

# UC Irvine

## UC Irvine Previously Published Works

### Title

Insights Into the Dynamics of Forest Succession and Non-Methane Hydrocarbon Trace Gas Emissions

### Permalink

<https://escholarship.org/uc/item/6vr0t2qd>

### Journal

Journal of Biogeography, 22(2/3)

### ISSN

0305-0270

### Authors

Martin, Philippe H  
Guenther, Alex B

### Publication Date

1995-03-01

### DOI

10.2307/2845946

### Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

# Insights into the dynamics of forest succession and non-methane hydrocarbon trace gas emissions

PHILIPPE H. MARTIN and ALEX B. GUENTHER\* *European Commission Joint Research Centre, TP 440, I-21020 Ispra (Varese), Italy; \*National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80307–3000, U.S.A.*

**Abstract.** Natural biogenic non-methane hydrocarbon (NMHC) emissions significantly influence the concentrations of free hydroxyl and peroxy radicals, carbon monoxide and tropospheric ozone. Present concerns with air pollution and the global carbon balance call for a better understanding of the respective roles of climate dynamics and vegetation succession in determining NMHC emissions. This constitutes the focus of the present paper. The approach consists in coupling the Energy, Water and Momentum Exchange and Ecological Dynamics model, a climatically sensitive, physically based gap phase forest dynamics model, and NMHC trace gas emission algorithms to assess possible changes in NMHC emissions from forests under stationary and changing climatic conditions. In summary, it is possible to follow the temporal evolution of foliar emissions over centuries using a vegetation dynamics model coupled with an NMHC emissions module.

Significant changes in isoprene and terpene emissions can take place as vegetation succession occurs under stationary climatic conditions and as climatic perturbations of the type and magnitude foreseen for global change alter the local microclimate. As illustrated by two examples, emissions may decrease or increase depending on the local climate and vegetation. The respective actions of changes in species absolute and relative abundance and changes in temperature interact very non-linearly making changes in emissions difficult to predict. None the less, coupled models of the kind described here may provide useful insights into the direction of such changes.

**Key words.** Non-methane hydrocarbon, climate dynamics, global carbon balance, gap-phase forest dynamics model, EXE.

## INTRODUCTION

Natural biogenic non-methane hydrocarbon (NMHC) emissions influence the concentrations of free hydroxyl and peroxy radicals, carbon monoxide (Zimmerman *et al.*, 1978; Chameides & Cicerone, 1978; Logan *et al.*, 1981) and tropospheric ozone (Crutzen, 1974), a strong oxidant and a radiatively active trace gas. The oxidation of foliar emissions of terpenes and isoprenes could contribute annually from 14% to possibly 88% of the total flux of CO into the atmosphere (Zimmerman *et al.*, 1978). Foliar emissions also constitute a small but significant flux of  $0.8 \text{ Pg(C)yr}^{-1}$  to the atmosphere (Warneck, 1988), compared to the  $7 \text{ Pg(C)yr}^{-1}$  due to fossil fuel burning, cement manufacturing and forest clearing (Brown *et al.*, 1994), and may represent a significant contribution of organic acids in rural and urban areas (Lamb *et al.*, 1987). Finally, it should be noted that vegetation is the dominant source of such natural hydrocarbons (Zimmerman *et al.*, 1978).

This short paper describes preliminary insights gained with EXE, the Energy, Water, and Momentum Exchange and Ecological Dynamics model (Martin, 1990; 1992), in combination with non-methane hydrocarbon (NMHC) trace gas emission algorithms to assess possible changes in

NMHC emissions from forests under stationary and changing climatic conditions.

## SIMULATING FOREST SUCCESSION AND LAND–SURFACE DYNAMICS

### A brief description of EXE

The Energy, Water, and Momentum Exchange and Ecological Dynamics model couples a physically and physiologically based water budget with an explicit treatment of ecological dynamics. In principle, EXE could be forced by atmospheric general circulation model output. EXE is made of two modules, ecological and physical. LINKAGES (Pastor & Post, 1984; 1986) provided the basis for the ecological module. Significant changes were made to couple physiology to physics in an effort to make the model realistically climatically sensitive. The physical module was built from scratch. It treats water uptake by the roots from the soil and atmospheric demand for water vapour explicitly. The forest hydrology and microclimate is computed once at daytime and once at night-time for the 365 days of the year. Information regarding the hydrology and the microclimate is transferred to the ecological module; the development of

TABLE 1. GCM climate change scenarios.

