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Biogenic hydrocarbon emissions and landcover/climate change in a subtropical savanna

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Abstract. Biogenic non-methane hydrocarbon (NMHC) emissions strongly influence the chemical composition of the troposphere. Thus, variations in emissions of these compounds are expected to cause changes in concentrations of important atmospheric trace gases. Here, we assess the relative magnitude of potential changes in NMHC (e.g., isoprene and monoterpene) emissions using field flux measurements from a subtropical savanna parkland/thorn woodland site in conjunction with model predictions of climate and landcover change. NMHC emissions of about 40 plant species were characterized. Grasses, as a group, had low emission rates. Several common woody species had high emission rates. However, there was little evidence of emissions being consistently related to woody plant taxonomy, growthform or functional groups. Above-canopy measurements were used to validate modeled isoprene flux predictions of about 2 mg C m^{-2} h^{-1} for savanna parkland/thorn woodland and ca. 0.7 mg C m^{-2} h^{-1} for the regional landscape, which is a mixture of savanna parkland/thorn woodland and cropland. Linkage of the biogenic emissions model with a plant succession model indicated that landcover change since the early 1800s has elicited a 3-fold increase in total NMHC emissions. This increase reflected changes in vegetation species composition (from domination by grasses which were typically 'low emitters', to shrubs and trees, many of which were 'high emitters') and increases in foliar density. Field measurements on two common shrub species indicated that isoprene emission increased exponentially with increases in leaf temperature from 20 to 40° C and were not suppressed by drought stress. Accordingly, our model predicted that projected increases in ambient temperature (3 to 6°C) emissions could

produce a 2-fold increase in biogenic NMHC emissions. Cloud cover, precipitation, relative humidity, and winds also exerted some control over NMHC emissions, but their influence was highly variable and difficult to estimate. Although our results are specific to southern Texas USA, they indicate the magnitude of change in NMHC emissions that could occur at other locations when climate and vegetation composition are altered.

1. Introduction

Non-methane hydrocarbons (NMHCs) have an important role in determining the oxidizing capacity and the aerosol burden of the atmosphere (Fehsenfeld et al. 1992). As such, they exert a strong influence on the chemical composition of the atmosphere and the global radiation balance. There are many sources of atmospheric NMHCs, but > 90% of the global annual emission is from vegetation (Guenther et al., 1995). NMHC emissions are therefore highly dependent on landcover (plant species composition and dominance) and environmental conditions (which influence species physiology and production) (Guenther et al., 1995).

The high temperatures and solar radiation fluxes associated with subtropical and tropical savannas make these bioclimatic regions large potential sources of biogenic NMHC emissions. Tropical savannas cover an eighth of the global land surface, over half the area of Africa and Australia, 45% of South America and 10% of India and Southeast Asia (Scholes and Archer 1997). Savannas contain a large and rapidly growing proportion of the world's human population and a majority of its rangelands and livestock (Young and Solbrig 1993). Consequently, landcover changes associated with grazing and crop production have been and continue to be substantial. Although the quantitative influence of changes in landcover and climate on NMHC emission will vary greatly for different sites, detailed case-studies can provide insights into the possible impacts of these factors on tropospheric chemistry and allow us to better prioritize research agendas.

Trends toward increasing woody plant abundance in temperate and tropical grasslands and savannas since the 1800s have been documented worldwide (Grover and Musick 1990, Archer 1994). Climatic change and changes in historical atmospheric CO_2 concentrations, fire regimes, rodent populations and livestock grazing have been suggested as driving forces in this shift in vegetation (Archer et al., 1995; Polley et al., 1996; Brown et al., 1997). This shift from grass- to woody plant-domination in savannas has been the focus of research at the La Copita subtropical savanna parkland/thorn woodland site in southern Texas, USA. Historical aerial photography (Archer et al., 1988) and ^{13}C analysis of soil organic carbon (Boutton et al., 1998) concur with observations made by early settlers (Inglis 1964) and have provided direct evidence that C_3 trees and shrubs have displaced C_4 grasses on this site. Plant growth (Archer 1989) and transition probability models (Scanlan & Archer 1991), substantiated by tree ring analysis (Boutton et al., 1998), indicate most woody plants have established over the past 100 y. Whereas pre-settlement landcover was grassland with scattered woodlands, present-day landscapes are dominated by trees and shrubs (Table 1).

Table 1. Reconstructed past (ca. 300 YBP), current (1983) and projected future (ca. 160 YAP) landcover of the La Copita site in subtropical southern Texas, USA (from Scanlan and Archer 1991).

