

The impacts of reactive terpene emissions from plants on air quality in Las Vegas, Nevada

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ABSTRACT

A three-part study was conducted to quantify the impact of landscaped vegetation on air quality in a rapidly expanding urban area in the arid southeastern United States. The study combines in situ, plant-level measurements, a spatial emissions inventory, and a photochemical box model. Maximum plant-level basal emission rates were moderate: 18.1 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$ (*Washingtonia* spp., palms) for isoprene and 9.56 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$ (*Fraxinus velutina*, Arizona ash) for monoterpenes. Sesquiterpene emission rates were low for plant species selected in this study, with no measurement exceeding 0.1 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$. The high ambient temperatures combined with moderate plant-level emission factors resulted in landscape emission factors that were low (250–640 $\mu\text{gC m}^{-2} \text{h}^{-1}$) compared to more mesic environments (e.g., the southeastern United States). The Regional Atmospheric Chemistry Mechanism (RACM) was modified to include a new reaction pathway for ocimene. Using measured concentrations of anthropogenic hydrocarbons and other reactive air pollutants (NO_x , ozone), the box model employing the RACM mechanism revealed that these modest emissions could have a significant impact on air quality. For a suburban location that was downwind of the urban core (high NO_x ; low anthropogenic hydrocarbons), biogenic terpenes increased time-dependent ozone production rates by a factor of 50. Our study demonstrates that low-biomass density landscapes emit sufficient biogenic terpenes to have a significant impact on regional air quality.

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1. Introduction

As the population of southern Nevada has grown, the increase in vehicle use has caused exceedances of US federal government air quality standards. Efforts to control air pollution sources require modeling both anthropogenic and biogenic sources of chemical species involved in ozone formation. Very little is currently known about biogenic volatile organic compounds (BVOCs) emissions from native desert and forest plants and non-native plants used in landscaping and the concomitant effects on air quality. To evaluate the contribution to ozone pollution of BVOCs from urban vegetation, we have conducted a unique three-part study, in which measurements, spatial modeling, and atmospheric chemistry modeling are

combined to assess the impact of BVOCs on air quality in Las Vegas, Nevada.

The majority of BVOCs emitted by vegetation make up the volatile component of a larger group of plant-produced chemicals known as terpenoids. These BVOC terpenoids can be classified into four categories: isoprene, monoterpenes (MTs), sesquiterpenes (SQTs), and oxygenated hydrocarbons (Guenther et al., 1995; Helmig et al., 1999; Fall, 2003). MTs and SQTs play a role in pollination or defense against herbivory (Gershenson and Croteau, 1991), while isoprene's hypothesized functions, including thermal and/or oxidant protection for plants or as a safety valve for the release of excess metabolites, are still under debate (Singsaas et al., 1997; Sharkey and Yeh, 2001; Loreto et al., 2001; Rosenstiel et al., 2004). Isoprene and MTs are the most well characterized BVOCs (Lerdau and Guenther, 1997). However, recent, indirect evidence suggests that reactive terpenoids are emitted in much higher amounts than MTs (see further discussion below).

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1.1. Atmospheric chemistry

BVOC fluxes are estimated to be on the order of 1150 Tg carbon yr⁻¹ on a global scale (Guenther et al., 1995), which is roughly an order of magnitude higher than anthropogenic volatile organic compound (VOC) emissions (Fuentes et al., 2000). North America has a BVOC flux of about 84 Tg carbon yr⁻¹ composed of roughly 35% isoprene, 25% MTs and SQTs, and 40% non-terpenoid compounds (Guenther et al., 2000). BVOCs are a key class of compounds in regard to tropospheric chemistry due to high emission rates and reactivities which are greater than those of anthropogenic hydrocarbons (Carter, 1994; Atkinson and Arey, 1998).

Nitrogen oxides (NO_x = NO + NO₂) react with VOC oxidation products to form ozone in the troposphere and thereby contribute to air pollution (Finlayson-Pitts and Pitts, 2000). The mechanism for ozone formation involves VOCs that react with either hydroxyl radicals (HO), ozone (O₃), or nitrate radicals (NO₃). Following this initial oxidation reaction, nitrogen oxide is converted to nitrogen dioxide (NO → NO₂), which then photolyzes to produce odd oxygen. The excited oxygen species produced combines with diatomic oxygen to form ozone. The majority of NO_x sources are anthropogenic, mainly from the burning of fossil fuels, while natural sources of these compounds include soil microbes, lightning, and forest fires (Monson and Holland, 2001). The main anthropogenic sources of VOCs are fueling operations, paints, and the burning of fossil fuels (EPA, 2007), while the natural sources include forest fires (Wiedinmyer et al., 2006) and BVOCs. Although biogenic sources of air pollution cannot be controlled, their contributions must be understood since concentrations of NO_x and VOCs in the atmosphere are an important component in devising air pollution control strategies. The VOC/NO_x ratio for a particular location determines the sensitivity of ozone concentrations to reductions in anthropogenic VOCs and NO_x emissions (Finlayson-Pitts and Pitts, 2000).

1.2. Plant BVOC production

Terpenoids are the largest and most diverse group of compounds produced by plants (Gershenson and Croteau, 1991), with two main biochemical pathways leading to their production. It is hypothesized that the acetate/mevalonate (MVA) pathway produces the precursors to SQTs and multiples thereof, such as triterpenes (Theis and Lerdau, 2003), while the deoxyxylulose-5-phosphate/methylerythritol phosphate pathway (DOXP/MEP) (Lichtenthaler, 1999) pathway leads to the production of isoprene and MTs. Certain terpenes, such as isoprene and a few MTs, are emitted directly after production, while most MTs and all SQTs are accumulated in specific, specialized structures for a period of time after production and before volatilization (Niinemets and Reichstein, 2003). This holds true for most MT and SQT emissions from vegetation in the Las Vegas area. *Pinus* spp. are among the most dominant vegetation in the Las Vegas metropolitan area, and BVOC emissions from two species *Pinus eldarica* (Mondel pine) and *Pinus halepensis* (Aleppo pine) were quantified in this study. *Pinus* spp. store terpenes in distinctive structures called resin ducts, as do many other conifers (Fahn, 1988; Trapp and Croteau, 2001). Resin cells are a simpler storage structure for terpenoids and are utilized by members of the family Cupressaceae. *Juniperus* spp. (juniper), which are members of this family, are also abundant in the Las Vegas area. Herbaceous, arid plants, such as *Rosmarinus officinalis* (rosemary), of the Labiatae family, and *Ambrosia dumosa* (white bursage), of the Compositae family, are also abundant and utilize glandular trichomes to store terpenoids (Fahn, 1988; Gershenson and Croteau, 1991).