GCM	J	F	M	A	M	J	J	A	S	O	N	D
St Paul, MN (45°N, 93°W) temperature changes (°C)												
GFDL	5.6	6.2	6.6	5.5	3.4	9.3	9.2	7.5	7.2	6.3	6.3	7.1
GISS	6.1	5.8	5.1	5.2	2.4	3.6	2.1	3.5	6.5	3.7	6.1	5.7
OSU	5.4	3.8	4.3	2.6	3.4	4.5	3.5	4.2	3.5	2.6	2.3	2.9
UKMO	10.0	10.3	9.0	9.3	7.0	6.3	7.3	10.7	8.8	7.1	9.1	10.9
St Paul, MN (45°N, 93°W) precipitation changes (mm)												
GFDL	129.0	116.0	109.0	96.0	103.0	63.0	73.0	76.0	89.0	83.0	119.0	119.0
GISS	116.0	103.0	130.0	103.0	106.0	106.0	106.0	103.0	76.0	96.0	113.0	123.0
OSU	123.0	129.0	113.0	89.0	76.0	89.0	106.0	96.0	113.0	139.0	109.0	89.0
UKMO	126.0	116.0	126.0	123.0	133.0	123.0	86.0	66.0	96.0	93.0	109.0	123.0
Duluth, MN (47°N, 92°W) temperature changes (°C)												
GFDL	6.5	7.5	7.6	6.3	3.6	9.4	9.4	7.9	7.4	6.8	6.4	7.5
GISS	5.1	6.0	4.9	5.2	2.0	3.7	2.2	3.1	5.5	3.7	6.0	5.1
OSU	5.1	3.9	4.3	2.5	3.5	4.3	3.5	4.1	3.3	2.6	2.5	2.7
UKMO	9.7	10.9	10.7	10.9	7.9	6.5	7.1	8.8	8.3	7.4	9.6	11.1
Duluth, MN (47°N, 92°W) precipitation changes (mm)												
GFDL	123.0	109.0	119.0	83.0	96.0	69.0	76.0	76.0	86.0	86.0	116.0	126.0
GISS	103.0	106.0	119.0	109.0	96.0	116.0	99.0	116.0	130.0	109.0	116.0	130.0
OSU	129.0	129.0	116.0	86.0	83.0	93.0	113.0	93.0	113.0	143.0	116.0	89.0
UKMO	126.0	123.0	126.0	136.0	136.0	126.0	96.0	83.0	106.0	89.0	109.0	123.0

the forest is then simulated. This results in new physical and physiological characteristics of the forest. At this point, the cycle can repeat itself.

### Input data, run specifications and computer requirements

Forest succession under 400 years of present climatic conditions are simulated, then numerical experiments to examine the sensitivity of model forests to climatic changes are performed using scenarios generated with the Geophysical Fluid Dynamics Laboratory (GFDL; Wetherald & Manabe, 1986; Manabe & Wetherald, 1987), the Goddard Institute for Space Studies (GISS; Hansen *et al.*, 1983), the Oregon State University (OSU; Schlesinger & Zhao, 1989), and the United Kingdom Meteorological Office (UKMO; Mitchell, 1983; Wilson & Mitchell, 1987) atmospheric general circulation models (GCMs). The changes in precipitation and temperature are displayed in Table 1.

EXE is driven by daily values of incoming solar and longwave radiation, air temperature, air humidity, precipitation and wind velocity. In addition, soil properties as well as water and nitrogen content of the soil are needed at the beginning of the simulation. So, present climate is simulated using daily micro-meteorological data for incoming solar radiation, ambient air temperature, ambient air humidity, and precipitation from the *Typical Meteorological Year* data set (National Climatic Center, 1981). The sites chosen for the simulations are the areas of St Paul and Duluth, MN, U.S.A.

The climate change scenarios only include monthly temperature and precipitation data. The perturbed climate is

constructed by applying absolute changes to present-day climatology. Each altered temperature is computed as the sum of the daily temperature value and the absolute monthly change for that month. Altered precipitation is also computed on the basis of present-day conditions. It was assumed that the temporal distribution of rain remains the same, but that amounts on a given day changed. Hence, the change in precipitation expected from climate change in