Vegetation Type	% Cover		
	Past	Present	Future
Wodland patches	19	59	86
Tree/shrub grove patches	14	17	6
Tree/shrub cluster patches	5	5	2
Herbaceous patches	62	19	6

To determine if biogenic NMHC emissions have changed as a result of the change in landcover from grass- to woody plant domination at the La Copita site, we screened most of the common plants along with plant species representing common growthforms for NMHC emissions. For two species shown to be high isoprene emitters, we then quantified isoprene emission as a function of light, temperature and drought stress. Site-specific information on vegetation change and plant NHMC emissions were then used in a numerical model to quantify NMHC emissions with respect to changes in vegetation composition, foliar density, leaf temperature, and leaf photosynthetic photon flux density (PPFD), as modulated by ambient temperature, cloud cover, precipitation, relative humidity, and wind speed. Model predictions of NMHC emissions were then compared with tower and tethered balloon NMHC flux measurements.

2. Methods

2.1 Site description

Field research was conducted in June and November 1991, March 1992, and June and November 1994 at the La Copita Research Area (27° 40' N; 98° 12' W; 75 to 90 m above sea level), 15 km south of Alice, TX, USA. The site, located in the eastern Rio Grande Plains of the Tamaulipan Biotic Province, has a subtropical climate characterized by warm winters and hot summers. Mean annual rainfall is 720 mm. Contemporary vegetation of the region has been described by Davis and Spicer (1965). Sandy loam uplands at the study site, which has

been grazed by cattle since the late 1800s, are savanna parklands consisting of clusters and groves of woody plants organized beneath the tree legume, *Prosopis glandulosa*. These gently grade (1-3% slopes) into clay loam intermittent drainages characterized by *Prosopis* woodlands (see Archer [1995] for additional details on vegetation, soils and climate). The database of Kinnee et al. (1997) indicated shrub and grassland comprise about 60% of the landscape surrounding the La Copita Research Area; the remainder was characterized by cropland, primarily sorghum.

2.2. NMHC flux measurements

2.2.1. Enclosure fluxes

Vegetation NMHC emission rates were estimated using three field-portable enclosure measurement systems. The first system, referred to here as the "hand-held screening" (HHS) system, provided an instantaneous, semi-quantitative measure of total NMHC emission rate. The HHS system was used to rapidly screen a large number of plant species and identify those with high total NMHC emission rates. The HHS system consisted of a transparent enclosure connected by Teflon tubing to a total NMHC analyzer with a photo-ionization detector (Thermo Environmental Instruments, Model 580B). The second system, a "bag enclosure measurement" (BEM), was used to quantify emission rates of a wide range of terpenoid compounds for individual plant species. The BEM system used a dynamic (open-flow) enclosure consisting of a rigid aluminum frame covered by a flexible, transparent Teflon bag. Guenther et al. (1996a) and Klinger et al. (1998) describe these systems in detail and have demonstrated that the HHS system can be reliably used to identify plants with high NMHC emissions. The third system, a "controlled leaf cuvette" (CLC) system, was used to precisely measure leaf isoprene emission rates associated with specific light and temperature conditions. The CLC system was a modified gas exchange measurement system (Harley et al., 1996) with environmental control (MPH1000, Campbell Scientific, Logan, UT).

2.2.2. Above-canopy fluxes

Above-canopy fluxes were estimated using surface layer gradient (SLG) and mixed layer mass balance (MLMB) methods (Guenther et al., 1996b, 1996c). Isoprene fluxes were estimated by the SLG method during 9 half-hour sampling periods, between 1000 and 1700 local standard time (LST), over 3 days in June 1994. Half-hour average isoprene fluxes were estimated by the MLMB method during 14 sampling periods, between 1200 and 1600 LST, over 5 days. The SLG flux estimates integrated over an area about 200 m upwind of the tower, whereas the MLMB flux estimates were representative of an area about

20 km upwind of the tethered balloon. The SLG method related NMHC fluxes to a vertical concentration gradient, based on air samples collected on a tower at heights of 4, 5.6 and 6.8 m above ground level (AGL), and an eddy diffusivity estimated by the Bowen Ratio technique (see Guenther et al. 1996b). The MLMB method related fluxes to the mixed-layer average NMHC concentration, based on air samples collected at heights between 200 and 1000 m AGL using a tethered balloon sampler, the NMHC chemical loss rate (due to reaction with OH and ozone), and the mixed-layer height. Chemical loss rates and mixed-layer average concentrations were calculated as described by Guenther et al. (1996b, 1996c) with estimates of mixed-layer height obtained from sonde and radar components of an Integrated Sounding System (ISS) developed at the National Center for Atmospheric Research (NCAR; Boulder, CO, USA). For both the SLG and MLMB flux methods, thirty minute average whole air samples were collected using timer-controlled, constant-flow air samplers developed at NCAR. Samples were either collected directly onto solid adsorption cartridges or were initially collected in 15 L Teflon bags and then transferred into electropolished stainless steel canisters.