1.3. Plant BVOC emission

For over 15 years, leaf-level studies have quantified volatile SQT emissions from different plants species and compared SQT emission rates to MT emission rates. Winer et al. (1992) found that emissions of SQTs were actually higher than those of MTs from cherry, peach, safflower, and other agricultural crops in southern California. This study specifically identified β-caryophyllene, α-humulene, and cyperene as SQTs emitted, but also detected several other C₁₅H₂₄ compounds which could not be positively identified. β-Caryophyllene was also detected in emissions from *Salvia mellifera* (black sage), a desert species native to California's South Coast Air Basin (Arey et al., 1995). Black sage emitted several other SQTs in concentrations equal to or greater than MTs emitted during the spring months of this study. Outside of California, Ciccioli et al. (1999) studied emissions of BVOCs from orange orchards in Spain, and found that emissions of β-caryophyllene made up the majority (50–70%) of total hydrocarbon emissions from orange species during the summer months. A recent study in Finland also showed high emissions of β-caryophyllene during the midsummer months from *Pinus sylvestris* (Scots pine). Total SQT emissions during late July were around 0.5 μgC gdw⁻¹ h⁻¹, while total MTs emissions were over twice this amount for the same time period (~1.3 μgC gdw⁻¹ h⁻¹, Hakola et al., 2006). A study of *Pinus taeda* (loblolly pine) in the southeastern United States showed emission of β-caryophyllene, α-humulene, α-bergamotene, and β-farnesene in amounts similar to those of emitted MTs (Helmig et al., 2006). Lastly, emissions from two clones of *Betula pendula* (silver birch) were measured, and the BVOC emissions from both clones in July were dominated by SQTs, including germacrene-D, (E,E)-α-farnesene, α-copaene, and β-bourbonene. In August, however, MTs made up the majority of the total BVOC emissions (Vuorinen et al., 2005). These leaf-level studies suggest that emissions of MTs are greater than or equal to SQT emissions for a variety of plant species, and that the magnitude of emissions has a seasonal variance.

In contrast, recent research at the whole-canopy scale has suggested that sesquiterpenes (SQTs) or perhaps other very reactive BVOCs comprise a much larger portion of total BVOCs than previously thought. For example, an ozone deposition study in California's Sierra Nevada foothills and a hydroxyl radical reactivity study in a northern Michigan forest both suggest that total reactive terpenoid emissions could be ten times higher than those of measured MTs (Goldstein et al., 2004; Di Carlo et al., 2004).

Very little is currently known about BVOC emissions from vegetation in the southwestern United States and the concomitant effects on air quality. This is due, in part, to national land cover databases biased by eastern U.S. vegetation studies which have poorly characterized the Southwest due to faulty assumptions of biomass density and rural/urban vegetation similarities (Kinnee et al., 1997; Diem and Comrie, 2000). Although relatively low in biomass density, the ecosystems of the arid southwest can emit significant BVOCs, since high air temperatures drive greater emission fluxes (Geron et al., 2006). Geron et al. report that peak summertime monoterpene emissions from arid ecosystems can reach 50% of values observed in eastern forests with much higher biomass densities. Southwestern cities contain many introduced plant species, and Diem and Comrie (2000) found that most of the BVOCs emitted within the city of Tucson, AZ were produced by introduced trees, such as eucalyptus, palm, and pine. These unique aspects increase the need for studies focused specifically on urban vegetation in the arid southwestern U.S.

We conducted a three-part study to investigate the impact of BVOC emissions on air quality in the Las Vegas area. (1) Field measurements of BVOCs in residential and commercial areas, golf courses, and parks were conducted to supplement published BVOC emission factor

databases. (2) This information was then entered into a GIS framework to produce an expanded emissions inventory for the Las Vegas, Nevada area. (3) Atmospheric chemistry box model simulations were employed to evaluate the contribution of BVOC emissions to tropospheric ozone production in urban and suburban areas.

2. Methodology

2.1. Measurements of BVOC emissions

Measurements of BVOC emissions from native and non-native vegetation were conducted between March and August 2006. Existing vegetation survey data were analyzed and species were selected for study that made up the top 85% of all plant species in the survey by area. Five sites within the Las Vegas metropolitan area were selected. BVOC leaf-level measurements were conducted with a field-portable gas chromatograph with flame-ionization detector (GC-FID), a novel glass chamber, and supplemental sample collection for compound identification in the laboratory by GC mass spectrometer (GC-MS).

2.1.1. Land use survey and plant species composition

A vegetation survey for the Las Vegas metropolitan area was obtained from Environmental Quality Management, Inc. (EQM). The urban area (208 690 acres; 84 454 ha) was divided into nine land use classes and vegetation surveys were conducted by EQM to determine vegetative, barren, and impervious coverages (EQM, 2006). This survey data was then processed into a percent coverage for each type of vegetation within each of the classes. These data were used to determine the top 85% of plant types in the urban area by spatial coverage. It was calculated that 21.9% of the urban area is barren of vegetation, 36.7% is made up of impervious surfaces such as roads and buildings, and 8.8% is composed of the Right of Way category which is defined to have no vegetation. Table 1 details the 15 plant types which make up the top 85% of foliage covering the remaining vegetated area.

Slightly less than 50% of the vegetation is made up of different species of grasses, wild and domestic. However, BVOC emissions from grasses were not measured during the field study. Several studies have examined BVOC emissions from lawn grasses in the past, and have found that only light-weight oxygenated BVOCs are emitted (Kirstine et al., 1998; Fall, 1999; Karl et al., 2001). Due to relatively long chemical lifetimes, these compounds are less important to local tropospheric chemistry and were not the focus of this study. Also, in the southwestern US, bermudagrass is the most common domesticated grass species (Bowman et al., 2006) and uses the C4 photosynthetic pathway. However, isoprene emission is associated with the C3 photosynthetic pathway (Wildermuth and Fall, 1996).

