Emission of Isoprene, Monoterpenes, Ethene and Propene by Vegetation

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Description and Implementation in the STOCHEM Model

Contents

1. Introduction

Isoprene (C_5H_8) and monoterpenes (general formula $C_{10}H_{16}$) are reactive volatile organic compounds (VOCs) which are emitted into the atmosphere by vegetation in large quantities. The magnitude of isoprene emissions on a global scale is of the same order as methane, and both compounds can strongly influence the oxidising capacity of the lower troposphere. Owing to their high reactivity, isoprene and monoterpenes can play an important role in surface chemistry even when their levels are lower than anthropogenic hydrocarbons. Plants also emit many other classes of compounds such as sesquiterpenes, aldehydes, and alcohols, but these will not be considered in this report.

The potential role of isoprene and other naturally emitted hydrocarbons in biosphere-climate-chemistry feedbacks has been summarised recently by Shallcross and Monks (2000) and Fuentes et al. (2001). In a future scenario with increased levels of CO_2 and warmer temperatures, isoprene emissions could increase by as much as a factor of four compared to the present day. Increased nitrogen oxide emissions (NO_x; = $NO + NO_2$) would mean that the surface levels of pollutants such as ozone and peroxyacetyl nitrate (PAN) could rise sharply. Under low NO_x conditions, isoprene and monoterpenes react to form acids and peroxides, which in turn lead to aerosol formation and a net cooling of the surface. However, Cox et al. (2000) have shown that there is a significant effect of global warming on plant growth, and that large areas of forest in the tropics could die away in the second half of the 21st century. If this were to happen, then natural VOC emissions would be much smaller, as most of these VOCs are emitted in tropical regions.

The products from reactions of the VOCs are often highly reactive as well. For example, when isoprene reacts with the hydroxyl radical (OH), the first stable products (depending on the reaction pathway) are methyl vinyl ketone and methacrolein (Atkinson, 2000), both of which contain an unsaturated carbon-carbon bond. These two products also react rapidly with the hydroxyl radical. Similarly, the degradation of monoterpenes produces a large number of peroxy radicals (RO_2). If sufficient levels of NO_x are present, these peroxy radicals will promote the formation of NO_2 and hence increase ozone levels. Conversely, if NO_x levels are low, isoprene and monoterpenes (and the products with carbon-carbon double bonds) can react with ozone directly and reduce its levels.

Not surprisingly, the lifetimes of isoprene and monoterpenes are small. Considering both day and night, the lifetime of isoprene ranges from 1.5 to 3 hours. For α-pinene, an important monoterpene, the lifetime may range from as little as 5 minutes to 3 hours. Other monoterpenes have even shorter lifetimes. For example, α-terpinene has a lifetime of just 2 - 5 minutes (Kesselmeier and Staudt, 1999, and references therein).

Isoprene emissions generally only affect surface chemistry, for two reasons. First, isoprene is only emitted during the hours of daylight. Secondly, its short lifetime means that very little if any isoprene escapes from the boundary layer. For example, Kesselmeier et al. (2000) measured vertical profiles of isoprene (and some monoterpenes) over pristine forest in Amazonia. The lowest mixing ratios were found at the highest altitudes (500 m), and the largest at the surface, the latter exhibiting considerable diurnal variation.

Monoterpenes are those molecules with the general formula $C_{10}H_{16}$. Plants emit a wide range of monoterpenes (Kesselmeier and Staudt, 1999); some examples are α- and β-pinene, and limonene. They generally contain at least one unsaturated carbon-carbon

bond, and often have one or more rings in their structure. In the case of α-pinene, one of these rings contains just four carbon atoms, which introduces strain in some of the carbon-carbon bonds and so increases the reactivity of the molecule.

Plants also emit a wide range of other VOCs, including many oxygenated species (Winer et al., 1992). Although many of these fluxes are small when compared to those of isoprene and monoterpenes, they are often of similar magnitude to the anthropogenic sources, and are emitted in locations far removed from anthropogenic activity. Many of these compounds are highly reactive. In this report, emissions of isoprene, mono-terpenes, ethene and propene from vegetation will be considered.

2. Model Descriptions: STOCHEM and MOSES

The model used for this work is the Met Office chemistry-transport model STOCHEM which has been described in detail elsewhere (Collins et al., 2000, and references therein), and so only a brief description is given here. In STOCHEM, a Lagrangian approach is used where the atmosphere between the surface and a pressure of 100 hPa is divided into 50,000 air parcels of equal mass which are advected with a one-hour time step. Each parcel contains the mixing ratios of 75 chemical species, including the important species which affect tropospheric ozone levels: methane, carbon monoxide, ozone, nitrogen oxides (NO and NO_2) and eight nonmethane hydrocarbons. A wide range of atomic and radical species are also included, such as the hydroxyl and perhydroxyl radicals, atomic oxygen (in both singlet and triplet states), peroxy radicals and alkoxy radicals formed from hydrocarbon oxidation. The concentrations of all these species are modelled explicitly within STOCHEM using 166 reactions, of which 17 are photochemical. No "lumping" or other approximations are used.

STOCHEM has a horizontal resolution of $5° \times 5°$, and nine vertical levels, and is coupled to the Hadley Centre climate model HadCM3 (Gordon et al., 2000) which in turn has a horizontal resolution of $3.75° \times 2.5°$ and 19 vertical levels. At each coupling step, fields of winds, temperature, specific humidity and many other data are passed to STOCHEM. The initial meteorological conditions were taken from a general climatology suitable for the 1990s, which in turn was generated as part of a long integration of HadCM3.