2.2.3. NMHC analysis

A photo-ionization detector was used in the HHS system for in-situ analysis of total NMHC. Air samples from the CLC enclosure system were analyzed for isoprene at the field site by gas chromatography (GC) with a reduction gas detector (Greenberg et al., 1993). Compound identification was accomplished by retention time comparison with known standards.

Air samples from the BEM enclosure and the above-canopy flux methods (SLG and MLMB) were stored using either electropolished stainless steel canisters or multistage solid adsorption cartridges and transported to the NCAR laboratory for analysis. Canister samples were analyzed for isoprene and monoterpenes by gas chromatography with cryogenic preconcentration using a flame ionization detector (GC-FID) to quantify concentrations (Greenberg et al., 1995). The cartridges contained layers of Carbotrap C, Carbotrap and Carbosieve S III whose preparation, conditioning, storage and transport has been described elsewhere (Helmig and Greenberg 1996). Cartridge sampling rates were 100 ml min^{-1} over 30 min periods, resulting in 3 L sample volumes. Air was pulled through sodium thiosulfate coated glass fiber filters upstream of the adsorbent cartridges for oxidant (ozone) removal (Helmig 1997). Several cartridges were loaded with higher sampling volumes for use in gas chromatography/mass spectrometry (GC/MS) analysis and compound identification. Quantitative cartridge analysis was performed by thermal desorption with cryogenic focusing and temperature-programmed GC/FID. NMHCs were identified with the FID instrument by computing their linear-programmed

retention indices and referring to the GC/MS measurements. Details of the cryogenic focusing and injection system and the GC parameters have been given elsewhere (Greenberg et al., 1995). Detector calibration was performed by loading and analyzing cartridges with known amounts of a hydrocarbon standard (10.5 ppb n-butane/ 10.3 ppb benzene, Scott Marrin, San Bernadino, CA).

2.3. Models

Biogenic NMHC emissions were predicted using a model based on the work of Guenther et al. (1995) and Guenther (1997). Area-average isoprene fluxes were calculated as the product of 1) foliar density, 2) an emission factor representing a weighted average for all plants within the landscape, and 3) emission activity factors that account for emission variations associated with changes in environmental conditions. A canopy environment model estimated PPFD for shaded and sunlit leaves at each of three canopy levels. Leaf temperatures were estimated using a leaf energy balance model that is similar to that described by Lamb et al. (1993). Landcover data for the source region of the MLMB measurements was derived from Kinnee et al. (1997). Landcover within the source region encompassed by SLG measurements was determined using belt transects and aerial photographs. Dimensional measurements were obtained for each woody plant encountered in belt transects and converted to leaf area and biomass using site-specific allometric relationships (Northup et al., 1996). Acreage of woody cover was measured on a 1990 low altitude, color-IR aerial photograph and multiplied by leaf area or biomass per unit ground area to generate estimates of total leaf area and total leaf biomass within the footprint.

A transition matrix model of vegetation dynamics developed for the La Copita site (Scanlan and Archer 1991) was used to estimate changes in woody plant cover associated with succession from savanna to woodland over the past century (Table 1). Changes in species composition and biomass accompanying the shift from grass- to woody plant-domination were based on relationships in Archer et al. (1988) and Schimel et al. (1995), respectively. Basically, the process of woody encroachment begins when *Prosopis glandulosa* establishes in the grass matrix. As this tree-legume grows, it modifies soils and microclimate to facilitate the ingress and establishment of other shrub species. Over time, as the shrub clusters organized around the *P. glandulosa* nucleus grow and new clusters form, canopies coalesce to form continuous woody cover. This process appears to have gone to completion on the moister lowland portions of the landscape and is still in progress on uplands. *P. glandulosa* typically dominates the overstory of upland and lowland woody patches; however, the understory shrubs contribute to its eventual demise via root competition (Barnes and Archer 1998). The shrubs

Zanthoxylum fagara, *Condalia hookeri*, and *Diospyros texana* typically dominate the understory of both upland and lowland sites. *Berberis trifoliolata* and *Ziziphus obtusifolia* are common, but subordinate understory species. Species such as *Aloysia gratissima* and *Celtis pallida* were more abundant in lowlands than uplands. Reconstructions of past grassland composition and productivity were based on relict communities (SCS 1979); changes subsequent to woody plant encroachment were based on Scanlan (1988). A standardized landscape consisting of 70% sandy loam upland and 30% clay loam lowland was used in the reconstructions and projections.