2.1.2. BVOC emission measurements

Measurements were conducted at five locations within the Las Vegas area (Table 2 and Fig. 1). Several instruments were used in conjunction to measure, identify, and quantify BVOC emissions. A novel glass leaf chamber was employed to enclose leaves and/or small branches for BVOC sample collection. The original design of Peter Harley, Ph.D. (National Center for Atmospheric Research, Boulder, CO) was modified to better suit the types of vegetation present in the Las Vegas area. Many of these plant species emit larger amounts of volatile compounds in response to leaf/needle disturbance, so the leaf chamber was re-designed to minimize disturbance during sample collection. The new design includes a 23 cm long cylinder with an I.D. of 7.5 cm and a two-piece glass lid that allows plants to slide into the chamber without being compressed. Glass was selected to provide an essentially inert surface. Well-mixed air was maintained in the chamber by a fan.

The motor of this fan was outside the chamber to avoid contamination. The air temperature of the chamber was modulated by two thermoelectric coolers and leaf temperature was monitored with a fine-wire thermocouple. High ambient temperatures prevented the coolers from maintaining a single leaf-temperature set-point, but were effective in keeping the enclosed plant material from going above ambient temperatures. The chamber was attached to a tripod which allowed leaves up to 2 m in height to be measured.

A Licor LI-6400 photosynthesis system (Licor, Lincoln, NE) was used as a pump and flow controller for air entering the leaf chamber and also to measure leaf physiology and ambient light levels. Inlet air was scrubbed of hydrocarbons twice to ensure a VOC-free background signal. The first scrubber (Refillable Hydrocarbon Trap, Restek, Bellefonte, PA) was placed on the inlet into the Licor, and the second (coconut charcoal Orbo filter, Supelco, Bellefonte, PA) was situated just before the leaf chamber. The Licor air pump also removed ozone from the inlet air (Geron et al., 2006), which is necessary due to the extremely rapid reaction time of certain BVOCs with ozone. Air flowed into the leaf chamber at a rate of 724 ml min^{-1} ($500 \mu\text{mol s}^{-1}$) and was drawn out of the chamber at a rate of $450\text{--}500 \text{ ml min}^{-1}$ by a second pump. These air flows kept the chamber under positive pressure and allowed for small gaps when sealing the plant stem.

Air was pulled from the glass leaf chamber into a field-portable GC-FID (8610C, SRI, Torrance, CA) and attached solid-phase hydrocarbon trap. Teflon tubing (1/8 in, 3.2 mm, O.D.) was used for all air sampling lines. The hydrocarbon trap was composed of about 7.5 cm of Tenax TA (60/80 mesh) centered in the middle of a 12.5 cm piece of 3.2 mm (1/8 in) O.D., 2.16 mm (0.085 in) I.D. fused-silica-lined stainless steel tubing. Samples were collected at a rate of 50 ml min^{-1} for 20 min for a total sample size of 1 L (STP). The hydrocarbon trap collection protocol was as follows: (1) ambient temperature for 20 min during air sample load, (2) 5 ml min^{-1} hydrogen back flush for 18 s, (3) heating the trap to $275 \text{ }^\circ\text{C}$, and then injection onto the GC column. The hydrogen flush removed ambient air since heating in the presence of oxygen quickly oxidizes SQTs and degrades the Tenax adsorbent. Since the hydrocarbon trap was not cooled below ambient temperatures ($27\text{--}38 \text{ }^\circ\text{C}$), a fraction of isoprene and MTs broke through the trap. To correct for this loss, algorithms were derived from laboratory tests using a gas standard of isoprene and α -pinene in nitrogen at a series of trap temperatures. The mean breakthrough amount (i.e., correction) for MTs was under 20%. The algorithm fit to the data explained 90% of the variance, and we calculate the uncertainty due to this breakthrough to be less than 5%. The breakthrough for isoprene was substantially higher, but the algorithm fit was very good (98%), so we estimate the uncertainty is much less than the variability inherent in the measurements.

The GC column was a 0.53 mm I.D. \times 30 m, 3.0 μm film MXT-624 capillary column (Restek). The GC oven temperature program was: $50 \text{ }^\circ\text{C}$ for 2.6 min, $10 \text{ }^\circ\text{C min}^{-1}$ to $225 \text{ }^\circ\text{C}$ (17.5 min), and $225 \text{ }^\circ\text{C}$ for 8.5 min. Additional sampling was performed on a subset of the measurements to identify compounds. Solid-Phase Micro Extraction (SPME, Supelco) fibers and SuperQ cartridges (Southern Scientific Inc., Micanopy, FL) were used in conjunction with a GC-MS (5890 Series II/5970, HP, Palo Alto, CA). Samples were collected by exposing SPME fibers for 45–60 min to the sample air stream, which were then refrigerated for transport back to the laboratory. Fibers were analyzed by GC-MS through gas-phase thermal desorption. Although some tentative BVOC identities were assigned through SPME analysis, the fibers did not hold samples well for extended periods (weeks), even when kept cold. Samples also were collected on SuperQ cartridges for 90–100 min at 100 ml min^{-1} and then kept in vials and refrigerated until transported back to the lab. Analytes were concentrated by liquid extraction with about 1.5 ml of dichloromethane and then evaporation with a steady

Table 1
Emission factors from species composing the top 85% of metropolitan vegetation.

