Application of the Canadian Emissions Processing System, Version 1.1, to Estimate Organic Aerosol Composition for North America

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ABSTRACT

Speciation processing for a detailed regional gas-phase mechanism that includes 81 individual and "lumped" VOC species has been implemented in Version 1.1 of the Canadian Emissions Processing System (CEPS). Like other regional gas-phase chemistry mechanisms, the species set was designed to capture the net reactivity of hundreds of individual emitted VOCs, but in addition, low-vapour-pressure, high-molecular-mass compounds with particulate-forming potential have also been represented in some detail in this species set. CEPS1.1 was then used to estimate VOC emissions for this species set from the 1990 Canadian and U.S. national emissions inventories for a grid covering most of North America with a 127/3-km grid spacing. The gridded and speciated VOC emissions were then used in conjunction with gas/particle partitioning theory to estimate the amount of organic aerosol that would result from four source types: (a) direct emissions of low-volatility condensable gases from anthropogenic sources; (b) direct emissions of low-volatility condensable gases from biogenic sources; (c) condensable gases formed from the reaction of non-condensable anthropogenic precursor gases; and (d) condensable gases formed from the reaction of non-condensable biogenic precursor gases. The results suggest that the composition of organic aerosol in North America should vary widely with spatial location, season, and source regime, that primary condensables contribute more to organic aerosol mass than secondary condensables, and that anthropogenic VOC emissions contribute more to organic aerosol mass than biogenic VOC emissions. The organic aerosol mass values predicted were found to be about 20% of measured values in several cities.

INTRODUCTION

Increasing attention is being paid to atmospheric particulate matter (PM) as a result of a number of epidemiological studies over the past decade that have shown associations between atmospheric fine PM (or $PM_{2.5}$) concentrations and human health effects, including morbidity and mortality. Chemical characterization of observed atmospheric $PM_{2.5}$ has suggested that carbonaceous matter, which consists of elemental carbon and organic matter, may contribute over 50% of $PM_{2.5}$ mass on an annual basis in some parts of North America (e.g., Malm et al., 1994; Eldred et al., 1997; Brook and Dann, 1999). Some of the organic matter is known to be emitted directly as PM, but some is believed to derive from gas-phase emissions of a number of VOC species that either condense directly to the particle phase or else undergo gas-phase reactions that yield condensable products (e.g., Turpin et al., 1991; Pankow, 1994a). There is thus a need to be able to estimate potential contributions from North American VOC emissions to ambient PM concentrations.

One important task of emissions processing systems (EPSs) is to speciate the total VOC mass emissions that are tabulated in various criteria-air-contaminant (CAC) emissions inventories. This is done in order to estimate emissions of each of the VOC species considered in the gas-phase chemistry mechanisms designed for use in urban, regional, and global air-quality (AQ) models (e.g., Middleton et al., 1990; Dickson and Oliver, 1991). To date these chemistry mechanisms have largely been designed to provide accurate simulations of tropospheric ozone, so that the key consideration has been to choose a set of individual and lumped VOC species that preserves the net reactivity of the full set of individual speciated VOC emissions using the minimum possible number of "model" VOC species (e.g., Kuhn et al., 1998; Dodge, 2000). However, additional information about VOC chemical and physical properties is required for gas-particle partitioning calculations, including chemical structure, molecular weight, vapour pressure, aqueous solubility, and organic solubility. Consequently, current hydrocarbon lumping strategies are not likely to be adequate to estimate VOC particulate-forming potential since they preserve reactivity but lose other crucial information.

This paper describes the use of (i) a regional emissions processing system, (ii) a new hydrocarbon lumping scheme designed specifically to preserve both reactivity and structural detail sufficient to resolve particulate-forming potential, and (iii) iterative thermodynamic calculations to estimate the potential contribution of North American VOC emissions, both anthropogenic and biogenic, to atmospheric organic PM for one selected day in each of the summer and winter seasons.

METHODOLOGY

Emissions Processing System

The Canadian Emissions Processing System (CEPS) is a regional emissions processing system used to process Canadian and U.S. national CAC emissions inventories (EIs) in order to prepare emissions input files for the Meteorological Service of Canada's (MSC) suite of regional AQ models (e.g., Moran et al., 1997; Scholtz et al., 1999, 2000a,b). The set of roughly 600 chemical speciation profiles currently used by CEPS includes a total of 822 individual VOC species. CEPS estimates biogenic emissions using a hybrid of the BEIS2 algorithms but BEIS1 biomass fields (Pierce et al., 1999; Scholtz et al., 2000a). The more detailed BEIS2 vegetation classes have not been employed because gridded data sets of these classes were not available for the entire North American continent.

