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HERBIVORE-INDUCED MONOTERPENE EMISSIONS FROM CONIFEROUS FORESTS: POTENTIAL IMPACT ON LOCAL TROPOSPHERIC CHEMISTRY

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Abstract. Herbivory results in an immediate increase in the rate of monoterpene emission from conifer tissues to the atmosphere. The current study uses simulated herbivory and a zero-dimensional photochemistry model with detailed treatment of monoterpene photooxidation to explore the potential impact of these herbivore-induced monoterpene emissions on local tropospheric chemistry dynamics. Measured monoterpene emission rates from undamaged current-year and year-old needles and wounded current-year needles of ponderosa pine and Douglas-fir trees were used to calculate whole-canopy fluxes expected from both a ponderosa pine and a Douglas-fir forest with 0%, 10%, and 25% damage to current-year needles. Fluxes from ponderosa pine forests with 10%- and 25%-damaged foliage are potentially 2- and 3.6-fold higher, respectively, than fluxes from forests with no herbivory. Douglas-fir forests experiencing 10% and 25% foliar damage can emit 1.6 and 2.5 times higher fluxes, respectively, than forests with no damaged foliage. The model simulations suggest that the fluxes resulting from even low-level herbivore damage (10% foliar damage) are large enough to increase local tropospheric production of ozone and organic nitrates and to suppress hydroxyl radical (OH) concentrations. In both Douglas-fir and ponderosa pine forests, the predicted magnitude of the perturbations to each of these chemical species increases linearly with the extent of foliar damage and is critically dependent on local mixing ratios of nitrogen oxides (NO_x). Ozone production is most sensitive to herbivore-induced emissions at NO_x concentrations between 0.3 and 7 nmol/mol. The presence of isoprene in coniferous-forest air diminishes the role herbivory plays in generating local ozone production. The results suggest that defoliation events should be considered to represent an important potential control over local oxidative tropospheric chemistry and to play an important role in perturbing local ozone dynamics in many rural coniferous forests throughout the United States.

Key words: biogenic hydrocarbons; coniferous forests; Douglas-fir; herbivory in coniferous forests; herbivory, simulated; hydrocarbons, non-methane; monoterpene emissions; oxidative capacity of the troposphere; photochemical model; ponderosa pine; tropospheric ozone production.

INTRODUCTION

Monoterpenes are 10-carbon, non-methane hydrocarbons produced by nearly all conifers (Banthorpe and Charlwood 1980). These compounds are stored internally in resin cells or ducts found throughout the needles, stems, roots, and buds (Fahn 1979), but because of their high vapor presures, they readily volatilize from conifer tissues into the atmosphere. Coniferous forests emit between 128 and 480 Tg C/yr, which makes them one of the largest global biogenic sources (Fehsenfeld et al. 1992, Guenther 1997).

Once in the atmosphere, monoterpenes are involved in a number of reactions that impact tropospheric chemistry on local, regional, and global scales. The rapid reactions of these compounds with ozone (O_3), hydroxyl radicals (OH), and nitrate radicals (NO_3) influence the production/consumption rate of ozone in the troposphere. These reactions also generate carbon monoxide (CO), organic nitrates, aerosols, acetone, and formaldehyde (Fishman and Seiler 1983, Kasting and Singh 1986, Trainer et al. 1987, Andreae et al. 1988, Jacob and Wofsy 1988, Fehsenfeld et al. 1992). Organic nitrates, such as peroxyacetyl nitrate (PAN), are of particular importance since they can sequester reactive nitrogen (NO and NO_2, which together will be referred to as NO_x), and release it into regions of the troposphere remote from reactive nitrogen sources (Sillman and Samson 1995). Since NO_x is the rate-limiting O_3 precursor in relatively clean air, this can cause ozone production even in regions far from NO_x sources (Fishman

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et al. 1979, Logan et al. 1981). In addition, the reaction of monoterpenes with OH can significantly suppress OH concentrations in the troposphere (Brasseur and Chatfield 1991, Fehsenfeld et al. 1992). OH initiates nearly all the oxidation paths in the troposphere. Suppressing OH concentrations will therefore influence the lifetimes and concentrations of many important chemical species, such as CH_4 and CO (Brasseur and Chatfield 1991, Fehsenfeld et al. 1992)

To quantify the influence monoterpenes have on these atmospheric processes, it is necessary to understand the major environmental factors controlling biogenic hydrocarbon fluxes from plant tissues. Emission of monoterpenes from conifer needles is a simple diffusive process controlled primarily by the influence of needle temperature on monoterpene vapor pressure, monoterpene concentration in the resin ducts, and the diffusive resistance of the tissue to volatile losses (Tingey et al. 1991, Lerdau 1991). Herbivory influences emissions from conifer needles in two ways. First, by damaging plant tissues, herbivores eliminate the diffusive resistance normally imposed by intact storage structures and trigger a large short-term increase in emissions. Fluxes measured from conifer needles of several species 2 h after tissue damage are as much as 60 times greater than those from undamaged needles (Litvak and Monson 1998). In addition, herbivory significantly increases the production of monoterpenes by directly increasing the activity of the enzymes that catalyze their synthesis (Litvak and Monson 1998). This increase in production, combined with the decrease in tissue resistance to flux, resulted in fluxes from needles wounded by either real or simulated herbivory that were still 10 times greater than undamaged controls 12 d after tissue damage.

Conifers are attacked by a wide variety of defoliating insects of which the lepidopterans and sawflies are the most common (Furniss and Carolin 1977). In temperate forests during non-outbreak periods, defoliators regularly consume 5–15% of the leaf area produced (Schowalter et al. 1986, Landsberg and Ohmart 1989). Yet foliage losses can reach 25–100% in herbivore outbreak years (Kulman 1971, Furniss and Carolin 1977, Schowalter et al. 1986, Mattson et al. 1991, Campbell 1993). The goal of the current study was to assess the role and potential impact of herbivory on the fluxes of monoterpenes from coniferous forest trees. Emission rates were measured from both undamaged and wounded needles from two conifer species: ponderosa pine (*Pinus ponderosa* Dougl. ex Laws) and Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco). These rates were then used to estimate the total fluxes expected from coniferous forests experiencing 0%, 10%, or 25% tissue damage due to herbivory. Finally, the impact of these fluxes on local tropospheric-chemistry dynamics was explored with a photochemical box model parameterized for the atmosphere above a coniferous forest in the Front Range of the Colorado Rocky Mountains (USA).