Botanical Name (common name)	Percent cover	ISO	API	CAM	SAB	BPI ^d	CAR	LIM ^e	PCY	BTE ^f	COC ^g	AOC	BEL	ACO	BCA	AHU	AFA
Grasses	48.4%																
<i>Pinus</i> spp. (pine) ^a	7.10%	0.00	0.53 (0.67)	0.01 (0.01)	0.01 (0.01)	0.25 (0.20)	0.18 (0.27)	0.11 (0.04)	0.00	0.00	4.83 (2.44)	0.18 (0.06)	0.002 (0.002)	0.00	0.01 (0.01)	0.00	0.00
<i>Washingtonia</i> spp. (palm)	3.50%	18.06 (0.00)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>Prosopis</i> spp. (mesquite)	3.20%	0.00	0.003 (0.01)	0.00	0.00	0.004 (0.01)	0.00	0.02 (0.03)	0.00	0.00	0.09 (0.11)	0.06 (0.07)	0.00	0.00	0.00	0.00	0.01 (0.01)
<i>Larrea tridentate</i> (creosote)	3.10%	0.00	0.02 (0.04)	0.06 (0.07)	0.00	0.00	0.00	0.09 (0.16)	0.00	0.04 (0.05)	0.10 (0.10)	0.03 (0.03)	0.00	0.00	0.00	0.00	0.00
<i>Atriplex</i> spp. (saltbush)	3.00%	0.00	0.01 (0.01)	0.004 (0.01)	0.00	0.01 (0.02)	0.01 (0.02)	0.03 (0.05)	0.21 (0.21)	0.00	0.003 (0.01)	0.07 (0.08)	0.00	0.00	0.00	0.00	0.00
<i>Morus alba</i> (mulberry)	2.90%	0.00	0.00	0.00	0.02 (0.03)	0.00	0.00	0.24 (0.32)	0.00	0.07 (0.09)	0.00	0.05 (0.05)	0.00	0.00	0.00	0.00	0.00
<i>Acacia</i> spp. (acacia) ^b	2.50%	0.00	0.00	0.01 (0.01)	0.00	0.00	0.00	0.00	0.02 (0.02)	0.00	0.00	0.03 (0.04)	0.00	0.00	0.00	0.00	0.00
<i>Fraxinus</i> spp. (ash)	2.40%	0.00	0.00	0.00	0.00	0.10 (0.09)	0.00	5.79 (4.25)	0.00	0.00	2.89 (2.57)	0.79 (1.31)	0.00	0.00	0.00	0.00	0.00
<i>Nerium oleander</i> (oleander)	2.30%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01 (0.002)	0.00	0.00	0.00	0.00	0.00
<i>Populus</i> spp. (cottonwood)	1.90%	14.26 (12.60)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>Rosmarinus officinalis</i> (rosemary)	1.70%	0.00	0.70 (0.62)	0.44 (0.39)	0.00	0.60 (0.68)	0.20 (0.24)	0.21 (0.17)	0.52 (0.48)	0.00	0.64 (0.67)	0.11 (0.12)	0.003 (0.01)	0.00	0.01 (0.01)	0.00	0.00
<i>Leucophyllum</i> spp. (barometer bush)	1.40%	0.00	0.00	0.00	0.00	0.00	0.00	0.23 (0.02)	0.04 (0.003)	0.00	0.02 (0.03)	0.07 (0.01)	0.00	0.00	0.01 (0.00)	0.00	0.00
<i>Ambrosia dumosa</i> (bursage) ^c	1.20%	0.00	1.6 (0.93)	0.06 (0.03)	0.00	3.00 (1.50)	0.00	2.00 (0.87)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>Juniperus</i> spp. (juniper)	1.10%	0.00	0.28 (0.26)	0.03 (0.03)	0.04 (0.04)	0.05 (0.06)	0.55 (0.75)	0.05 (0.04)	0.00	0.04 (0.04)	0.06 (0.07)	0.04 (0.03)	0.00	0.05 (0.03)	0.03 (0.02)	0.06 (0.03)	0.01 (0.01)

Units are $\mu\text{gC gdw}^{-1} \text{h}^{-1}$ and standard deviations are in parentheses. ISO = isoprene, API = α -pinene, CAM = camphene, SAB = sabinene, BPI = β -pinene, CAR = 3- Δ -carene, LIM = Δ -limonene, PCY = p-cymene, BTE = β -terpinene, COC = cis-ocimene, AOC = allo-ocimene, BEL = β -elemene, ACO = α -copaene, BCA = β -caryophyllene, AHU = α -humulene, AFA = α -farnesene.

^a Pines category is a combination of the BVOC emissions from Mondel pine (2/3) and Aleppo pine (1/3). See text for rationale.

^b *Acacia stenophylla* (shoestring acacia) BVOC emissions were used to represent all species of acacia in metropolitan area.

^c Emission factors from Geron et al. (2006) were used to represent *Ambrosia dumosa* (white bursage).

^d Beta-pinene co-elutes with myrcene, however, SuperQ cartridge samples and GC-MS library match identified this peak as β -pinene for those sampled with this technique.

^e This peak could be trans-ocimene for ash and a combination of trans-ocimene and limonene for Mondel pine as these compounds elute 0.06 min apart. Trans-ocimene has two peaks according to library match.

^f Beta-terpinene and β -thujene also coelute. Juniper emits β -thujene, while it is uncertain which compound is emitted by creosote and mulberry.

^g Cis-ocimene, trans-ocimene, and eucalyptol elute within 0.06 min of each other and overlap on the GC-FID. From SuperQ cartridge sampling, Mondel pine emits trans-ocimene, creosote emits cis-ocimene, and rosemary emits eucalyptol. Ash emits a light-dependent compound which is likely an ocimene.

Table 2
Field research sites.

Name	Species Studied	Latitude/Longitude
Angel Park Golf Course	Mesquite, cottonwood, shoestring acacia, and creosote bush	36° 10' 20.49" N, 115° 17' 13.56" W
Sunset Park	Saltbush, mesquite, Arizona ash, Mondel and Aleppo pine, oleander, palm, mulberry, and barometer bush	36° 04' 16.80" N, 115° 07' 06.24" W
Deerbrook neighborhood	Juniper, rosemary, and palm	36° 14' 26.77" N, 115° 15' 36.36" W
Desert Research Institute	Shoestring acacia	36° 06' 52.23" N, 115° 08' 49.53" W
Clark County Complex	Mesquite and Mondel pine	36° 09' 59.53" N, 115° 09' 18.39" W

stream of nitrogen. Sample volume was then adjusted by adding 10 μ l of hexane, and 1 μ l volumes were injected onto the GC–MS. Retention time analysis was used to identify compounds from samples when no SPME fibers or SuperQ cartridges were employed. Two liquid, authentic standards (β -caryophyllene and α -humulene) and a gas-phase standard of isoprene (5.25 ppm) and α -pinene (0.737 ppm) in nitrogen were run on the GC–MS and the GC–FID for identification. Other BVOCs were tentatively identified by comparing spectra to the HP NBS75K library (MS Chemstation software).

Calibration was performed with the gas-phase isoprene and α -pinene standard and other compounds were quantified by assuming a uniform carbon FID response. The instrument was determined to have a detection limit of 1 ng carbon. All emission rates were then based on the dry leaf weight (gdw = grams dry weight) of each leaf sample collected. Leaf samples were collected for each set of measurements on all plant species except for the majority of the *Larrea tridentata* (creosote bush). Leaf samples were stored in a cool location and brought back to the laboratory for leaf area and dry weight measurements (70 °C, 24–48 h).