In the HadCM3 model, the surface processes and exchange of carbon and water between the surface and the atmosphere are simulated by the MOSES 2.2 sub-model (Essery et al., 2001). In MOSES 2.2, the sub-grid scale surface heterogeneity is represented by dividing the surface of each model grid box into one or more of nine different surface types, called tiles. These are listed in Table 1.

Table 1. Surface types defined in MOSES 2.2

Tile Number	Surface type	Tile Number	Surface type
1	Broadleaf Forest	6	Urban
2	Needleleaf Forest	7	Water (land only)
3	C3 grass	8	Bare Soil
4	C4 grass	9	Ice
5	Shrub		

Except for those classed as land-ice, each grid cell on land may be subdivided into any combination of tiles 1 to 8. On the global scale, the urban category (tile 6) is virtually absent, and is treated as bare desert in STOCHEM. At each coupling time step, fields of leaf-area indices, surface temperatures and radiation fluxes are passed from MOSES to STOCHEM. The leaf phenology was active for these simulations.

3. Factors affecting Natural VOC Emissions

Emission of isoprene and monoterpenes varies considerably between different species of plant. The emission of isoprene from plants is controlled by temperature, and levels of photosynthetically active radiation (PAR), which lies within the wavelength range 400 - 700 nm; isoprene is thus only emitted during hours of daylight. Monoterpene emissions, however, seem to be controlled by temperature only (Guenther et al., 1993, 1995), although some recent measurements indicate that there may also be a light dependence (Rinne et al., 2002). Ethene and propene are produced by different mechanisms.

4. Isoprene and Monoterpene Emission Model

The model used in STOCHEM to calculate emission of isoprene and monoterpenes from vegetation is based on the scheme developed by Guenther et al. (1995), which in turn is an improved form of the earlier model of Guenther et al. (1993). The two emission models have been used successfully by many other researchers to simulate experimental data and perform global chemistry modelling studies (Lamb et al., 1996; Street et al., 1996; Pier and McDuffie, 1997; Wang and Shallcross, 2000; Lehning et al., 2001; Pétron et al., 2001; Karlik and Winer, 2001; Boissard et al., 2001). The model formulation involves the calculation of two dimensionless coefficients which depend on temperature and the flux of PAR respectively. The calculation of these two coefficients is independent of plant species. The emissions of isoprene and monoterpenes are obtained by multiplying the product of these coefficients by ecosystem dependent emission factors and foliar densities.

4.1 Basic Emission Model

In the model of Guenther et al. (1995), the VOC emission flux is calculated from the following equation:

$$F = D\varepsilon\gamma \qquad\qquad\qquad (1)$$

where F is the VOC emission flux (μg C m^{-2} h^{-1}; i.e. per m^2 of ground), D is the foliar density (g dry matter m^{-2}), ε is an ecosystem dependent emission factor (μg C g^{-1} h^{-1}; i.e., emission per gram of dry foliar matter), and γ is a dimensionless activity factor which accounts for the influence of leaf temperature and PAR. In their global modelling study of natural VOC emissions, Guenther et al. (1995) used the Olson World Ecosystems database (Olson, 1992) to identify different ecosystems. Each ecosystem was assigned one of three specific leaf weights, and one of five base emission factors which were derived from a review of emission fluxes reported in the literature.

A slightly different approach was necessary in STOCHEM, because the foliar density D is not available. Guenther et al. (1995) list specific leaf weights (in g m^{-2} of leaf) and base emission factors (ε) for isoprene and monoterpenes for the ecosystems identified in the Olson (1992) database. Using the data presented by Guenther et al. (1995), leaf weights and emission factors were assigned to the five plant functional types (tiles 1-5 in Table 1) used in MOSES. These data are summarised in Table 2.

For isoprene emissions in the model of Guenther et al. (1995), the activity factor γ is the product of two coefficients C_L and C_T, which account for the effects of PAR levels and leaf temperature respectively. This definition has been modified for use in STOCHEM to account for the areas of leaves which are directly lit by the sun, and which are shaded. Although these leaf areas are calculated by Guenther et al. (1995), it is not clear how they were used in the calculation of the isoprene emissions. The equation used to calculate γ in STOCHEM is given later in section 5. The parameters C_L and C_T are discussed in further detail in sections 4.2 and 4.3. respectively. Monoterpene emissions are controlled by temperature only, and require a different formula for the calculation of γ which is described in section 4.4.

Table 2. Ecosystems, specific leaf weights and emission factors used in STOCHEM to calculate fluxes of isoprene and monoterpenes.

Tile Number	Ecosystem	Leaf Weight, w / g m^{-2}	Emission Factor, ε / μgC g^{-1} h^{-1} Isoprene	Monoterpenes
1	Broadleaf Forest	125	24	0.4, 0.8[a]
2	Needleleaf Forest	150	8	2.4
3	C$_3$ Grass	125	16	0.8
4	C$_4$ Grass	125	16	0.8
5	Shrub	125	16	0.8

[a]Broadleaf forests have a base monoterpene emission factor of 0.4 μgC g^{-1} h^{-1} in the tropics, and 0.8 μgC g^{-1} h^{-1} in temperate zones.

