Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons

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Abstract. The results from a series of outdoor chamber experiments establishing the atmospheric aerosol-forming potential of fourteen terpenoid hydrocarbons have been used to estimate the annual amount of secondary organic aerosol formed globally from compounds emitted by vegetation. Hydroxyl radical, ozone, and nitrate radical oxidation each contribute to aerosol formation in full-photooxidation experiments; because oxidation by nitrate radical under ambient, remote conditions is likely to be negligible, parameters describing aerosol formation from hydroxyl radical and ozone reaction only are developed. Chamber results, temporally and spatially resolved, compound-specific estimates of biogenic hydrocarbon emissions, and hydroxyl radical and ozone fields are combined to lead to an estimate for atmospheric secondary organic aerosol formed annually from biogenic precursors of 18.5 Tg, a number smaller than the previously published estimate of 30-270 Tg [Andreae and Crutzen, 1997].

1. Introduction

Biogenic hydrocarbons emitted by vegetation play an important role in the chemistry of the urban- and regional-scale atmosphere [Fehsenfeld et al., 1992]. These compounds are among the most reactive in the atmosphere as measured by their reaction rate constants with ozone (O3) and the hydroxyl (OH) and nitrate (NO3) radicals [Atkinson et al., 1995; Shu and Atkinson, 1995; Atkinson, 1997]. Biogenic hydrocarbons contribute to tropospheric ozone formation in regions of extensive vegetation [Chameides et al., 1988; Roselle et al., 1991] and yield relatively non-volatile secondary oxidation products that form aerosols [Hoffmann et al., 1997; Griffin et al., 1999].

The aerosol-forming potential of biogenic hydrocarbons was first noted by Went [1960]. However, a quantitative understanding of aerosol formation from these molecules was lacking until recently [Hoffmann et al., 1997; Griffin et al., 1999]. Griffin et al. [1999] investigated the predominant aerosol-forming compounds emitted by vegetation [Arey et al., 1991, 1995; Guenther et al., 1994, 1996; König et al., 1995], the majority of which are monoterpenes that apparently function as defensive agents against herbivory [Lerdau, 1991]. Understanding the aerosol-forming potential of these compounds is imperative to assess the contribution of biogenically derived aerosol to regional particulate levels and the global aerosol burden.

Liousse et al. [1996] included formation of organic aerosol from biogenic precursors in their global study of carbonaceous aerosols; they employed a constant aerosol yield of 5% for all biogenic species except isoprene, which does not form aerosol upon oxidation. Based on previous chamber data, Andreae and Crutzen [1997] provided an estimate of the global amount of aerosol formed annually from biogenic precursors of 30 to 270 Tg yr

2. Secondary Organic Aerosol Formation

Experiments investigating the aerosol-forming potential of fourteen biogenic compounds have been described previously [Hoffmann et al., 1997; Griffin et al., 1999]. SOA forms through adsorptive and/or absorptive condensation or nucleation of products of gas-phase hydrocarbon oxidation [Pankow, 1994; Odum et al., 1996]. The SOA yield, Y, defined as the dimensionless ratio of the mass concentration of SOA formed, AMo, to the mass concentration of the parent hydrocarbon reacted, measures the aerosol-forming potential of a compound. Gas-aerosol partitioning of oxidation products depends on the mass concentration of an absorbing organic phase. As a result, Y is a function of the final equilibrium organic mass concentration of this absorbing phase, M0 (µg m

where αi is the mass-based stoichiometric yield of oxidation product i and Kp,0 (m3 µg

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Yield data for over 30 individual aromatic and biogenic parent hydrocarbons have been fit to equation (1) on the basis of a two-product model, that is, by parameters $\alpha_1$, $\alpha_2$, $K_{\text{com,1}}$, and $K_{\text{com,2}}$ (Odum et al., 1996, 1997; Hoffmann et al., 1997; Griffin et al., 1999). Many products capable of partitioning into the aerosol phase are formed during the atmospheric oxidation of such hydrocarbons (Yu et al., 1998). However, the remarkably close fit of yield data to equation (1) for the compounds studied indicates that two generic products approximate well the stoichiometry and volatility of the final product mix. While yield scales linearly with $M_o$ in the range of atmospheric applicability (small $M_o$), experiments must be performed over the entire range of organic mass concentrations to obtain the yield parameters for each parent hydrocarbon (see Table 1). Calculated yields are also shown in Table 1 for values of $M_o$ between 5 and 40 $\mu$g m$^{-3}$. These yields encompass the range of 5-40% used by Andreae and Crutzen (1997).