G93 temperature and light-temperature dependent algorithms (Guenther et al., 1993) were used to scale emissions to their basal rate, which is defined as 30 °C. Temperature dependent algorithms were used to scale BVOC emissions from plant species that did not emit isoprene, while isoprene emitters were scaled using light-temperature dependent algorithms. Different temperature coefficients (β) were used for MTs ($\beta_{MT} = 0.09 \text{ K}^{-1}$) and SQTs

($\beta_{SQT} = 0.15 \text{ K}^{-1}$) according to current literature (Guenther et al., 1993; Helmig et al., 2006). Growth temperature affects the parameterization of the G93 algorithm (Petron et al., 2001), and desert plants have been observed to have a higher T_{max} value than temperate species (Geron et al., 2006). Because of the high air temperatures observed in Las Vegas, the selection of the T_{max} value has a strong influence on extrapolating observed emission rates. We used two values for T_{max} in this study: 41 °C and 51 °C. Changing T_{max} from 41 °C to 51 °C increases the algorithm's prediction by 70% at 40 °C when starting from a basal emission rate of 30 °C (Fig. 2). Unless explicitly noted, we used $T_{max} = 41$ °C.

Several steps were taken to ensure accurate BVOC emissions data. Most importantly, care was taken in leaf chamber placement around branches and leaves and replicate measurements for every species were collected to minimize and detect any disturbance emissions. Blank runs without enclosed vegetation were collected before and after individual plant species measurements to ensure BVOCs were not carried over on the Tenax trap or leaf chamber walls. If any carryover was detected (when observed, blank peak area was typically <10% of the measurement peak area), the leaf chamber was cleaned and a new blank run was performed before the next individual was measured. A Licor 6400 photosynthesis system was employed to collect photosynthesis and stomatal conductance measurements. These data were collected, logged, and archived to ensure that all plants were physiologically active at the time of measurement.

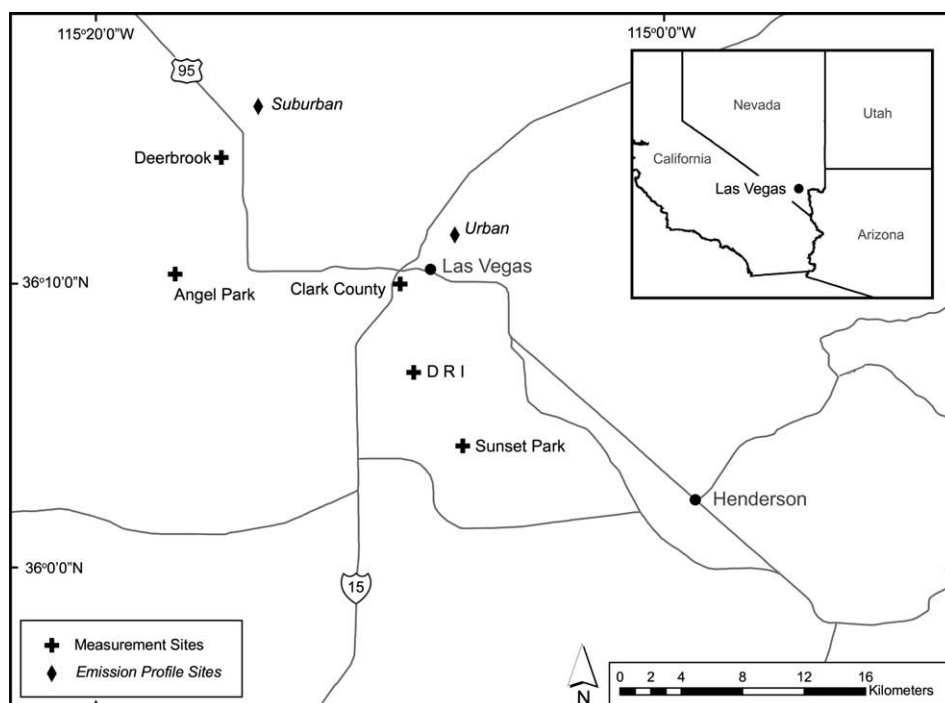


Fig. 1. Field research sites and emission profile sites within the Las Vegas metropolitan area.

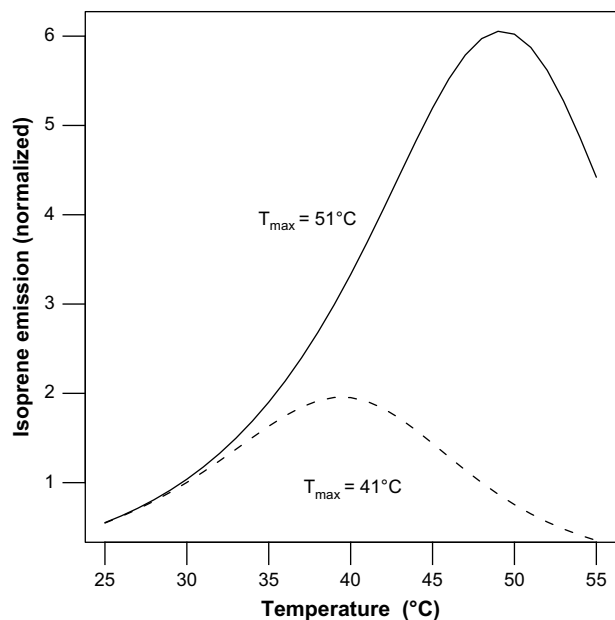


Fig. 2. Effect of T_{\max} on the isoprene emission algorithm of Guenther et al. (1993).

Ortega and Helmig (2008) reviewed current techniques for measuring BVOC emissions from plants and summarized a set of recommendations (Table 4, Ortega and Helmig, 2008). We followed the majority of their recommendations in our study, with the following three groups of exceptions. First, we use a glass cuvette instead of the recommended Teflon branch bag, which decreases our leaf sample mass and hence the detected BVOC concentration. We offset this decreased concentration by lowering the flow rate of air entering the cuvette. This relates to the second deviation from the review study's recommendations—controlling condensation within the enclosure. They recommend high flow rates and drying incoming air to prevent condensation. The extremely low relative humidity and low transpiration rates in our study area result in a situation where condensation does not occur. The third area is sample collection and concentration. As suggested, we use a solid absorbent and a field-portable GC-FID, but we supplement this with the SMPE fibers and SuperQ cartridges. We support this choice with two lines of reasoning. First, we are only performing compound identification with these techniques, and peaks matched with the GC-FID measurements. Second, the SuperQ method was thoroughly explored in several studies (Matsunaga et al., 2008, 2009).

