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Permalink
https://escholarship.org/uc/item/8dd368hb

Journal
EARTH INTERACTIONS, 10(3)

ISSN
1087-3562

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Publication Date
2006

DOI
10.1175/EI174.1

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Peer reviewed
Future Changes in Biogenic Isoprene Emissions: How Might They Affect Regional and Global Atmospheric Chemistry?

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Received 31 August 2005; accepted 18 November 2005

ABSTRACT: Isoprene is emitted from vegetation to the atmosphere in significant quantities, and it plays an important role in the reactions that control tropospheric oxidant concentrations. As future climatic and land-cover changes occur, the spatial and temporal variations, as well as the magnitude of these biogenic isoprene emissions, are expected to change. This paper presents a study of the change in biogenic isoprene emissions that would result from both anthropogenic land-cover and climate-driven changes. Annual global isoprene

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emissions were estimated to be 522 Tg yr\(^{-1}\) under current climatological and land-cover conditions. When climate-driven land-cover changes are predicted, but climate does not change, total global emissions did not change significantly, although regional impacts were important. However, the use of future temperature and land-cover drivers to estimate isoprene emissions produced a global estimate of 889 Tg yr\(^{-1}\). Anthropogenic land-cover changes, such as urbanization and changes of natural vegetation to plantation forests, can also have substantial impacts on isoprene emissions (i.e., up to 717 Tg yr\(^{-1}\), a 37% increase, when land-cover changes but temperature remains at current-day values). The Model for Ozone and Related Tracers, version 2 (MOZART-2) was run with the different isoprene emission scenarios to simulate the potential changes in global atmospheric chemical composition. The simulated regional surface ozone concentrations changed as much as −9 to 55 ppbv under certain emission and climate scenarios. These results were used to evaluate changes in the ozone production chemistry under different emission scenarios. As expected, the impacts of changing isoprene emissions are regionally dependent, with large changes in China, the Amazon, and the United States.

KEYWORDS: Isoprene emissions; Land-cover change; Ozone production

1. Introduction

Biogenic emissions, including volatile organic compounds (VOCs) and particulate matter (PM), play an important role in regional air quality processes and global atmospheric chemistry. Isoprene (C\(_5\)H\(_8\)) is the predominant VOC emitted by vegetation. This compound is very reactive in the atmosphere and contributes to the reactions that control the concentrations and lifetimes of longer-lived species. In certain regions, it has been shown that isoprene plays a key role in the reactions that form tropospheric ozone (O\(_3\)), which is both a pollutant and a greenhouse gas (e.g., Chameides et al. 1988; Fehsenfeld et al. 1992; Pierce et al. 1998). Ozone formation, however, is nonlinear. The collocation of anthropogenic sources of oxides of nitrogen (NO\(_x\)) with biogenic sources of reactive VOC (particularly isoprene) can generate large amounts of tropospheric O\(_3\), whereas biogenic sources located in areas without the presence of anthropogenic NO\(_x\) will not (Ryerson et al. 2001) and can, in some instances, reduce O\(_3\) concentrations (e.g., Fiore et al. 2005; von Kuhlmann et al. 2004).

Biogenic emissions of isoprene are controlled by environmental variables, most notably temperature and light. The quantity of isoprene emissions is also dependent on the type of land cover (i.e., grassland, forest, shrubland) and the species of the vegetation within those land covers. High isoprene emission potentials are confined to roughly one-third of woody tree species and are much less common in crops and grasses (e.g., Guenther et al. 1995). It is therefore expected that future biogenic isoprene emissions will change as climate and land cover changes. For example, increases in temperatures will lead to increased isoprene emissions. Also, as forested areas are converted to croplands, savannahs, and grasslands, isoprene emissions in those regions are expected to decrease. Potential changes and impacts of biogenic isoprene emissions must be considered as we evaluate potential future climate and chemistry scenarios to better understand the drivers and impacts and to design pollution control strategies. Currently, the Intergovernmental Panel on
Climate Change (IPCC) does not include future projections of isoprene in their modeling scenarios. However, it is well recognized that these emissions are important and should be included in coupled climate and chemistry simulations (Prather and Ehhalt 2001).

We know that isoprene emissions are likely to change in future years, but predicting the magnitude and spatial distribution of these changes with any certainty is quite challenging. We can look at the sensitivity of global emissions and chemistry to changes in the driving variables to gain a better understanding of the importance of the emissions in future years. The aim of this research is to better understand the differences in isoprene emissions that may occur as the result of changes in climate and land cover. We have performed a study to evaluate the sensitivity of total global isoprene emissions to anthropogenic and climate-driven land-cover changes. We investigate the impact of these changes on atmospheric chemistry, particularly surface $O_3$ concentrations, using a global chemical transport model. By assessing the sensitivity of $O_3$ formation to changes in the concentrations of VOCs, we can address the importance of future isoprene emission scenarios on air quality and discuss the implications in designing future $O_3$ abatement strategies. We understand that these estimates of potential emission scenarios are highly uncertain, but present these results to show the importance of possible changes. To investigate the emissions of isoprene under future land-cover and climate scenarios, we used a series of offline models to simulate changes in vegetation, isoprene emissions, and atmospheric chemistry.