3. Individual Oxidant Contributions to Aerosol Formation

The unsaturated carbon-carbon bonds inherent to the monoterpenes structure induce a high level of reactivity with OH, NO$_3$, and O$_3$. At NO$_3$ levels characteristic of chamber photooxidation experiments, NO$_3$ contributes significantly to oxidation if a sufficient amount of NO$_3$ forms prior to complete consumption of the hydrocarbon by OH and O$_3$. Of the compounds of interest, this is the case only for $\alpha$-pinene, $\beta$-pinene, $\Delta^2$-carene, and sabineine.

In remote areas, NO$_3$ concentrations are expected to be very low as there is little impact from anthropogenic NO$_x$ sources. Therefore, in order to extrapolate smog chamber data to ambient conditions for these four bicyclic alkenes, the contribution of NO$_3$ to chamber aerosol formation must be removed from that measured. To do so, the amount of parent hydrocarbon that reacted with each oxidant in each experiment must be determined. Despite the complexity of the gas-phase chemistry in these experiments, it is possible to simulate hydrocarbon consumption patterns using the SAPRC90b chemical mechanism of Carter (1990).

In order to assess the importance of each oxidant to aerosol formation for the bicyclic alkenes, experiments in which either O$_3$ or NO$_3$ was the only available oxidant (a scavenger was used to consume any OH formed in the O$_3$-alkene reaction) were performed in the dark, but at daytime temperatures. On the basis of the resulting yield information for single-oxidant systems and the gas-phase simulations, it is possible to determine the amount of organic aerosol formed from reaction with each oxidant in full-photooxidation experiments (Hoffmann et al., 1997; Griffin et al., 1999). By subtracting the NO$_3$ contribution, yield parameters for aerosol formation in the absence of NO$_3$ for bicyclic alkenes have been developed (Table 1).

In order to extrapolate chamber data to the ambient, it is important to determine if the relative hydrocarbon oxidation by OH and O$_3$ observed in the chamber is consistent with that expected in the ambient. Global average estimates of 50 ppbv for O$_3$ and 2.6x10$^6$ molecules cm$^{-3}$ for OH do lead to relative hydrocarbon consumption patterns similar to those observed in the smog chamber for bicyclic alkenes (Griffin et al., 1999) (Table 2). Therefore, we assume that relative consumption patterns for the other biogenic parent compounds studied in the chamber will approximate those expected in the ambient. Because the atmospheric oxidation of bicyclic alkenes seen in experiments are similar to those derived using global-average oxidant concentrations, further oxidation of first-generation products in the chamber should mimic appropriately such reactions occurring in the ambient. Yu et al. (1998) have shown evidence of these reactions in our chamber. Thus, it can be assumed that the aerosol yield parameters in Table 1 can be used to describe ambient aerosol formation even though experimental conditions do not mimic exactly ambient conditions in all situations. While it is expected that aerosol yield will decrease with increasing temperature, there are currently no quantitative data available to describe this phenomenon. Therefore, the parameters given here (derived for an average temperature of 310K) are used in all cases. Given that the majority of biogenic emissions occur in hot, tropical regions, this assumption may not induce a large amount of error.