Detailed VOC Species Set

As described by MSC (2001) and Makar et al. (2001a), a table of properties was first constructed for the 822 individual VOC species included in the CEPS speciation profiles. The table includes Chemical Abstract Service registry codes, molecular structure codes, OH reactivities, vapour pressures with respect to the pure liquid at 253, 273, and 298 K, experimental or estimated freezing and boiling points, and solubilities. This properties table plus North American domain totals for the mass emissions of the individual VOC species generated by CEPS were then used as the basis with which to group the 822 VOC species into 80 VOC classes (plus one extra class for species for which insufficient information was available). Some of the classes consist of single species with significant emissions (e.g., propane, ethene, benzene, isoprene, alpha-pinene) while others are made up of numerous species (e.g., “C11-19 Alkanes”, “Internal C6-8 Alkenes”, “High-reactivity Esters”). Consideration of the total emissions for the individual species avoids too many VOC classes being used for species with very small emissions and provides useful information for choosing representative species and for calculating emission-weighted average class properties such as molecular weight (e.g., Middleton et al., 1990; Makar et al., 2001a,b).

This set of 81 VOC species is believed to have sufficient detail to capture both gas-phase reactivity and physical characteristics relevant to particle formation of the most commonly emitted biogenic and anthropogenic VOCs in the atmosphere. These species are referred to as the AURAMS81 set, after the regional air quality model AURAMS (“A Regional Unified Air Quality Modelling System”) in which the emissions files are to be used (Moran et al., 1998). Such a level of VOC detail is considerably higher than that used previously in regional air quality modelling: for example, Middleton et al. (1990) considered 32 VOC species, and these were further lumped when used for regional AQ modeling (e.g., Lurmann et al., 1986; Stockwell et al., 1997).

Emissions Inventory Data Sets

The 1990 Canadian national CAC point- and area-source EI files that were processed by CEPS were obtained from the Environmental Protection Service of Environment Canada in Hull, Quebec (Deslauriers, 1996; Scholtz et al., 1999, 2000a). On-road mobile-source emissions were estimated by CEPS using seasonal files of MOBILE5C-generated emission factors (Philpott, 1993) and annual vehicle-miles-travelled (VMT) files by province (Scholtz et al., 2000a). Canadian biogenic emissions were estimated using the CBEIS2 module of CEPS based on gridded, hourly surface temperature and solar insolation fields for two representative days obtained from the Canadian Meteorological Centre of Environment Canada in Dorval, Quebec (Scholtz et al., 2000a,b; Scholtz and Taylor, 2001).

The 1990 U.S. national CAC EI point-, area-, and on-road mobile source EI files processed by CEPS were obtained from the Office of Air Quality Planning and Standards of the U.S. Environmental Protection Agency (EPA) in Research Triangle Park, North Carolina. These files were extracted from the U.S. EPA’s 1987-91 Regional Interim Emission Inventory (U.S. EPA, 1993; Scholtz et al., 1999, 2000a). The U.S. biogenic emissions were estimated using the CBEIS2 module of CEPS and the same gridded, hourly surface temperature and solar insolation fields used for estimating the Canadian biogenic emissions.

CEPS Setup and Calculations

The processing domain considered in this work spanned most of North America, as shown in Figure 1. The map projection used was a polar stereographic projection true at 60°N, and the 153 by 171 grid used 127/3 km (~ 42 km) grid spacing.

Relatively few modifications were required to implement the AURAMS81 species set in CEPS. The main one was to create a chemical data-base file assigning each of the 822 individual VOC species to one of the AURAMS81 VOC classes (cf. Scholtz et al., 1999). Molecular weights also had to be assigned for each VOC class.