### 2. Estimation of isoprene emissions

Emissions of isoprene were modeled based on the algorithms developed by Guenther et al. (Guenther et al. 1995). The flux (mgC m$^{-2}$ ground h$^{-1}$) of isoprene from vegetation was estimated with the following equation:

$$\text{Flux} = DE \gamma,$$

where $D$ is the vegetation density (g dry mass m$^{-2}$ ground); $E$ is an emission factor ($\mu$gC g$^{-1}$ dry mass h$^{-1}$), or the rate at which isoprene is emitted under some standardized set of conditions; and $\gamma$ is an activity factor that takes into account the effects of environmental variables, such as temperature and photosynthetically active radiation (PAR) (Guenther et al. 1995). Generally, isoprene emissions increase with increasing temperatures and PAR up to a saturation point. Foliar density is equivalent to the product of the leaf area index (LAI; m$^2$ leaf m$^{-2}$ ground) and average specific leaf mass (SLM; g dry mass m$^{-2}$ leaf). Emission factors are assigned to different land-cover classifications based on the type of vegetation expected within each class. A global emissions inventory developed by Guenther et al. (Guenther et al. 1995) was used for our base case (hereafter called BASE). This emissions inventory is commonly used by global modelers (e.g., Horowitz et al. 2003) and is part of the inventories of the Global Emissions Inventory Activity (GEIA; available online at http://www.geiacenter.org). The uncertainties associated with the BASE case can be quite large (up to a factor of 3 in some regions) (Guenther et al. 1995).

Maps of the spatial distribution of natural land cover from the Mapped Atmo-
sphere–Plant–Soil System (MAPSS) model (Neilson 1995) were used to investigate the impact of climate-driven changes on isoprene emissions. MAPSS is a biogeographic model that simulates the distribution of 45 different vegetation types using input climate drivers, including temperature, precipitation, and radiation. We used the output from one MAPSS model run for our study: a future run, which used a mean climate for 2070–99 predicted by the Hadley HADCM2SUL global circulation model (GCM) (e.g., Kattenberg et al. 1996; Neilson and Drapek 1998). The HADCM2SUL GCM simulation has a global temperature increase of 1.7°C at the time of CO₂ doubling, with the largest increases in temperatures at latitudes between −20° and 20°N and at latitudes greater than 50°N (Neilson and Drapek 1998; Kattenberg et al. 1996). The future vegetation map represents simulated vegetation under an approximate doubling of atmospheric CO₂ concentrations and associated climate. The vegetation map had a 0.5° × 0.5° spatial resolution and showed natural vegetation only: agriculture and other managed land uses were not identified with this model output. Differences between the MAPSS land-cover map and the land-cover data used by Guenther et al. (Guenther et al. 1995) for our BASE scenario were observed globally: the differences were not only due to the fact that MAPSS only includes natural vegetation, but also changes in the MAPSS land cover driven by a future climate.

Two isoprene emission scenarios were estimated with the MAPSS output vegetation map. These were selected to evaluate the impact of changes in temperatures and the spatial distribution of vegetation on isoprene emissions. For both scenarios, isoprene emission factors were assigned to each of the 45 MAPSS land-cover categories. The first scenario used the future MAPSS vegetation map and current temperatures (1990–2000) to simulate global isoprene emissions (hereafter called FUTVEG-CURCLIM). The second emissions scenario (hereafter called FUTVEG-FUTCLIM) was produced with the future MAPSS vegetation map and the average monthly temperatures (from 2070 to 2099) from the Hadley HADCM2SUL GCM. Only land cover and temperature were changed in these emission scenarios, and all other input variables were kept constant.

In future years, anthropogenic influences, including urbanization and agriculture, are expected to have a large impact on land-use and vegetation coverage. To investigate the impact of anthropogenic land-cover change on isoprene emissions, we investigated two different land-use change scenarios. The first is the replacement of natural forested areas with urban, suburban, and pasture landscapes, which often results in a decrease in regional isoprene emissions. The second circumstance investigated was the replacement of natural vegetation with large-scale tree plantations, which is occurring worldwide. Many of the plantation tree species used throughout the globe, including Populus (poplar), Eucalyptus, and Elaeis (oil palm), are high isoprene emitters. Thus, replacement of natural vegetation with plantations often results in elevated regional isoprene emissions. We simulated these types of changes in two regions in the world where the potential for such land uses exists, but where the implications for atmospheric chemistry may differ: the United States and the Amazon basin. In the United States, there are large sources of nitrogen oxides (NOₓ) and higher background O₃ concentrations, as compared to the Amazon, which is considered more pristine and has lower O₃ and NOₓ background concentrations.

