

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⁻¹. Recent work has expanded greatly the understanding of secondary organic aerosol (SOA) formation beyond that available to Andreae and Crutzen [1997]. Accounting for new data on the aerosol-forming potential of biogenic organics, spatially and temporally resolved, compound-specific global emissions profiles, and the nonlinear nature of SOA formation allows for a sharpening of this estimate.

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, ΔM_o , 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, M_o ($\mu\text{g m}^{-3}$). For the experiments considered, M_o equals ΔM_o as the absorbing medium is generated completely by the parent hydrocarbon oxidation. The relationship between Y and M_o is

$$Y = M_o \sum_i \left(\frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_o} \right) \quad (1)$$

where α_i is the mass-based stoichiometric yield of oxidation product i and $K_{om,i}$ ($\text{m}^3 \mu\text{g}^{-1}$) is the gas-particle equilibrium coefficient that describes the partitioning of oxidation product i between the absorbing organic aerosol phase and the gas phase [Pankow, 1994; Odum *et al.*,

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1996]. 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 α_1 , α_2 , $K_{om,1}$, and $K_{om,2}$ [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 $\mu\text{g m}^{-3}$. 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 monoterpene structure induce a high level of reactivity with OH, NO₃, and O₃. At NO_x levels characteristic of chamber photooxidation experiments, NO₃ contributes significantly to oxidation if a sufficient amount of NO₃ forms prior to complete consumption of the hydrocarbon by OH and O₃. Of the compounds of interest, this is the case only for α -pinene, β -pinene, Δ^3 -carene, and sabinene.

In remote areas, NO₃ 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 NO₃ 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

Table 1. Aerosol yield parameters for biogenic organics

Parent	α_1	α_2	$K_{om,1}$	$K_{om,2}$	Yield
Δ^3 -Carene	0.057	0.476	0.063	0.0042	2.3-10.9%
β -Caryophyllene	1.000	N/A	0.0416	N/A	17.2-62.5%
α -Humulene	1.000	N/A	0.0501	N/A	20.0-66.7%
Limonene	0.239	0.363	0.055	0.0053	6.1-22.8%
Linalool	0.073	0.053	0.049	0.0210	1.9-7.3%
Myrcene ¹	0.100	0.275	0.513	0.0032	7.6-12.7%
Ocimene	0.045	0.149	0.174	0.0041	2.4-6.0%
α -Pinene ²	0.038	0.326	0.171	0.0040	2.4-7.8%
β -Pinene	0.113	0.239	0.094	0.0051	4.2-13.0
Sabinene	0.060	0.376	0.406	0.0038	4.7-10.6%
α - & γ -Terpinene	0.091	0.367	0.081	0.0046	3.4-12.7%
Terpinene-4-ol	0.049	0.063	0.159	0.0045	2.3-5.2%
Terpinolene	0.046	0.034	0.185	0.0024	2.3-4.4%

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

²SOA formation by NO₃ oxidation is negligible [Griffin *et al.*, 1999].

Table 2. OH and O₃ oxidation patterns for bicyclic alkenes

Parent	Chamber		Global Average	
	O ₃	OH	O ₃	OH
Δ^3 -Carene	18.0%	82.0%	16.2%	83.8%
α -Pinene	41.1%	58.9%	42.5%	57.5%
β -Pinene	12.6%	87.4%	8.0%	92.0%
Sabinene	16.9%	83.1%	25.2%	74.8%

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 O₃ or NO₃ was the only available oxidant (a scavenger was used to consume any OH formed in the O₃-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 NO₃ contribution, yield parameters for aerosol formation in the absence of NO₃ 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 O₃ observed in the chamber is consistent with that expected in the ambient. Global average estimates of 50 ppbv for O₃ and 2.6x10⁶ 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 hydrocarbon oxidation consumption patterns 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.

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

Table 3. Estimated species contributions to global emissions

MONOTERPENES		ORVOC	
Monoterpene ¹	Contribution	ORVOC ²	Contribution
α -Pinene	35%	Terpenoid Alcohols	9%
β -Pinene	23%	C ₇ -C ₁₀ n-Carbonyls	7%
Limonene	23%	Aromatics	6%
Myrcene	5%	Sesquiterpenes	5%
Sabinene	5%	Terpenoid Ketones	4%
Δ^3 -Carene	4%	Higher Olefins	1%
Ocimene	2%		
Terpinolene	2%		
α - & γ -Terpinene	1%		

¹Guenther *et al.* [1995] estimate a total monoterpene emission rate of 127 TgC yr⁻¹; Müller [1992] estimates 147 Tg yr⁻¹. ²Only those capable of forming aerosol are included; Guenther *et al.* [1995] estimate an ORVOC emission rate of 260 TgC yr⁻¹; Müller [1992] estimates 94 Tg yr⁻¹.

emissions of the most important 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 monoterpene 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 concentrations simulated by IMAGES [Müller and Brasseur, 1995]. IMAGES oxidant concentrations are given for specific times and, if needed, are scaled by factors ranging from 3 to 10 to reflect values at times when oxidation, and therefore aerosol formation, is expected to be maximum [Mount *et al.*, 1997]. Because biogenic emissions are given as hourly averages for each month, diurnal oxidant concentration is neglected, and each scaled value is used for an entire day. Vertical cells are thus defined by increasing values of the scale heights for the compounds of interest. For example, the lowest three-dimensional cell, in which all compounds are present and well mixed, has a height equal to the scale height of the most reactive compound. The second cell will then extend from the top of the first cell to the scale height of the second most reactive compound. In this second cell, all

compounds except the most reactive are present. This development of vertical cell heights is extended until the scale height of the least reactive compound is reached. These vertical cell heights are derived for each surface cell since 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]. Andreae and Crutzen [1997] considered an annual emissions rate of 300-500 Tg C yr⁻¹, which is greater than that predicted by Müller [1992] and essentially equal to that predicted by Guenther *et al.* [1995] (see Table 3).

5. Global Aerosol Formation from Biogenic Hydrocarbons

Individual α_i and $K_{om,i}$ values have been shown to simulate the amount of SOA formed from mixtures as complex as evaporated gasoline [Odum *et al.*, 1997]. M_{oT} , the mass concentration of SOA formed from the oxidation of the mixture of n hydrocarbons, can be found by solving

$$\sum_j^n \left[\Delta HC_j \sum_i \left(\frac{\alpha_{i,j} K_{om,i,j}}{1 + K_{om,i,j} M_{oT}} \right) \right] = 1 \quad (2)$$

where ΔHC_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 sabinene 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 carbonyls 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 [*Lioussé 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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