonpoint Sources | | | |
| reported as individual species | 3167 | | |
| estimated missing species | 6 | | |
| reported as POM or 16-PAH ^b | 185 | | |
| missing SCCs ^c within PAH-emitting profiles | 46 | | |
| sub-total: nonpoint sources | 3404 | 4730 | 5161 |
| Mobile Sources | | | |
| Onroad | | | |
| reported as individual species | 185 | | |
| estimated missing species | 0 | | |
| reported as POM or 16-PAH ^b | 0 | | |
| missing SCCs ^c within PAH-emitting profiles | 27 | | |
| subsub-total: onroad mobile sources | 212 | 468 | 523 |
| Nonroad | | | |
| reported as individual species | 184 | | |
| estimated missing species | 0 | | |
| reported as POM or 16-PAH ^b | 8 | | |
| missing SCCs ^c within profiles | 0 | | |
| subsub-total: nonroad mobile sources | 192 | 394 | 474 |
| sub-total: mobile sources | 404 | 862 | 997 |
| Total | | | |
| total reported | 4102 | | |
| total reported or estimated | 8213 | 16423 | 18273 |

^a Reported values have been rounded to the nearest whole number. ^b Taken as 32% of reported value (see text). ^c Emission factors for the speciation profiles with missing SCCs were determined as Σ 6PAH/ Σ TOG in the 2002 NEI for the reported SCCs associated with those profiles.

utilities), and mobile sources (e.g., SCC 2280003000, commercial residual oil-powered marine vessels). As broken down by source type, this study estimates emissions of 12 115 Mg/year for point sources, 5161 Mg/year for nonpoint sources, 523 Mg/year for onroad mobile sources, and 474 Mg/year for nonroad mobile sources, and the split between Canadian and U.S. sources is similar to that reported for the overall total emissions (see Table 2).

Comparison with U.S. NEI. Every 3 years, the U.S. EPA releases an updated National Emissions Inventory (NEI)

comprising estimates of emissions for a variety of criteria and hazardous air pollutants. These are based on information collected from lower levels of government, other emission inventory programs, industry, and models (6), each of which employs different estimation methods as opposed to the uniform source type specific emission factors used in this study.

The most recent NEI estimates were produced for 2002 (15) and provide a basis of comparison for the estimates made in this study. The 2002 NEI files were queried in a