4.2 Dependence of Emissions of Isoprene on Photosynthetically Active Radiation (PAR)

The factor C_L is a function of the PAR flux, and is defined in equation (2),

$$C_L = \frac{a\,C_{L1}\,PAR}{\sqrt{1+a^2 PAR^2}}$$

(2)

where $a = 0.0027$ and $C_{L1} = 1.066$; these are empirical constants derived by Guenther et al. (1993) by fitting the above expression to measured emission rates. For this expression, PAR should be in units of μmol photons m^{-2} s^{-1}. The PAR flux from MOSES 2.2 is in units of W m^{-2}, and is converted to μmol photons m^{-2} s^{-1} by multiplying by 4.57 μmol PAR photons J^{-1} (Cox et al., 1998)[¶].

[¶] The conversion factor is calculated as follows: 1 mol PAR photons (J mol^{-1}) $= L \times h \times c / \lambda$, where L is Avogadro's number, 6.022×10^{23} mol^{-1}, h is Planck's constant, 6.626×10^{-34} J s, c is the speed of light, 3×10^{8} m s^{-1}, and λ is a wavelength in the middle of the PAR range, assumed to be 543 nm. The reciprocal of this result gives the factor quoted in the text, in units of mol photons J^{-1}.

Equation (2) is plotted in Figure 1(a). Isoprene emissions (normalised) increase linearly with PAR at first, with a slope equal to a, and then approach a saturation point. The constant C_{LI} ensures that C_L equals 1 at a PAR flux of 1000 µmol photons m^{-2} s^{-1}.

A further complication arises because the fluxes of both direct beam and scattered (diffuse) PAR are required. Clearly, not all leaves in a vegetative canopy will be lit directly by sunlight. Shaded leaves receive only diffuse PAR, whereas those at the top of the canopy receive both direct and diffuse PAR. Shaded leaves produce considerably less isoprene than unshaded ones, as the diffuse PAR levels are generally much smaller than the direct beam PAR. A simple canopy radiative transfer model to calculate the flux densities of direct and diffuse PAR on sunlit and shaded leaves, as well as the areas of sunlit and shaded leaves, is described in section 5.

4.3 Dependence of Isoprene Emissions on Temperature

The temperature dependence of isoprene emissions is controlled by the factor C_T, which is defined in equation (3). This type of equation has been used to describe the temperature response of enzymatic activity (Guenther et al., 1993).

$$C_T = \frac{\exp\dfrac{C_{T1}(T-T_S)}{RT_ST}}{1+\exp\dfrac{C_{T2}(T-T_M)}{RT_ST}} \tag{3}$$

In equation (3), T is the leaf temperature, R is the Ideal Gas Constant (= 8.31 J mol^{-1} K^{-1}), C_{T1} = 95 kJ mol^{-1}, C_{T2} = 230 kJ mol^{-1}, and T_M = 314 K; the values of these coefficients were again determined by Guenther et al. (1993) by fitting equation (3) to experimental data. T_S is a standard temperature, 303 K. Equation (3) is plotted in Figure 1(b). The (normalised) isoprene emission rate increases with temperature until it reaches a maximum at about 310 K (37 °C), after which it falls. The leaf temperature is not available as a diagnostic from the MOSES 2.2 surface scheme; instead, the surface temperature of each tile is used.

4.4 Dependence of Monoterpene Emissions on Temperature

Monoterpene emissions appear to be controlled by temperature only (Guenther et al., 1993, and references therein). In this case, the activity factor γ is given by equation (4),

$$\gamma = \exp\left[\beta(T-T_S)\right] \tag{4}$$

where β (in units of K^{-1}) is an empirical coefficient, and T_S is the standard temperature defined earlier. Guenther et al. (1993) cite many estimates of β, which range from 0.057 to 0.144 K^{-1}. However, half of these values lie within the range 0.090 ±0.015 K^{-1}. A value of 0.09 K^{-1} was used for all vegetation by Guenther et al. (1995), and this value was also used in STOCHEM.

Many of the experimental studies of isoprene and monoterpene emissions from various species of plants have fitted the models of Guenther et al. (1993, 1995) to the data, and obtained quite different values of the coefficients described above (for example, Street et al., 1996; Pier and McDuffie, 1997). In a global model, it is not possible to distinguish many different plant species. The model of Guenther et al. (1995) produces a similar annual global emission to other estimates, although the authors state that the error in their estimate is a factor of 3.

5. Canopy Radiative Transfer Model

When considering emissions of isoprene from vegetation, it is also necessary to calculate the areas of leaves which are lit directly by the sun, and those which lie in the lower part of the canopy and are shaded by leaves higher up. Shaded leaves receive considerably less PAR than the sunlit ones, and hence emit less VOCs (Figure 1(a)). The proportion of sunlit and shaded leaves will also change with time of day, as the sun moves across the sky. The equations used to calculate the astronomical quantities necessary to compute the solar zenith angle, equations (5) - (9), are taken from Iqbal (1983). The solar zenith angle is then used in equations (10) - (14) to calculate the areas of sunlit and shaded leaves. The cosine of the solar zenith angle θ may be calculated from equation (5),

$$\cos\theta = \sin\delta \sin\phi + \cos\delta \cos\phi \cos ha \tag{5}$$

where δ is the solar declination angle (the angle between the sun at solar noon and the plane of the Earth's equator), ϕ is the geographic latitude, and ha is the hour angle, which is zero at noon, and positive in the morning. To calculate the solar declination angle δ, it is first necessary to calculate the day angle, Γ, which is defined in equation (6),

$$\Gamma = 2\pi(d - 1) / 365 \tag{6}$$

where d is the day number, and equals 1 on 1st January and 365 on 31st December. The solar declination angle (in radians) may then be calculated using equation (7),

$$\delta = 0.006918 - 0.399912 \cos\Gamma + 0.070257\sin\Gamma$$
$$- 0.006758 \cos2\Gamma + 0.000907\sin2\Gamma \tag{7}$$

