Radiative forcing of phytogenic aerosols

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[1] The principal objective of this study is to investigate the radiative influences produced by phytogenic aerosols over a forested area in eastern Canada where measured aerosol concentrations resulted from α-pinene and β-pinene oxidation processes. The studied forest ecosystem produced moderate amounts of biogenic hydrocarbons, with isoprene and pinene mixing ratios reaching 1.6 parts per billion. Once oxidized, these pinene levels gave rise to maximum phyrogenic aerosol concentrations of circa 5000 particles per cm³. The amount of diffuse and attenuated solar irradiance resulting from the interaction of aerosols with incoming irradiance was quantified using a one-dimensional spectral radiative transfer model and measured aerosol sized distributions and concentrations. Results show that aerosols in the atmospheric boundary layer contributed to only moderate levels of diffuse irradiance but generated substantial attenuation of the incoming solar irradiance stream. For the irradiance levels measured in eastern Canada during cloudless days in July and with aerosol concentrations in the range of 2000 to 5000 particles per cm³, average daytime solar irradiance attenuation amounted to 0.04 W m⁻² with a diffuse component of 0.01 W m⁻². The maximum solar irradiance extinction reached 0.2 W m⁻². Assuming a uniform spatial aerosol distribution, this negative radiative influence could offset substantial fractions of the regional thermal forcing resulting from increased levels of greenhouse gases such as carbon dioxide. It is concluded that greater radiative influences (cooling) could be present over regions dominated by hydrocarbon productive forest ecosystems.

INDEX TERMS: 0315 Atmospheric Composition and Structure: Biosphere/athmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0330 Atmospheric Composition and Structure: Geochemical cycles; 3307 Meteorology and Atmospheric Dynamics: Boundary layer processes; KEYWORDS: biogenic hydrocarbons, biogenic aerosols, radiative forcing, energy balance, Mie scattering, monoterpenes


1. Introduction

[2] Tree plant species release many and large amounts of nonmethane hydrocarbons (NMHCs) into the atmosphere [Fuentes et al., 2000; Guenther et al., 2000; Sharkey and Yeh, 2001]. Throughout the growing season numerous NMHCs, including isoprene (C₅H₈), monoterpenes (C₁₀H₁₈), sesquiterpenes (C₁₅H₂₈), and oxygen-containing (C₅H₈O₂) compounds are released into the atmospheric boundary layer at rates (825–1150 Tg C yr⁻¹) exceeding those from anthropogenic sources (100 Tg C yr⁻¹) [Guenther et al., 1995; Müller, 1992]. These biogenic NMHCs are environmentally important because they exert great influences on three related atmospheric processes. First, NMHCs such as isoprene are produced as part of the carboxylation process in plants and as such play key roles in the biospheric carbon cycle [Crutzen et al., 1999; Fuentes et al., 1999; Goldstein et al., 1998; Monson and Fall, 1989]. Second, they are highly reactive with the major atmospheric oxidizing species of hydroxyl radicals (HO·), ozone (O₃), and nitrate radicals (NO₃⁻). Reactions involving these chemical species lead to the formation of alkylperoxy (RO₂·) radicals, which can effectively convert nitric oxide (NO) to nitrogen dioxide (NO₂) [Atkinson, 2000; Fuentes et al., 2000] and hence enhance the production of O₃ in the atmospheric boundary layer. The oxidation of NMHCs also generate carbonyl compounds such as formaldehyde (HCHO) [Biesenthal et al., 1998; Montzka et al., 1995], which further contribute to atmospheric chemistry processes that ultimately lead to O₃ production. Therefore in regions such as eastern North America, oxidation of biogenic NMHCs can contribute to and exacerbate the problem of smog [Chameides et al., 1988; Pierce et al., 1998]. Third, the oxidation of monoterpenes and sesquiterpenes produces high (10–30%) yields of fine carbonaceous aerosols [Andreae and Crutzen, 1997; Hoffmann et al., 1997; Went, 1960] whose diameter range is <0.4 μm. In the atmospheric...
boundary layer, these fine aerosols can influence many atmospheric processes. For instance, through light scattering and absorption phytogenic aerosols can modify the quality and quantity of incoming solar irradiance thereby impacting the energy balance of the lower atmosphere. (In this manuscript, phytogenic aerosols refer to particulate organic carbon resulting mostly from monoterpenes oxidation.) Because of their size and chemical characteristics, these aerosols can also serve as condensation nuclei and thus influence cloud formation processes.

The principal goal of this study is to evaluate the hypothesis that phytogenic aerosols within the atmospheric boundary layer produce sufficient forcing of the incoming solar irradiance to alter the surface energy balance. To evaluate this hypothesis, diurnal patterns of ambient isoprene and pinene levels above a mixed deciduous forest are studied to understand the local and temporal dynamics of fine aerosols. In addition, utilizing measured aerosol concentrations above the forest canopy and a spectral radiative transfer model, the amounts of diffuse and net attenuated solar irradiance are quantified for two consecutive days during July 1996.