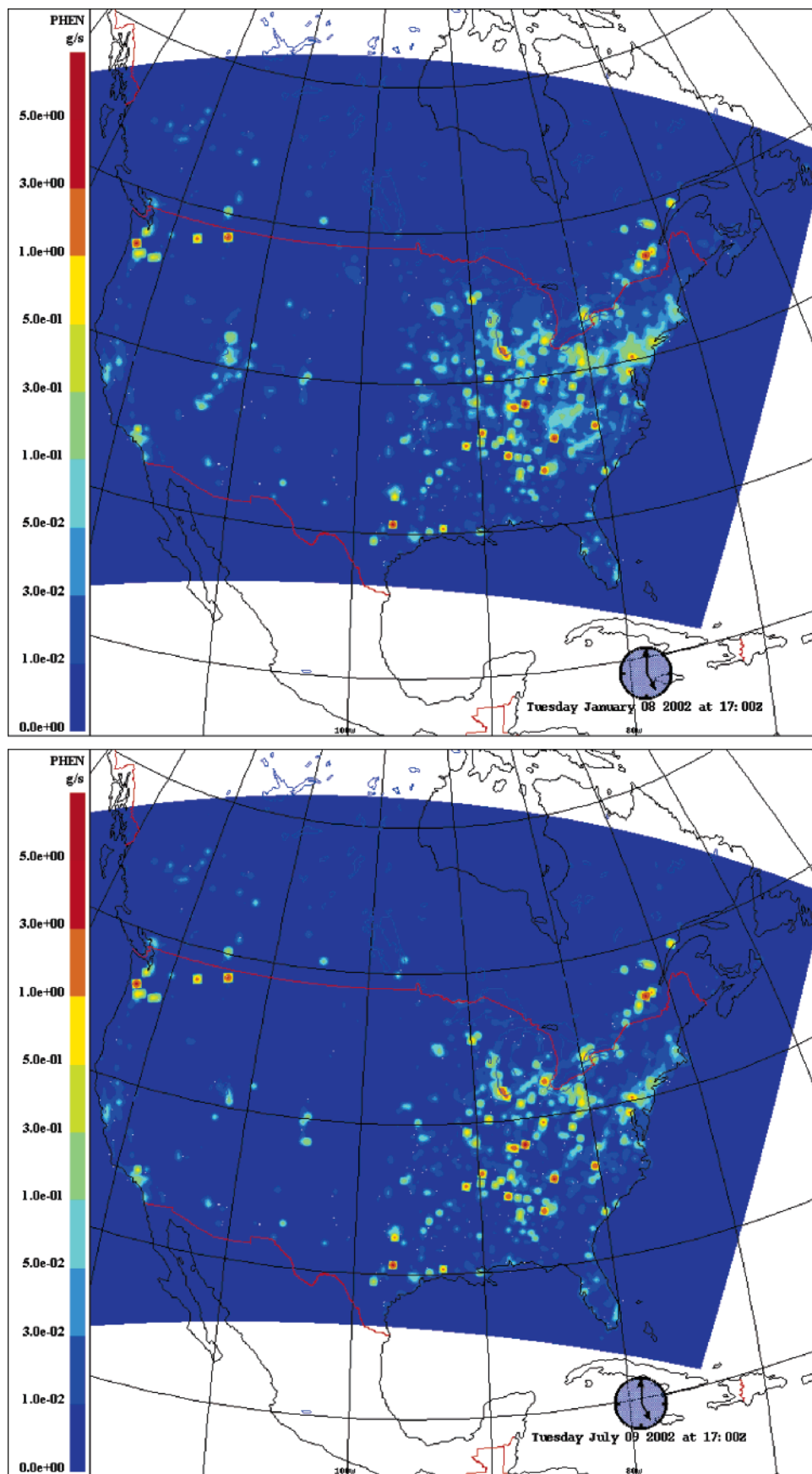


FIGURE 2. Total phenanthrene emission rates (g/s) at 17:00 UTC for (a) January 8 and (b) July 9.

database format. The total national emission for each PAH was calculated on the basis of SCC as this allowed for the

assignment of speciation profiles for the sake of comparison to the results of this study.