For the first emissions scenario (hereafter called URB), we assumed that 50%
of the current land area in the southeastern United States, and 50% of the current land area in the Amazon basin, was replaced by urban and pasture landscapes. Both of these areas currently have substantial forests with the potential for large land-use changes. Large areas throughout the southeastern United States have been converted from natural pine and hardwood forests to urban and suburban landscapes, and this is expected to continue in future years as the population grows and more people move into urban areas (e.g., Theobald 2005). In the Amazon basin, the natural forest is being replaced by pastures used for cattle grazing and by cropland. To calculate the emissions for URB, 50% of the isoprene emissions in the BASE scenario were reduced by a factor of 8 in large areas of the southeastern United States and the Amazon. This represents the change in isoprene emissions that would result from converting the natural forests in the regions, which are moderately high isoprene-emitting land covers [with isoprene emissions on the order of 24 \( \mu g C g^{-1} h^{-1} \) (e.g., Guenther et al. 1995)], to pasture, cropland, and urban land uses, which have lower isoprene emission potential [isoprene emission factors on the order of 3 (0 to 8) \( \mu g C g^{-1} h^{-1} \) (e.g., Guenther et al. 1995)]. This change assumes a factor of 8 reduction in the number of trees in these regions and no change in the percentage of trees that are isoprene emitters.

In the second scenario (hereafter called PLANT), we assumed that 25% of the current land area in the western United States was replaced by poplar (\textit{Populus}) plantations, and 25% of the current land area in the Amazon was replaced by oil palm (\textit{Elaeis guineensis}) and \textit{Eucalyptus} plantations. Throughout the United States, poplar plantations that are grown for pulp production have increased in number and size. Alig et al. (Alig et al. 2000) used an economic agricultural model to show that future U.S. poplar plantations will likely be concentrated in the Pacific Northwest. We have chosen a scenario where the maximum potential land area in this region is covered with poplar plantations. For the PLANT scenario, 25% of the isoprene emissions of the BASE emissions in the northwestern United States were increased by a factor of 32. This estimated increase is based on the replacement of natural land cover, with an emission factor of about 0.53 mg m\(^{-2}\) h\(^{-1}\) (Guenther et al. 2000), with poplar plantations that have an emission factor of about 17 mg m\(^{-2}\) h\(^{-1}\) (Guenther et al. 2000).

Also in the PLANT scenario, 50% of the isoprene emissions of BASE in the Amazon were increased by a factor of 4 to represent the replacement of natural forests with oil palm and eucalyptus plantations. Forest plantations cover approximately \(6 \times 10^6\) ha in Brazil, and \textit{Eucalyptus} accounts for 59% of this area (see FAO Web site at http://www.fao.org/forestry/site/23747/en/bra). The increase assigned to the Amazon is based on replacing forested areas that have 25% isoprene-emitting trees with a plantation that is 100% isoprene-emitting trees. The much larger increase applied for the northwestern United States is the combination of a factor of 8 increase in the number of trees, due to the replacement of open shrubland and cropland with plantations, and a factor of 4 increase in the percentage of trees that emit isoprene (from 25% to 100%). We recognize that these anthropogenically driven land-cover changes were chosen arbitrarily and may not be realistic. However, these potential changes in different areas of the world allow for an evaluation of the importance of land-use change. We investigate only the impact of land-use change on the emissions, and so these cases are driven by current (1990–2000) meteorological inputs.
The BASE, URB, and PLANT scenarios were estimated using land-cover maps that include urban and agriculture land uses. The FUTVEG-CURCLIM and the FUTVEG-FUTCLIM scenarios are based on natural vegetation only. A summary of the global isoprene emissions predicted under each of these scenarios is shown in Table 1.

3. Estimated isoprene emissions scenarios

Emissions of biogenic isoprene were estimated for each of the five scenarios (Table 1). The annual global emissions predicted for FUTVEG-CURCLIM were increased by only 1% from the BASE estimate. When both temperature and natural vegetation are changed (FUTVEG-FUTCLIM), a large increase in global isoprene emissions was observed (+70%). Figure 1 shows the changes from the BASE isoprene emissions that were simulated with the natural vegetation and climate drivers. When only land cover is changed (FUTVEG-CURCLIM), regional changes in isoprene emissions were observed (Figure 1b). The largest decreases in isoprene emissions were in South America, northern Australia, India, and the south-central United States where natural forests that have high isoprene emissions were replaced by shrubs, savannas, and grasslands, which have much lower emissions. Small increases in isoprene emissions were simulated in China, India, Europe, and the northeastern United States, where forested vegetation types replaced areas with low-emitting vegetation.

When future temperature was changed with natural land cover (FUTVEG-FUTCLIM), biogenic isoprene emissions were increased in most regions, with the exception of northern Australia, central South America, and the central United States (Figure 1c). Although in some localities, land-cover change alone caused a reduction in isoprene emissions, increases in temperature had a larger overall effect.

Figure 2 shows the differences in isoprene emissions of URB and PLANT from the BASE case. Even regional anthropogenic changes in land cover (URB and PLANT) changed the total global isoprene emission substantially (−9 and +37%, respectively). The changes in emissions occurred only in the areas where we applied the anthropogenic land-cover conversions.