MATERIALS AND METHODS

Trees and wounding protocol

Monoterpene emission rates were measured from wounded and unwounded needles of ponderosa pine trees that were part of an ongoing study in Placerville, California, USA, that was dedicated to understanding the response of tree growth to elevated tropospheric CO_2 concentrations (for details see Ball [1990]). Emission-rate measurements were made on trees growing in several different CO_2 and nitrogen-fertilization treatments, though no significant treatment effects were found (see Constable et al. [1999] for results for unwounded needles, and *Results,* below, for results for wounded needles). For the purpose of this study, these measurements were pooled to provide characteristic undamaged and wounded emission rates for this species. The Douglas-fir trees were part of a similar ongoing experiment in Corvallis, Oregon, USA (for details see Tingey et al. [1995]). In this case, emission-rate measurements were made on trees from two different CO_2 treatments. Once again, no significant treatment effects were found, so measurements for undamaged and for wounded needles were pooled to provide characteristic emission rates for this species (see *Results,* below, for statistical details).

Mechanical wounding of the needle tissue, by cutting the needles in half and removing the distal portion, was used to simulate herbivory in both species. In previous laboratory experiments monoterpene fluxes from ponderosa pine needles damaged in this way did not significantly differ from those eaten by herbivores (Litvak and Monson 1998; wounded needles emitted fluxes of 91 ± 8 μg C·g (dry mass [DM])$^{-1}$·h^{-1} (mean ± 1 SE) 8 d after tissue damage, compared to fluxes of 105 ± 8 μg C·g DM^{-1}·h^{-1} emitted from needles half eaten by tiger moth larvae (last instar) (*Halisdota ingens* Hy. Edwards) 8 d after herbivory). Simulating herbivory in this way limits the applicability of our model to outbreaks of herbivores that consume needles in a fashion that severs the resin storage structures. In both species, emission rates were measured from undamaged controls and the remaining portion of the wounded needles 8 d after they were wounded, on two trees (one measurement per tree) per chamber.

Monoterpene collection and analysis

Monoterpene emission rates were measured on needles enclosed in a temperature-, and light-controlled cuvette coupled to a flow-through portable gas-exchange system (Campbell MPH 1000 [Campbell Scientific, Logan, Utah, USA]) plumbed with teflon tubing (described in Lerdau et al. [1997]). Hydrocarbon-free air supplied from a gas cylinder was delivered to the cuvette at flow rates of 750–950 standard cm^3/min. The

TABLE 1. Chemical reactions and kinetic rates added to the Master Mechanism model in this study.

Reaction†	Rate constant
β-pinene + $OH \rightarrow C_9H_{14}(OO\cdot)CH_2OH$	7.9×10^{-11}
$C_9H_{14}(OO\cdot)CH_2OH + NO \rightarrow C_9H_{14}(OONO)CH_2OH$	4.5×10^{-13}†
$C_9H_{14}(OO\cdot)CH_2OH + NO \rightarrow$ nopinone + $CH_2O + HO_2 + NO_2$	7.5×10^{-12}†
$C_9H_{14}(OO\cdot)CH_2OH + HO_2 \rightarrow C_9H_{14}(OOH)CH_2OH + O_2$	3.0×10^{-12}†
$C_9H_{14}(OOH)CH_2OH + h\nu \rightarrow$ nopinone + $CH_2O + OH$	· · ·
$C_9H_{14}(OOH)CH_2OH + OH \rightarrow C_9H_{14}(OO\cdot)CH_2OH + H_2O$	6.0×10^{-12}†
Nopinone + $OH \rightarrow C_9H_{15}OCO(OO\cdot) + H_2O$	14.3×10^{-12}‡
β-pinene + $O_3 \rightarrow$ criegee radical	1.5×10^{-17}‡
β-pinene + $NO_3 \rightarrow C_9H_{12}CH_3(OO\cdot),H(ONO_2)$	2.5×10^{-12}‡
δ-3-carene + $OH \rightarrow CH_3C(OO\cdot)CH_2CHCHCH_2CH(OH)CCH_3CH_3$	8.8×10^{-11}
$CH_3C(OO\cdot)CH_2CHCHCH_2CH(OH)CCH_3CH_3 + NO \rightarrow C_9H_{14}(OONO)CH_2OH + NO_2$	4.5×10^{-13}†
$CH_3C(OO\cdot)CH_2CHCHCH_2CH(OH)CCH_3CH_3 + NO \rightarrow CH_3COCH_2CHCHCH_2CHOCCH_3CH_3 + HO_2 + NO_2$	7.5×10^{-12}†
$CH_3(OO\cdot)CH_2CHCHCH_2CH(OH)CCH_3CH_3 + HO_2 \rightarrow CH_3COOHCH_2CHCHCH_2CH(OH)CCH_3CH_3 + O_2$	3.0×10^{-12}†
$CH_3COOHCH_2CHCHCH_2CH(OH)CCH_3CH_3 + h\nu \rightarrow CH_3COCH_2CHCHCH_2CHOCCH_3CH_3 + OH$	· · ·
$CH_3COOHCH_2CHCHCH_2CH(OH)CCH_3CH_3 + OH \rightarrow CH_3C(OO\cdot)CH_2CHCHCH_2CH(OH)CCH_3CH_3 + H_2O$	6.0×10^{-12}†
$CH_3COCH_2CHCHCH_2CHOCCH_3CH_3 + h\nu \rightarrow CH_3COCHCH_2CH(CH_2OO\cdot)CCH_3CH_3 + CO + HO_2$	· · ·
$CH_3COCH_2CHCHCH_2CHOCCH_3CH_3 + OH \rightarrow C_9H_{15}OCO(OO\cdot) + H_2O$	1.9×10^{-11}‡
$CH_3COCH_2CHCHCH_2CHOCCH_3CH_3 + NO_3 \rightarrow C_9H_{15}OCO(OO\cdot) + HNO_3$	2.5×10^{-15}‡
δ-3-carene + $O_3 \rightarrow$ criegee radical	3.7×10^{17}‡
δ-3-carene + $NO_3 \rightarrow C_9H_{12}CH_3(OO\cdot),H(ONO_2)$	9.1×10^{-12}†

Note: Solar radiation is indicated in the reactions by ''*hv*''; ''OO·'' means that the species is a radical. Rate constants were adapted from Atkinson (1997). (No rate constants are provided for the three reactions driven by solar radiation.)

† The rate constants were from corresponding reactions with α-pinene.

‡ The reaction products are from corresponding reactions with α-pinene.

carbon dioxide content of the air stream entering the cuvette was maintained at growth treatment levels. Relative humidity in the chamber was held constant at 60% and needle temperature was maintained at 30°C (ponderosa pine) or 25°C (Douglas-fir). Light intensities for the measurements varied between 900 and 1100 $\mu mol \cdot m^{-2} \cdot h^{-1}$.

Monoterpene emission rates were measured on ~4–6 ponderosa pine needles and 20 Douglas-fir needles. For each species, emission rates were measured on undamaged old needles, undamaged current-year needles, and wounded current-year needles. The closed-cell foam pads that sealed the needles in the cuvette were replaced after every measurement to minimize the possibility of monoterpene cross contamination between measurements. In addition, the cuvette was heated to 45°C and flushed with hydrocarbon-free air at ~1 cm^3/min for at least 1 h between measurements. Measurements of air drawn through an empty cuvette after conducting these procedures indicated the absence of possible monoterpene contaminants. Trapping and analysis of monoterpenes was conducted as previously described (Constable et al. 1999).