The maximum error in equation (10) is 0.0006^c (Iqbal, 1983). The hour angle ha is calculated using equation (8),

$$ha = 2\pi(0.5 + (UT + E_t) / 1440 + \lambda /360.0) \tag{8}$$

where UT is Universal Time in minutes, λ is the longitude (in degrees) and E_t is the equation of time (in minutes) which accounts for the variation in the solar day throughout the year (Iqbal, 1983). E_t is calculated from the day angle Γ as shown in equation (9). The terms in round brackets represent E_t in radians, and the factor 229.18 converts E_t into minutes.,

$$E_t = 229.18 \times (0.000075 + 0.001868 \cos\Gamma - 0.032077 \sin\Gamma$$
$$- 0.014615 \cos2\Gamma - 0.04089 \sin2\Gamma) \tag{9}$$

The areas of leaves in direct sunlight, and those which are shaded may now be calculated (Guenther et al., 1995). The sunlit portion is calculated using equation (10),

$$LAI_{SUN} = \left[1 - \exp\left(\frac{-0.5 LAI}{\cos\theta} \right) \right] \frac{\cos\theta}{\cos\alpha} \qquad (10)$$

where LAI is the total leaf area index of the vegetated tile, and α is the mean leaf-sun angle. Assuming a spherical leaf angle distribution within the canopy, the mean leaf-sun angle is $60°$. The area of shaded leaves is obtained by simple subtraction,

$$LAI_{SHADE} = LAI - LAI_{SUN} \qquad (11)$$

The flux density of PAR on the sunlit leaves is given by

$$Q_{SUN} = PAR_{DIR} \frac{\cos\alpha}{\cos\theta} + Q_{SHADE} \qquad (12)$$

where PAR_{DIR} is the flux of direct PAR above the canopy, and Q_{SHADE} is defined as

$$Q_{SHADE} = PAR_{DIFF} \exp\left(-0.5 LAI^{0.7} \right) + Q_1 \qquad (13)$$

where PAR_{DIFF} is the flux of diffuse PAR above the canopy. The factor Q_1 appears owing to multiple scattering of direct beam radiation, and is given by equation (14),

$$Q_1 = 0.07 PAR_{DIR} (1.1 - 0.1 LAI) \exp(-\cos\theta) \qquad (14)$$

The canopy can be divided into a number of layers, and equations (10) - (14) evaluated for each layer. However, Guenther et al. (1995) compared two isoprene emission models which had one and five layers respectively, and found a difference between the two of just 5 %. MOSES considers the whole canopy and no layering information is available.

To calculate emission of isoprene, the areas of sunlit and shaded leaves for each vegetated tile are calculated, along with the appropriate fluxes of direct and diffuse PAR received by the leaves, Q_{SUN} and Q_{SHADE}, as defined in equations (12) and (13). These two fluxes are used in place of 'PAR' in equation (2) to calculate the factor C_L for sunlit and shaded leaves ($C_{L,SUN}$ and $C_{L,SHADE}$). The dimensionless activity factor γ is then calculated for each tile using equation (15),

$$\gamma_i = C_T(i) \left[LAI_{SUN}(i) C_{L,SUN}(i) + LAI_{SHADE}(i) C_{L,SHADE}(i) \right] \qquad (15)$$

The total emission from the UM grid cell is obtained by summing the emission fluxes from each tile and weighting them by the fractional area of that tile, as shown in equation (16),

$$F = \sum_{i=1}^{NPFT} \nu_i w_i \varepsilon_i \gamma_i \qquad (16)$$

F is the total VOC flux ($\mu gC\ m^{-2}\ s^{-1}$), v_i is the tile fraction (i.e. the fraction of the area of the grid cell which is occupied by that tile), w_i is the leaf weight and ε_i is the emission factor. The constant NPFT refers to the number of plant functional types, and equals 5; only the first five tiles are vegetated (Table 1). The foliar density D (equation (1)) is not used directly in this calculation.

The total PAR flux is available from the MOSES sub-model, but the individual fluxes of direct and diffuse PAR reaching the surface (PAR_{DIR} and PAR_{DIFF}) are not, and so are obtained from the radiation section of the STOCHEM model. These fluxes are converted to fractions, and multiplied by the total PAR flux. The STOCHEM PAR fluxes are calculated on a 5° x 5° grid. The position of the centre of a UM grid cell on the 5° x 5° grid is found, and the appropriate PAR flux used. No interpolation or re-gridding of the STOCHEM PAR fluxes is performed. The radiation section of STOCHEM also only calculates radiation fluxes up to 660 nm; however, as the STOCHEM fluxes are only used to calculate the fractions of direct and diffuse PAR, this should not present a problem.

6. Results: Emission of Isoprene and Terpenes Calculated in STOCHEM

The above isoprene and monoterpene model was implemented in STOCHEM which was then integrated for two years. Results from both years of the simulation were analysed. This particular integration also used methane emissions from wetlands and rice paddies which were generated interactively at each time step (Gedney and Cox, 2002). The isoprene emissions were also used interactively in the chemistry. The monoterpene emissions react with OH, O_3 and NO_3, but do not affect the levels of these three species.