Five major emissions streams were processed: point sources; on-road mobile sources; anthropogenic area sources; non-anthropogenic area sources; and biogenic sources (MSC, 2001; Scholtz and Taylor, 2001). Anthropogenic and non-anthropogenic area sources were separated on the basis of ASC code: the latter consisted of wind-blown dust, geysers and geothermal activity, volcanoes, and wildfires. Two days, one in the winter (15 January 2000) and one in the summer (15 July 2000), were selected for calculating day-specific biogenic emissions while winter and summer season-day averages were calculated for the various anthropogenic streams. [Clearly, the use of biogenic emissions for only two days raises the issue of representativeness, but these data should be sufficient to illustrate the relative importance of biogenic vs. anthropogenic VOC emissions to organic aerosol formation.] CEPS was then run to produce estimates of hourly AURAMS81 species emissions on the North American grid for the winter and summer days. In the biogenics processing, this included the use of hourly gridded surface temperature and cloud-adjusted solar insolation fields for 15 January 2000 and 15 July 2000.

CEPS Post-Processing

Once gridded AURAMS81 emissions were prepared by CEPS, a simple approach was used to convert VOC emission fluxes to VOC air concentrations. The daily emitted mass of each of the 81 VOC classes was assumed to be uniformly mixed into each grid-cell volume, with a 500-meter-deep boundary layer assumed above the surface. The masses and volumes so obtained were used to estimate mass concentrations (ug m^{-3}) in each grid square. The diurnal averages of the hourly temperatures for January 15, 2000, and July 15, 2000 used to determine daily biogenic emissions were also used to calculate partitioning and reaction rate parameters (see below).

The transport of mass between grid cells or into the free troposphere, wet and dry removal, and accumulation of emissions from previous days were not considered. All of these processes could be considered within the framework of a regional air-quality model. However, the thrust of the present work was to carry out an exploratory calculation using an emissions processing model in conjunction with detailed chemical and thermodynamic calculations but a simple representation of other atmospheric processes with the goal of obtaining a rough quantitative estimate of the relative seasonal contributions of biogenic and anthropogenic VOC sources and primary and secondary condensation pathways to organic PM mass in the troposphere.

Calculation of Organic PM Mass from Primary Condensable VOC Species Air Concentrations

As discussed in MSC (2001) and Makar et al. (2001b), an iterative form of the Pankow absorption partitioning equation (Pankow, 1994a) was used to determine the mass of primary condensable VOC species in the particle phase from ambient concentrations of those species in each grid cell of the North American domain. A subset of 23 AURAMS81 VOC species plus water vapour was used for these calculations. These species were selected from the full set of 81 species on the basis of pre-existing observations confirming their presence in the aerosol phase and/or the physical properties of the compounds (e.g., low vapour pressure with respect to the pure liquid, or high solubility with respect to water). Water was included in the calculations in order to determine the extent to which hydrophilic VOCs such as the "Diacids" (represented by adipic acid) could influence the aerosol water content at relative humidities below 100%.

An important restriction of the Pankow equation is that it requires that the identities of the partitioning gases be known in order to be able to supply values of molecular weights, vapour pressures, and activity coefficients. For those AURAMS81 VOC model species consisting of more than one of the 822 VOC species considered by CEPS, a representative individual VOC species was specified (Makar et al., 2001a). Vapour pressures were then calculated through methods outlined in Makar (2000) and activity coefficients were calculated through functional-group-contribution techniques (UNIFAC: Sandler, 1999). Temperatures were held constant at the diurnal average temperature appropriate for each grid cell for the selected winter day and summer day and the relative humidity was assumed to be 50%.

Calculation of Organic PM Mass from Secondary Condensable VOC Species Air Concentrations

Secondary organic aerosol (SOA) formation potential depends upond both the reactivity of the "parent" or precursor compound and on the volatility of the product species. Because the atmospheric chemical reaction pathways for hydrocarbons are complex and many of the numerous possible oxidation products are difficult to identify analytically at this time, an empirical "yield" approach based on laboratory measurements has been used to quantify SOA formation potential. In this approach, the SOA yield is defined simply as the ratio of the amount of organic aerosol mass produced to the mass of the original precursor VOC species reacted. Controlled smog-chamber experiments have been carried out to determine yield data for a number of VOC species (e.g., Odum et al., 1997; Hoffman et al., 1997; Griffin et al., 1999). Many of these experiments have shown that the yield may be expressed as a function of the pre-existing organic aerosol mass (ORGM)

As discussed in MSC (2001) and Makar et al. (2001b), the ORGM-dependant formula of Odum et al. (1996) was used to calculate the contribution of SOA precursors to organic aerosol mass. This formula is preferable to earlier approaches using fixed yields, which tend to overestimate aerosol yield. SOA formation has been observed for a subset of 19 of the AURAMS81 species, so SOA formation potential was estimated for these VOC classes. Measured stoichiometric coefficent ($\acute{a}_i$) values and absorption equilibrium partitioning coefficient (K_i) values were available for nine of these species, while for the others, values for the species closest in structure for which ORGM-dependant yields were available were used.