The analytical box model

The reaction scheme of the National Center for Atmospheric Research's Master Mechanism model developed and described by Madronich and Calvert (1989, 1990) was used to examine the impact of herbivore outbreaks in ponderosa pine and Douglas-fir forests on tropospheric chemistry. This model in its original form includes a comprehensive reaction scheme for the oxidation of α-pinene, and its intermediate oxygenated products at one point in the troposphere (i.e., a zero-dimensional [box] model). In both ponderosa pine and Douglas-fir, the three most abundant monoterpenes emitted from needles are α-pinene, β-pinene, and δ-3-carene. To accommodate oxidation of the additional monoterpene compounds, limited reaction schemes were added for the gas-phase photooxidation of β-pinene and δ-3-carene. The reactions and rate constants added to the model were adopted from Atkinson (1997) and are listed in Table 1. If rate constants were not available for reactions specific to the immediate or secondary reaction products of β-pinene and δ-3-carene, values for the corresponding reactions for the oxidation of α-pinene were used. Due to limited information on the removal of the major products formed in monoterpene oxidation, the reactions that remove the major oxygenated intermediates of β-pinene and δ-3-carene (which are nopinone and 2,2-dimethyl-3-(2-oxopropyl)-cyclopropaneacetalehyde, respectively) were modified to produce the same compounds as the corresponding reactions of pinonaldehyde (the major aldehyde formed in the oxidation of α-pinene). The same procedure was followed for the oxidation of β-pinene by NO_3 and of δ-3-carene by O_3 and NO_3. The rate constants for each reaction are specific to the re-

TABLE 2. Environmental conditions and initial species concentrations in model simulations (chosen to be representative of the Colorado Front Range, USA).

a) Environmental conditions

Environmental variable	Condition
H_2O	50% relative humidity
Pressure	101.325 kPa†
UV radiation	40°N, −105°W; 15 June; clear skies
Temperature	varies diurnally
Light	varies diurnally

b) Initial species concentrations

Chemical species	Concentration‡
N_2	79%
O_2	20.9%
CO_2	350 μmol/mol
H_2	0.6 μmol/mol
O_3	40 nmol/mol
CH_4	1.8 μmol/mol
CO	120 nmol/mol
H_2O_2	1 nmol/mol
α-pinene	0.1 nmol/mol
β-pinene	0.1 nmol/mol
δ-3-carene	0.1 nmol/mol
NO_x	0.01–100 nmol/mol; fixed in simulations

† 1 atmosphere = 101.325 kPa.

‡ μmol/mol = parts per million by volume, ppmv; nmol/mol = parts per billion by volume, ppbv.

actions with β-pinene and δ-3-carene, but the reactions produce the same compounds as the corresponding reactions with α-pinene.

The chemical rate equations were integrated with a Gear-type solver as described in Madronich and Calvert (1990) and integration was carried out for eight simulation days, starting at midnight. All species concentrations reported in the results are the maximum concentration recorded on the eighth simulation day, unless otherwise noted. A radiative-transfer model developed by Madronich (1987) was used to calculate photodissociation coefficients (*J* values) for all photolysis reactions for each time step assuming a solar zenith angle for 15 June, at latitude 40° and longitude −105°, 1.6-km altitude, 10% ground albedo, and clear skies. The environmental conditions and initial species concentrations used in the model runs are listed in Table 2. Both the environmental conditions and initial species concentrations were chosen to be representative of the Colorado Front Range (USA), as determined from past empirical measurements (see Table 2). The model maintained constant pressure but with a full temperature and diurnal light cycle. Temperature varied according to diurnal measurements recorded in a subalpine pine-fir forest at a weather station ∼5 km west of Boulder (Colorado, USA), designated ''A-1'' and maintained by the Institute of Arctic and Alpine Research.

This model in its original form neglects transport and surface deposition. We assumed a daytime planetary boundary layer (PBL) of 1 km, and a nighttime PBL of 300 m. The daytime rise in the PBL was programmed to begin at 0800 and increase linearly to a height of 1 km at solar noon. At 1800, the top of the PBL was programmed to decrease linearly until it reached 300 m at 2000. One consequence of increasing the depth of the PBL during the day is that trace gases are diluted due to entrainment of clean air from above. The mixing ratios of trace gases above the PBL are assumed to be those of clean continental air: 40 nmol/mol (parts per billion [10^9] by volume [ppbv]) O_3, 120 nmol/mol CO, 1600 nmol/mol CH_4, and 1 nmol/mol CH_2O. The mixing ratios of monoterpenes, isoprene, and their oxidation products are assumed to be negligible in the air above the PBL. Surface deposition for trace gases was determined by adding sink terms equal to the piston velocities of each compound divided by the thickness of the PBL. Other heterogeneous processes were ignored.

The monoterpene emission rates included in the model are estimates of the fluxes of α-pinene, β-pinene and δ-3-carene expected from a ponderosa pine or Douglas-fir forest in the Colorado Front Range experiencing an outbreak in which 0%, 10%, or 25% of the total foliage is damaged. To calculate whole-canopy fluxes, rates were determined for three needle classes: old undamaged needles (all needles at least 1 yr old), current-year undamaged needles, and current-year wounded needles. Current-year needles were assumed to account for 35% and 33% of all needles on ponderosa pine and Douglas-fir trees, respectively (Borghetti et al. 1986, Margolis et al. 1995). In both species, it was also assumed that all needles ≥1 yr old emitted monoterpenes at the same rate.

The emission rates for each terpene from undamaged current-year and 1-yr-old needles were measured directly in both ponderosa pine and Douglas-fir. The current-year wounded-needle emission rate for each terpene was calculated as the average daily flux from wounded needles expected over an 8-d period after wounding. Litvak and Monson (1998) showed that 2 h after needle damage, emission rates from wounded needles of several species were 60 times greater than rates from undamaged needles. In the same study, in the period from 3–8 d after wounding, emission rates were consistently 6–10 times greater (depending on the species) than rates from undamaged needles. We used this pattern, assuming an exponential decline in emission rates between 2 h and 3 d, and the emission rates measured from undamaged current-year needles and damaged current-year needles 8 d after tissue damage, to calculate the total emissions expected from wounded needles for 8 d after wounding. Because it is not realistic to assume that wounding of all 10% or 25% of needles in our herbivory scenarios is initiated at the same time, the average flux from the 8-d period for which we have measurements was chosen to represent the wounded-needle emission rate from each species.