2. Monoterpene Chemistry

Monoterpenes are phytogenic organic compounds released to the atmosphere as gaseous compounds. Under favorable meteorological conditions they can undergo transformation chemistry leading to the production of polar compounds whose low vapor pressures (Table 1) contribute to secondary organic aerosol formation through gas-to-particle partitioning. While recent advances in chemical analytical techniques have led to substantial progress in the identification of monoterpene-reaction products, much more work is needed to delineate the exact nature and details of this gas-to-particle transformation process. The \(\alpha\)-pinene and \(\beta\)-pinene constitute the two most abundant monoterpenes present over forest environments [Geron et al., 2000; Kesselmeier and Staudt, 1999] and represent approximately 30% of the total NMHCs found in the North American atmosphere [Fuentes et al., 2000; Guenther et al., 2000]. Because of their double bond structure, monoterpenes are highly reactive in the atmospheric boundary layer where their residence time, because of the reactions with HO\(_3\), O\(_3\), and NO\(_3\), amounts to a few hours (Table 1). An overview of this chemistry is summarized in Figures 1 and 2 to identify the most relevant monoterpene-reaction products often found in phytogenic aerosols and used in the radiative transfer model described in section 4. As shown in Figure 1, a key product from reaction of \(\alpha\)-pinene with HO is pinonaldehyde (cis-3-acetyl-2,2-dimethyl-cyclobutyl)-acetaldehyde [Hatakeyama et al., 1989], which has been identified as a major component of phytogenic aerosols over forested environments [Kavouras et al., 1998; Yu et al., 1999a]. Reaction of \(\beta\)-pinene with HO follows a similar mechanism, except that nopinone (see Table 1) (dimethylbicyclo[3.1.1]heptan-2-one) is the major...
reaction product [Hatakeyama et al., 1989]. Oxidation of pinenes with NO$_3^-$ similarly starts with addition of the radical to the double bond as the rate limiting step. Low stability of resulting nitrated products makes experimental identification in either the gas or aerosol phase difficult. Nevertheless, NO$_3^-$-initiated oxidation of pinenes results in aerosol formation [Hallquist et al., 1999], primarily during the nighttime when NO$_3^-$ is more abundant.

The reaction of pinenes with O$_3$ proceeds through the formation of primary, cyclic ozonides that decompose into so-called Criegee biradicals. Possible pathways (schemes) following the formation of these highly reactive intermediates are outlined in Figure 2 (see schemes 1 and 2). These pathways indicate the formation of several oxygenated compounds that have been identified in phytogenic aerosols. These compounds include aldehyde and nor-pinonaldehyde from α-pinene-based reactions, and the ketones of 3-hydroxynopinones and 3-keto-nopinones from β-pinene-based reactions. Carboxylic acids such as pinonic acid, pinic acid, and nor-pinonic acid have been identified in phytogenic aerosols [Kamens et al., 1999; Yu et al., 1999b]. As part of the oxidation of pinenes, low molecular weight products such as carbon monoxide (CO), carbon dioxide (CO$_2$), and HCHO [Hatakeyama et al., 1989] are also produced.

Much of the present understanding of monoterpene gas phase to aerosol conversion has come from laboratory studies. Hatakeyama et al. [1989] reported smog chamber studies indicating that reaction of α-pinene and β-pinene with HO had substantially larger aerosol yields than reaction with O$_3$. It is now established [Paulson et al., 1998] that the latter reaction can also lead to the production of HO radicals (see Figure 2), thereby raising the possibility that aerosol formation might be augmented because of monoterpene-HO chemistry. However, on the basis of recent laboratory investigations, Bonn and Moortgat [2002] and Bonn et al. [2002] concluded that aerosol formation is largely the result of monoterpene-O$_3$ reactions. Further investigations are required to verify these latest laboratory results. Nonetheless, the available data [Andreae and Crutzen, 1997; Hoffmann et al., 1997, Pandis et al., 1992] indicate that the oxidation of monoterpenes and sesquiterpenes leads to maximum aerosol yields of about 40%. On the basis of field observations in southern Nova Scotia, Canada, Leaitch et al. [1999] deduced an aerosol mass yield of only 13% from the oxidation of α-pinene and β-pinene. These latter aerosol yields are likely underestimates because monoterpene gas-phase conversion to aerosols does not necessarily occur within the same spatial domain where monoterpene oxidation takes place. After the initiation of monoterpane-oxidation reactions, it may take several hours for aerosol nucleation and coagulation processes to take place. Therefore aerosol formation processes require a much larger fetch than that for monoterpane emissions. Results from field measurements are provided below.