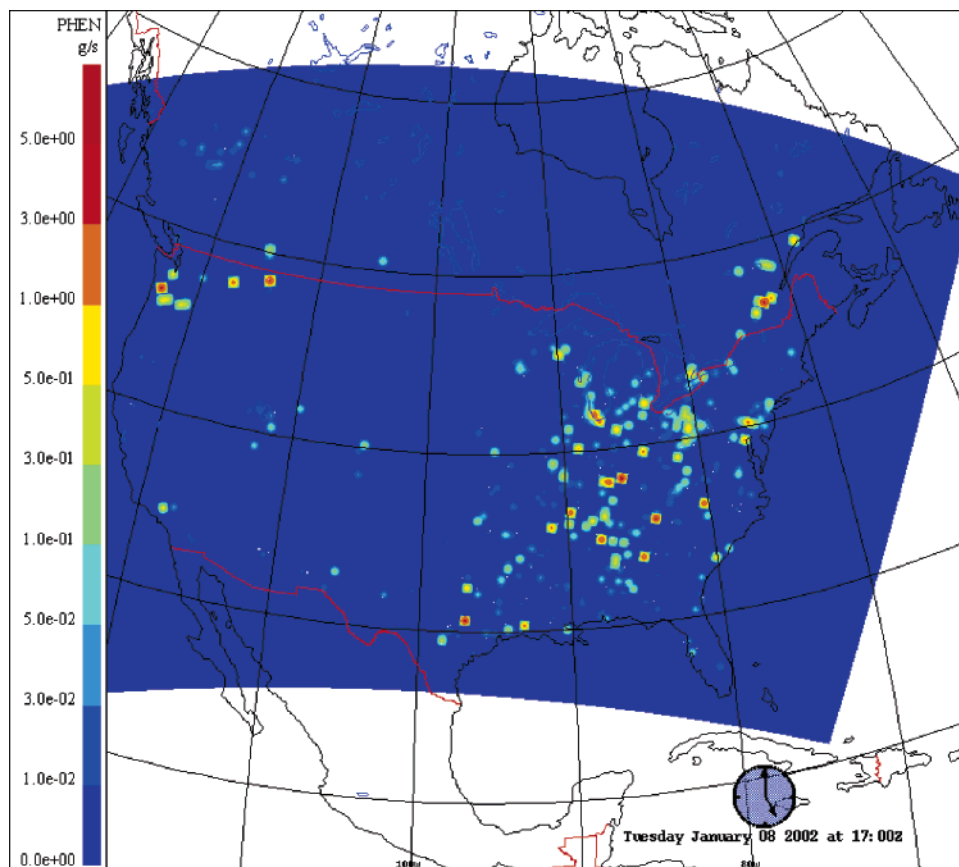


FIGURE 3. Total point source phenanthrene emission rates (g/s) on January 8 at 17:00 UTC.

The target PAHs discussed here are reported by the NEI either as individual species or as part of an aggregate parameter such as POM (polycyclic organic matter) or 16-PAH (Pope, A., U.S. EPA, Office of Air Quality Planning and Standards, personal communication, 2006). On the basis of the emission factors from the EPA (8, 9) and the motor vehicle emission factors used in the 1999 NEI (10), the target six PAHs represent an average of 31.8% of 16-PAH with a standard deviation of 25.0%. This average factor was used to scale down the 16-PAH and POM estimates in the 2002 NEI with the result contributing only 4% to the total annual Σ 6PAH estimate.

As can be seen in Table 2, the 2002 NEI reported a total annual Σ 6PAH emission of 4102 Mg/year, which is a factor of 4 lower than the total U.S. estimate from this study. Three important differences in the information included in each set of estimates could narrow this gap substantially.

The first difference relates to the completeness of speciated PAH information in the 2002 NEI. As often seen in studies of environmental media and emission sources, it is highly unlikely that any particular commonly measured species will be absent if the others are present (e.g., refs 3, 16, and 17). In fact, the U.S. EPA's compendium of emission factors for POM states that the PAHs targeted in this study are routinely detected and reported in source tests (8). However, there are many instances in the 2002 NEI, and almost exclusively in the point source data, where one or more PAH is reported as zero, while nonzero estimates appear for the other species. If the approach used for the development of this study's emission factors (step 3 in Materials and Methods) is applied to the zero data in the NEI, an additional 333 Mg/year would be added to its estimates. These estimates are reported in Table 2 as estimated missing species.

Second, the lists of SCCs used for the 2002 NEI and this study's inventory estimates differ; the PAH emissions lit-

erature suggests that the number of SCCs that should be associated with PAH emissions is larger than the number reported in the 2002 NEI. For the example of point sources, the NEI reports speciated PAH data for 442 SCCs and 16-PAH or POM data for a further 237 SCCs, whereas this study had 1085 SCCs assigned to PAH-emitting profiles based on the type of emitting activity. If equivalent emission factors are calculated for the data reported in the NEI (viz. $EF = \Sigma PAH / \Sigma TOG$ within each speciation profile), and then applied to the TOG emissions associated with the SCCs missing from the NEI, an additional 3705 Mg/year of target PAHs would be reported. This is 40% more than the total reported PAH from all sources in the 2002 NEI. Over 98% of these additional emissions is associated with two speciation profiles that relate to the metals industry: 76% is derived from SCCs associated with profile 0016b (basic oxygen furnace), and a further 22% is associated with profile 9010b (secondary metal production). These estimates are included in Table 2 as missing SCCs within PAH-emitting profiles.