Several assumptions were made in calculating these rates: (1) only the current-year foliage was damaged (many herbivores prefer the youngest needle tissue of conifers (Miller et al. 1991, Campbell 1993, McCullough et al. 1993, Carisey and Bauce 1997, Clancy et al. 1998*a*, *b*); (2) the herbivores damaged the needles according to the pattern we observed in the laboratory where only a distal portion of the needle is initially removed by the herbivore, leaving the remaining portion of the needle damaged on the tree for a period of time (Litvak and Monson 1998); (3) the change in monoterpene fluxes from wounded needles over an 8-d period follows the pattern described in Litvak and Monson (1998); and (4) the simulations will only tell us the *potential* impact herbivory could have on local tropospheric chemistry during an outbreak.

Emission rates were added to the Master Mechanism model by assuming a constant source for each terpene, equivalent to the calculated emission rates for each herbivory scenario in units of molecules per square centimeter per second, divided by the thickness of the PBL. Monoterpene emission rates in the model, from both undamaged and damaged needles, were programmed to vary with diurnal temperature according to the algorithms developed by Guenther et al. (1993). The calculated fluxes for each terpene were multiplied by a leaf-area index (LAI) of 9.8 and 17.3 for ponderosa pine and Douglas-fir, respectively, based on the average of at least three reported values for each species (Whittaker and Niering 1975, Grier and Running 1977, Gholz 1982, Larsson et al. 1983, Owen et al. 1987, McLeod and Running 1988, Gower et al. 1992, Runyon et al. 1994, O'Hara 1996). Simulations were run for three herbivory scenarios (0%, 10%, and 25% damaged needles) and seven atmospheric NO_x concentrations (0.01, 0.1, 0.3, 1.0, 3.0, 10.0, 100.0 nmol/mol NO_x). These NO_x concentrations were fixed in the simulations to avoid problems associated with modeling NO_x transport to and from sites. In this way, it was possible to assess the impact of herbivore-induced emissions on tropospheric chemistry in a variety of sites typical of both clean-air and polluted regions.

In most rural coniferous ecosystems, monoterpenes occur in the atmosphere along with the hemiterpene, isoprene (Kleinman et al. 1994, Mount and Williams 1997). To test if this presence of isoprene modifies the impact that herbivore-induced emissions have on tropospheric-chemistry dynamics, isoprene flux was added to several simulations. The added flux, $14\ \mu g\ C \cdot g^{-1}\ DM \cdot h^{-1}$, is the normalized leaf-level emission rate designated as ''low emissions'' in the classification system used in Guenther et al. (1994). Simulations were run for four isoprene concentrations: 0.1, 0.5, 1.0, 10.0 nmol/mol. These fluxes were added to the model assuming a constant source equivalent to the emission rate divided by the thickness of the PBL between 0700 and 1900. Isoprene emission rates during these daytime hours were temperature dependent, and varied according to the algorithm described by Guenther et al. (1993). Isoprene fluxes were set to zero throughout the night period.

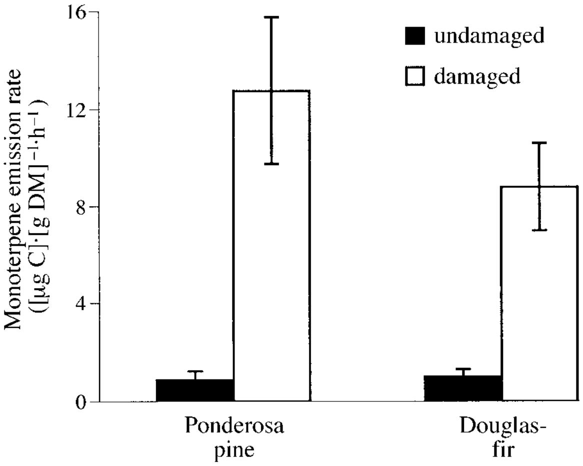

FIG. 1. Total monoterpene emission rates (means ± 1 SE) from undamaged and damaged needles of both ponderosa pine and Douglas-fir. Results presented are averages across all growth treatments for undamaged and wounded needles (n = 12 for ponderosa pine; n = 6 for Douglas-fir). DM = dry mass.

Statistical analyses

To examine the influence of nitrogen and carbon dioxide treatments on emission rates from ponderosa pine and carbon dioxide treatment on Douglas-fir emission rates, we used a two-way ANOVA and a one-way ANOVA, respectively. Wounded and control needles in both species were analyzed separately. Emission rates from wounded needles 8 d after tissue damage were statistically compared to emission rates from undamaged controls in both species using a simple t test. Because growth treatment did not significantly influence emission rates in either control or wounded needles, mesurements from all growth treatments were grouped together for this analysis. All statistics were performed on SAS statistical package (SAS Institute 1990).

RESULTS

The influence of simulated herbivory on monoterpene emissions

Wounded needles from both ponderosa pine and Douglas-fir trees have significantly higher monoterpene fluxes than undamaged needles for at least 8 d after tissue damage (Fig. 1; ponderosa pine: $F = 31.74$, df = 1, 11, $P = 0.0002$; Douglas-fir: $F = 34.34$, df = 1, 5, $P = 0.004$). Growth treatments did not significantly alter the emission rates from either undamaged

TABLE 3. Monoterpene fluxes from (A) different-aged undamaged wounded needles and (B) total canopy for simulations of 0%, 10%, and 25% foliar herbivory damage.

Species	α-pinene	β-pinene	δ-3-carene
A) Needle fluxes (μg C·g DM^{-1}·h^{-1})			
Ponderosa pine			
Old undamaged	0.24	1.05	0.18
Current-year undamaged	0.18	0.56	0.11
Current-year wounded	4.0	13.4	2.4
Douglas-fir			
Old undamaged	0.83	2.591	0.28
Current-year undamaged	0.44	0.61	0.28
Current-year wounded	5.58	11.4	2.09
B) Total canopy fluxes (molecules·cm^{-2}·s^{-1})			
Ponderosa pine			
0% foliar damage	1.7×10^{10}	7.3×10^{10}	1.3×10^{10}
10% foliar damage	3.8×10^{10}	1.5×10^{11}	2.6×10^{10}
25% foliar damage	6.9×10^{10}	2.6×10^{11}	4.6×10^{10}
Douglas-fir			
0% foliar damage	6.8×10^{10}	1.9×10^{11}	2.8×10^{10}
10% foliar damage	1.2×10^{11}	2.9×10^{11}	4.6×10^{10}
25% foliar damage	1.9×10^{11}	4.5×10^{11}	7.2×10^{10}

Notes: Emission rates shown here are for 25°C. Ponderosa pine emission rates were measured at 25°C, and Douglas-fir emission rates were converted from 30°C to 25°C using the Guenther et al. (1993) algorithms. Current-year wounded-needle rates are daily averages calculated for the 8-d period after wounding (see *Materials and Methods: The analytical box model* for details).

or wounded needles in either species (ponderosa pine ANOVA results: control needles $F = 0.92$, df = 1, 11, $P = 0.47$; wounded needles $F = 0.85$, df = 1, 11, $P = 0.50$; Douglas-fir ANOVA results: control needles $F = 4.401$, df = 1, 5, $P = 0.13$; wounded needles $F = 0.97$, df = 1, 5, $P = 0.97$). Thus, measurements from all trees within the wounded or undamaged categories were pooled for each species.