3. Current NMHC emissions

3.1. Enclosure measurements

NMHC emissions were determined for some 40 plant species representing 16 families, and several growthforms (grasses, forbs, or shrubs and trees with evergreen and deciduous leaf habits) (Table 2). The HSS system (detection limit ca. 0.5 μg C g^{-1} h^{-1} [Guenther et al. 1996a]) was used to screen 26 plant species and categorize their total NMHC emission as either 'high' if detected or 'low' if not detected. About 30% of these 26 species had high total NMHC emissions. Most of the species classified as 'high' emitters were evergreen shrubs. A notable exception was *Quercus stellata*, a deciduous tree. All grass species screened were 'low' emitters.

The BEM and CLC systems were subsequently used to quantify isoprene and monoterpene emission rates for 22 woody species. The observed emission rates (Table 2) were normalized using temperature and PPFD-dependent algorithms (Guenther et al., 1993) to estimate emissions representative of leaves at 30°C receiving a PPFD of 1000 μmol m^{-2} s^{-1}. Among the seven leguminous (Fabaceae) shrubs inventoried, only *Eysenhardtia texana* was a high isoprene emitter. High isoprene emission rates, between 8 and 80 μg C g^{-1} h^{-1}, were observed for five other woody species: *Berberis trifoliolata*, *Condalia hookeri*, *Karwinskia humboldtiana*, *Quercus stellata*, and *Ziziphus obtusifolia*. Three of these species, *C. hookeri*, *K. humboldtiana*, and *Z. obtusifolia*, are in the family Rhamnaceae. Although some genera in this family may symbiotically fix atmospheric N_2 in root nodules containing actinomycetous *Frankia* sp., those at the La Copita do not appear to do so (Zitzer et al., 1996). *B. trifoliolata* is an evergreen sclerophyllous shrub, *C. hookeri* and *K. humboldtiana* are facultative evergreen shrubs, and *Z. obtusifolia* is a drought deciduous shrub. *Q. stellata* is deciduous tree. Thus, there was no consistent relationship between isoprene emission and plant taxonomy or growthform. About half of the 22 shrub and tree species had significant monoterpene emission rates. The observed monoterpenes included α-pinene, β-pinene,

sabinene, camphene, myrcene, α-thujene, and d-limonene. High monoterpene emissions (>2 μg C g^{-1} h^{-1}) were observed for three shrub/tree species (*Acacia rigidula, Tamarix aphylla*, and *Ziziphus obtusifolia*); seven shrub/tree species were low or moderate (0.1 to 2 μg C g^{-1} h^{-1}) monoterpene emitters.

Six grass and one cactus species were investigated using a surface chamber that enclosed all plants within a ground surface area of approximately 0.4 m^2 (Table 3). Although surface chambers were placed so that targeted plant species contributed >90% of the total foliar density, some contributions from other plant species within the chamber were possible. These measurements, which integrated the terpenoid emissions from a variety of co-occurring herbaceous plant species, tended to be low (<0.1 μg C g^{-1} h^{-1}). However, monoterpene emissions of about 7 μg C g^{-1} h^{-1} were observed for ground surfaces dominated by *Bouteloua rigidiseta*, an unpalatable early seral grass, and *Setaria texana*, a palatable late seral grass. However, there was a significant occurrence of forbs in each of these plots and these herbaceous dicots may have contributed to the high emission rates rather than the grasses.

The PPFD and temperature dependence of isoprene emission for three of the shrub species at La Copita (Figure 1) was similar to that reported for other plants (Guenther et al., 1993). In most cases, isoprene emission increased linearly with PPFD at low light levels, then saturated at 1000 μmol m^{-2} s^{-1} (about 50% full sunlight). An exception was observed for *Condalia*, probably a result of its shoot geometry. The PPFD response of isoprene emission tracked that of net photosynthesis. For light saturated leaves, isoprene emission increased exponentially at leaf temperatures above 20°C, peaked at 40°C, then declined slightly (Figure 1). Laboratory studies have shown that short term decreases in stomatal conductance do not influence isoprene emission rates (Monson and Fall 1989). In contrast, field measurements by Steinbrecher et al. (1997) in the Mediterranean region indicated isoprene emission from *Quercus pubescens* exhibited a "mid-day depression" pattern typical of that observed for stomatal conductance and photosynthesis. We investigated whether this might be the case at the semi-arid La Copita site, by comparing gas exchange and water relations of adult *Berberis trifoliolata* and *Condalia hookeri* plants (n= 6 leaves per species) which had been growing in plots receiving supplemental water (ca. 30 cm of water every 2-4 weeks since May 1994) to that of plants receiving only natural rainfall (Figure 2). At the time of our measurements (late September 1994), there had been 81 mm of natural rainfall in August and 46 mm in September, of which 5 mm had fallen during the 2 weeks preceding our physiological measurements. Differences in levels of plant water stress between the irrigated and non-irrigated plots were reflected in higher pre-dawn water potentials among plants on the irrigated plots (mean water potential = - 0.9 and - 0.7 MPa for *Condalia* and *Berberis*,