4. Chemical modeling

In this study, we used a global chemistry transport model [Model for Ozone and Related Chemical Tracers, version 2 (MOZART-2)] to assess the impacts of the

| Name         | Input temperature | Land-cover scenario                              | Isoprene (Tg yr⁻¹) | Percent change from BASE |
|--------------|-------------------|-------------------------------------------------|--------------------|--------------------------|
| BASE         | Current           | Current (based on Guenther et al. 1995)         | 522                |                          |
| FUTVEG-CURCLIM| Current           | Future MAPSS                                    | 529                | 1                        |
| FUTVEG-FUTCLIM| Future           | Future MAPSS                                    | 889                | 70                       |
| URB          | Current           | Pasture/urban replace natural vegetation        | 475                | –9                       |
| PLANT        | Current           | Plantations replace natural vegetation         | 717                | 37                       |
changes in biogenic isoprene emissions on tropospheric oxidant concentrations. MOZART-2 was developed at the National Center for Atmospheric Research (NCAR) together with the National Oceanic and Atmospheric Administration (NOAA) Geophysical Fluid Dynamics Laboratory (Princeton, New Jersey) and the
Max Planck Institute for Meteorology (Hamburg, Germany). This model simulates the distribution of tropospheric ozone and its chemical precursors. In its standard configuration, MOZART-2 calculates the concentrations of 63 chemical species from the surface up to the middle stratosphere. The model is described by Horowitz et al. (Horowitz et al. 2003), who provide an extensive evaluation of MOZART-2, including a comparison of calculated concentrations with CMDL surface measurements (CO and O₃), global O₃ sonde data, and measurements from aircraft (O₃, CO, NOₓ, PAN, HNO₃, various nonmethane hydrocarbons, CH₂O, etc.). In this study, the hydrocarbon chemistry in the model is updated from the version of Horowitz et al. (Horowitz et al. 2003). The primary changes are that more hydrocarbon species are added in the chemistry scheme, such as toluene (C₇H₈), C₅H₁₂, and C₄H₈.

MOZART-2 is developed in the framework of the transport model MATCH (Model of Atmospheric Transport and Chemistry) (Rasch et al. 1997), which includes a representation of advection, convective transport, boundary layer mixing, and wet and dry deposition. Surface emissions of chemical species include those from fossil fuel and industrial activity, biomass burning, biogenic emissions.
from vegetation and soils, aircraft emissions, lightning, and oceanic emissions. The chemical scheme used in MOZART-2 accounts for the oxidation of ethane, propane, propene, isoprene, \( \alpha \)-pinene (as a surrogate for all terpenes), and n-butane (as a surrogate for all hydrocarbons with four or more carbons, excluding isoprene and terpenes). Heterogeneous reactions of \( \text{N}_2\text{O}_5 \) and \( \text{NO}_3 \) on sulfate aerosols are included, using prescribed sulfate aerosol distribution (Tie et al. 2001). Photolysis frequencies are determined using a precalculated “lookup” table (Brasseur et al. 1998).

In this study, each of the different isoprene emission scenarios was input and run for a 1-yr period with the MOZART-2 model. All inputs to the model other than isoprene emissions, including anthropogenic emissions and meteorology, were kept constant. The MOZART-2 simulations were driven by the NCAR Community Climate Model, version 2 (CCM2). These drivers provided meteorology and climate representative of current conditions (1990–2000). The MOZART-2 simulations were run at the T42 configuration, with a horizontal grid resolution of approximately 2.8° by 2.8°. Isoprene emissions from the MAPSS scenarios were created with a 0.5° resolution and the BASE emission inventory at 1°. Both were averaged over each MOZART model grid. The URB and PLANT scenarios were created directly by scaling the BASE emissions at the MOZART grid resolution.

5. Chemical model output

Each emissions scenario was run with the MOZART-2 model for a 1-yr period, and the monthly averaged results for July are presented here. The month of July has been chosen as the focus of this discussion since it represents the peak of the ozone season in the Northern Hemisphere. Although the total global isoprene emissions in the FUTVEG-CURCLIM scenario did not change significantly from the BASE (Table 1), the changes in emissions had a significant impact on regional \( \text{O}_3 \) surface concentrations. For the month of July, differences in surface \( \text{O}_3 \) concentrations ranged from \(-6\) to 39 ppbv (Figure 3). Thus, regional changes in isoprene emissions driven only by land-cover changes can alter \( \text{O}_3 \) chemistry. The \( \text{O}_3 \) concentrations simulated with FUTVEG-FUTCLIM isoprene emissions differed more notably from the BASE simulation. For July, the differences in monthly averaged surface \( \text{O}_3 \) concentrations ranged from \(-9\) ppbv to 52 ppbv (Figure 3). In this case, monthly averaged \( \text{O}_3 \) concentrations for July were decreased as much as 25% in some areas (southern China, Indonesia, central Africa, and Brazil) and increased as much as 95% in other areas (Europe and northeastern China).