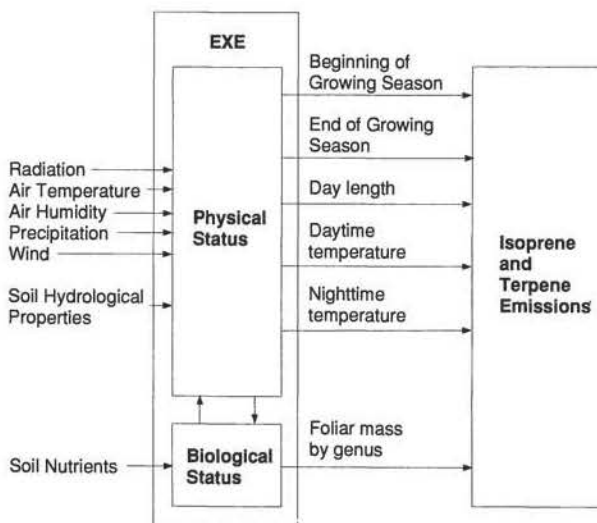


FIG 1. Information flow diagram describing the NMHC calculation.

TABLE 2. Standardized NMHC fluxes for twenty-nine tree genera.

<i>i</i>	Genus	Isoprene $a_{i,1}$	Terpene $a_{i,2}$
1	Fir ( <i>Abies</i> )	0.0	3.0
2	Maple ( <i>Acer</i> )	0.0	3.0
3	Birch ( <i>Betula</i> )	0.0	0.2
4	Hickory ( <i>Carya</i> )	0.0	1.6
5	American chestnut ( <i>Castanea dentata</i> )	0.0	0.6
6	Sugarberry ( <i>Celtis laevigata</i> )	0.0	0.2
7	Flowering dogwood ( <i>Cornus florida</i> )	0.0	1.6
8	American beech ( <i>Fagus grandifolia</i> )	0.0	0.6
9	Ash ( <i>Fraxinus</i> )	0.0	0.0
10	Plum and cherry ( <i>Prunus</i> )	0.0	0.0
11	Walnut and butternut ( <i>Juglans</i> )	0.0	3.0
12	Eastern red cedar ( <i>Juniperus virginiana</i> )	0.0	0.6
13	Sweetgum ( <i>Liquidambar styraciflua</i> )	70.0	3.0
14	Yellow poplar ( <i>Liriodendron tulipifera</i> )	0.0	0.2
15	American hornbeam ( <i>Carpinus caroliniana</i> )	0.0	1.6
16	Spruce ( <i>Picea</i> )	14.0	3.0
17	Pine ( <i>Pinus</i> )	0.0	3.0
18	Sycamore ( <i>Platanus occidentalis</i> )	35.0	0.0
19	White oak ( <i>Quercus alba</i> )	70.0	0.2
20	Red oak ( <i>Quercus rubra</i> )	70.0	0.2
21	Basswood ( <i>Tilia</i> )	0.0	0.6
22	Eastern hemlock ( <i>Tsuga canadensis</i> )	0.0	0.2
23	Elm ( <i>Ulmus</i> )	0.0	0.0
24	Yellow buckeye ( <i>Aesculus octandra</i> )	0.0	0.6
25	Tamarack ( <i>Larix laricina</i> )	0.0	1.6
26	Aspen and poplar ( <i>Populus</i> )	70.0	0.0
27	Northern white cedar ( <i>Thuja occidentalis</i> )	0.0	0.6
28	Black tupelo ( <i>Nyssa sylvanica</i> )	14.0	0.6
29	Eastern hop hornbeam ( <i>Ostrya virginiana</i> )	0.0	0.6

The emission rates are in  $\mu(\text{C}) \text{ g}^{-1}$  (dry weight foliar mass)  $\text{h}^{-1}$ . They represent emissions from leaves for a temperature of 30°C and a photosynthetically active radiation flux of 1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$  (source: Guenther, Zimmerman & Wildermuth, 1994). To account for canopy light interception, these numbers are divided by 1.75 in the calculations.

that month is added to each rainy day in the present climate. Radiation is held identical to present-day conditions, as well as wind velocity. Humidity can be assumed either to behave so that specific humidity remains constant (the number of water molecules in a parcel of air does not change) or that relative humidity stays the same (the number of water molecules changes with temperature). Since no drought stress is experienced in the simulations with the fixed humidity case, the fixed humidity case is not simulated.

Simulating forest dynamics with EXE on one plot for 500 years takes about 1 hour of IBM RISC 6000/580 CPU time. EXE therefore ran for a total of approximately 160 hours (= 20 plots per simulation  $\times$  2 sites  $\times$  4 scenarios per site  $\times$  1 hour per 500 year simulation) to complete this sensitivity analysis exercise.