### Table 1. Aerosol yield parameters for biogenic organics

<table>
<thead>
<tr>
<th>Parent</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$K_{\text{com,1}}$</th>
<th>$K_{\text{com,2}}$</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta^2$-Carene</td>
<td>0.057</td>
<td>0.476</td>
<td>0.063</td>
<td>0.0042</td>
<td>2.3-10.9%</td>
</tr>
<tr>
<td>$\beta$-Caryophyllene</td>
<td>1.000</td>
<td>N/A</td>
<td>0.0416</td>
<td>N/A</td>
<td>17.2-62.5%</td>
</tr>
<tr>
<td>$\alpha$-Humulene</td>
<td>1.000</td>
<td>N/A</td>
<td>0.0501</td>
<td>N/A</td>
<td>20.0-66.7%</td>
</tr>
<tr>
<td>Limonene</td>
<td>0.239</td>
<td>0.363</td>
<td>0.055</td>
<td>0.0055</td>
<td>6.1-22.8%</td>
</tr>
<tr>
<td>Linalool</td>
<td>0.073</td>
<td>0.053</td>
<td>0.049</td>
<td>0.0210</td>
<td>1.9-7.3%</td>
</tr>
<tr>
<td>Myrcene$^1$</td>
<td>0.100</td>
<td>0.275</td>
<td>0.513</td>
<td>0.0032</td>
<td>7.6-12.7%</td>
</tr>
<tr>
<td>Ocimene$^2$</td>
<td>0.045</td>
<td>0.149</td>
<td>0.174</td>
<td>0.0041</td>
<td>2.4-6.0%</td>
</tr>
<tr>
<td>$\alpha$-Pinene$^2$</td>
<td>0.038</td>
<td>0.326</td>
<td>0.171</td>
<td>0.0040</td>
<td>2.4-7.8%</td>
</tr>
<tr>
<td>$\beta$-Pinene</td>
<td>0.113</td>
<td>0.239</td>
<td>0.094</td>
<td>0.0051</td>
<td>4.2-13.0</td>
</tr>
<tr>
<td>Sabineine</td>
<td>0.060</td>
<td>0.376</td>
<td>0.406</td>
<td>0.0038</td>
<td>4.7-10.6%</td>
</tr>
<tr>
<td>$\alpha$ &amp; $\gamma$-Terpinene</td>
<td>0.091</td>
<td>0.367</td>
<td>0.081</td>
<td>0.0046</td>
<td>3.4-12.7%</td>
</tr>
<tr>
<td>Terpinene-4-ol</td>
<td>0.049</td>
<td>0.063</td>
<td>0.159</td>
<td>0.0045</td>
<td>2.3-5.2%</td>
</tr>
<tr>
<td>Terpinolene</td>
<td>0.046</td>
<td>0.034</td>
<td>0.185</td>
<td>0.0024</td>
<td>2.3-4.4%</td>
</tr>
</tbody>
</table>

$^1$These values are an estimate as only two experiments were performed.

$^2$SOA formation by NO$_3$ oxidation is negligible (Griffin et al., 1999).

### Table 2. OH and O$_3$ oxidation patterns for bicyclic alkenes

<table>
<thead>
<tr>
<th>Parent</th>
<th>OH</th>
<th>O$_3$</th>
<th>OH</th>
<th>O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chamber</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Global Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta^2$-Carene</td>
<td>18.0%</td>
<td>82.0%</td>
<td>16.2%</td>
<td>83.8%</td>
</tr>
<tr>
<td>$\beta$-Pinene</td>
<td>41.1%</td>
<td>58.9%</td>
<td>42.5%</td>
<td>57.5%</td>
</tr>
<tr>
<td>$\beta$-Pinene</td>
<td>12.6%</td>
<td>87.4%</td>
<td>8.0%</td>
<td>92.0%</td>
</tr>
<tr>
<td>Sabineine</td>
<td>16.9%</td>
<td>83.1%</td>
<td>25.2%</td>
<td>74.8%</td>
</tr>
</tbody>
</table>

4. Compound-Specific Emissions Inventory for Biogenic Compounds

Because the biogenic species considered exhibit a wide range of SOA yields, it is necessary to assess global-scale...
emissions of the most monoterpenes and other reactive volatile organic compounds (ORVOC) in order to estimate the amount of global, biogenically derived SOA formed annually. The global emissions of monoterpenes and ORVOC have been estimated by ecosystem [Guenther et al., 1995]. By determining the predominant plant species associated with these ecosystems and identifying and quantifying the specific monoterpenes and ORVOC emissions from these individual species [Arey et al., 1991, 1995; Guenther et al., 1994, 1996; König et al., 1995], the contributions of individual compounds to emissions of monoterpenes or ORVOC on a global scale can be inferred (Table 3). Less important compounds are grouped with others expected to have similar aerosol-forming potentials.