The initial value of ORGM used in the SOA calculations was the condensed mass created from the primary-condensable calculations. The amount of ORGM created, and the amount of SOA precursor species lost in each hour, was calculated assuming an hour-dependent oxidant concentration and solving the relevant analytic exponential decay equations. VOC precursor and ORGM values were updated each hour, as were the OH and O_3 concentrations used to determine the SOA mass produced in each hour. The initial SOA precursor species concentrations were derived in a similar fashion to the initial primary-condensable species concentrations: the uniform mixing of 24 hours of emissions into a 500-meter-deep boundary layer giving the mass per unit volume.

RESULTS

VOC Mass Emissions

Figure 1 shows the spatial distribution across North America of summertime total VOC emissions (summed over all 81 VOC classes) from anthropogenic and biogenic sources for base year 1990. As shown in Table 1, in the summer biogenic VOC emissions are larger in magnitude and more widespread than anthropogenic emissions. The latter tend to be emitted from population centers, (Figure 1a), and in Figure 1c a number of cities are identifiable as VOC "hot spots", suggesting the importance of anthropogenic emissions at these locations. In terms of the AURAMS81 species set, in the summer biogenic VOC emissions dominate about eight VOC classes ("Isoprene", four classes of monoterpenes, "Internal C_{6-8} Alkenes", "C_{6+} Aldehydes", and "High-Reactivity Esters") whereas the anthropogenic emissions contribute to a much wider range of VOC classes (see also Figures 3.9 and 3.10 in MSC (2001)). In the winter, with the loss of deciduous foliage and lower temperature and sunlight levels, net biogenic emissions are much lower than in summer while anthropogenic emissions are about 15% lower (Table 1).

However, as shown below, the VOC classes with the greatest emissions by mass are not necessarily those with the greatest contributions to PM formation. As noted above, the extent to which an emitted species partitions directly to the condensed phase will be a function of its structural and physical properties. A relatively low total mass emission may be offset by a high potential to partition to the condensed phase. SOA precursor species have a similar variability: their emitted mass, reactivity, and the precursor-dependant SOA yield all impact on their relative contribution towards the net organic material formed from a given mixture of gases.

Potential Organic Aerosol Formation from Primary Condensable VOC Species

According to Table 1, 17% (=11,435/66,427) of the wintertime and 27% (=73,520/273,586) of the summertime VOC emissions belong to the 23 AURAMS81 classes considered to be semi-volatile and to have the potential at atmospheric conditions to condense directly onto aerosol particles. Anthropogenic sources dominate biogenic sources in the winter but are dominated in turn by biogenic sources in the summer. The overall aerosol mass fraction from these primary condensable VOC emissions (i.e., total primary-condensable VOC condensed/total primary-condensable VOC emitted) is estimated to be 0.04 (=446/11,435) in the winter but only 0.002 (=129/73,520) in the summer. This large seasonal variation is due to temperature effects (i.e., volatility depends directly on termperature) and not to the seasonal variation in emissions since emissions of the primary condensable species are over six times larger in the summer than the winter. Interestingly, biogenic VOC emissions are calculated to contribute virtually no organic aerosol mass for the two season-days considered. If only anthropogenic sources are considered, then the overall mass fraction from anthropogenic primary condensable VOC emissions is 0.05 (=446/8,244) in the winter and 0.01 (=129/11,230) in the summer, that is, a smaller seasonal variation.

Figure 2a shows the summertime spatial distribution of condensed-phase organic aerosol mass from primary condensable VOC species.

Potential Organic Aerosol Formation from Secondary Condensable VOC Species

According to Table 1, 35% (=23,563/66,427) of wintertime and 37% (=100,598/273,586) of summertime VOC emissions belong to the 19 AURAMS81 classes considered to be SOA precursors. However, the overall aerosol mass fraction from these SOA precursor emissions is estimated to be only 0.0004 (=10/23,563) in the winter and 0.0002 (=16/100,598) in the summer. The larger seasonal variation than for primary condensable emissions is due to the greater contribution of biogenic VOC emissions.