3. Field Measurements

The field data used in this study were obtained during 7–8 July 1996 in a forested region within Kejimkujik National Park, Nova Scotia, Canada (44°26’N, 65°12’W) as part of the NARSTO-CE (North American Research Strategy for Tropospheric Ozone-Canada East) project (for additional details see Biesenthal et al. [1998] and Leaitch et al. [1999]). The site is 155 m above mean sea level.
and forested with birch (*Betula alleghaniensis*), red maple (*Acer rubrum L.*), black spruce (*Picea mariana*), and other coniferous tree species with an average canopy height of 18 m. In 1996, the forest had an estimated leaf area index (LAI) of 4 and coniferous species constituted approximately 67% of the vegetation surrounding the measurement site. Given this tree species composition, this forest ecosystem is considered “moderately” productive in terms of NMHC emissions (see further details below).

The two days included in this study represented both cloudless and cloudy conditions (Figure 3). On 7 July 1996 the site was situated behind a cold front and thus under the influence of a weak anticyclonic system. This predominant sinking motion was interrupted by midmorning on 8 July 1996, when a warm front passed the measurement site, followed by the cold front of a cyclonic system, which was associated with considerably cloudiness as reflected in the low solar irradiance levels (Figure 3). These synoptic features impacted the magnitude and diurnal patterns of air temperature (Figure 4). Air temperature measured at 15 m above ground exhibited diurnal variations ranging from 10 to 20°C (Figure 4). During 7 July in the morning hours the wind direction (measured at 20 m above the ground) changed gradually from the southwest through west to the northwest. The wind speed varied between 2 and 4 m s\(^{-1}\) (Figure 5). Around 18 hours AST (Atlantic daylight saving time), the winds gradually shifted to produce flows primarily from west-southwest. Southerly winds dominated during 8 July, with an abrupt change in speed and direction around 15–16 hours (Figure 5) as the cold front passed the measurement site. These wind flow patterns and temperature regimes impacted the local availability of monoterpenes (Figure 6).

To derive a qualitative understanding of the forest hydrocarbon production and associated aerosol formation processes, the diurnal trends in NMHCs were studied during two consecutive days. The mixing ratios for \(\alpha\)-pinene and \(\beta\)-pinene (Figure 6) exhibited strong diurnal variations ranging from minimum values of circa 100 parts per trillion (Figure 3). Time series of solar irradiance during 7 (circles) and 8 (squares) July 1996 at Kejimkujik National Park, Nova Scotia, Canada. See color version of this figure in the HTML.
on a volume basis (pptv) during the daytime to maximum levels of 1600 pptv at night. These monoterpene diurnal trends resulted because of the combined effects of forest emission rates and chemical sink processes. Monoterpene emission is normally at a maximum during the daytime in response to higher temperatures [Guenther et al., 1994], but chemical sinks and atmospheric turbulent transport are greatest during the daytime as well and contribute to lower pinene levels than nighttime mixing ratios. On 7 July during 8–18 hours the pinene levels stayed nearly constant but around 18 hours both α-pinene and β-pinene sharply increased with time. Even though at that time of day (18 hours) emission rates were likely reduced because of lower temperatures (Figure 4), the increases in monoterpene levels probably resulted because of increased advection that coincided with southwesterly flow (Figure 5).

This scenario is supported by the measured diurnal trends in isoprene during 7 July 1996 (Figure 7). As commonly observed, peak isoprene levels coincide with the time of day when photosynthetically active irradiance (PAR) and temperature reach maximum values (plants do not release isoprene at night). In this instance (Figure 7), however, an additional isoprene peak appeared later in the day on 7 July (20 hours), indicating advection of isoprene from a stronger source region. The observed monoterpene (Figure 6) and isoprene (Figure 7) levels reflect a moderate source from the underlying forest. Under the influence of environmental conditions reported in this study (Figures 3, 4, and 5), highly hydrocarbon productive forest ecosystems can give rise to ambient pinene and isoprene levels in the 2 to 10 ppbv and 5 to 30 ppbv range, respectively [e.g., see Baldocchi et al., 1995; Fuentes et al., 1996].