The FUTVEG-FUTCLIM scenario included large increases in isoprene emissions in the Amazon and central Africa and a subsequent reduction of \( \text{O}_3 \) concentrations, similar to what was shown by von Kuhlmann et al. (von Kuhlmann et al. 2004) in the Amazon. Ozone was reduced in these regions when isoprene was increased because \( \text{O}_3 \) reacts with the available isoprene and is not regenerated due to a lack of \( \text{NO}_x \). This effect was enhanced in the Amazon, where there are reduced levels of OH, which leads to longer lifetimes of isoprene, and thus higher concentrations. In Asia, isoprene emissions were predicted to increase by the FUTVEG-FUTCLIM scenario. However, the modeled \( \text{O}_3 \) concentrations in southern China decreased, despite the fact that this is an area with relatively high
anthropogenic emissions of VOC and NO\textsubscript{x}. The decrease also occurred as a result of isoprene–O\textsubscript{3} reactions, since the modeled O\textsubscript{3} chemistry in the region is NO\textsubscript{x} limited and less sensitive to changes in VOC concentrations (Tie et al. 2005, manuscript submitted to Atmos. Environ.). Kang et al. (Kang et al. 2003) also have shown that in some regions, VOC increases can cause a reduction in O\textsubscript{3} production due to increased reactions with NO\textsubscript{2} that produce stable organic nitrogen compounds that result in a reduction of available NO\textsubscript{x}. It should be noted that anthropogenic NO\textsubscript{x} emissions were kept constant in our simulations, although these emissions, particularly in Asia, are expected to increase in future years.

Figure 4 shows the difference in modeled O\textsubscript{3} concentrations between the URB and PLANT cases and the BASE case. Because the emission changes were more localized in these scenarios, the changes in O\textsubscript{3} concentrations for these simulations were not as spatially extensive as those from the model simulations when the isoprene emissions were changed globally. The changes in surface O\textsubscript{3} concentrations with the reduction of isoprene emissions (URB scenario) were relatively small: decreases as much as \(-4\) ppb in the southeastern United States and an increase of up to \(4\) ppbv in the Amazon. Ozone was decreased in the southeastern
United States when isoprene emissions were decreased because, in this region, the 
O_3 chemistry is sensitive to both NO_x and VOC concentrations (see next section). 
Since there are NO_x sources in this region, reductions in isoprene here result in a 
reduction in the O_3 production. These results differ from those reported by Fiore 
et al. (Fiore et al. 2005) who show a reduction in isoprene emissions and a 
corresponding increase, although small, in simulated surface layer O_3 concentrations 
in the southeastern United States. The discrepancies between the two studies 
are primarily the result of varying emissions inputs, meteorological drivers, and 
chemical mechanisms. However, in both studies, changes in isoprene emissions 
did not have a substantial impact on the simulated O_3 concentrations.

By removing isoprene emissions in the Amazon (URB scenario), an increase in 
O_3 concentration was observed. In this region, ozonolysis of isoprene is a sink for 
O_3; therefore, when isoprene is removed, O_3 is not removed as efficiently and 
concentrations are higher. Similar results were reported by von Kuhlmann et al. 
(von Kuhlmann et al. 2004).

The PLANT scenario led to decreases in monthly averaged (July) surface O_3 
concentrations up to 7 ppbv in the Amazon and in the Pacific Northwest. However, 
increases as much as 24 ppbv O_3 were simulated in the southwestern United States.
and the Baja region of Mexico. As mentioned above, isoprene reactions with O$_3$ in the Amazon act as a sink for O$_3$. As isoprene emissions increase in this region, more O$_3$ is destroyed and average surface concentrations are lowered. In the northwestern United States, a similar situation exists. However, in the southwestern United States and Baja Mexico, more NO$_x$ is available and the O$_3$ chemistry is highly sensitive to changes in VOC concentrations (see next section). Therefore, as isoprene concentrations were increased, O$_3$ concentrations increased significantly. Note that regional changes in emissions can have very localized impacts.

6. Ozone chemistry

The sensitivity of the modeled O$_3$ chemistry to changes in isoprene emissions was investigated using methods explained by Kleinman et al. (Kleinman et al. 1997; Kleinman et al. 2001), who present a method to evaluate the sensitivity of O$_3$ production to changes in NO$_x$ and VOC concentrations by looking at different radical loss pathways. The assumption is

$$Q = L_N + L_R,$$

where $Q$ is the sum of all radical sinks, $L_N$ is the loss of radicals from reactions with NO and NO$_2$, and $L_R$ is the loss rate of free radicals from radical–radical reactions. Kleinman et al. (Kleinman et al. 1997) show that O$_3$ production is dependent on the ratio $L_N/Q$ and that when this ratio is less than 0.5, the O$_3$ production is more sensitive to NO$_x$. When the ratio is more than 0.5, the O$_3$ production is sensitive to changes in VOC concentrations. This sensitivity is important in some regions when designing pollution control strategies: knowing the sensitivity of the O$_3$ production in an area can provide guidance to the most effective control strategies (NO$_x$ controls, VOC controls, or a combination of both). We applied this methodology to our global model outputs to identify regions where the O$_3$ production changes under different emission scenarios.