Figure 2b shows the summertime spatial distribution of SOA mass from anthropogenic VOC sources while Figure 2c shows the summertime spatial distribution of SOA mass from biogenic sources. As expected from Table 1, the mass distributions for both panels are lower in magnitude than the Figure 2a mass distribution.

Potential Organic Aerosol Formation from Total Condensable VOC Species

Considering both condensation pathways in Table 1, up to 53% (=34,998/66,427) of wintertime and 64% (=174,119/273,586) of the summertime VOC emissions are estimated to have some potential to form organic aerosol mass. [This is an upper bound because the three AURAMS81 species “Phenol”, “Cresol”, and “Aromatic Aldehydes” may contribute to both primary and secondary condensables.] The seasonal variation is large: summertime condensable VOC emissions are almost five times larger than wintertime condensable VOC emissions. However, the overall aerosol mass fraction from total condensable VOC emissions is low: only 0.0013 (=456/34,998) of the wintertime and 0.0008 (=145/174,119) of the summertime condensable VOC emissions were estimated to have partitioned to the particle phase. The organic aerosol mass contributed by primary condensable VOC emissions is much larger than that contributed by secondary precursors: 98% (=446/456) in the winter and 89% (=129/145) in the summer. Similarly, the organic aerosol mass contributed by anthropogenic VOC emissions is much larger than that contributed by biogenic VOC emissions: nearly 100% (=454/456) in the winter and 96% (=139/145) in the summer. Major urban areas have the highest values (approximately 1 μg m^{-3}).

Figure 2d shows the summertime spatial distribution of condensed-phase organic aerosol mass from both primary and secondary condensable VOC species. As in Figure 1c, many major urban centres appear as “hot spots”.

DISCUSSION

Observational support for the above calculations is difficult to obtain: measurements of aerosol composition usually include total organic material but do not attempt to provide a detailed speciation of the organics. Other observational work may be used to infer indirectly the presence of condensed-phase organic material in aerosols. For example, the partitioning of organic matter to the condensed phase may occur to other surfaces besides aerosols – deposition to buildings, plants, etc. near the ground may occur either as direct condensation of the gases or as deposition of organic aerosol. Recent measurements of organic films found on buildings in Toronto show that both “High-reactivity low-vapour-pressure PAHs” and “High-carbon-number Alkanes”, two of the primary condensable VOC classes considered in the present study, are present in these surface films (Diamond et al., 2000).

If the estimates of total condensable organic PM mass from VOC emissions are examined for the grid cells corresponding to some urban centers, they are found to correspond to roughly 20% of the average organic PM mass measured in these cities. For example, the estimated values for Toronto and Los Angeles were 0.6 and 1.5 $\mu g\ m^{-3}$, respectively, compared to measured values of 3.2 and 6.2–7.0 $\mu g\ m^{-3}$ (MSC, 2001; Rogge et al., 1993). Of course, primary emissions of organic aerosol have not been considered here, and primary sources are expected to dominate on average (e.g., Turpin and Huntzicker, 1991; Schauer et al., 1996). One important consequence of neglecting the primary organic aerosol emissions is that their presence would enhance aerosol formation from organic gases (Pankow, 1994b), suggesting that the estimates presented in this study should be viewed as conservative (i.e., underestimates).

The result that biogenic VOC emissions contribute little to organic PM mass does not mean that vegetation does not contribute at all to atmospheric organic PM mass. For example, waxes coating plant leaves are known to be shed directly as particles during leaf agitation. More generally, there is considerable uncertainty over whether emissions of primary condensable VOCs will be reported as primary PM emissions or as VOC emissions in available emission factors and speciation profiles. For example, many VOC species emitted from combustion processes may be volatile at exhaust temperatures but semi-volatile at ambient temperatures. Thus, the testing methodology used to obtain process-specific VOC speciation profiles and PM emission factors and speciation profiles can affect how primary condensable VOC emissions are reported, depending upon whether the exhaust stream is diluted to ambient conditions before the speciation measurements are made. Given the temperature dependence of gas/particle partitioning, the actual ambient temperature also needs to be known. Details of testing methodology are seldom provided but are very relevant today when both VOC and PM emissions are of interest.