The α-pinene, β-pinene, and δ-3-carene emission rates measured from the three needle classes used to calculate total forest fluxes, as well as the total forest fluxes for each herbivory scenario, are listed in Table 3 for both ponderosa pine and Douglas-fir. In both species, old needles emit all three terpenes at higher rates than current-year needles (Table 3). In Douglas-fir the average daily fluxes of α-pinene, β-pinene, and δ-3-carene from current-year wounded needles are all roughly 10 times greater than the fluxes from undamaged control needles. In ponderosa pine the average daily flux of all three terpenes from wounded current-year needles is at least 20 times greater than those from controls. However, Douglas-fir has almost twice the LAI (leaf-area index) of ponderosa pine, which results in higher predicted total forest fluxes (Table 3).

Diurnal variation of important tropospheric species in the model

The diurnal variation in O_3, and O_3-forming precursors from the last 2 d of a simulation with no herbivory in a ponderosa pine forest with NO_x concentrations fixed at 1.0 nmol/mol is shown in Fig. 2. Ozone concentrations decrease at night due to dry deposition in the relatively shallow mixed layer (Fig. 2A). At 0800, O_3 concentrations tend to increase as the nighttime PBL (planetary boundary layer) breaks down, and the surface layer is diluted with air from above the PBL that contains 40 nmol/mol O_3. This increase is augmented by photochemical production which takes O_3 concentrations above 40 nmol/mol in this scenario. Simulated O_3 concentrations peak in the late afternoon and early evening, then decrease as photochemical production subsides and the top of the PBL breaks down to form the shallow nighttime mixed layer.

Simulated mixing ratios for OH and HO_2 radicals have daytime maxima near noon and nighttime minima just before dawn (Fig. 2B). Simulated mixing ratios for RO_2 radicals also increase from dawn to midday, but exhibit their highest peak during the night. Terpene concentrations in the model are at a minimum during the day, continually increase from 1800 to sunrise, then rapidly decrease (Fig. 2C). The diurnal change in NO and NO_2 (Fig. 2D) reflects the method chosen to fix NO_x concentration. With NO_x fixed at 1.0 nmol/mol, the sum of NO + NO_2 is set to unity. Mixing ratios of NO_2 are highest at night, but the maximum value is constrained by the fixed mixing ratio. During the day as NO_2 photolyzes, NO mixing ratio increases until the sum of NO + NO_2 reaches unity.

The predicted influence of herbivore-induced emissions on tropospheric chemistry

The model simulations indicate that even with low-level herbivory (10% damage) in both ponderosa pine and Douglas-fir forests, emissions of monoterpenes are large enough to increase the daily maximum O_3 concentration (Figs. 3A and 4A). The predicted increase

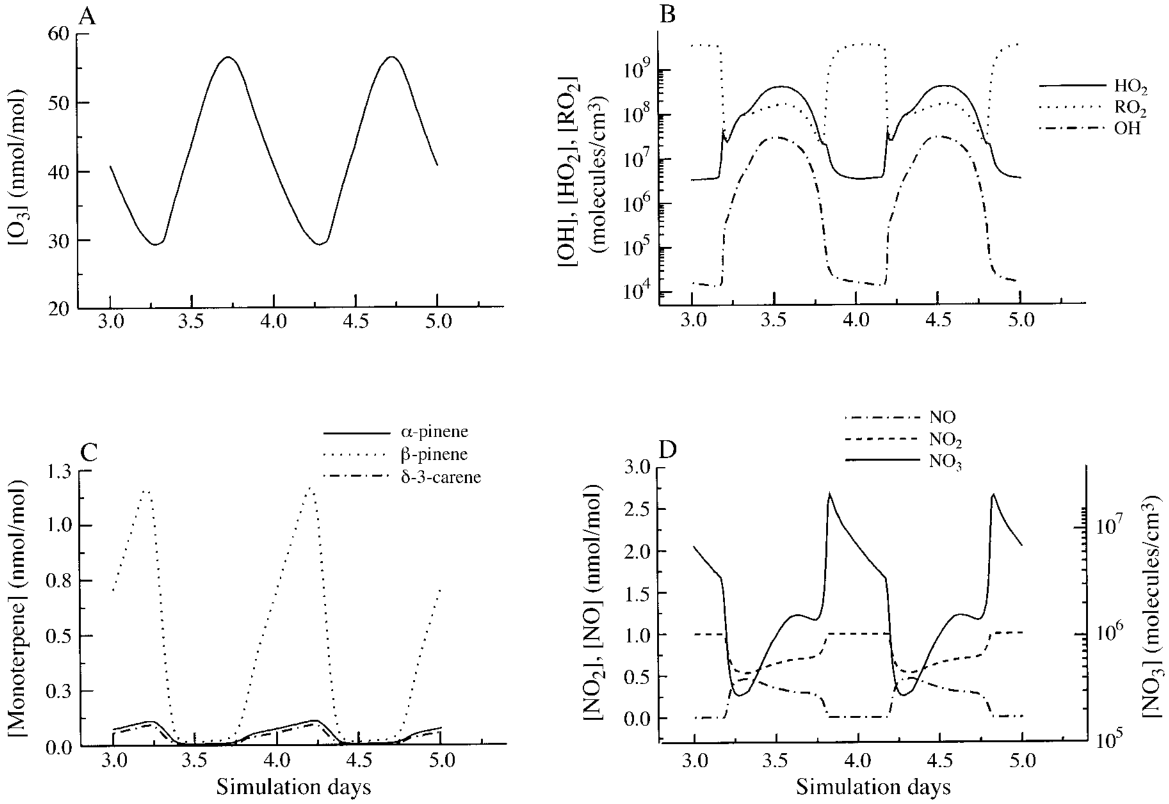

FIG. 2. Diurnal variation in concentrations of (A) O_3, (B) OH, HO_2, and RO_2, (C) α-pinene, β-pinene, and δ-3-carene, and (D) NO, NO_2, and NO_3 from a simulation with no herbivory in a ponderosa pine forest with NO_x fixed at 1.0 nmol/mol.

in O_3 is critically dependent on ambient NO_x concentration (Figs. 3 and 4). In both Douglas-fir and ponderosa pine forests, at low NO_x concentrations (<0.1 nmol/mol), O_3 production is limited by the availability of NO_x, and is therefore not sensitive to herbivory. At these low NO_x concentrations, O_3 mixing ratios remain below background (40 nmol/mol). However at NO_x concentrations >0.1 nmol/mol, the maximum O_3 concentration reached each day increases in a first-order fashion with extent of herbivory. The model predicts that the higher total forest fluxes from Douglas-fir forests, from both wounded and undamaged needles, should result in higher concentrations of O_3, compared to ponderosa pine forests.