For our evaluation, we assumed that peroxy acetyl nitrate (PAN) was in equilibrium and was neither a source nor a sink for radicals. Also, we assumed that the primary loss of radicals to reactions with NO$_x$ was with the reaction of NO$_2$ with OH, so that $L_N = k(\text{OH})(\text{NO}_2)$. Following Kleinman et al. (Kleinman et al. 1997), we assume that $L_R$ is dominated by the loss of radicals due to the production of H$_2$O$_2$ and organic peroxides, and that the loss of radicals to all other radical–radical reactions, including OH+HO$_2$, was inconsequential. Therefore,

$$L_R = \sum_i k_i [\text{RO}_2][\text{HO}_2] + 2k_3[\text{HO}_2]^2.$$  \hspace{1cm} (3)

We used the 11 most important RO$_2$–HO$_2$ reactions within the MOZART chemical mechanism to calculate the first term in the equation for $L_R$. With these assumptions, we calculated $L_N/Q$ from the monthly averaged output of MOZART for each scenario.

Figure 5 shows the ratios $L_N/Q$ for the BASE case. As shown, the ratio was less than 0.5 (NO$_x$ limited) over most of the globe. However, there are areas where the O$_3$ chemistry was sensitive to both VOC and NO$_x$, or predominantly VOC (e.g.,
areas within Europe and the United States). Based on this map, areas identified with green have NO$_x$ sensitive O$_3$ formation under current land use and climate. In these regions, controls on sources of NO$_x$ would be most effective at controlling elevated O$_3$ concentrations. Those areas in pink have VOC-limited O$_3$ production, and controls of VOC emissions in these regions would be most effective at controlling O$_3$ production. The transitional areas (with ratios 0.4–0.6) can use a combined control strategy to have effective reduction of O$_3$. Monthly averaged concentrations simulated by MOZART were applied for these calculations. This type of analysis should be completed with output from shorter time scales, as the O$_3$ production chemistry changes during the course of a day. However, our global monthly averaged results are shown here as a general indicator of the overall chemistry.

We looked at how these sensitivities would change if the emissions of isoprene change according to the scenarios we put forth. A comparison of calculated $L_n/Q$ between the BASE case and the FUTVEG scenarios revealed regional changes in $L_n/Q$ resulting from changes in natural vegetation only and resulting isoprene emissions (for the month of July). Changes in isoprene emissions due to future land-cover mapping only (FUTVEG-CURCLIM) and changes in land cover and temperature (FUTVEG-FUTCLIM) led to varied responses in the global map of $L_n/Q$. The most significant changes occurred in Europe, Asia, and the northeastern United States, where the ratio was reduced, and O$_3$ formation became less sensitive to changes in VOC concentrations and more sensitive to changes in NO$_x$. The opposite happened in a small area of northern Australia, where both emission scenarios predicted a reduction in isoprene emissions. It is important to note that the most substantial changes in O$_3$ production chemistry was predicted to occur in populated regions of the world.

For the URB and PLANT scenarios, the change in O$_3$ formation sensitivity was localized to the areas in which we assigned anthropogenic land-cover changes, and
those changes were relatively small. In both cases, the change in the O\textsubscript{3} production sensitivity in the Amazon was less than 0.05. In the Amazon, NO\textsubscript{x} concentrations are generally low. Because the O\textsubscript{3} chemistry is greatly limited by NO\textsubscript{x} concentrations, large changes in isoprene concentrations in either direction did not have an impact. However, when isoprene emissions were reduced in the southeastern United States (replacing natural vegetation with urban and suburban landscapes), \(L_{N/Q}\) was increased as much as 0.13, and the O\textsubscript{3} chemistry became more sensitive to changes in VOC concentrations. When isoprene emissions were increased in the western United States due to increased plantation area (URB), the O\textsubscript{3} production became more sensitive to NO\textsubscript{x} concentrations, with \(L_{N/Q}\) reduced as much as 0.61. However, since the coast of southern California and northwestern Mexico is highly VOC limited, the reduction in \(L_{N/Q}\) did not have a significant impact on the O\textsubscript{3} production, which remained highly sensitive to increases in isoprene emissions.

### 7. Discussion

In our modeling exercise, we used well-established algorithms that simulate the immediate light and temperature dependence of isoprene emissions (Guenther et al. 1993; Guenther et al. 1995). Rosenstiel et al. (Rosenstiel et al. 2003) recently suggested that leaf-level isoprene emissions may be repressed under elevated ambient CO\textsubscript{2} concentrations. However, the canopy-scale responses to increased CO\textsubscript{2} are not known, including potential variations associated with changes in plant species composition. Increases in CO\textsubscript{2} concentrations are expected to increase vegetation density and LAI, which will directly increase isoprene emissions in some forests. However, since isoprene emission from vegetation is light dependent, increases in LAI can prevent light from reaching lower canopies, thus reducing the emissions per unit LAI. Isoprene emission response to increased CO\textsubscript{2} was not included in our model simulations, since algorithms that describe this dependence are unavailable. Regardless, the direct and indirect effects of increased atmospheric CO\textsubscript{2} concentrations should be considered when looking at future isoprene emissions. Other less understood effects of drought, altered biomass, and long-term temperature trends should be incorporated into these studies as the mathematical algorithms that simulate these effects are developed. We also did not look at the impact of changing radiation regimes on isoprene emissions, although, as noted above, changes in radiation and subsequent PAR can control isoprene emissions.