The calculated isoprene emissions in the first model integration were too high, at about 1000 Tg yr^{-1}. Some plant species do not emit isoprene (Kesselmeier and Staudt, 1999), so the fact that the emission was overestimated is not surprising. The isoprene emission factors were adjusted by multiplying by 0.565 to give a total similar to that calculated by Guenther et al. (1995), who estimated 570 Tg yr^{-1}. The natural hydrocarbon emission model in STOCHEM now calculated annual emissions of isoprene of 565 and 554 Tg yr^{-1} in the first and second years of the integration. Kesselmeier and Staudt (1999) cite other estimates of annual isoprene emissions, which range from 198 Tg yr^{-1} to 574 Tg yr^{-1}. Wang and Shallcross (2000) also implemented a similar model to that of Guenther et al. (1995) into a GCM which contained a land-surface model, and calculated an annual isoprene emission of 601 Tg yr^{-1}. The adjusted values calculated in STOCHEM lie at the upper end of the range of previous estimates.

There have been fewer estimates of the annual global monoterpene emissions. In the present study, values of 133 and 127 Tg yr^{-1} were calculated in the first and second years of the integration; no adjustment to the emission factors has been made. Kesselmeier and Staudt (1999) cite several estimates which range from 144 Tg yr^{-1} to 544 Tg yr^{-1}. The values calculated in the present work lie just outside the lower limit of other estimates.

The latitudinal distribution of the isoprene and monoterpene emissions from the second year of the integration are shown in Figure 2. The only other known plot of the latitudinal variations of these emissions is given by Guenther et al. (1995). The maximum isoprene emissions in STOCHEM occur at the equator, whereas Guenther et al. (1995) predict a maximum at about 5° S. Both models predict isoprene emissions between 20° N and

65° N which are about 3 times smaller than those in the tropics. Overall, the latitudinal distribution of isoprene emissions predicted in STOCHEM and by Guenther et al. (1995) are similar. However, the monoterpene emissions in STOCHEM show only a small variation with latitude, whereas those predicted by Guenther et al. (1995) have a similar pattern to the isoprene emissions. It is not immediately clear why the two models give such different results. Although temperatures in the tropics are greater than those at temperate latitudes, which implies greater emissions, the largest source of monoterpenes are coniferous trees.

The monthly variation in isoprene and monoterpene emissions are shown in Figure 3. The isoprene emissions have two maxima, one in March, and a larger one in August and September, and do not vary by a large amount throughout the year. Guenther et al. (1995) also predict only a small variation in isoprene emissions throughout the year from some ecosystems. The monoterpene emissions change more smoothly throughout the year, with a maximum in September and a minimum in January and February. The variation for this group of species is smoother, as it is only affected by temperature changes.

The annual emissions over the surface of the Earth from the calculations of Guenther et al. (1995), and the new interactive scheme in STOCHEM, are shown in Figures 4 and 5 respectively. Both schemes have maximum emissions from tropical rain forests. The isoprene emissions calculated by Guenther et al. (1995) are greatest from Amazonia, whereas those calculated by the new scheme are more evenly spread over all regions of tropical forest. The interactive scheme has increased emissions from southern parts of the USA and Central America, and also from India and Australia. Both data sets predict a small isoprene emission from vegetation in Europe, Asia and North America.

7. Emission of Ethene and Propene

Plants emit a large number of other VOCs as well as isoprene and monoterpenes, including many hydrocarbons and a range of oxygenated compounds (Winer et al., 1992). There have been few measurements of emissions of other VOCs by plants, and correspondingly few estimates of natural emissions of these compounds. In most cases, only an estimate of total 'OVOC' (Other volatile organic compounds) or 'ORVOC' (Other reactive volatile organic compounds) is given, usually in $TgC\ yr^{-1}$, and no information on speciation is supplied. In this section, estimates of the magnitudes of the ethene and propene emissions by plants are reviewed and recommended values for STOCHEM are given. The emissions are distributed using fields of monthly ORVOC emissions from Guenther et al. (1995).

Ehhalt and Rudolph (1984) estimate the biogenic source of ethene to be $1\ Tg\ yr^{-1}$, but do not indicate how they obtained this value. Sawada and Totsuka (1986) used measurements of ethene emissions per unit biomass, and estimates of total biomass in 14 different ecosystems to derive a global source of $17 - 29\ Tg\ yr^{-1}$. Singh and Zimmerman (1992) reviewed the sources and sinks of many NMHCs. They state that both ethene and propene have biogenic sources, but only give a total flux from all sources. They also state that combustion is the principal source of propene. From their data, an upper limit on the biogenic source of propene of $4\ Tg\ yr^{-1}$ may be estimated.

Goldstein et al. (1996) measured ethene and propene emissions from a deciduous forest in Massachusetts, and obtained 24 hour averaged fluxes of 2.63×10^{10} and 1.13×10^{10} molecules $cm^{-2} s^{-1}$ respectively. These fluxes were linearly correlated with levels of PAR, indicating a photosynthetic source. Using these fluxes, and the ecosystem areas tabulated by Sawada and Totsuka (1986), global biogenic sources for ethene and propene of 21.0 and 11.9 Tg yr^{-1} respectively may be calculated. This value is similar to the estimates of Hough (1991) and Sawada and Totsuka (1986) (Table 3). The ethene and propene fluxes listed by Poisson et al. (2000), 11.8 and 7.7 Tg yr^{-1} respectively, are lower than many of the estimates discussed above, and it is not clear how these values were calculated.