2.2. Spatial emissions inventory

Up-to-date vegetation surveys of the urban area were recently conducted by Environmental Quality Management, Inc. (EQM) as part of the State Implementation Plan (SIP) for ozone exceedances in Clark County, Nevada. EQM defined nine urban land use classes (Table 3), and percent cover was assigned to the vegetation types present. These land use classes included categories for barren and impervious surfaces as well. The urban land use classes, associated vegetation types, and BVOC emission factors were combined using ArcGIS 9.0 software (ESRI, Redlands, CA) to map BVOC emissions over the metropolitan area with the following equation:

$$\text{Emission}_i = \sum_k \sum_j \text{PC}_{jk} \times \text{EF}_{ij} \times \text{BD}_j \times C_i \quad (1)$$

in which (i) represents BVOC chemical species, (j) represents vegetation type, (k) represents land use class, (PC) is percentage

Table 3

Urban land use classes and associated geographic coverage.

Urban Land Use Class	Code	Coverage (acres)	Percent of total area	Percent with vegetation
Industrial	IND	3548	1.7%	21%
Light Industrial	LIND	13 660	6.5%	16%
Suburban Residential	SUB	34 083	16.3%	8%
Urban Residential	URB	10 311	4.9%	19%
Rural Residential	RUR	25 057	12.0%	20%
Public Facilities and Parks	PARK	69 645	33.4%	22%
Commercial	COM	15 154	7.3%	9%
Major Development	MD	18 918	9.1%	8%
Right of Way	RoW	18 314	8.8%	0%
		208 690	100%	

Percent with vegetation is the percent area excluding barren cover, grasses, and impervious surfaces.

cover, (EF) is emission factor, (BD) is biomass density, and (C) is the temperature and light correction discussed above. The biomass density was calculated by dividing the leaf area index (LAI, m^2 leaf area m^{-2} ground area) by the specific leaf area (SLA, m^2 leaf area gdw^{-1}) measured during the field campaigns. Vegetation-specific LAI estimates were taken from the US EPA's Biogenic Emission Information System (BEIS, v3.12) database. Because the PC was determined by local survey data, this is a significant improvement over the landscape LAI estimates employed in BEIS. The temperature utilized for C was 37.8°C (100°F) since average summertime temperatures in Las Vegas are regularly at or above 37.8°C . Fig. 3 contains the results of these calculations summed over all BVOC species.

2.2.1. Emission profile sites

To compare the effects of BVOC emissions on air quality in urban and suburban areas, two representative locations within the metropolitan region were selected (Fig. 1). The Urban site (JD Smith, code JD) is located in the North Las Vegas area and the Suburban site (Joe Neal, code JO) is located north of Ann Road just east of Highway 95, which is often downwind of the Las Vegas urban core. These locations were selected because of the availability of ambient source profile data (T&B Systems, 2006b, see below; Clark County network).

The BVOC emissions for each site were derived from the spatial inventory by averaging over a $3\text{ km} \times 3\text{ km}$ box (total of nine grid cells) centered on the sites. An area of 9 km^2 was chosen to represent the diversity of vegetation in urban and suburban areas. Ambient temperatures were used for C in Equation (1): 44°C (111°F) at the Urban site and 41°C (106°F) for the Suburban site. These temperatures were recorded on July 15, 2005 at the JD Smith and Joe Neal monitoring stations, respectively, and source profile data from this date were used for the atmospheric modeling detailed below. July 15, 2005 was selected for the model since an ozone exceedance occurred. Winds of $3\text{--}13\text{ km h}^{-1}$ from the southeast were recorded between 9:00 and 18:00 at the Joe Neal monitoring station on this date, in agreement with the downwind characterization of this site. At these high air temperatures, the selection of the T_{\max} parameter in the G93 algorithm is very significant. We investigated the impact by changing T_{\max} from 41°C , the standard value, to 51°C for some model runs.

2.3. Atmospheric chemistry modeling

An atmospheric box model (SBOX, Seefeld and Stockwell, 1999) was applied to isolate the effects of BVOC emissions on ozone production using RACM2 for the chemical mechanism portion of the model (Regional Atmospheric Chemistry Mechanism, version 2;

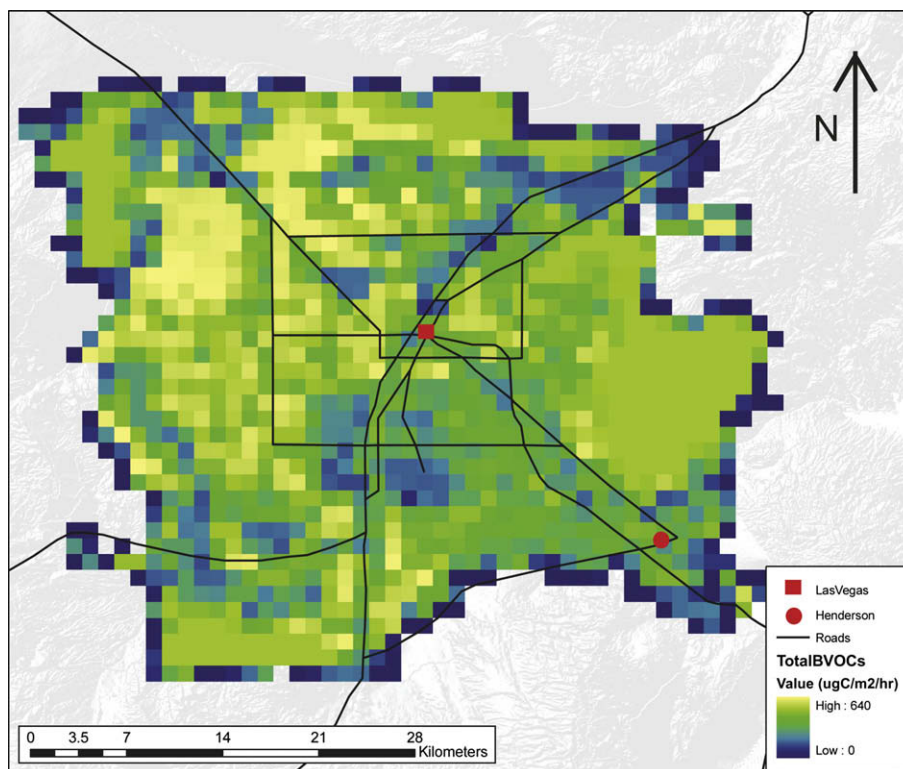


Fig. 3. Total BVOC emissions for Las Vegas metropolitan area.