The final difference between this study and the NEI is the choice of PAH emission factors themselves. Emission factors are listed in Table S5 for those profiles having PAH data reported in the 2002 NEI. Note that the factors listed for the NEI were not necessarily used by the agencies reporting data but, rather, they have been calculated a posteriori in the current work from the total reported annual PAH and TOG emissions as a basis of comparison to this study. Data were available in the 2002 NEI such that emission factors could be calculated for 55 speciation profile source type combinations. A total of 29 (53%) of those 55 paired emission factors were of different orders of magnitude, and of those 29, 24 were higher in this study relative to the values inferred in the NEI. This may be a misleading comparison, however, since it essentially assumes that all U.S. PAH emissions were reported through the 2002 NEI, but as detailed earlier, there

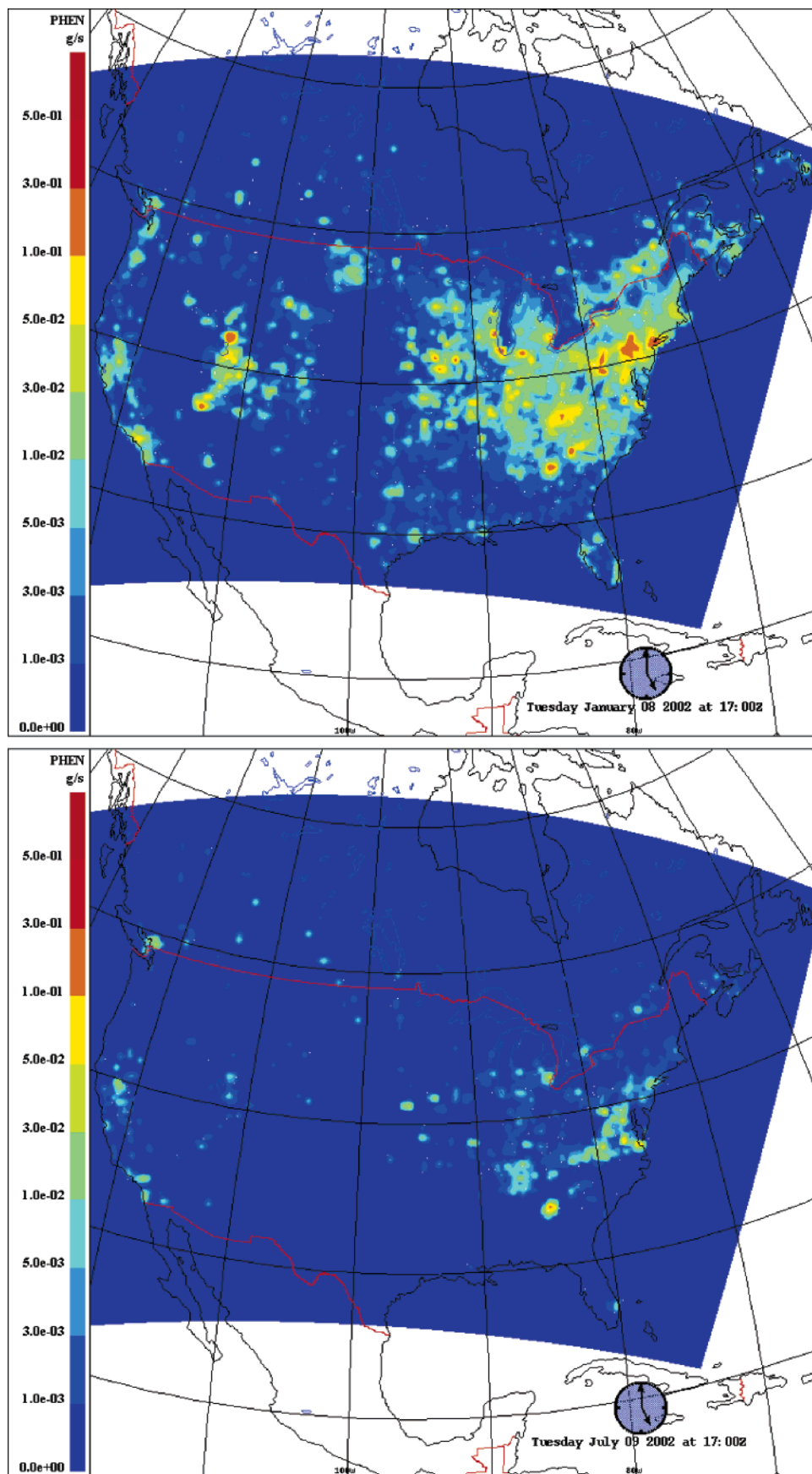


FIGURE 4. Total nonpoint source phenanthrene emission rates (g/s) at 17:00 UTC on (a) January 8 and (b) July 9.

appears to be substantial mass missing from that inventory. Alternatively, the information contained in the compilations

of emission factors may now be out-of-date since the determination of such factors is still an active area of research.