## CALCULATING NON-METHANE HYDROCARBON EMISSION FROM FORESTS

### Input data

Biogenic NMHC emissions are a function of the foliar mass of the tree species present (Zimmerman *et al.*, 1978).

irradiance and canopy temperature (Lamb *et al.*, 1987). As summarized in Fig. 1, the EXE output data used as input in the NMHC trace gas emission calculations are daytime and night-time canopy temperatures averaged over twenty forest plots of one-twelfth of hectare each, live leaf biomass by genus averaged over the twenty forest plots, day length and the dates for the beginning and end of the growing season as computed by EXE.

### NMHC emission algorithms

From the regressions presented in Lamb *et al.* (1987), the hourly NMHC emission rate by genus and by emission type in  $\mu\text{g}(\text{C})\text{g}^{-1}$  (dry weight foliar mass)  $\text{h}^{-1}$ , can be expressed as

$$e_{i,j}(T) = a_{i,j}10^{b_j(T-30)}, \quad (1)$$

where *i* refers to the genus (see Table 2 for the twenty-nine tree genera considered); *j* refers to the emission type (*j* = 1 for isoprene and *j* = 2 for terpene); *T* is temperature, in °C;  $a_{i,j}$  is the emission rate for genus *i* and emission type *j*, standardized at 30°C (values for  $a_{i,j}$  may be found in Table 2); and  $b_j$  is a constant characteristic of the change in

emission type  $j$  with temperature.  $b_1 = 0.0415$  (isoprene) and  $b_2 = 0.0172$  (terpene) (Lamb *et al.*, 1987).

Emission rates by genus and by emission type on a daily basis are computed as

$$E_{i,j,k}(T_k^{\text{daytime}}, T_k^{\text{night-time}}) = 24 [f_k e_{i,j}(T_k^{\text{daytime}}) + (1 - f_k) \delta e_{i,j}(T_k^{\text{night-time}})], \quad (2)$$

where  $k$  is the Julian day;  $T_k^{\text{daytime}}$  is the daytime temperature, in °C;  $T_k^{\text{night-time}}$  is the night-time temperature, in °C;  $f_k$  is the fraction of the day during which there is light; and  $\delta$  is zero for isoprene at night-time and one otherwise.

Yearly emissions by NMHC emission type, in  $\mu\text{g}(\text{C})\text{g}^{-1}(\text{dry weight foliar mass}) a^{-1}$ , are calculated as

$$F_j = \sum_{k=1}^{365} \sum_{i=1}^5 r_i B_i E_{i,j,k}, \quad (3)$$

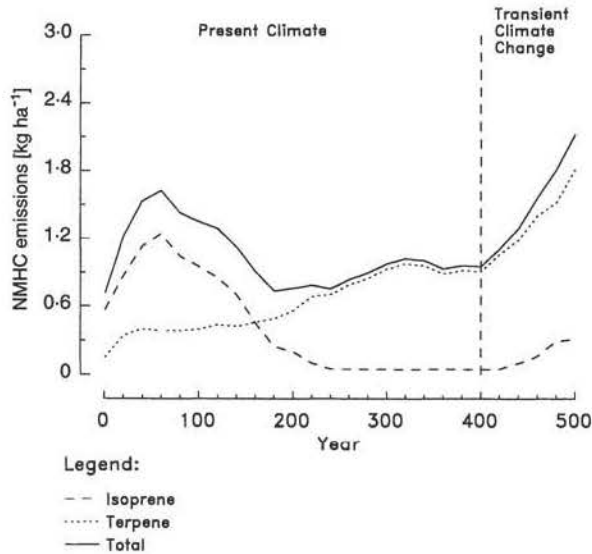


FIG. 2. NMHC emissions for St Paul, MN: Present climate and GFDL climate change scenario.

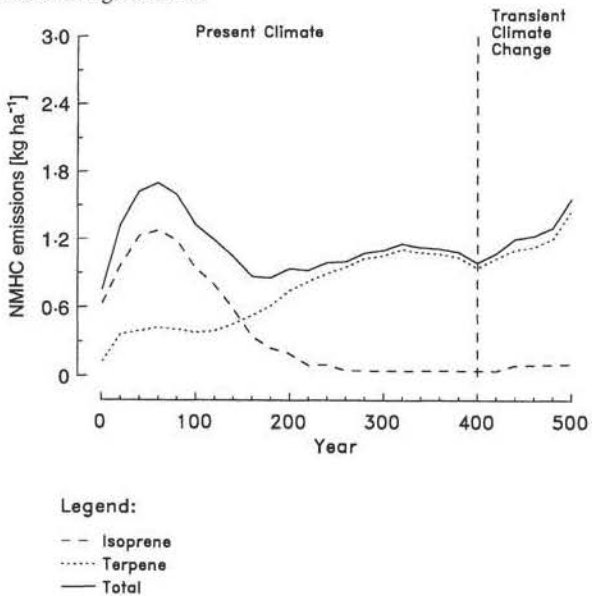


FIG. 3. NMHC emissions for St Paul, MN: present climate and GISS climate change scenario.

where  $r_i$  is the ratio of dry weight foliar mass to live weight foliar mass for genus  $i$  and  $B_i$  is the live weight foliar mass for genus  $i$ .