respectively) compared to those on the non-irrigated plots (mean water potential = -2.0 and -1.9 MPa). Although drought stress significantly reduced stomatal conductance in both species and reduced net photosynthesis rates 40% in *Berberis* compared to that of well-watered plants, leaf level isoprene emission rates were not affected. Our observations were consistent with short-term experiments on potted *Liquidambar styraciflua* plants (Fang et al., 1996) which found that photosynthesis and stomatal conductance were more severely affected than isoprene emission by repeated cycles of drying.
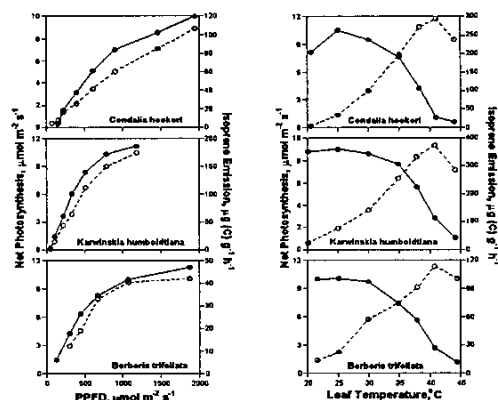

Figure 1. Net photosynthesis, μmol m^{-2} total leaf area s^{-1} (filled circles), and isoprene emission μg C g^{-1} dry weight h^{-1} (open circles), as a function of leaf temperature and photosynthetic photon flux density (PPFD) for three shrub species at La Copita.
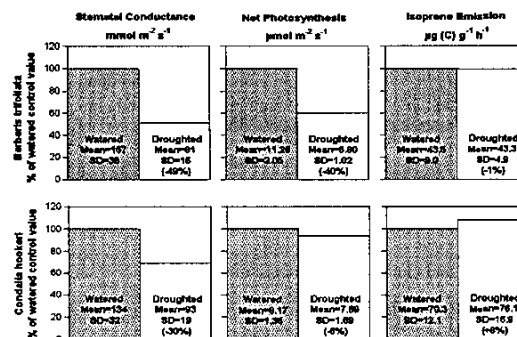

Figure 2. Mean (SD; n= 6 leaves per species) net photosynthesis, stomatal conductance and isoprene emission for shrubs growing on plots receiving supplemental water (30 cm every 2-4 weeks) compared to plants growing on plots receiving only natural rainfall.

3.2. Above-canopy flux measurements and model evaluation

Isoprene fluxes of 1.9 ± 0.5 mg C m^{-2} h^{-1} (mean ± standard deviation) estimated by the SLG method were associated with ambient temperatures of 29.0 ± 1.7°C and an above-canopy PPFD of 1090 ± 400 μmol m^{-2} s^{-1}. The MLMB estimates of mean isoprene fluxes were 0.56 ± 0.08 and associated with ambient temperatures of 32.4 ± 0.5°C and an above-canopy PPFD of 1620 ± 60 μmol m^{-2} s^{-1}. The two sets of above-canopy flux measurements were used to evaluate emission model predictions for the two general types of landcover that presently dominate southern Texas. The SLG measurements are primarily representative of savanna parkland/thorn woodland, whereas the source region of the flux estimated by the

MLMB method is that of cropland (primarily sorghum) with some contribution from the savanna parkland/thorn woodland. The emission model prediction of isoprene fluxes for La Copita savanna parkland/thorn woodland with an ambient temperature of 29°C and an above-canopy PPFD of 1090 μmol m^{-2} s^{-1} was 2.2 mg C m^{-2} h^{-1}. This is about 20% higher than the flux measured by the tower-based SLG flux system. The predicted isoprene flux for mixed cropland-thorn woodland, with an ambient temperature of 32°C and an above-canopy PPFD of 1620 μmol m^{-2} s^{-1}, was 0.72 mg C m^{-2} h^{-1}. This is about 30% higher than the flux measured by the tethered balloon based MLMB flux system. Both of these results demonstrate good agreement between model predictions and field measurements of above-canopy isoprene fluxes.