Goliff et al., 2006). RACM2 is a gas-phase atmospheric chemistry mechanism that was developed to simulate the remote and urban troposphere. To simplify complex tropospheric chemistry, RACM2 aggregates similar compounds into groups according to their chemical characteristics (e.g., alkanes and alkenes) with a few exceptions for compounds with unique properties (Finlayson-Pitts and Pitts, 2000). RACM2 has been updated from the original RACM module with the Geiger isoprene mechanism and speciation of certain compounds, including benzene, methyl vinyl ketone, acetaldehyde, methanol, ethanol, and benzaldehyde (Goliff et al., 2006). RACM2 was implemented with these steps: (1) RACM2 was modified to include a new reaction scheme for the MT ocimene; (2) RACM2 was initialized with continental and site-specific chemical species data and meteorological information; and (3) the atmospheric model was run using RACM2 inputs and photolysis rate simulations.

2.3.1. Modifications to RACM2

Reactions involving the MT ocimene were added to RACM2. A detailed literature search was undertaken to collect current rates of reaction and reaction products with three atmospheric oxidants (O_3 , HO, and NO_3). These reactions, rates of reaction, and literature

references are listed in Table 4. A new category (OCI) was created to represent acyclic MTs measured in this study: cis-ocimene and allo-ocimene. The OCI category also includes another acyclic MT, myrcene that was not detected. Several studies have determined the reaction products for myrcene with O_3 and HO (Atkinson and Arey, 2003 and refs. therein; Lee et al., 2006a, 2006b), and the combined myrcene reaction products from these studies were used to represent the OCI category (Reactions (1) & (2)). Reaction rates were obtained from Calogirou et al. (1999) and references therein. Reaction (3) involves oxidation of OCI by NO_3 radicals. The RACM2 aggregation category DIEN represents the chemistry of smaller carbon compounds with two carbon-carbon double bonds (Stockwell et al., 1997), and so the reaction products for DIEN- NO_3 reactions were used as surrogates for Reaction (3).

The ten MTs quantified in this study were split into four groups based on their structures, reaction rates, and reaction products: API includes α -pinene, β -pinene, camphene, and 3- Δ -carene; LIM includes D -limonene, β -terpinene, and sabinene; OCI includes cis-ocimene and allo-ocimene; XYL includes p-cymene and other anthropogenic xylene compounds. The reaction rates and products of the API, LIM, and XYL groups were previously defined in RACM2.

Table 4

New BVOC reactions and rates of reaction for RACM2 chemical mechanism.

Reactions	Rate constant ($cm^3 \text{ molecule}^{-1} s^{-1}$)
1 $OCI + O_3 \rightarrow 0.51HCHO + 0.15ACD + 0.039ORA1 + 0.23ACT + 0.053ORA2 + 0.7UALD + 0.63HO$	5.6×10^{-16}
2 $OCI + HO \rightarrow 0.36ACT + 0.3HCHO + 0.05ORA1 + 0.19OLIP + SOA (25\%)$	2.52×10^{-10}
3 $OCI + NO_3 \rightarrow 0.90OLNN + 0.10OLND + 0.90MACR$	2.2×10^{-11}

Abbreviations: OCI = ocimene, HCHO = formaldehyde, ACD = acetaldehyde, ORA1 = formic acid, ACT = acetone, ORA2 = acetic acid, UALD = unsaturated aldehydes, OLIP = peroxy radicals from olefins, SOA = secondary organic aerosol, OLNN = organic nitrate adducts, OLND = organic nitrate adducts, MACR = methacrolein & unsaturated monoaldehydes. All rate constants from Calogirou et al. (1999) and references therein. Reaction (1) UALD and HO yields from myrcene- O_3 from Atkinson and Arey (2003); other products and yields from myrcene- O_3 from Lee et al. (2006a). Reaction (2) myrcene-HO products and yields from Atkinson and Arey (2003). OLIP represents unidentified gaseous products from the Lee et al. (2006b) study. The SOA yield was added to maintain carbon balance.

2.3.2. Initialization of RACM2 and modeling procedure

RACM2 was initialized according to the following steps. (1) Continental background concentrations were utilized to represent nitrogen (N₂), oxygen (O₂), methane (CH₄), carbon monoxide (CO), water vapor (H₂O), and sulfur species in RACM2. (2) Background VOC (including isoprene and α -pinene) and NO_x concentrations were obtained from the Clark County Regional Ozone Precursor Study (T&B Systems, 2006b) and ozone data taken from the Clark County ozone monitoring network (JD Smith/Urban and Joe Neal/Suburban sites) for July 15, 2005 were used to represent these compounds in RACM2. (3) BVOC emission fluxes compiled above for the Urban and Suburban sites were converted to concentration changes (ppb min⁻¹) by scaling them to a boundary layer height of 800 m. Although at its highest the boundary layer reaches 4400 m during the summer months (Mark Green, DRI, personal correspondence) a constant height of 800 m was used in this study (but see the sensitivity test described below). All BVOC emissions were constant in time, and only isoprene and α -pinene were initialized due to their presence in the source profile data noted above. (4) Two model simulations were performed per site for a total of four unique simulations. One was performed without BVOCs and the other included the BVOC emissions.

SBOX, an atmospheric photochemistry box modeling system using RACM2, treats an air mass as an arbitrarily shaped 'box,' but has no spatial dimension and is therefore completely well mixed. Model simulations were run with SBOX based on the simulations explained above, modeled photolysis rates, and the updated RACM2 mechanism. The photolysis rate simulations were calculated at the latitude for Las Vegas and for clear sky conditions. Simulations were 6 h in length, and ran from 10:00 to 16:00 local time to capture the time period at which BVOCs would have the largest effect on atmospheric chemistry due to higher air temperatures. Ozone exceedances in the Las Vegas Valley occur as the result of one of two situations: transport from the Los Angeles, CA area on days with strong southwest winds, or as the result of local urban sources on days with light and variable winds (T&B Systems, 2006a). An ozone exceedance is defined by the EPA as an 8 h average concentration exceeding 80 ppb. Data from July 15, 2005 was selected because an ozone exceedance due to 'local sources' occurred on this date.