### NMHC EMISSIONS FROM FORESTS OVER CENTURIES UNDER STATIONARY AND PERTURBED CLIMATIC CONDITIONS

Secondary succession as simulated by EXE starts with an empty area which is progressively invaded by so-called

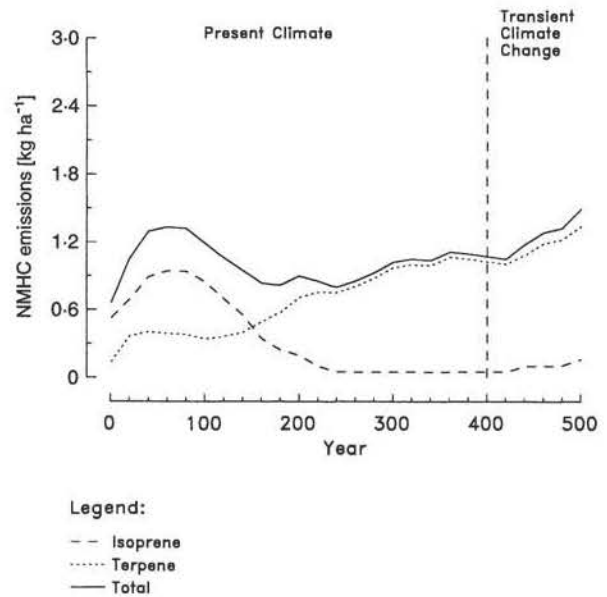


FIG. 4. NMHC emissions for St Paul, MN: present climate and OSU climate change scenario.

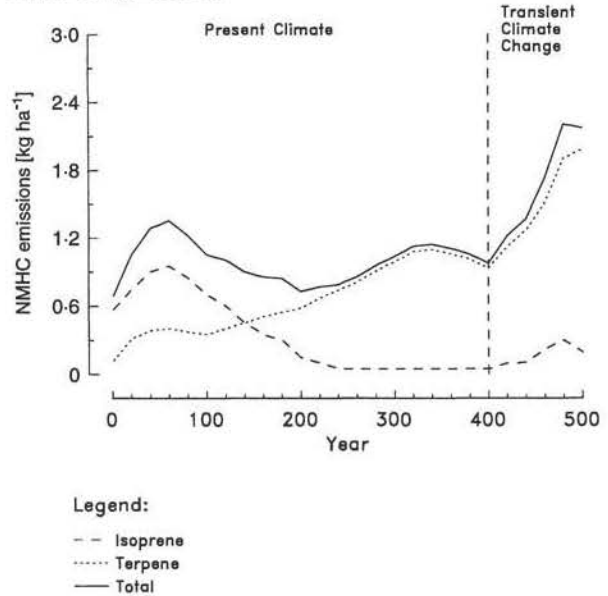


FIG. 5. NMHC emissions for St Paul, MN: present climate and UKMO climate change scenario.

pioneer species. After having reached maturity, these pioneer species are progressively replaced, in general, by other species. After about 400–500 years, in the northern temperate/boreal forest transition zone chosen for the simulation, a relatively stable vegetation assemblage is attained which can maintain itself for long periods of time. At this point in the simulation, the climate change scenarios are used to evaluate the effects of climatic perturbations on stable mature forests.

**St Paul, MN area**

In the St Paul, MN region, by year 400, EXE produces the maple–basswood (*Acer–Tilia*) forest most typical of the

area with an early abundance of aspen (*Populus grandidentata*, *P. tremuloides*) and yellow birch (*Betula alleghaniensis*).

Between year 400 and year 500, the climate change scenarios are used. Although not always at the same time, the biomass of the dominant maple decreases in all cases.