[10] The observed aerosol concentration and size characteristics followed complex diurnal patterns (as represented by dN/dlogD), which were largely modulated by meteorological conditions and chemical processing. The greatest particle concentrations were measured during the evening of 7 July when two modal size distributions (10–50 nm and 100–200 nm) dominated the aerosol population (Figure 8). Particle nucleation commenced within the local area during the early afternoon of 7 July when particles in the 10–50 nm size range grew until 21 hours through coagulation and condensation. The aerosol volume increases observed during the early evening coincided with the large increases in α-pinene and β-pinene mixing ratios during the same period (Figure 6). Aerosol volume (Figure 8) continued to grow until 04 hours on 8 July and thereafter aerosol volume grew slowly with particle modes centered at 80–90 nm and >150 nm. The aerosol growth dynamics are almost entirely attributed to local gas-particle conversion as reflected in the linear increases in aerosol volume with decreases in α-pinene and β-pinene mixing ratios. Except for the early morning on 7 July particle numbers mostly ranged between 2000–5000 per cm$^2$ over the 2-day period. Assuming that the local changes in aerosol concentrations resulted because of the oxidation of α-pinene and β-pinene, Leaitch et al. [1999] deduced an aerosol mass yield of approximately 13%. The ozone data (Figure 9) provide an indication of the photochemical activity that prevailed during the aerosol measurements. The ozone data offer additional evidence to indicate that (during 7–8 July 1996) a relatively clean air mass dominated the region.
while aerosol measurements were made. On the basis of measurements of aerosol chemical characteristics [Leaitch et al., 1999], it is concluded that the aerosols were produced within the local forest fetch (>10 km). Through a statistical combination of measurement uncertainties, the average uncertainty in field data was estimated to be ±15 (for additional details see Biesenthal et al. [1998]). The aerosol data (Figure 8) are included in the radiative model described below to study solar irradiance attenuation by biogenic aerosols.

4. Radiative Forcing Model

[11] The principal objective of this study is to quantify the radiative influence resulting from phytogenic aerosols in the atmospheric boundary layer. We note that while numerous studies [e.g., Kikas et al., 2001; Intergovernmental Panel on Climate Change (IPCC), 2001; Jacobson, 2001; Penner et al., 2001; Pilinis et al., 1995; Yu et al., 2001] have investigated the radiative forcing of anthropogenic and natural aerosols, little attention has been paid to the radiative influences of phytogenic aerosols. In this study to quantify the radiative influences resulting from phytogenic aerosols, a one-dimensional spectral model was developed and applied to the atmospheric column extending from the forest canopy to the top of the convective boundary layer. The functional relationships to estimate aerosol solar irradiance scattering and absorption were adopted from previously applied and tested Mie theory [Seinfeld and Pandis, 1998]. With this model the combined effect of solar irradiance scattering and absorption was quantified. Once these two processes were expressed per unit surface area of the shadow cast by the irradiated aerosols, the light extinction efficiency ($Q_{\text{ext}}$) was defined as the sum of scattering ($Q_{\text{scat}}$) and absorption ($Q_{\text{abs}}$) efficiencies as shown in equation (1):

$$Q_{\text{ext}} = Q_{\text{scat}} + Q_{\text{abs}}.$$  

Mie scattering is governed by the wavelength of incident irradiance ($\lambda$) and particle size, nominally represented by the particle diameter ($D_p$). These two variables can be combined to establish the ratio ($\alpha$) of the particle circumference ($\pi D_p$) to the light wavelength:

$$\alpha = \frac{\pi D_p}{\lambda}. \quad (2)$$

An additional governing variable in Mie scattering is the particle optical property (Table 1), which can be quantified by a refractive index, $\eta$, as shown in equation (3):

$$\eta = n + i\kappa. \quad (3)$$

The real part, $n$, and the imaginary part, $\kappa$, of the refractive index depend on the light wavelength. Ordinarily, $\eta$ is normalized to the refractive index of the aerosol medium (in this case air), $\eta_0$, and is given as $m = \eta/\eta_0$. For all the light wavelengths considered in this study a representative $m$ value of 1.45 was considered (because the visible and near infra red part of the electromagnetic spectrum are included in the analysis, negligible $\kappa$ values are considered in the model). Larson et al. [1988] and Jacobson [1997], who also dealt with organic aerosols, used a similar value (1.55).

[12] Returning to the light scattering and extinction efficiencies, the dimensionless quantities of $Q_{\text{scat}}$ and $Q_{\text{ext}}$ for individual spherical aerosols depend on $m$ and $\alpha$. Scattering and extinction efficiencies are defined as the ratio of radiant power scattered or absorbed by a single particle to the radiant power geometrically intercepted by the particle cross-section. Wickramasinghe [1973] and Bohren and Huffman [1983] originally developed the $Q_{\text{scat}}$ and $Q_{\text{ext}}$ functional relationships as defined in equations (4) and (5):

$$Q_{\text{scat}}(m, \alpha) = \frac{2}{\alpha^2} \sum_{k=1}^{\infty} (2k + 1) \left[ |a_k|^2 + |b_k|^2 \right]$$

$$Q_{\text{ext}}(m, \alpha) = \frac{2}{\alpha^2} \sum_{k=1}^{\infty} (2k + 1) \text{Re}(a_k + b_k).$$