The three most reactive oxidative components of the troposphere are OH, HO_2, and RO_2. Radicals of OH react rapidly with all monoterpenes (see Table 1 for rate constants). Figs. 3 and 4 show that the emissions released from either ponderosa pine or Douglas-fir forests experiencing even low-level foliar damage are sufficient to reduce local concentrations of OH. The impact of monoterpene emissions on OH concentration is dependent on the local abundance of NO_x, and is only evident at NO_x concentrations below 10 nmol/mol (Figs. 3 and 4). Results from the model suggest that the maximum noontime concentrations of both HO_2 and RO_2 are also sensitive to monoterpene emissions from ponderosa pine and Douglas-fir needles and increase linearly with the extent of herbivory (Figs. 3 and 4). The proportion of nitrogen that ends up in organic nitrates relative to HNO_3 increases with the extent of herbivory in both ponderosa pine and Douglas-fir (Fig. 5). However, the impact of herbivory on this ratio is only evident at NO_x concentrations below 1.0 nmol/mol.

When isoprene is added to the model, the impact of monoterpene emissions on O_3 production decreases (Table 4). With no isoprene in the model, increased emissions that result from 25% foliar damage increase maximum daily O_3 concentration by 18% compared to simulations with no foliar damage. However, when daytime isoprene concentrations are 1.0 nmol/mol, O_3 concentrations in the simulation with 25% foliar damage were only 6% higher than the simulation with no herbivory. Herbivory has no impact on O_3 production when isoprene concentrations are 10 nmol/mol.

DISCUSSION

The results of this study predict that defoliation events in either a ponderosa pine or Douglas-fir forest could markedly increase monoterpene emissions, which in turn could strongly modify several aspects of

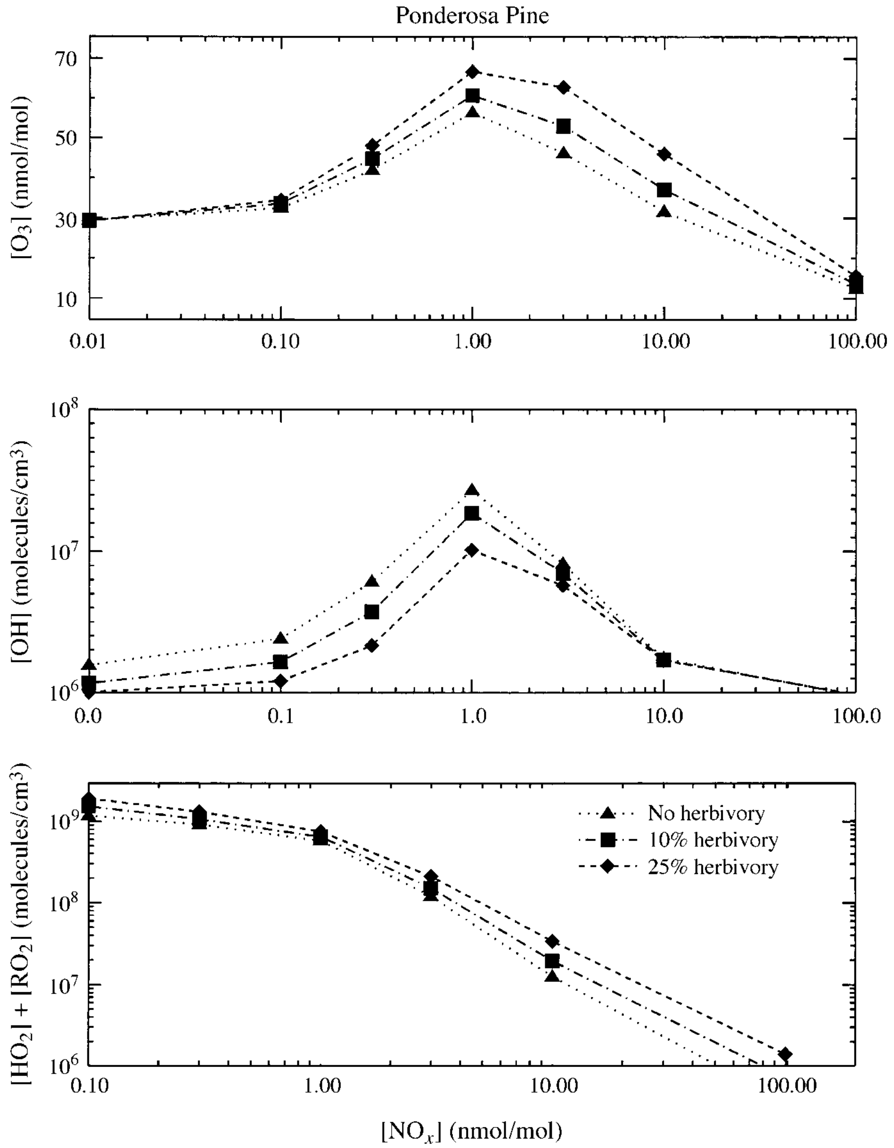

FIG. 3. Model predictions of the influence of foliar damage on concentrations of ozone, OH radical, and HO_2 and RO_2 radicals in a ponderosa pine forest, as a function of NO_x concentration. Values reported for O_3, OH, and HO_2 are maximum concentrations reached on the eighth simulation day; values reported for RO_2 are the noontime maxima on the eighth simulation day.

local tropospheric chemistry. As herbivory was allowed to increase in the simulations, the primary reactant, OH, decreased in concentration, while daily maximum concentrations of the primary products of oxidative photochemistry, including O_3 and organic nitrates, increased (Figs. 3, 4, and 5). Tropospheric O_3 is an important component of photochemical smog that can be detrimental to both human health and crop productivity, and a potent greenhouse gas with an infrared absorption maximum in an optically thin region of the atmosphere (Mustafa 1990, NRC 1991, Tingey et al. 1994). The OH radical is the single most important component behind most daytime tropospheric photochemistry (Logan et al. 1981, Crutzen 1995). It controls the lifetimes, and therefore the concentrations, of CH_4, CO, and most non-methane hydrocarbons (Levy 1971, Crutzen 1973, Logan et al. 1981, Kley 1997). Organic nitrates are major sinks for NO_x in rural environments (Sillman and Samson 1995). Additionally, organic nitrates such as PAN (peroxyacetyl nitrate) can transport NO_x over long distances in the free troposphere, effectively redistributing it from polluted, near-urban forests to cleaner, distant forests (Sillman and Samson 1995). Given that the O_3-forming capacity of each NO_x molecule is highest at low NO_x concentrations (Liu et al. 1987), transport of NO_x by organic nitrates creates