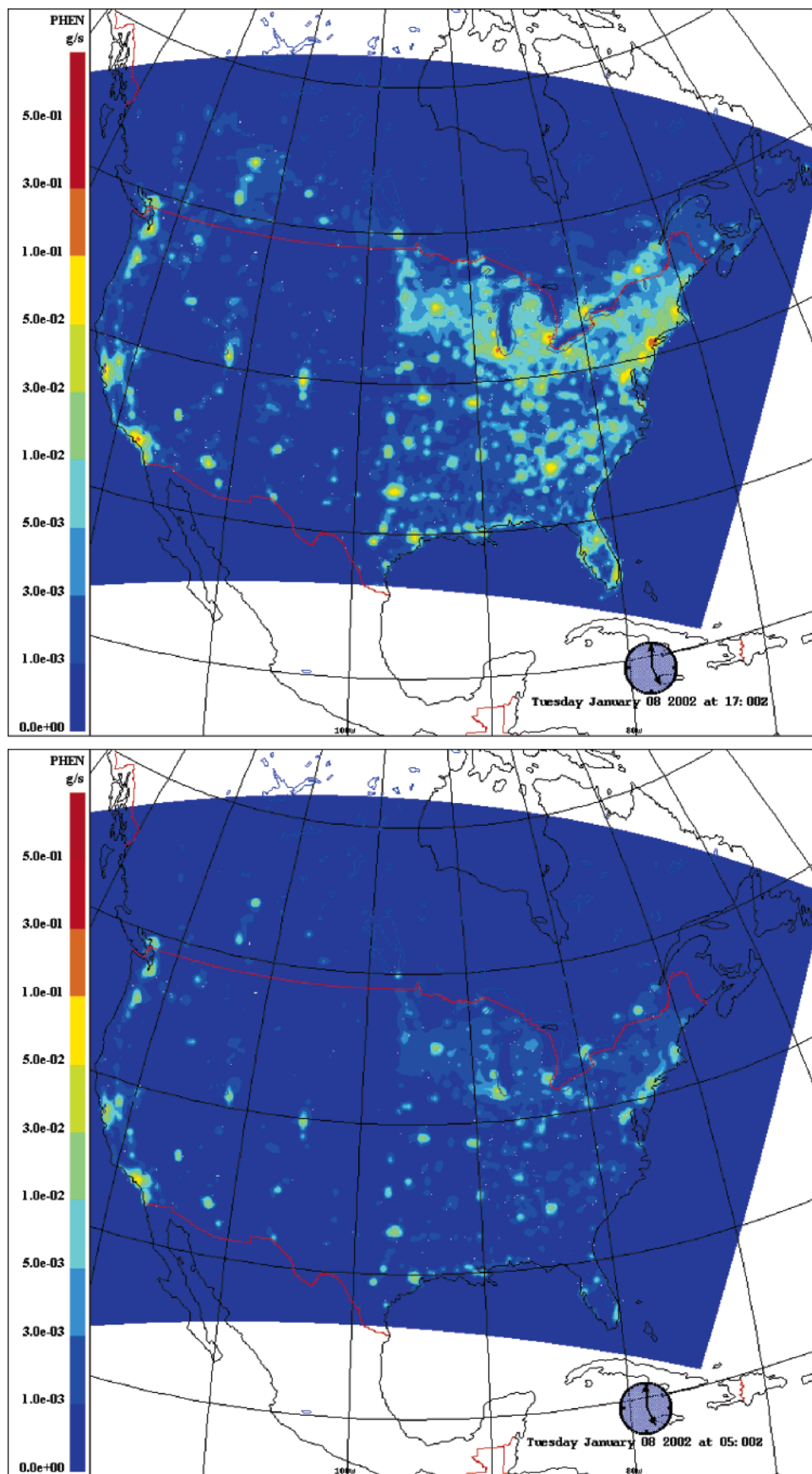


FIGURE 5. Total mobile source phenanthrene emission rates (g/s) on January 8 at (a) 17:00 UTC and (b) 05:00 UTC.