All known estimates of the global fluxes of ethene and propene from vegetation are summarised in Table 3. Given the lack of data these estimates are subject to large uncertainties. However, the magnitudes of the emission fluxes are comparable with if not larger than the anthropogenic sources. For STOCHEM, the emission fluxes calculated using the data from Sawada and Totsuka (1986) and Goldstein et al. (1996) are recommended; an ethene flux of 21 Tg yr^{-1} and a propene flux of 11.9 Tg yr^{-1}. There are a few data which indicate that ethene and propene are released by soils (Warneck (1999) and references therein). Fluxes from soils are estimated as 3.3 and 0.9 Tg yr^{-1} for ethene and propene respectively (Warneck, 1999). The flux of propene from soils is negligible, but the ethene flux is of similar size to that produced from biomass burning, and so may be important.

Table 3. Estimates of global emissions of ethene and propene from vegetation[a].

Ethene	Propene	Reference
1	-	Ehhalt and Rudolph (1984)
23.3[b]	-	Sawada & Totsuka (1986)
20	20	Hough (1991)
5	1	Müller and Brasseur (1995)
21.0[c]	11.9[d]	Goldstein et al. (1996)
11.8	7.7	Poisson et al. (2000)

[a]Units are Tg yr^{-1}.
[b]Mean value given by authors. Range quoted is 16.6 - 29.0 Tg yr^{-1}.
[c]Calculated using ecosystem areas given by Sawada and Totsuka (1986), a growing season of 184 days (May - October; Goldstein et al., 1996), and the flux measured by Goldstein et al. (1996) given in the text.
[d]Derived from ethene flux using ethene : propene flux ratio of 1.76 (Goldstein et al., 1996).