Figure 9. Time series of ozone mixing ratios measured at 2 m above ground during 6–8 July 1996 at Kejimkujik National Park, Nova Scotia, Canada.
The $a_k$ and $b_k$ are coefficients, defined below, and $\text{Re}$ represents the real part of the $a_k$ and $b_k$ quantities. In equations (4) and (5) the index $k$ is an integer whose value increases by one until numeric convergence is achieved. The $a_k$ and $b_k$ relationships are expressed in terms of Ricatti-Bessel functions [Wickramasinghe, 1973] as defined in equations (6) and (7):

$$a_k = \left( \frac{A_k(y)}{m} + \frac{k}{\alpha} \right) \text{Re}(\zeta_k(\alpha)) - \text{Re}(\zeta_{k-1}(\alpha))$$

(6)

$$b_k = \left( \frac{A_k(y)m + k}{\alpha} \left[ \text{Re}(\zeta_k(\alpha)) - \text{Re}(\zeta_{k-1}(\alpha)) \right] \right).$$

(7)

To generate the required $A_k(y)$ values in equations (6) and (7), a recursive relationship is needed as shown in equation (8) [Bohren and Huffman, 1983]:

$$A_k(y) = \frac{-k + \frac{1}{y} - A_{k-1}(y)}{y}.$$  

(8)

The $A_k(y)$ is defined as $A_0(y) = \cos(y)/\sin(y)$, with $y = \alpha m$. Also, the Ricatti-Bessel function $\zeta_k(\alpha)$ represents a recursive relationship and is given in equation (9):

$$\zeta_k(\alpha) = \frac{2k - 1}{\alpha} \zeta_{k-1}(\alpha) - \zeta_{k-2}(\alpha).$$

(9)

When $k$ has the value of $1$, then $\zeta_0(\alpha)$ and $\zeta_1(\alpha)$ take the complex functions shown in equations (10) and (11):

$$\zeta_{-1}(\alpha) = \cos \alpha - i \sin \alpha$$

(10)

$$\zeta_0(\alpha) = \sin \alpha - i \cos \alpha.$$  

(11)

The scattering efficiencies in equations (4) and (5) must be determined by summing terms and incrementing $k$ until a desired convergence is achieved. In this study, the maximum $k$ value of 30 was considered to ensure convergence for all scattering efficiencies.

[13] The relationships described above provide estimates of light scattering and extinction efficiencies for individual aerosols. For a population of spherical particles, spectral light extinction coefficients ($b_{\text{ext}}(\lambda)$) can be defined for different sized aerosols of identical refractive properties with a number size distribution function defined in terms of aerosol size characteristics, $n(D_p)$. Thus for a population of spherical aerosols ranging in size from nearly zero nm in diameter (e.g., 10 nm) to maximum diameter ($D_p^{\text{max}}$), the $b_{\text{ext}}(\lambda)$ depends on the representative aerosol surface area ($\pi D_p^2/4$), the $Q_{\text{ext}}$ in function of both $m$ and $\alpha$ ($Q_{\text{ext}}(m, \alpha)$), and $n(D_p)$ as described in equation (12):

$$b_{\text{ext}}(\lambda) = \int_0^{D_p^{\text{max}}} \frac{\pi D_p^2}{4} Q_{\text{ext}}(m, \alpha)n(D_p)dD_p.$$  

(12)

The light scattering modification ($b_{\text{scat}}(\lambda)$) is similarly defined as shown in equation (13):

$$b_{\text{scat}}(\lambda) = \int_0^{D_p^{\text{max}}} \frac{\pi D_p^2}{4} Q_{\text{scat}}(m, \alpha)n(D_p)dD_p.$$  

(13)

Both $b_{\text{scat}}(\lambda)$ and $b_{\text{ext}}(\lambda)$ have units of $m^{-1}$. At a given light wavelength, the $b_{\text{scat}}(\lambda)$ and $b_{\text{ext}}(\lambda)$ coefficients represent the fractional loss or modification in the light intensity per incremental path length through the aerosol layer. It is then useful to express the $b_{\text{scat}}(\lambda)$ and $b_{\text{ext}}(\lambda)$ functions in terms of aerosol mass ($m(D_p)$) distribution, rather than number size distribution $n(D_p)$. The results are shown in equations (14) and (15) [Ouimette and Flagan, 1982]:

$$b_{\text{ext}}(\lambda) = \int_0^{D_p^{\text{max}}} \frac{3}{2\rho_p D_p} Q_{\text{ext}}(m, \alpha)m(D_p)dD_p.$$  

(14)

$$b_{\text{scat}}(\lambda) = \int_0^{D_p^{\text{max}}} \frac{3}{2\rho_p D_p} Q_{\text{scat}}(m, \alpha)m(D_p)dD_p.$$  

(15)

In equations (14) and (15), $\rho_p$ represents the particle density. When multiplied by the atmospheric layer thickness ($\partial Z$), the derived quantities in equations (14) and (15) represent spectral optical depths.