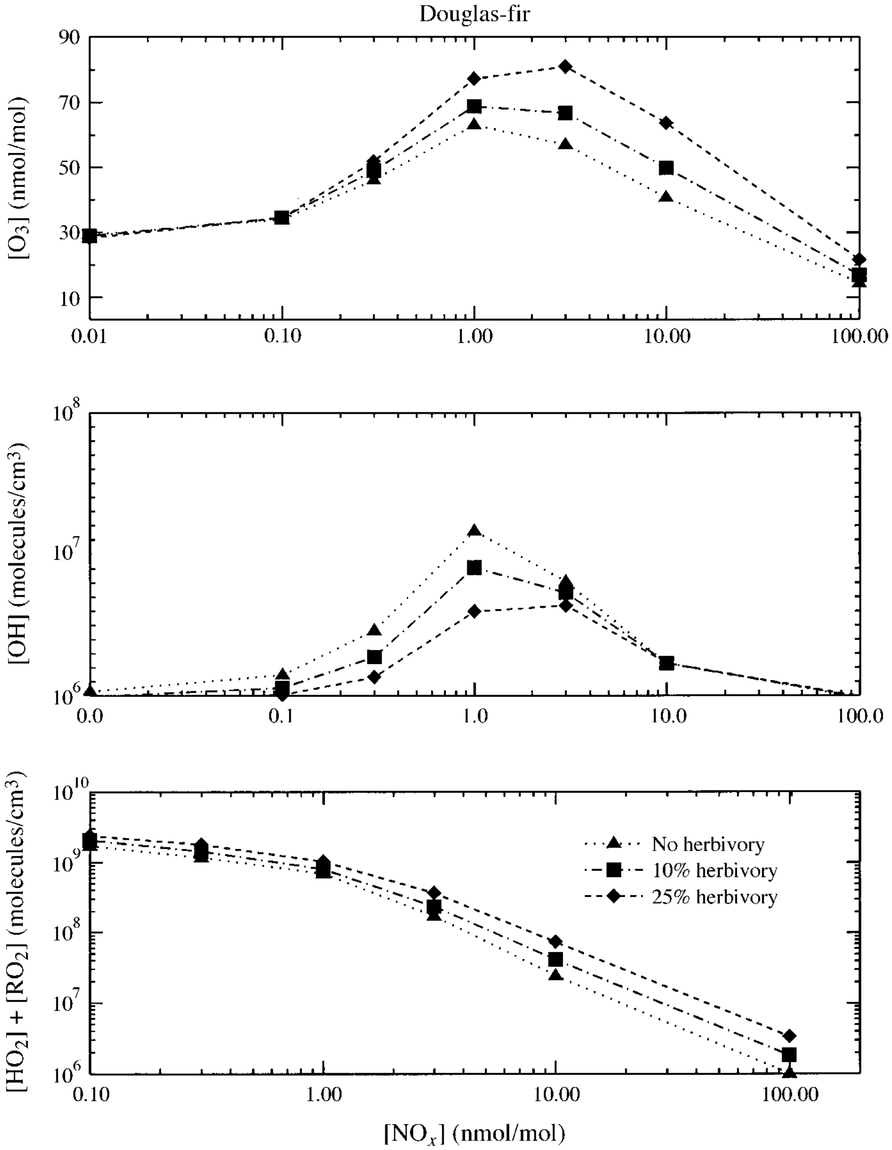

FIG. 4. Model predictions of the influence of foliar damage on concentrations of ozone, OH radical, and HO_2 and RO_2 radicals in a Douglas-fir forest, as a function of NO_x concentration. Values reported for O_3, OH, and HO_2 are maximum concentrations reached on the eighth simulation day; values reported for RO_2 are the noontime maxima on the eighth simulation day.

an important spatial dimension in the relationship between NO_x concentration and tropospheric O_3.

The degree to which herbivore-induced monoterpene emissions affect these oxidative compounds is dependent on the local abundance of NO_x. The dependence of O_3 production on concentrations of both NO_x and non-methane hydrocarbons is well documented (Levy 1971, Crutzen 1974, Chameides 1978, Fishman et al. 1979, Liu et al. 1987, Lin et al. 1988). When monoterpenes are oxidized, HO_2 and RO_2 radicals are formed, both of which oxidize NO to NO_2 by the following reactions (Crutzen 1973, Fishman et al. 1979, Trainer et al. 1987):

$$HO_2 + NO \rightarrow NO_2 + OH \tag{1}$$

$$RO_2 + NO \rightarrow NO_2 + RO. \tag{2}$$

These reactions lead to ozone production during the day as NO_2 photolysis generates a ground-state oxygen atom that combines with molecular oxygen (O_2) to produce O_3 (Leighton 1961). Because HO_2 and RO_2 radical concentrations are dependent on the extent of defoliation (Figs. 3 and 4), the magnitude of increase in daily O_3 concentration is as well. Within the model, when NO_x concentrations are too low for reactions (1) and (2) to occur, O_3 production is not sensitive to herbivory and O_3 mixing ratios drop below background (40 nmol/