This would cause the estimated factors in this study to be slightly outdated and, since technological improvements tend to reduce PAH emissions, overestimated as well.

Given the differences in methods and information sources between the two inventories, it is encouraging that the adjusted estimates are within a factor of 2 of each other.

However, the assumptions involved in comparing the two inventories and the differences in the results show that further research in the determination of PAH emissions is necessary.

Spatial and Temporal Distribution of Emissions. The focus of this study was to develop and implement a method to adapt the speciation profiles used by an emissions processing system to estimate emissions of individual semivolatile toxic substances in time and space. To be useful as input for a regional air quality model, the spatial and temporal variation of emissions must be well-represented. With the aim of examining this facet of emission estimates, two sample runs of the modified SMOKE configuration were conducted for a typical weekday (Tuesday) in January and July. The TOG emissions on which the estimates are based are identical to those used to estimate annual PAH emissions, and these TOG emissions were temporally disaggregated as noted in the Materials and Methods.

Output from the sample runs of SMOKE was sorted by primary source sector (viz., point, nonpoint/area, mobile). Although the emissions for each of the target PAH species were determined separately, the spatial and temporal variations were similar for all species. As such, a single species (phenanthrene) is used as an example in the following discussion.

Figure 2 shows the spatial distribution of the total phenanthrene emissions in January and July at 17:00 UTC. As expected, the gridded results show emissions intensities that are similar to the distribution of population since emissions are predominantly anthropogenic. The maximum total emission rates tend to occur at the same locations as the maximum rates for point sources (Figure 3). The latter contribute to the highest grid cell emission rates of all source types and are an order of magnitude higher at their peak than those for nonpoint and mobile sources.

Point source estimates were similar in January and July (not shown) since industrial activities are largely unaffected by seasonal variations in activity. However, non-point source emissions did differ considerably between January and July (Figure 4a,b) due to seasonal differences in energy production. The spatial variation of the latter is affected not only by the population distribution but also by the differences in activity levels (e.g., heating and cooling) of the geographical area under consideration. As seen in Figure 4a, the southern U.S. is disproportionately light in winter non-point emissions with respect to its population, which is consistent with expectations related to its warmer climate.

Winter mobile source emissions, shown in Figure 5a,b, reflect the spatial distribution of population as might be expected. The temporal resolution available through this study's approach to estimating emissions is illustrated in this figure, where emissions during day and night hours contrast human activity between these two times of day (17:00 UTC and 5:00 UTC, respectively).

This study presented the methods used to adapt the speciation profiles used by an existing emissions processing system to estimate the emissions of semivolatile PAH compounds and their variation in time and space. The methods presented could be applied to any class of pollutants for which emission factor information is available. Novel approaches were taken to estimating missing information and aggregating emission factors for each speciation profile. The results presented for southern Canada are the first for that country to include all known sources. The results of the study for the U.S. were compared with the annual emission estimates produced by the 2002 NEI and illustrated similarities as well as some important differences. Total emissions are dominated by relatively few source types and, as such, it would be useful for the emission factors associated with these sources to be re-examined. Spatial and temporal variations of these largely anthropogenic pollutants conform

to expectations based on population distribution, diurnal human activity cycles, and climate. As such, PAH emissions can be estimated using an emissions processing system and subsequently used as input to regional air quality models.

Acknowledgments

E.G. is grateful to Terry Bidleman for helpful discussions regarding the development of the emission factors used in this study.

Supporting Information Available

(a) Detailed explanation of the calculation of emission factors used in this study. (b) Speciation profiles associated with PAH emissions. (c) SCCs with available PAH emission factors in consulted compilations. (d) Variability in emission factors aggregated by speciation profile. (e) Full results of the total annual estimated PAH emissions. (f) Comparison of emission factors in this study and those calculated a posteriori from U.S. NEI data. (g) Sample calculation of emission factors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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