Our study only focused on the biogenic emissions of isoprene, although it is well known that vegetation emits a variety of trace gases, including monoterpene. Biogenic monoterpene emissions are dependent on temperature, LAI, and, in some cases, PAR, so that, as temperature, PAR, and LAI increase, emissions of these compounds are expected to increase. Monoterpenes can react in the atmosphere and have the potential to form secondary organic aerosol. It is not immediately clear, however, what impacts increased monoterpene emissions will have on atmospheric chemistry and climate; this topic will be the focus of future studies.

Other studies have looked at potential isoprene emissions under future climate scenarios. Turner et al. (Turner et al. 1991) produced the first study of potential changes in global isoprene emissions driven by climate change. They predicted isoprene emission estimates for a current climate and land cover (representative of
1988), and further, potential land-cover changes that might occur under the precipitation and temperatures predicted by the output of four different GCMs simulated with a doubling of CO₂. Turner et al. (Turner et al. 1991) estimated an increase in isoprene emissions from 323 to 379–408 Tg isoprene yr⁻¹ with the predicted changed landscapes. More recently, Sanderson et al. (Sanderson et al. 2003) performed a similar study to this one, using emissions predicted with a dynamic global vegetation model that was coupled with a global chemical transport model. Sanderson et al. (Sanderson et al. 2003) applied the Hadley Centre Climate Model (HadCM3) with a dynamic global vegetation model. In these simulations, CO₂ levels were prescribed according to the IS92a scenario and the future emissions applied were based on the IPCC SRES A2 scenario. The current meteorology and land cover were representative of the 1990s and the future meteorology and land cover of the 2090s. When looking at changes in global isoprene emissions from future land-cover changes only, they reported a small decrease in isoprene emissions of 39 Tg yr⁻¹ (7% decrease). When both temperature and land cover were considered, Sanderson et al. (Sanderson et al. 2003) report total global isoprene emissions of 697 Tg yr⁻¹, whereas we predict much higher emissions (889 Tg yr⁻¹) in our uncoupled model (Table 2). The large discrepancies between these studies are the result of using different input meteorological and land-cover data to drive the emission algorithms, as well as differences in the applied modeling systems. Sanderson et al. (Sanderson et al. 2003) used a coupled modeling system where the land surface and the atmospheric processes were simulated simultaneously. Our study applied an offline approach in which the meteorology and land surface processes were simulated without feedbacks and then were used as input to the chemical transport model.

Sanderson et al. (Sanderson et al. 2003) report similar changes in O₃ concentrations to those reported by this study. Differences between the model results by Sanderson et al. (Sanderson et al. 2003) are probably the result of the inclusion of future NOₓ emissions and temperatures in their coupled climate–chemistry simulations. The model simulations performed in this study used changes in biogenic isoprene emissions only and did not consider changes in biogenic and anthropogenic NOₓ emissions. However, spatially, both models show similar areas with increases in surface O₃ concentrations. The primary exception to this is that Sanderson et al. (Sanderson et al. 2003) report increases in O₃ concentrations in southern China and in the Amazon, where we estimated decreases in O₃ concentrations.

**Table 2. Comparison of reported global annual isoprene emission estimates under future climate and land-cover predictions.**

| Reference               | Land cover | Temperature | Isoprene emission (Tg yr⁻¹) |
|-------------------------|------------|-------------|-----------------------------|
| Turner et al. (Turner et al. 1991) | Current    | Current     | 323                         |
|                         | Future     | Current     | 379–408                     |
| Sanderson et al. (Sanderson et al. 2003) | Current | Current | 549                         |
|                         | Current    | Future      | 736                         |
|                         | Future     | Future      | 697                         |
| This study              | Current    | Current     | 522                         |
|                         | Future     | Current     | 529                         |
|                         | Future     | Future      | 889                         |
This is most likely due to the differences in modeling techniques (coupled versus uncoupled), as well as differences in anthropogenic emission inputs and meteorology for these regions. The differences in the results warrant further investigation of the emissions and chemistry in these particular regions.

Von Kuhlmann et al. (von Kuhlmann et al. 2004) report that the uncertainties associated with isoprene in global chemical transport models are substantial, and differences in chemical, deposition, and source schemes can have a dramatic impact on the output. The differences between the model outputs reported by Sanderson et al. (Sanderson et al. 2003) and here do identify regions with higher uncertainty than others, and we recommend further investigation into the emissions and chemistry of these regions, particularly in eastern Asia and in the Amazon. While we agree that the use of a fully coupled model, such as the one used by Sanderson et al. (Sanderson et al. 2003), is a logical approach to investigating this system, we feel that the offline approach presented here is useful to identify and better understand the effects of individual parameters of the system.