Table 2. Isoprene and monoterpene emission factors, representative of 30°C and 1000 μmol m^{-2} s^{-1}, measured with the BEM or CLC system. Total VOC emission level estimated with the HSS system. NM indicates that no measurement was made. Plant nomenclature follows Correll and Johnston (1979).

Family	Species	Growth Form	Isoprene μg C g^{-1} h^{-1}	Monoterpene μg C g^{-1} h^{-1}	Total VOC
Fabaceae	*Acacia berlandieri*	deciduous shrub	< 0.1	< 0.1	NM
Fabaceae	*Acacia farnesiana*	deciduous shrub/tree	< 0.1	< 0.1	Low
Fabaceae	*Acacia greggii*	deciduous shrub	< 0.1	< 0.1	Low
Fabaceae	*Acacia rigidula*	deciduous shrub	< 0.1	2.8	NM
Verbenaceae	*Aloysia gratissima*	deciduous shrub	< 0.1	1.4	NM
Chenopodiaceae	*Atriplex canescens*	evergreen shrub	< 0.1	< 0.1	NM
Asteraceae	*Baccharis texana*	deciduous shrub	< 0.1	< 0.1	NM
Berberidaceae	*Berberis trifoliolata*	evergreen shrub	36	0.1	High
Poaceae	*Bouteloua curtipendula*	C4 grass	NM	NM	Low
Sapotaceae	*Bumelia celastrina*	evergreen shrub/tree	NM	NM	Low
Ulmaceae	*Celtis laevigata*	deciduous tree	< 0.1	< 0.1	Low
Ulmaceae	*Celtis pallida*	deciduous shrub	NM	NM	Low
Poaceae	*Cenchrus ciliaris*	C4 grass	NM	NM	Low
Rhamnaceae	*Colubrina texensis*	deciduous shrub	< 0.1	< 0.1	NM
Rhamnaceae	*Condalia hookeri*	evergreen shrub	25	< 0.1	High
Euphorbiaceae	*Croton lindheimerianus*	herb	NM	NM	High
Poaceae	*Cynodon dactylon*	C4 grass	NM	NM	Low
Ebenaceae	*Diospyros texana*	evergreen shrub	< 0.1	1.0	Low
Fabaceae	*Eysenhardtia texana*	deciduous shrub	35	0.9	NM
Asteraceae	*Helianthus annuus*	herb	NM	NM	High
Poaceae	*Heteropogon contortus*	C4 grass	NM	NM	Low
Rhamnaceae	*Karwinskia humboldtiana*	evergreen shrub	43	< 0.1	High
Fabaceae	*Leucaena retusa*	deciduous tree	< 0.1	< 0.1	NM
Solanaceae	*Lycium berlandieri*	deciduous shrub	NM	NM	Low
Cactaceae	*Opuntia engelmanii*	cactus	NM	NM	Low
Asteraceae	*Palafoxia texana*	herb	NM	NM	Low
Fabaceae	*Prosopis glandulosa*	deciduous tree	< 0.1	0.1	Low
Fagaceae	*Quercus stellata*	deciduous tree	80	NM	High
Lamiaceae	*Salvia ballotaeflora*	deciduous shrub	< 0.1	< 0.1	Low
Poaceae	*Schedonnardus paniculatus*	C4 grass	NM	NM	Low
Poaceae	*Sorghum bicolor*	C4 grass	NM	NM	Low
Tamaricaceae	*Tamarix aphylla*	evergreen tree	< 0.1	2.5	NM
Asteraceae	*Xanthocephalum dracunculoides*	herb/shrub	< 0.1	0.7	NM
Asteraceae	*Zexmania hispida*	evergreen herb	NM	NM	High
Rutaceae	*Zanthoxylum fagara*	evergreen shrub	< 0.1	0.4	High
Rhamnaceae	*Ziziphus obtusifolia*	deciduous shrub	8.1	2.5	Low

Table 3. Isoprene and monoterpene emissions from surface chamber enclosing 0.4 m² ground area. Plots dominated by *Setaria texana* and *Bouteloua rigidiseta* also had significant forb components which may have contributed to their elevated emissions.