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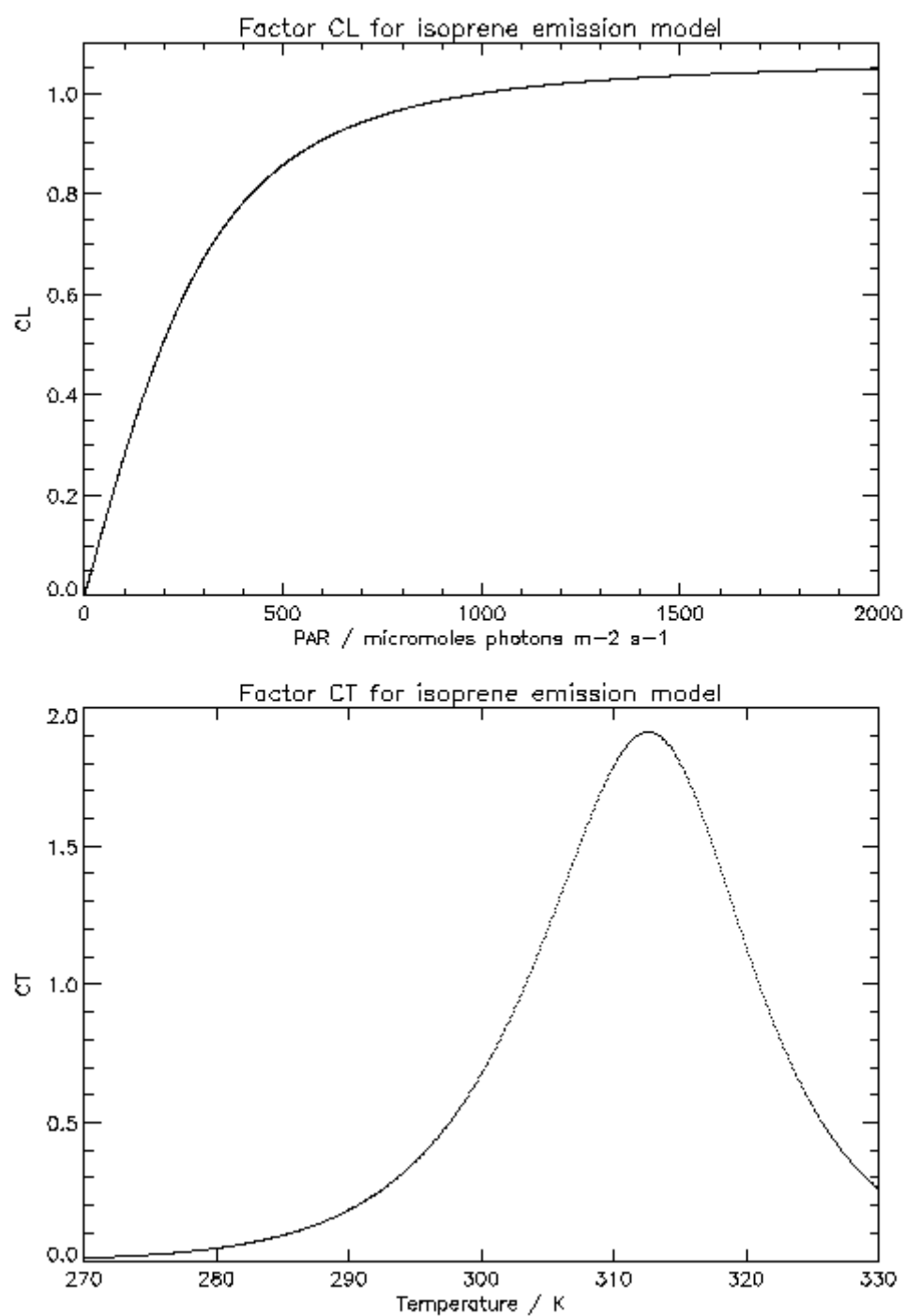
Figure 1. (a) Normalised isoprene emission rate (C_L) as a function of PAR; (b) normalised emission rate (C_T) as a function of leaf temperature.
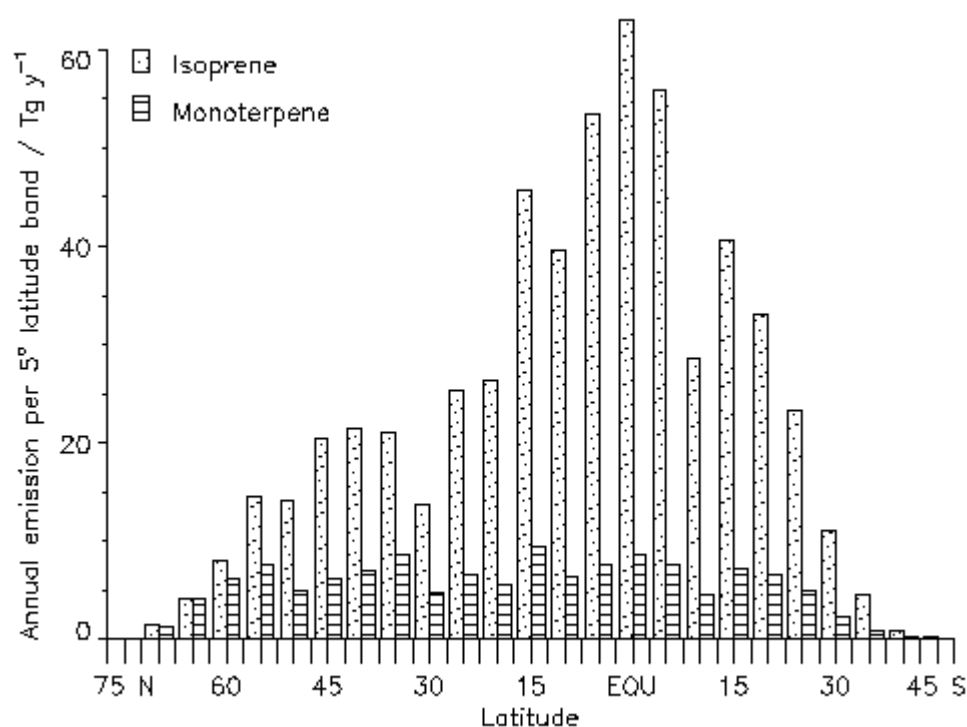
Figure 2. Latitudinal variations of isoprene and monoterpene emissions generated in STOCHEM.
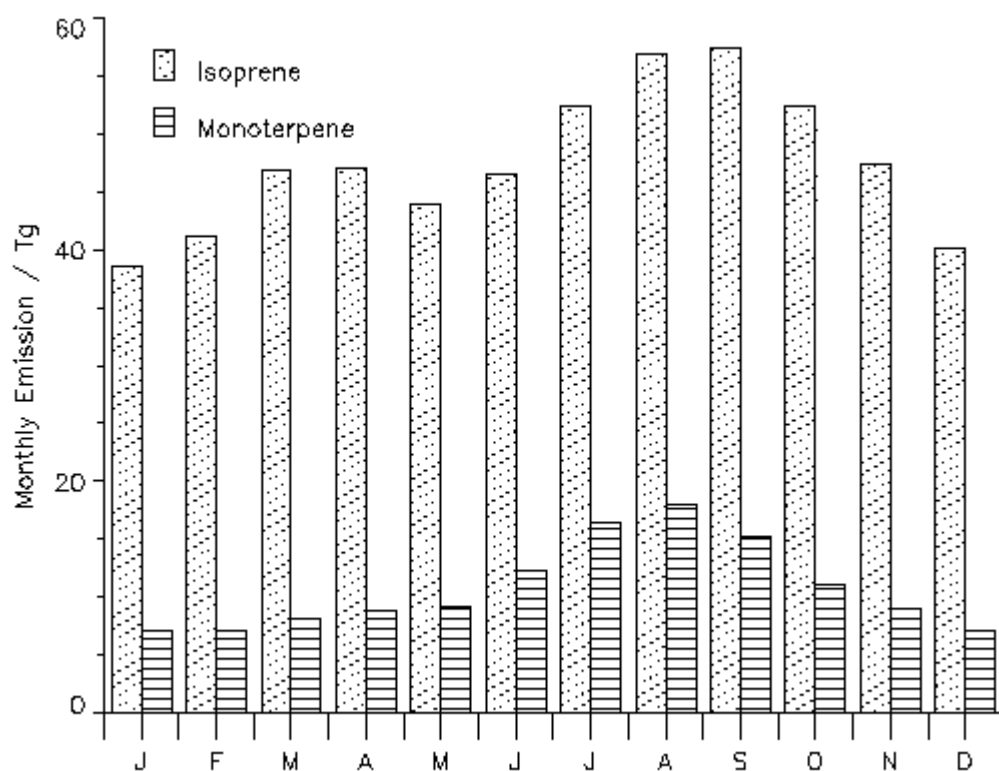