The World Health Organization (WHO) has set an 8-h \( \mathrm{O}_3 \) standard at 120 \( \mu \mathrm{g} \, \mathrm{m}^{-3} \) (\( \sim 61 \) ppbv), levels of \( \mathrm{O}_3 \) above which are considered unhealthful (World Health Organization 2000). Areas throughout the world, including populated regions in Europe and the United States, currently do not meet these standards. The results from this study show that changes in land cover and climate, and the resulting isoprene emission scenarios, can cause increased \( \mathrm{O}_3 \) in areas with already elevated concentrations. In all cases except URB, where \( \mathrm{O}_3 \) decreased in most areas, increases in the potential number of people living in areas with monthly averaged \( \mathrm{O}_3 \) concentrations (averaged for July) greater than 61 ppbv were observed (Table 3). Thus, even small and localized changes in isoprene emissions can produce detrimental health impacts for large populations. With this type of analysis, we can identify the areas that will be under unhealthy \( \mathrm{O}_3 \) concentrations when different land-cover changes occur and target these places with control strategies that would be effective at preventing \( \mathrm{O}_3 \) concentrations from rising above the standard.

### 8. Conclusions

Land cover and temperature both control biogenic isoprene emissions. Anthropogenic changes in land cover can have a large impact on the emissions, and these changes should be considered in future climate and chemistry scenarios along with

| Millions of people | Global population with \( \mathrm{O}_3 > 61 \) | Difference | Percent difference |
|--------------------|-----------------------------|------------|--------------------|
| BASE               | 704                         |            |                    |
| FUTVEG-CURCLIM     | 1382                        | 678        | 96%                |
| FUTVEG-FUTCLIM     | 1741                        | 1037       | 147%               |
| URB                | 675                         | -29        | -4%                |
| PLANT              | 717                         | 13         | 2%                 |
the climate-driven changes. Our results show that future temperature estimates have a potentially stronger influence on isoprene emissions than do future predictions of climate-driven changes in natural land cover. However, there are still uncertainties linked to the general MAPSS vegetation classifications, which are very broad and may not realistically represent isoprene emission categories. Also, there may be large regional and local land-cover changes that are not identified in a global modeling exercise. We recommend regional studies to better quantify the impacts of land-cover and climate change on isoprene emissions and O$_3$ chemistry. Specific regions where large changes are observed, therefore warranting further study at regional scales, include eastern Asia, the Amazon, and the United States. It should also be noted that the isoprene emissions predicted as part of this study may be underestimated. The algorithms of Guenther et al. (Guenther et al. 1995) used to predict emissions do not account for the acclimation of plants to higher temperatures (i.e., Petron et al. 2001), which can have an increasing effect on the emissions. There is, however, little known about the long-term temperature effects on isoprene emissions, and these need to be studied further in the laboratory and the field before they can be incorporated into modeling studies.

Changes in isoprene emissions can have a significant impact on atmospheric chemistry, including tropospheric O$_3$ production. By evaluating the sensitivity of O$_3$ production in different regions to changes in concentrations of NO$_x$ and VOC, we can better assess the changes in atmospheric chemistry that result from changing sources and identify more effective air pollution control strategies for these different scenarios. Since biogenic and anthropogenic NO$_x$ emissions were unchanged in our exercise, increasing isoprene emissions, as was the case in the FUTVEG-FUTCLIM and PLANT simulations, caused most areas to become more sensitive to NO$_x$ concentrations. When planning future air quality control strategies, changes in both NO$_x$ and VOC emissions must be considered in order to determine the most effective means for reducing surface O$_3$ under future climates. In areas where the O$_3$ sensitivity is expected to be affected by anthropogenic and climate-driven changes in emissions, O$_3$ abatement plans should be designed to take the changes into account. Specifically, plans that reduce both VOC and NO$_x$ emissions, or only NO$_x$, should be identified in developed and developing regions.

We show here that anthropogenic changes in land cover can have a substantial impact on emissions and chemistry. Regions with larger affected populations can also be identified and targeted for pollution controls. By sharing this knowledge, these results can be used to guide planners to use more effective land management practices that could reduce or prevent potential air quality problems in the future. We plan to next compare the magnitude of the chemical effects of potential future isoprene emission scenarios to those from anthropogenic scenarios at the regional scale and to evaluate the differences in observed results from coupled and uncoupled modeling systems.

Acknowledgments. This paper was presented at the International 2003 Young Scientists’ Global Change Conference, organized by START (www.start.org) and hosted by the Third World Academy of Sciences/ICTP in Trieste, Italy, 16–19 November 2003. The authors thank Peter Harley and Peter Hess for their useful reviews of the manuscript. This work was partly supported by the Biogeosciences Initiative at the National Center for Atmospheric Research (NCAR), which is sponsored by the National Science Foundation.
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