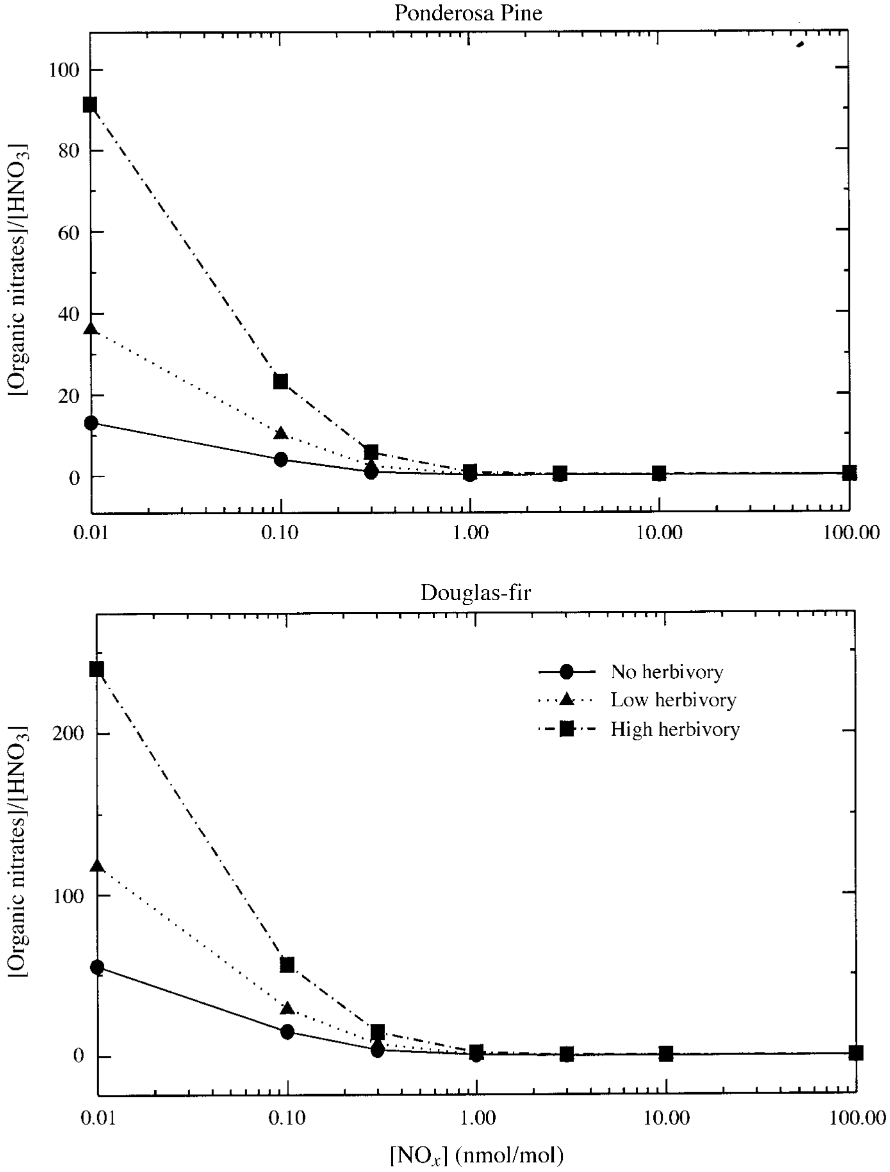

FIG. 5. Model predictions of the influence of foliar damage on the ratio of organic nitrates to HNO_3 as a function of NO_x for both ponderosa pine and Douglas-fir.

mol) as O_3 is consumed through the following reaction with HO_2 radicals:

$$HO_2 + O_3 \rightarrow OH + 2O_2. \quad (3)$$

These model results are consistent with past studies of relatively clean rural air, in which NO_x has been demonstrated as the rate-limiting O_3 precursor (Fishman et al. 1979, Logan et al. 1981, Lurmann et al. 1983, Liu et al. 1987). In the modeled simulations, O_3, OH, RO_2, and HO_2 all decreased at NO_x mixing ratios >1 nmol/mol (Fig. 1). This can be understood through two additional reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (4)$$

$$NO_2 + OH \rightarrow HNO_3. \quad (5)$$

Thus, when NO_x mixing ratios get high enough, photochemistry virtually collapses due to the removal of NO_x, OH, and O_3 (Trainer et al. 1987, Finlayson-Pitts and Pitts 1997).

The model predicts net O_3 production will occur and be sensitive to herbivore-induced emissions at NO_x concentrations between 0.3 and 7 nmol/mol (Figs. 3 and 4). NO_x concentrations in coniferous forests of the Colorado Front Range and other non-urban areas in the United States typically vary from 0.1 to 3 nmol/mol,

TABLE 4. Maximum daily ozone concentrations reached on the eighth simulation day in ponderosa pine forests as a function of foliar damage and isoprene concentrations.

Isoprene concentration (nmol/mol)	Maximum O_3 concentration (nmol/mol)		
	0% damage	10% damage	25% damage
No isoprene	56.4	60.7	66.7
0.1	61.7	65.7	71.4
0.5	78.3	81.3	85.8
1.0	92.5	94.7	98
10.0	128	128	128

but have occasionally been measured as high as 8 nmol/mol (Roberts et al. 1983, Finlayson-Pitts and Pitts 1986, Liu et al. 1987, Chameides et al. 1992, Mount and Williams 1997). Thus, forests in the United States are likely to exist at NO_x concentrations that make local oxidative chemistry sensitive to herbivore outbreaks.

The model suggests that the presence of isoprene in coniferous forests could diminish the role herbivory plays in generating local O_3 production. Adding isoprene to the simulations increases the maximum O_3 concentration reached per day, but decreases the fraction of the increase that is due to monoterpene flux from wounded foliage (Table 4). Without isoprene, the model suggests that in most rural areas O_3 production would be hydrocarbon limited, and in the case of coniferous forests would be sensitive to increases in monoterpene emissions due to herbivory. The presence of isoprene however, even at low mixing ratios, causes the chemistry to change, so that O_3 production is NO_x limited, and not responsive to dynamics in forest monoterpene emissions. This result is due to the extremely high reactivity of isoprene, compared to monoterpenes. Typical daytime isoprene mixing ratios in rural coniferous forests in the Colorado Front Range are between 0.05 and 0.15 nmol/mol (Mount and Williams 1997, Goldan et al. 1993), but in other non-urban forests in the United States isoprene mixing ratios can be as high as 2 nmol/mol (Cantrell et al. 1992, Kleinman et al. 1994). The latter forests tend to be in the southeastern United States, where oak (*Quercus* spp.) and sweetgum (*Liquidambar styraciflua*), which are both isoprene-emitting taxa, frequently occur with various species of pine. In these mixed forests tropospheric O_3 production would be, to some degree, uncoupled from herbivore-induced increases in monoterpene production from pines.

This study is a first attempt at estimating the potential influence of herbivory in coniferous forests on local tropospheric-chemistry dynamics. The model specifically evaluates emission rates induced by insects that sever the resin storage structures of current-year needles, and only attempts to predict the impact due to an insect outbreak in which 10% or 25% of the total foliage is damaged during an 8-d period. No attempt was made to simulate herbivore population dynamics or long-term effects of herbivory on overall tree performance due to the short time period of the model simulation (8 d).

By using fluxes induced by simulated herbivory and assuming only current-year needles are wounded in the model, we suggest the results generated here are conservative estimates of the potential impact of defoliation in coniferous forests on local tropospheric chemistry. Year-old needles of both tree species have higher monoterpene concentrations than current-year needles (Table 3). Therefore, if we assume that fluxes from damaged needles are proportional to the initial concentration of monoterpenes in undamaged foliage, outbreaks on older foliage should produce higher monoterpene fluxes, and have a greater impact on local tropospheric dynamics than outbreaks predominantly on current-year foliage. The mechanical herbivory treatment used here, in which the distal portion of the needle is removed in a single cut, does not reflect the more gradual removal rate of needle tissue that occurs with actual chewing. Given that continual bites could each result in an instantaneous large release of monoterpenes to the atmosphere, we are likely underestimating in the model the total flux expected from damaged needles due to real herbivory, by allowing only one short-lived 60-fold increase in monoterpene flux per damaged needle. The model is in need of further constraint using data on the type and magnitude of monoterpene emissions from actual insect outbreaks, and on the oxidative pathways of monoterpenes in the atmosphere. If, however, the estimates from this study are at least roughly realistic, it must be concluded that defoliation events could play an important role in the dynamics of local oxidative tropospheric chemistry, and in perturbing local O_3 dynamics.

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