Figure 3. Monthly isoprene and monoterpene emissions generated in STOCHEM. The annual totals are 570 Tg yr^{-1} for isoprene and 133 Tg yr^{-1} for monoterpenes.
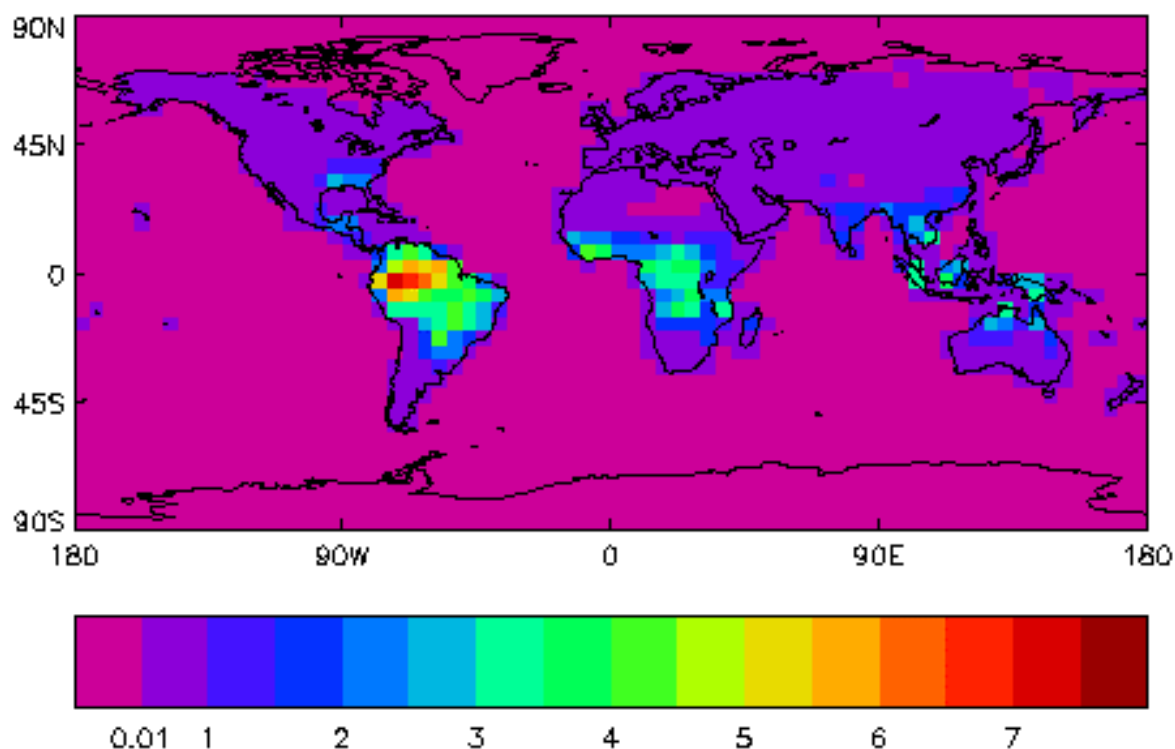
Figure 4. Annual isoprene emissions in Tg yr^{-1} from model of Guenther et al. (1995), as originally used in STOCHEM. The total is 521 Tg yr^{-1}.
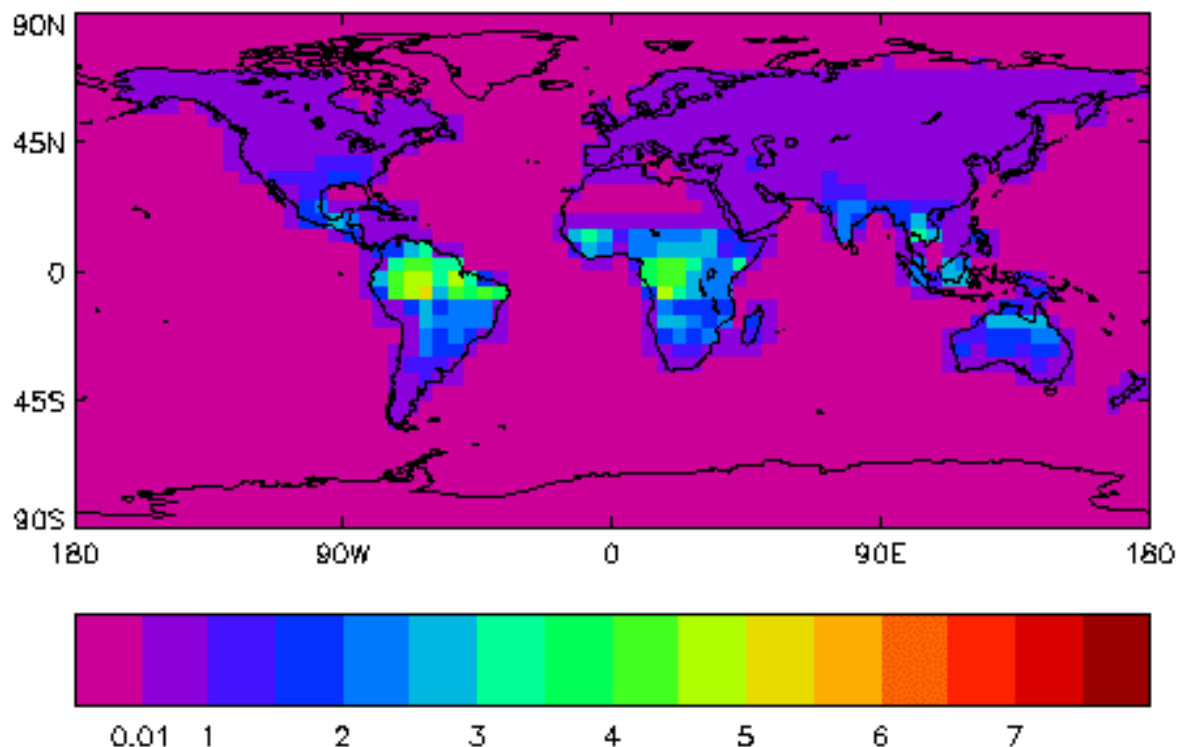

Figure 5. Annual isoprene emissions in Tg yr^{-1} from new interactive scheme in STOCHEM, based on model of Guenther et al. (1995) but using MOSES 2.2 surface types. The annual total is 570 Tg yr^{-1}.