Dominant Species	Growth Form	Emision Rate (μg C g⁻¹ h⁻¹)	
		Isoprene	Monoterpenes
Bouteloua rigidiseta	grass	< 0.1	7.0
Chloris cucullata	grass	< 0.1	< 0.1
Chloris plurifloraa	grass	< 0.1	< 0.1
Opuntia lindheimeri	cactus	< 0.1	0.9
Schizachyrium scoparium	grass	< 0.1	< 0.1
Setaria texana	grass	< 0.1	6.9
Stipa leucotricha	grass	< 0.1	0.1

4. Land-use and climate change

In this section, we consider how changes in vegetation and climate might affect NMHC emissions. Certainly, there are large uncertainties associated with both future land-use and climate predictions and the simulated response of biogenic NMHC to these. However, a reconstruction of changes in NMHC emissions which may have accompanied well-documented changes in land cover in recent history would give a sense of the magnitude of change that may occur with future changes in land cover. Further, this exercise serves to demonstrate the relative importance of variables governing NMHC emissions (e.g., PPFD, leaf temperature, foliar density, and plant species composition) and the relative importance of factors that modulate these driving variables (e.g., ambient temperature, cloud cover, precipitation, relative humidity, wind speed, land-use, and disturbance regime).

4.1 PPFD

PPFD strongly influences the emissions of some, but not all, NMHCs (Guenther et al., 1995). The discussion in this section is directed at those light dependent compounds (e.g., isoprene). As shown in Figure 1, leaf isoprene emission increased with increasing PPFD at low PPFD levels but saturated at PPFD levels about half of full sunlight. The PPFD at any height within a plant canopy is determined primarily by the solar constant (the radiation flux output by the sun), the solar angle (the angle between the sun and the earth surface), atmospheric aerosol and trace gas concentrations, and plant canopy structure. Changes in the solar constant and interannual variations in the daily and annual patterns of solar angle are negligible in comparison to the other potential changes in PPFD. Both canopy structure and atmospheric composition are factors that fluctuate considerably and are susceptible to directional changes with time.

Atmospheric concentrations of aerosols and trace gases, particularly water vapor (i.e., cloud cover), strongly influence both transmissivity, the fraction of PPFD transmitted through the atmosphere, and the relative proportion of direct and diffuse PPFD at the top

of the canopy. An increase in cloud cover will decrease total PPFD, but will increase the fraction of diffuse PPFD. The canopy environment model used for this study predicted that increasing cloud cover would result in a lower PPFD for leaves at the top of a canopy, but may increase PPFD levels in the lower canopy because scattered photons more effectively penetrate to the canopy interior. Cloud cover similarly influences total solar radiation, which can impact isoprene emission rates by changing the radiant energy levels that determine leaf temperature. Consequently, increasing cloud cover decreased isoprene emissions in the upper canopy but increased isoprene emissions in the lower canopy. Sensitivity studies with the isoprene emission model (see section 2.3) indicated the influence of cloud cover on isoprene emission was dependent on LAI and solar angle. The average daytime PPFD transmissivity at the La Copita site was about 0.6. A simulated 50% increase (50% decrease) in transmissivity resulted in a predicted 48% increase (67% decrease) in isoprene emission

4.2 Leaf temperature

The leaf energy balance model used for this study predicted that an increase in ambient temperature would result in a leaf temperature increase of the same magnitude. The large increase in isoprene emission with increasing leaf temperature, shown in Figure 1, demonstrates the potential sensitivity of isoprene emission to short term changes in ambient temperature. It is not yet clear whether this temperature response will be sustained or if acclimation will occur. The annual ambient temperature at the La Copita site, predicted by general circulation models for a doubled CO_2 climate scenario, ranges from about 3 to 6°C above the present 21.3°C (e.g., VEMAP 1995). The corresponding predicted increase in total terpenoid emissions for this magnitude of temperature change would be 50 to 100%, respectively. Leaf temperatures are also sensitive to changes in radiation flux, leaf water potential (strongly related to soil moisture and rainfall), relative humidity and wind speed. The emission model predicted that isoprene emission would increase by about 25% with a) a decrease in wind speed from 3 to 2 m s⁻¹; b) an increase in relative humidity from 50 to 65%; or c) an increase in solar radiation flux from 300 to 340 W m⁻².

4.3 Foliar density and species composition

Changing land-use practices can alter landcover and thereby influence biogenic NMHC emissions. Although the vegetation changes reconstructed for the La Copita site cannot be directly extrapolated to other regions, they illustrate the direction and relative magnitude of the NMHC emission changes that can occur with land cover change. As noted in Section 3.2, the SLG above-canopy flux estimates representative of the present-day savanna parkland/thorn woodland landscape at La Copita were in good agreement with the emission model estimates. This suggests our estimates of species foliar density and NMHC emission were reasonable and that parameterization of the emission model for this site was sound.