[14] To apply this spectral radiative forcing model, the incoming global solar irradiance values reported in Figure 3 were considered to be in the wavelength range 0.305 < $\lambda$ < 4.045 $\mu$m and partitioned over 119 wave bands. To determine the aerosol spectral radiative influence, the measured global solar irradiance values were converted to spectral irradiance quantities and denoted by $R(\lambda_i)$. The $R(\lambda_i)$ values were determined as the product of measured total solar irradiance ($R_{\text{tot}}$) and the ratio of modeled irradiance per wave band ($R_{\text{mod}}(\lambda_i)$) and the modeled sum of energy over all wave bands (see equation (16)). The modeled irradiance values were computed for a location at 37°N during solar noon. In equation (16) it was assumed that the computed spectral characteristics of irradiance do not change with time of day. The $R(\lambda_i)$ values for any time of day were estimated for the periods when measurements of solar irradiance were available:

$$R(\lambda_i) = R_{\text{tot}} \left( \frac{R_{\text{mod}}(\lambda_i)}{\sum_{\lambda_i=0.305 \mu m}^{\lambda_i=4.045 \mu m} R_{\text{mod}}(\lambda_i)} \right).$$  

(16)

Spectral irradiance values were obtained from the American Society for Testing and Materials (ASTM), Table G159-98 Standard Tables for References Solar Spectral Irradiance at Air Mass 1.5: Direct Normal and Hemispherical for a 37° Tilted Surface. The ASTM utilized the model output of Bird et al. [1983]. The specified atmospheric conditions included an absolute air mass of 1.5, Angstrom turbidity at 500 nm of 0.27, total column water vapor equivalent of 1.42 cm, total column ozone equivalent of 0.34 cm, and surface albedo of 0.2 (assuming that the surface has a cosine (Lambertian) distribution of reflectivity).
In this study, it is assumed that the solar irradiance values apply to the level above the boundary layer. The solar irradiance extinction and scattering for the atmospheric column, defined from the forest canopy to the top of the mixed layer ($Z^*$), were computed using equations (17) and (18). In this atmospheric layer, the light attenuation was considered to obey the Beer-Lambert law [Psiloglou et al., 1997]:

$$R_{	ext{ext}}(\lambda) = R(\lambda)(1 - e^{-b_{\text{ext}}(\lambda)Z^*M})$$  

$$R_{\text{sca}}(\lambda) = R(\lambda)(1 - e^{-b_{\text{sca}}(\lambda)Z^*M}).$$  

In the estimation of solar irradiance extinction and scattering, aerosol concentrations were assumed to be uniformly mixed within the atmospheric boundary layer whose depth varied with time [Gong et al., 2000], reaching a maximum altitude of 1200 m around 14 hours. To account for the increased path length that the solar beams take through the depth of the boundary layer, when the solar beam angle of incidence deviates from the zenith ($\theta_i$), the optical air mass ($M$) had to be calculated. The $M$ is given by Kasten and Young [1989] and is shown in equation (19):

$$M = \left[ \cos \theta_i + 0.50572(96.07995 - \theta_i)^{-1.6364} \right]^{-1}. $$  

To find the total diffuse and extinction of solar irradiance, the quantities in equations (17) and (18) were summed over the solar wave band interval between 0.305 and 4.045 $\mu$m. The solar irradiance extinction and scattering were determined for each hour, starting at sunrise and ending at sunset during 7–8 July 1996.

5. Aerosol Radiative Forcing

In this investigation, the entire size distribution of aerosols measured over the forest canopy was considered to come from monoterpane oxidation products. Aerosol growth dynamics and chemical characteristic measurements provided evidence in support of this assumption [Leaitch et al., 1999] (Leaitch et al. [1999] give additional details). This assumption was made to incorporate in the model the refractive properties of phytogenic aerosols. Table I includes the available refractive information for $\alpha$-pinene and $\beta$-pinene and several key monoterpane oxidation products. The similarities in the refractive indices for all these compounds are fortuitous because a single bulk refractive index can be employed to represent every aerosol particle without the detailed knowledge of aerosol chemical composition. In the results reported below, all particles were assumed to have a spherical shape.

To evaluate the hypothesis that phytogenic aerosols in the boundary layer produce measurable radiative influence, the diurnal solar irradiance attenuation was studied for the two days when aerosol measurements were made (Figure 8). The estimated diurnal solar irradiance attenuation trends (Figure 10) were strongly modulated by temporal changes in the atmospheric boundary layer depth, aerosol concentrations, and different aerosol size characteristics. During 7 July calculated maximum solar irradiance attenuation reached 0.07 W m$^{-2}$ during 14–15 hours, one hour after the peak in incoming solar irradiance. During 8 July the maximum light attenuation attained the value of 0.19 W m$^{-2}$ and coincided with maximum levels of incoming solar irradiance (Figure 3). The higher irradiance attenuation estimated for 8 July resulted in response to greater fine (<100 nm in diameter) aerosol concentrations than the ones observed during 7 July. Here it is important to recognize that the Mie scattering model implies a one-to-one correspondence between particle concentration and irradiance attenuation. The light extinction relationships in equations (12) and (13) scale directly with particle concentration because the Beer-Lambert extinction laws in equations (17) and (18) appear linear at low ($<1$) optical spectral depths.