Under stationary climatic conditions, as shown in Figs 2, 3, 4 and 5, isoprene emissions are significantly greater than the terpene emissions during the first 160 years of the simulation. At this point, terpenes start dominating the signal. This result is explained by the early dominance of aspen which, with a standardized rate of  $70 \mu\text{g}(\text{C})\text{g}^{-1}$  (dry weight foliar mass)  $\text{h}^{-1}$ , is a high isoprene emitter. The later high rates of terpene emissions are explained by the late

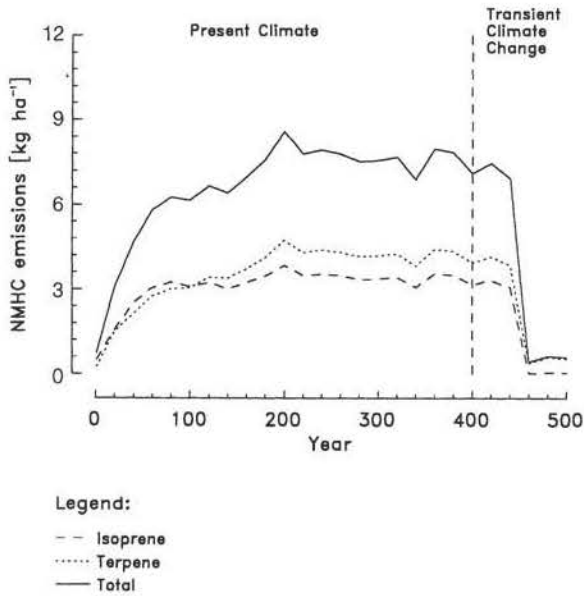


FIG. 6. NMHC emissions for Duluth, MN: present climate and GFDL climate change scenario.

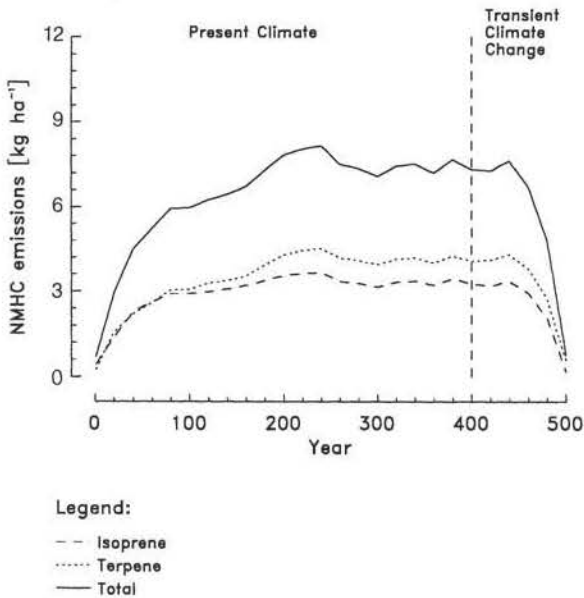


FIG. 7. NMHC emissions for Duluth, MN: present climate and GISS climate change scenario.

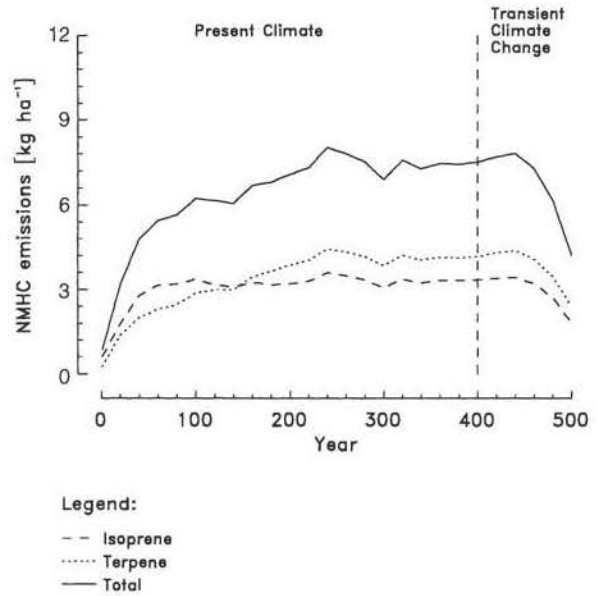


FIG. 8. NMHC emissions for Duluth, MN: present climate and OSU climate change scenario.