A subsequent coupling of a vegetation change model to the biogenic NMHC emissions model (see Section 2) indicated total terpenoid (isoprene plus monoterpene) emissions from the present-day landscapes characterized by savanna parkland/thorn woodland has increased by a factor of three (from about 0.6 to 1.7 mg C m^{-2} h^{-1} for a canopy average temperature of 30°C) over that of the historical C$_4$ grassland which dominated this area 100-200 years ago. An assessment of the region surrounding La Copita indicates that agricultural activities such as sorghum farming dominate land-use. The terpenoid emissions associated with this landcover type (also a C$_4$ grass) were predicted to be about a factor of 3 lower than that of the current savanna parkland/thorn woodland and comparable to that estimated for the historical native C$_4$ grassland. This prediction was validated by the MLMB above-canopy flux measurements.

Our estimates of changes in NMHC emissions associated with the conversion of grassland to woodland at the La Copita site are in accordance with estimates in other ecosystems. Klinger et al. (1998) documented a 4-fold increase in total terpenoid emissions per unit foliar mass along a grassland savanna to *Isoberlinia*-dominated woodland transect in Central Africa. Changes in NMHC emissions associated with vegetation change in subtropical Texas and tropical Africa also mirror those reported for temperate forest. Martin and Guenther (1995) used a forest succession model to predict changes in foliar density and species composition at two sites in Minnesota USA over a 500 year period (400 years with the present climate; then 100 years with various future climate scenarios). The predicted changes in forest structure were then evaluated with a biogenic emission model. A 2- to 4-fold increase in isoprene emission was predicted for the successional sequences under the present climate. An additional 2- to 4-fold increase was predicted for a transient change in climate.

5. Conclusions

Biogenic NMHC emissions from a subtropical savanna parkland/thorn woodland landscape in southern Texas were characterized and the site was used as a case study for investigating the magnitude and relative importance of changes in biogenic NMHC emissions associated with landcover and climate change. NMHC emission rates of about 40 plant species were characterized, including many that have not been previously investigated. Grasses, as a group, were typically low emitters. Emission rates among woody plants were highly variable. Although there was a tendency for evergreen shrubs to have higher emission rates than deciduous species, there were several important exceptions. As a result, there were no clear or consistent emission rate patterns associated with woody plant taxonomic, growthform or functional groups.

Savannas are a globally significant source of biogenic NMHC emissions and are susceptible to changes in climate and landcover. Several of the primary factors controlling biogenic NMHC emissions can be strongly influenced by changes in landcover and climate. A biogenic NMHC emission model, similar to the ones described by Guenther et al. (1995) and Guenther (1997), predicted isoprene emissions from the present-day savanna parkland/thorn woodland vegetation (1.7 mg C m^{-2} h^{-1}) that were within 20% of those measured by a tower based flux system. A vegetation dynamics model (Scanlan and Archer (1991) linked with the biogenic NMHC emission model, predicted that vegetation changes at this subtropical site over the past century (replacement of savanna grassland dominated by 'low emitters' by a thorn woodland complex containing many 'high emitters') would have increased isoprene emissions by a factor of three (from about 0.6 to 1.7 mg C m^{-2} h^{-1} for a canopy average temperature of 30°C). The conversion of savanna grassland to cropland represents another dominant landcover change in this region. The emission model predicted very little change (<25%) in isoprene emission associated with this landcover change. The isoprene emission predicted for cropland, mixed with some thorn savanna/woodland, was 0.72 mg C m^{-2} h^{-1} which is within 30% of emissions estimated by a tethered balloon based flux system.

The biogenic emission model also predicted that the increase in ambient temperature of 6°C, predicted for this region by a general circulation model for a doubled CO$_2$ climate scenario, could elicit a 2-fold increase in isoprene emissions from this subtropical savanna parkland/thorn woodland site. Model experiments indicated that cloud cover, precipitation, relative humidity, and winds exerted some control over NMHC emissions, but difficulties in predicting future changes in their dynamics makes it difficult to assess their impact on future emissions.

Results of this study demonstrated that isoprene emissions from this subtropical savanna parkland/thorn woodland landscape can be significant and are strongly linked to landcover and climate variables that have

changed in the past and may change in the future. Isoprene and other biogenic VOC have a major role in determining the chemical composition of the atmosphere and changes in emissions of these compounds associated with landcover change in grasslands, savannas and woodlands are likely to have a significant impact. A better understanding of the potential changes in biogenic emissions from this, and other globally important landscapes, is needed in order to predict the impact of human induced and natural global change.

Acknowledgments

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