By applying the contributions of each species listed in Table 3 to the emissions in each 5° x 5° horizontal cell in a global model, a compound-specific and temporally and spatially resolved emissions profile for monoterpenes and ORVOC is established. These emissions are converted to concentration units by using appropriate reactive layer heights specific to each compound. These heights are derived from an estimate of vertical eddy diffusivity [Seinfeld and Pandis, 1998] and appropriate time scales inferred from reaction rate constants and OH and O₃ levels vary spatially. For simplicity, ground level concentrations of OH and O₃ are used. NO₃ is assumed not to contribute to oxidation.

Since the formation of organic aerosol depends on the relative amounts of monoterpenes and ORVOC emitted, a second emissions scenario was constructed by using the other major biogenic inventory of Guenther et al. [1995]. In the second scenario, emissions of each species in each cell were found simply by using the ratio of emission values predicted by Müller [1992] and Guenther et al. [1995] (see Table 3). The major difference between these two estimates is that Guenther et al. [1995] predict almost three times as much ORVOC emission as Müller [1992].

5. Global Aerosol Formation from Biogenic Hydrocarbons

Individual αᵢ and Kᵢᵢ values have been shown to simulate the amount of SOA formed from mixtures as complex as evaporated gasoline [Odum et al., 1997]. Mᵢᵢ, the mass concentration of SOA formed from the oxidation of the mixture of n hydrocarbons, can be found by solving

\[
\sum_j \left( \Delta \text{HC}_j \sum_i \left( \frac{\alpha_{i,j} K_{i,j}}{1 + K_{i,j} M_{oT}} \right) \right) = 1 \quad (2)
\]

where \( \Delta \text{HC}_j \) is the concentration of parent compound j reacted. To estimate the \( M_{oT} \) in each cell from biogenic compounds, equation (2) is used with the yield parameters from Table 1 and the daily biogenic concentrations derived in each cell. The yield parameters of sabine were used for ten-carbon, bicyclic terpenoid ketones because each species exhibits an exocyclic double bond. Yield parameters for aromatics with multiple methyl groups were employed for aromatics [Odum et al., 1997]. First, the compounds listed in Table 1 and these aromatics and ketones are considered. If the left-hand side is greater than unity for \( M_{oT} \) equal to zero, equation (2) is solved iteratively to find the appropriate \( M_{oT} \) for the cell of interest. (Otherwise, \( M_{oT} \) is set to zero for that cell.) In the non-zero cases, additional SOA formation from straight-chain olefins and carboxyls is considered. For these two classes, a flat yield of 5% is assumed for SOA formation [Wang et al., 1991]. The concentration of SOA formed in each cell is thus calculated on a daily basis, converted to mass using cell volume, and summed spatially to provide the global daily amount of SOA formed. At the end of each day, it is assumed that the SOA is released to the free troposphere. The amount of SOA generated from the oxidation of biogenic species annually is found by summing the results of each day of the year.
Using the emissions profiles of both Guenther et al. [1995] and Müller [1992] to account for possible differences in the distribution between monoterpenes and ORVOC, the estimated range of global biogenically derived SOA is 13-24 Tg yr\(^{-1}\). In the absence of additional information, the best estimate can be taken as the average, 18.5 Tg yr\(^{-1}\). The range estimated here is likely a lower bound since products of biogenic oxidation will partition to primary organic aerosol mass and anthropogenic SOA.

The majority of this biogenically derived SOA will be formed in forested regions. However, because of their extensive conversion to aerosol, biogenic hydrocarbons can also contribute substantially to aerosol burdens in any areas with significant vegetation. On average, if a one-week lifetime is assumed, the predicted burden of SOA from biogenic oxidation is 0.36 Tg, which is slightly less than but of the same order of magnitude as the predicted burdens for primary carbonaceous aerosols from biomass and fossil fuel burning [Liousse et al., 1996]. This burden is smaller than those predicted for sea salt, soil dust, and sulfate aerosols but is the same order of magnitude as those predicted for black carbon, nitrate, and ammonium aerosols [Tegen et al., 1997; Adams et al., 1999].

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References


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