The representativeness of these calculations should also be kept in mind. For example, only two days of biogenic emissions were considered, the same constant-depth mixing height was assumed for both winter and summer days, and horizontal homogeneity and an idealized diurnal variation was assumed for the OH and O_3 fields in the SOA formation calculations. Nevertheless, this approach allows the importance of VOC contributions to organic aerosol mass to be estimated and the relative contributions of (i) the primary and secondary condensation pathways and (ii) anthropogenic and biogenic sources to be compared while avoiding the complications of having to use a full-blown AQ model in addition to an emissions processing system.

CONCLUSIONS

This study constitutes a first attempt to use national emissions data sets and an emissions processing system to estimate the overall contribution of VOC emissions to organic aerosol mass on a North American scale. The organic aerosol mass estimates are about 20% of observed aerosol mass for several cities for which measurements are available, but primary organic aerosol emissions have not been considered. The results suggest that primary condensable VOC species make a greater contribution to organic aerosol mass than do secondary precursor species, and that anthropogenic VOC species make a greater contribution than biogenic secondary precursor species. One limit on these results is the consistency with which primary condensable VOC species are reported in the available VOC speciation profiles as VOC emissions rather than as (already condensed) primary PM emissions. Finally, emissions speciation and chemical reaction mechanisms lacking this level of VOC detail will fail to reproduce the contribution of the primary-condensation pathway to organic aerosol formation found here.

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Table 1. North American VOC emissions (tonnes/day) and amount of organic aerosol mass estimated to partition from these emissions for a winter and summer day in base year 1990.

	Winter		Summer	
Emission Category	Emitted	Condensed	Emitted	Condensed
Total VOC Emissions	66,427	456	273,586	145
Anthropogenic Emissions	57,180	454	68,135	139
Biogenic Emissions	9,247	2	205,451	6
Total Primary Condensables	11,435	446	73,520	129
Anthropogenic Emissions	8,244	446	11,230	129
Biogenic Emissions	3,191	0	62,290	0
Total Secondary Condensables	23,563	10	100,598	16
Anthropogenic Emissions	17,924	8	18,964	10
Biogenic Emissions	5,639	2	81,634	6
Total Condensable Emissions	34,998	456	174,119	145
Anthropogenic Emissions	26,168	454	30,195	139
Biogenic Emissions	8,830	2	143,924	6

Figure 1. Net summer daily emission rates per grid cell of (a) anthropogenic VOCs, (b) biogenic VOCs, and (c) total VOCs (g/day).