One key goal of this study is to investigate the spectral radiative influence resulting from biogenic aerosols, particularly in the PAR region as this type of irradiance can impact processes such as forest carbon uptake [Gu et al., 1999; Hollinger et al., 1994; Hollinger et al., 1998]. The results indicate that the greatest spectral light extinction occurred between the wavelengths of 300 and 700 nm, with...
light extinction values ranging from 0.05 to 0.40 W m\(^{-2}\) μm\(^{-1}\) (Figure 11). These variations in spectral radiative influence resulted in response to both the dominant aerosol concentrations in the size range of <300 nm and variable levels of incoming solar irradiance. The spectral light scattering also exhibited strong diurnal variations, with greatest scattering occurring during the time periods with highest incoming solar irradiance. Maximum diffuse light attenuation reached 0.09 W m\(^{-2}\) μm\(^{-1}\) and generally occurred in the PAR spectral range (Figure 12). On average the diffuse irradiance component, resulting from light scattering processes only, amounted to 12% of the total attenuated solar irradiance. The overall conclusion of these modeling results is that phytogenic aerosols do not directly contribute to large amounts of diffuse irradiance. However, phytogenic aerosols can indirectly impact processes such as cloud formation [Penner et al., 2001] and thus convert direct to diffuse irradiance.

6. Discussion and Implications

The results presented above (Figures 10, 11, and 12) apply to a forest ecosystem with moderate monoterpenes emission capabilities. The prevailing environmental conditions (e.g., temperature and PAR) observed over the Kejimkujik forest do not necessarily promote large monoterpenes emission rates and therefore limited aerosol production rates should be expected. Moreover, at the time of measurements, the site was not impacted by anthropogenic activity that could usually provide key chemical substrates for aerosol nucleation and coagulation processes over more NMHC productive ecosystems. Consequently, there is the potential for both larger sized particles (due to stronger NMHC source strength) and higher number concentrations (due to “polluted” air masses) than those measured over this eastern Canadian forest. Therefore the measured aerosol concentrations and estimated radiative influences reported here pertain to remote locales. Even in this region with potentially weak aerosol radiative influence, midday irradiance extinction levels support the hypothesis that these locally produced aerosols may modify the energy balance of the lower troposphere.

To generalize our results and make them applicable to other regions with larger monoterpenes emissions, several scenarios are considered to investigate the potential phytogenic aerosol radiative influence. The first set of scenarios considers increases in aerosol concentration of 5-, 10-,
will likely result in higher aerosol concentrations greater levels of boundary layer ozone and monoterpenes photochemical activity to generate aerosols. Air masses with greater levels of boundary layer ozone and monoterpenes will likely result in higher aerosol concentrations [Bonf et al., 2002]. In rural places such as Appalachian Mountains (where the blue haze due to phyogenic aerosols is frequently observed) in the eastern United States, or regions with warmer climates [Kavouras et al., 1998], particle numbers can be 3- to 5-fold higher than the levels measured at Kejimkujik [Went, 1960; Yu et al., 2000]. Under the same environmental conditions reported in Figure 3, using the assumed aerosol concentrations, the instantaneous maximum light extinction attained 6.5 W m⁻² (Figure 13) for 7 July. These results are within the reported aerosol radiative influence for the southeastern United States [Yu et al., 2001], where the atmospheric-column light attenuation over land can be as high as 13.4 W m⁻².

The second scenario entails 5-, 10-, 20-, 60-, and 100-fold increases in the total aerosol loading by considering uniformly larger particle sizes and holding particle numbers the same as those measured over the Kejimkujik forest. These particle size increase scenarios are based on the realization that aerosols in the lower atmosphere can grow via several physical processes, including aerosol wetting and nucleation on aerosol seeds (as often observed in more polluted atmospheres). A 100-fold increase in mass is achieved by considering that all the particles increase their diameter by a factor of 4.64. Thus the particle mode that grows to 150 nm on 8 July would have a diameter centered at 700 nm (which in reality may result when aerosols become wet). The modeling results indicate that irradiance attenuation does not scale directly with particle size increase and the light extinction reaches a 1 W m⁻² maximum on 7 July (Figure 14) under the 100-fold size increase scenario. From these scenarios it is evident that increase in particle growth is a less efficient process to enhance light attenuation than particle nucleation. In part, this owes to the fact the physical shadow cast by a growing aerosol increases as the square of particle diameter, but the amount of material needed to support this growth increases as the cube of particle diameter. Thus there is a decrease in the incremental level of light attenuation for each additional amount of aerosol mass loading as the particles grow. This size effect may be partially offset by an increase in particle scattering efficiencies (see equations (4) and (5)). In general, however, particle nucleation is a more efficient aerosol partitioning process in providing light attenuation than particle growth for a given aerosol mass loading. The most notable outcome of these two theoretical calculations is that higher levels of light extinction and diffuse irradiance resulted from greater fine aerosol concentrations.