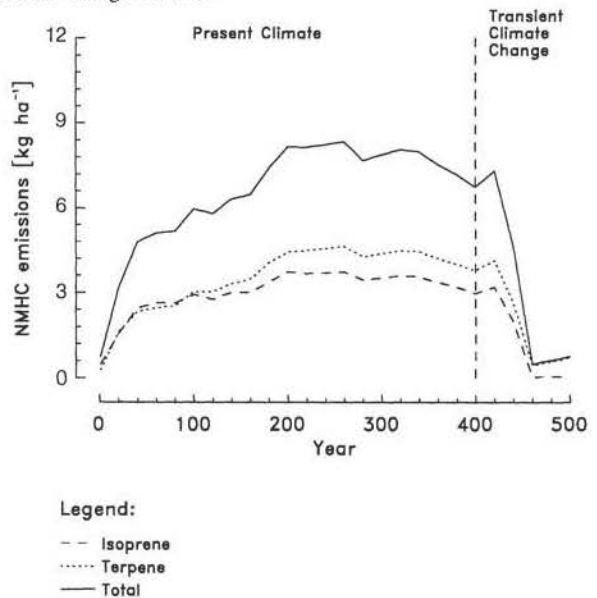


FIG. 9. NMHC emissions for Duluth, MN: present climate and UKMO climate change scenario.



successional dominance of maple which, with a standardized rate of  $3 \mu\text{g}(\text{C})\text{g}^{-1}(\text{dry weight foliar mass}) \text{h}^{-1}$ , is a high terpene emitter.

As climate change takes place, it was pointed out that biomass of this mature maple forest decreases. This is more than compensated by the rise in temperature which leads to a steep increase in terpene emissions with each of the GCM scenarios used.

### Duluth, MN area

In the Duluth, MN area, the abundance of aspen (*Populus grandidentata*, *P. tremuloides*) during the first 150 years of the simulation is very high. By year 400, the forest is dominated by a spruce (*Picea glauca*, *P. mariana*) forest with some yellow birch in the understorey.

The dominant spruce die back and are replaced by maple between year 400 and year 500. The timing of the disappearance of the spruce and the appearance of a (young) maple-dominated forest depends entirely on the GCM scenario used.

The first comment to make regarding the simulation on the Duluth site is that, as can be seen in Figs 6, 7, 8 and 9, NMHC emissions are higher than on those on the St Paul site by one order of magnitude. The results obtained for the Duluth area are also different from those for the St Paul area in that, during the 500 years of the whole simulation, isoprene and terpene emissions have the same order of magnitude, with terpene emissions being slightly higher than isoprene emissions after the first 100 years.

As previously pointed out, between year 400 and 500, spruce disappears and is replaced by maple as climate change takes place. Although the exact timing of this switch is a function of the GCM climate change scenario used, similar patterns emerge. The spruce produces isoprene at a standardized rate of  $14 \mu\text{g}(\text{C})\text{g}^{-1}(\text{dry weight foliar mass}) \text{h}^{-1}$  and terpenes at a rate of  $3 \mu\text{g}(\text{C})\text{g}^{-1}(\text{dry weight foliar mass}) \text{h}^{-1}$ , while maple produces no isoprene and emits terpenes at a standardized rate of  $3 \mu\text{g}(\text{C})\text{g}^{-1}(\text{dry weight foliar mass}) \text{h}^{-1}$ . Therefore, despite the emission enhancement effect of temperature, the relatively low NMHC emission rate of the maple and the low leaf biomass of the young maples explain a very sharp reduction in total NMHC emissions.

### DISCUSSION AND CONCLUSION

These preliminary results show that it is possible to follow the temporal evolution of NMHC trace gas emissions under stationary and perturbed climatic conditions over time-scales of centuries to millenia using climatically sensitive, physically based gap dynamics forest models such as EXE coupled with NMHC trace gas emissions algorithms.

The results of the simulations presented here indicate that significant changes in isoprene and terpene emissions can occur both as vegetation succession takes place under stationary climatic conditions and as climatic changes come about. These results, moreover, point out that emissions may either decrease or increase depending on the forest microclimate and the successional stage of the vegetation

on the site. Recent formulations of biogenic NMHC emissions make the emission rate light-dependent (cf. Guenther *et al.*, 1993). In the present simulations, a simple temperature-based algorithm was used. Although this simplification significantly affects quantitative estimates of yearly emissions at the continental scale, it should minimally alter the qualitative patterns of biogenic NMHC emissions described here.

Because of the synergistic interaction of changes in species absolute and relative abundance, and changes in temperature, the impact of global change on NMHC emissions rates is difficult to predict. Nevertheless, coupled models of the kind described here may provide useful insights into the possible direction of such changes.