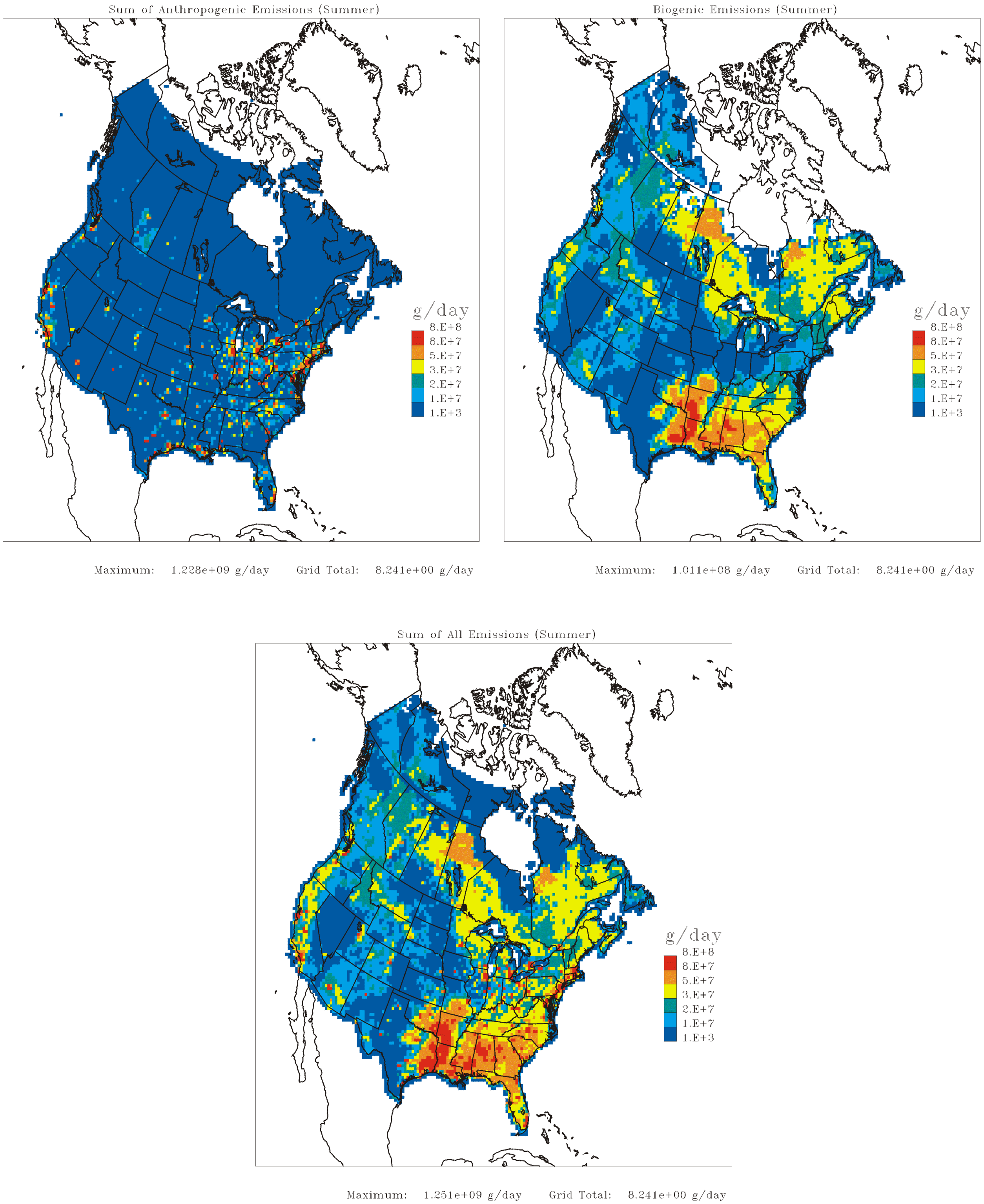
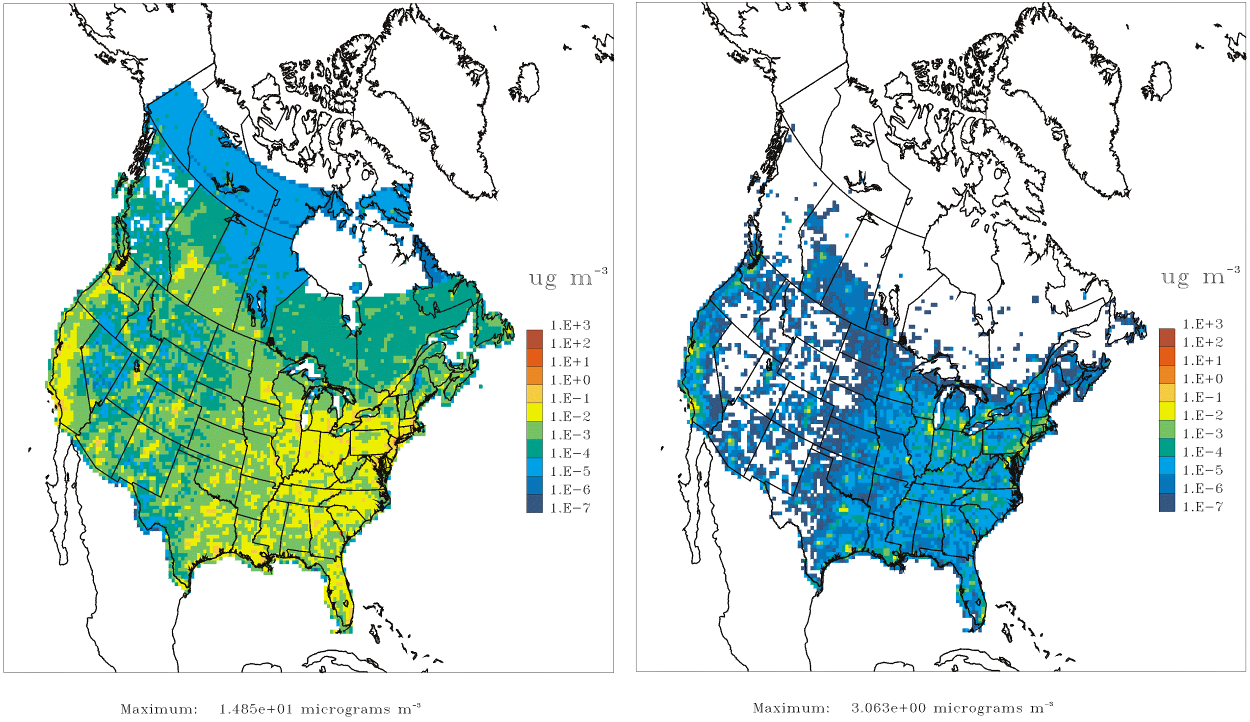