The phyogenic aerosol irradiance influences estimated in this study pertain to regions dominated by forest ecosystems that effectively emit monoterpenes and sesquiterpenes. Such regions may include eastern North America where hydrocarbon aerosol precursors are abundantly produced [Geron et al., 2000]. The baseline radiative influences can be even greater under the influence of higher aerosol loadings. For example, for the aerosol concentration scenarios based on five fold increases above the Kejimkujik ambient particle concentrations, the resulting diurnal averages and associated standard deviations are 0.3 ± 0.3 W m⁻². This radiative influence is comparable to the values (~0.31 W m⁻²) resulting from total natural (e.g., organics) aerosol constituents over continental regions [Jacobson, 2001]. This is likely the radiative (cooling) influence to be expected over regions such as the Blue Ridge Mountains” in the Carolinas and Virginia (USA) where the blue haze is conspicuously and frequently observed during the summer time [Went, 1960]. In addition, this radiative influence could offset a substantial fraction of the (1.46 W m⁻²) thermal perturbation resulting from increased levels of carbon dioxide during the last 200 years [IPCC, 2001].

7. Summary and Conclusions

During the 2-day study period, forest biogenic hydrocarbon emissions resulted in maximum ambient α-pinene...
and β-pinene mixing ratios of 1.6 ppbv. The oxidation of these monoterpenes gave rise to local aerosol formation. The onset of aerosol nucleation processes resulted from the local gas-to-particle conversion as reflected in the linear increases in aerosol volume with corresponding decreases in α-pinene and β-pinene mixing ratios. The oxidation of local monoterpenes produced aerosol yields in the 13% level. Following the onset of intense photochemical activity in the early afternoon, particles grew slowly until characteristic diameters reached >150 nm. Aerosol concentrations mostly ranged from 2000 to 5000 particles per cm$^3$.

[24] Once uniformly distributed throughout the convective boundary layer, phytogenic aerosols contributed to an estimated maximum solar irradiance attenuation of 0.2 W m$^{-2}$. This radiative influence applies to the conditions experienced over Nova Scotia, Canada during July 1996. The estimated radiative influence could offset a fraction of the regional thermal influence resulting from increased levels of carbon dioxide in the last 200 years. Therefore we conclude that phytogenic aerosols can impact the energy balance of the lower atmosphere and produce a net cooling effect, which could be a measurable fraction of the thermal forcing resulting from the most important greenhouse gases such as carbon dioxide. This is the first attempt to estimate the radiative influence of phytogenic aerosols. For more complete studies, comprehensive radiative transfer modeling systems and detailed field data sets are required to adequately ascertain the impact of phytogenic aerosols on the energy balance of the lower troposphere. Nonetheless, when scaling the present results to more biogenic-hydrocarbon productive forest ecosystems, the aerosol solar radiative forcing can reach several Watts per m$^2$. It is expected that these latter radiative influences might be present over regions experiencing high (>5000 particles per cm$^3$) aerosol concentrations. Eastern North America, in particular, might be experiencing shifts in the surface energy balance due to current rates of reforestation with tree species that are more effective in emitting hydrocarbons than the indigenous plant species that were essentially eradicated in the early 1900s to support agriculture.

[25] As an additional working hypothesis, we propose that phytogenic aerosols can potentially alter regional climate through two related processes. First, carbonaceous aerosols can effectively act as cloud condensation nuclei, thereby influencing cloud formation processes. Increased cloud formation will result in reduced solar irradiance reaching the surface. Because of aerosol-cloud interactions, this light attenuation may produce regional surface energy balance changes comparable to the thermal energy trapping by greenhouse gases. Additionally, clouds contribute to transform direct to diffuse solar irradiance. Because forests increase their carbon uptake in response to large levels of diffuse irradiance, there could be a novel and “positive” feedback loop operating over forest ecosystems. This loop may give rise to reduced levels of solar irradiance reaching the Earth’s surface and result in lowering the thermal radiative forcing due to increased removal of greenhouse gases such as carbon dioxide. These regional processes outlined in this study are not presently quantified and remain unaccounted for in modeling systems designed to investigate the energy balance of the lower atmosphere. Detailed field investigations may provide valuable information on the magnitude of these feedback loops operating over forested regions.

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