### REFERENCES

- Chameides, W.L. & Cicerone, R.J. (1978) Effects of non-methane hydrocarbons in the atmosphere. *J. geophys. Res.* **83**, 947–952.
- Crutzen, P.J. (1974) Estimates of possible variations in total ozone due to natural causes and human activities. *Ambio*, **3**, 201–210.
- Brown, L., During, A., Flavin, C., French, H., Lenssen, N., Lowe, M., Misch, A., Postel, S., Renner, M., Starke, L., Weber, P. & Young, J. (1994) *State of the World 1994: A Worldwatch Institute Report on progress towards a sustainable society*. W.W. Norton & Company, New York.
- Guenther, A.B., Zimmerman, P.R., Harley, P.C., Monson, R.K. & Fall, R. (1993) Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analysis. *J. geophys. Res.* **98**, (D3), 12609–12617.
- Guenther, A.B., Zimmerman, P.R. & Wildermuth, M. (1994) Natural volatile organic compound emission rate estimates for U.S. woodlands. *Atmos. Environ.* **28**, 1197–1210.
- Hansen, J., Russell, G., Rind, D., Stone, P., Lacis, A., Lebedeff, S., Ruedy, R. & Travis, L. (1983) Efficient three-dimensional global models for climate studies: Models I and II. *Monthly Weather Rev.* **111**, 609–662.
- Harte, J. (1985) *Consider a spherical cow: a course in environmental problem solving*. William Kaufmann Inc., Los Altos, CA.
- Houghton, J.T., Callander, B.A. & Varney, S.K. (eds) (1992) *Climate change 1992: The supplement report to the IPCC scientific assessment*. Cambridge University Press, Cambridge.
- Houghton, J.T., Jenkins, G.J. & Ephraums, J.J. (eds) (1990) *Climate Change: The IPCC scientific assessment*. Cambridge University Press, Cambridge.
- Lamb, B., Guenther, A., Gay, D. & Westberg, H. (1987) A national inventory of biogenic hydrocarbon emissions. *Atmos. Environ.* **21**, 1695–1705.
- Lieth, H. & Wittaker, R.H. (eds) (1975) *Primary productivity of the biosphere*. Springer-Verlag, New York.
- Logan, J.A., Prater, M.J., Wofsky, S.C. & McElroy, M.B. (1981) Tropospheric chemistry: a global perspective. *J. geophys. Res.* **86**, 7210–7254.
- Manabe, S. & Wetherald, R.T. (1987) Large-scale changes in soil wetness induced by an increase in carbon dioxide. *J. Atmos. Sci.* **44**, 1211–1235.
- Martin, P.H. (1990) *Forest succession and climate change: coupling land-surface processes and ecological dynamics*. Cooperative Thesis between the University of California at Berkeley and the National Center for Atmospheric Research (NCAR), Boulder, CO. University Microfilms International (UMI) Catalog Number 9126692.

- Martin, P.H. (1992) EXE: a climatically sensitive model to study climate change and CO<sub>2</sub> enrichment effects on forests. *Aust. J. Bot.* **40**, 717–735.
- Mitchell, J.F.B. (1983) The seasonal response of a general circulation model to changes in CO<sub>2</sub> and sea temperature. *Q. J. Roy. Meteorol. Soc.* **109**, 113–152.
- National Climatic Center (1981) *Typical meteorological year: User's manual*. TD-9734, Ashville, North Carolina.
- Pastor, J. & Post, W.M. (1984) *Development of a linked forest productivity–soil process model*. ORNL TM-9519, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.
- Pastor, J. & Post, W.M. (1986) Influence on climate, soil moisture, and succession on forest carbon and nitrogen cycles. *Biogeochemistry* **2**, 3–27.
- Schlesinger, M.E. & Zhao, Z.C. (1989) Seasonal climatic changes induced by doubled CO<sub>2</sub> as simulated by the OSU atmospheric GCM/mixed-layer ocean model. *J. Climate* **2**, 459–495.
- Warneck, P. (1988) *Chemistry of the natural atmosphere*. Academic Press, New York.
- Wetherald, R.T. & Manabe, S. (1986) An investigation of a cloud cover change in response to thermal forcing. *Climat. Change* **8**, 5–23.
- Wilson, C.A. & Mitchell, J.F.B. (1987) A doubling CO<sub>2</sub> climate sensitivity experiment with a global climate model including a simple ocean. *J. geophys. Res.* **92**, 13315–13343.
- Zimmerman, P.R., Chatfield, R.B., Fishman, J., Crutzen, P.J. & Hanst, P.L. (1978) Estimates of CO and H<sub>2</sub> from the oxidation of hydrocarbon emissions from vegetation. *Geophys. Res. Lett.* **5**, 679–682.