Figure 2. Estimated summer spatial distribution across North America of VOC-derived ambient organic aerosol matter concentration (µg m^{-3}) from (a) primary condensable VOC emissions, (b) anthropogenic secondary condensable VOC emissions, (c) biogenic secondary condensable VOC emissions, and (d) sum of three preceding categories.

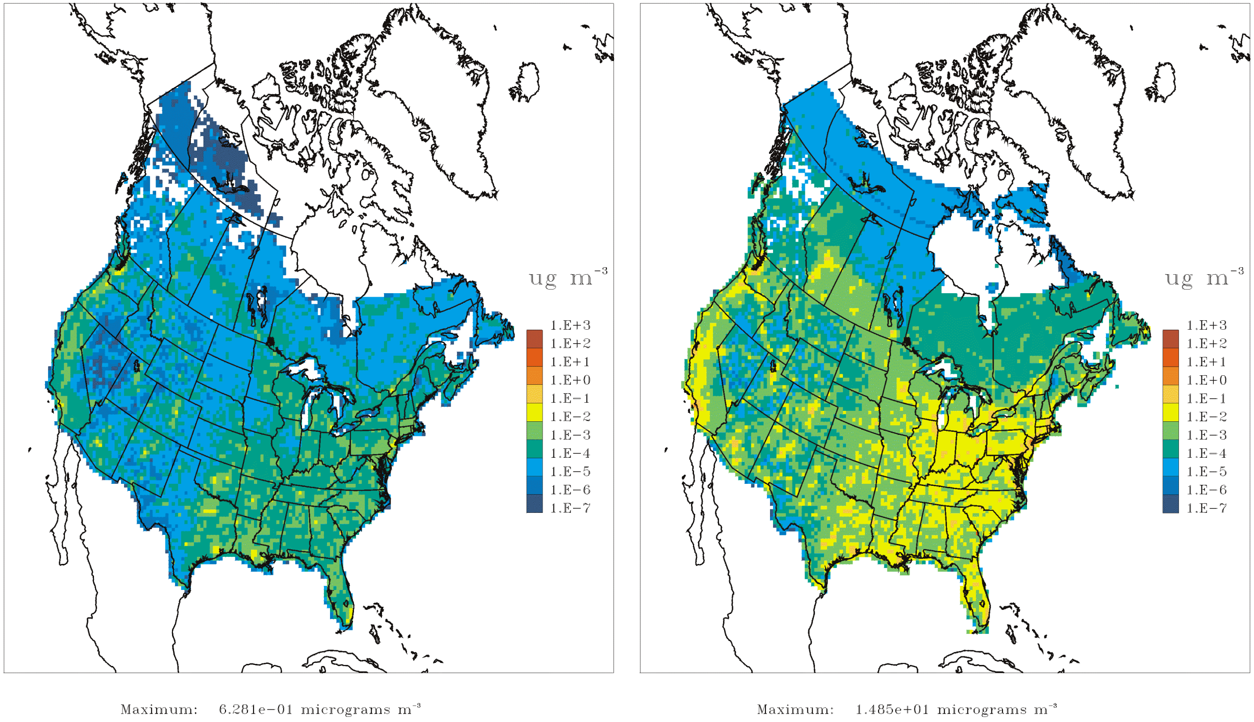
(a) Anth. POM Mass (summer)

(B) Anth. SOA Mass (summer)



(c) Biog. SOA Mass (summer)

(d) Total Condensable Organic Matter (summer)



KEYWORDS

emissions processing
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organic aerosol
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