2.3.3. Sensitivity tests

A series of additional runs were also performed to test the sensitivity of the model to changing inputs and assumptions. The first set evaluated the separate impact of adding only isoprene or MTs. Another set tested the impact of changing T_{\max} to 51 °C (see section 2.1). An additional set explored adding a dynamical boundary layer. The impact of a static boundary layer was tested by running a model simulation with a dilution rate equivalent to the boundary layer increasing 72% during the 6 h model run. Because this would also dilute the available NO_x, a NO_x source equal to 0.035 ppb min⁻¹ was also included in these model runs.

3. Results and discussion

3.1. Leaf-level measurements

A variety of BVOCs were emitted from the vegetation measured. Isoprene, ten MTs, and five SQTs were tentatively identified, and there were indications that other compounds were emitted as well. Table 1 details the plant types measured, the emission factors for each BVOC emitted and the associated standard deviations. Juniper had the highest total SQT emissions of the vegetation measured and emitted four unique SQTs; α -copaene, β -caryophyllene, α -humulene, and α -farnesene. Juniper also had the highest total number of

compounds emitted (13 MTs and SQTs combined). Overall, *Washingtonia* spp. (palm species) and *Populus* spp. (cottonwood species) had the highest total BVOC emissions, with isoprene emission factors of 18.1 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$ and 14.3 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$, respectively. *Fraxinus velutina* (Arizona ash) had the highest non-isoprene emissions (MTs and/or SQTs) with 9.56 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$, followed by Mondel/Aleppo pine with 6.11 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$, rosemary with 3.43 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$, and juniper with 1.27 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$. Arizona ash had the highest emission factor for a single compound (after isoprene) at 5.79 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$. Limonene and allo-ocimene were emitted from the highest number of plant species measured, and β -caryophyllene was measured most frequently of the SQTs. Our leaf-level dataset is beneficial in that novel isoprene and MT emission factors have been obtained that are specific to the climate of Las Vegas, and SQT emissions have been measured from these plants for the first time.

3.1.1. Isoprene emitters (palms and cottonwood)

Palm species and cottonwoods were the only plant types that emitted isoprene with no other BVOCs detected. The isoprene emission factor for the palm species (18.06 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$) is in reasonable agreement with the number reported by Guenther et al. (1994): 14 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$, and they also reported no significant MT emissions. Our rate for isoprene emission for cottonwoods is lower than another report in the literature (32.68–37 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$, Evans et al., 1982), but again there is agreement on a lack of MT emissions. Our lower emission rate could be due to drought stress typical for the Las Vegas area; extreme drought has been shown to suppress isoprene emissions after an initial stimulation (Pegoraro et al., 2007). The lack of SQT emissions from cottonwoods was confirmed by concurrent measurements reported by Matsunaga et al. (2009).

Due to time limitations caused by long run times and an emphasis on studying SQT emissions, we did not perform any temperature response curves for the two species emitting isoprene. As noted in the method section, desert plants have been shown to have higher values of T_{\max} in the G93 algorithm (Geron et al., 2006). Using a higher value for T_{\max} gives lower basal emission rates: increasing T_{\max} to 51 °C reduces the cottonwood basal emission rate by 33%–9.6 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$, which is even lower compared to the literature value cited above. The palm emission rate decreases by 30%–12.7 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$, and this is very close to the cited emission rate. We speculate that the standard value of $T_{\max} = 41$ °C is appropriate for the species measured in our study, because irrigation provides some water moisture and results in lower leaf temperatures due to evaporative cooling.

3.1.2. Pines

Mondel and Aleppo pines are the only genera present in each of the eight urban land use classes, and are often the highest percentage cover for these classes (after grasses). Only two SQTs were emitted by pines, but MT emissions from both species were moderate (defining low < 1 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$, moderate 1–10 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$, high > 10 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$, following the scheme of Benjamin et al. (1996)) with an emission factor of 4.829 \pm 2.444 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$ for cis-ocimene. SQT emissions have been measured from two other species of pine, Scots and Loblolly, in recent studies. Hakola et al. (2006) found emissions of β -caryophyllene and two other SQTs, tentatively identified as α -farnesene and α -humulene, from Scots Pine in southern Finland. They reported β -caryophyllene emission rates during the summer of 0.054 \pm 0.03 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$ (30 °C), which compares reasonably with our results (0.011 \pm 0.006 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$). Sampling from the same chamber employed during our study, Matsunaga et al. (2009) found similarly low total SQT emissions (0.016 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$). Helmig et al. (2006) found much higher β -caryophyllene emissions from loblolly pine, 0.30 $\mu\text{gC gdw}^{-1} \text{h}^{-1}$ (30 °C). Conversely, emissions of α -pinene, β -pinene, and δ -limonene

reported for loblolly pine were lower than in our study (Helmig et al.: α -pinene = 0.25, β -pinene = 0.12, δ -limonene = 0.013; current study: α -pinene = 0.53, β -pinene = 0.25, and δ -limonene = 0.11, all $\mu\text{gC gdw}^{-1} \text{h}^{-1}$). These differences could indicate variations within this genus, variability due to environmental factors such as temperature regime, nutrients, herbivory, precipitation, and phenology, or measurement error. Both the Scots and Loblolly pine studies examined emissions from trees in forest environments, while the Mondel and Aleppo Pines measured were located within a park and irrigated. Many parks and golf courses in the Las Vegas area are watered with reclaimed water, which we speculate may have a higher salt load and could thereby stress plants. On the other hand, irrigation for these park trees may reduce the water stress experienced by pines in their native environments.

3.1.3. Arizona ash

Arizona ash and its two cultivars, Fan-Tex and Modesto, are popular trees in Las Vegas and are present in large numbers in parks and residential areas due to their rapid growth rates and drought tolerance (Modesto and Fan-Tex, respectively, *Trees for Tomorrow*, 2005). BVOC emissions from Arizona ash were measured in Sunset Park in May, June, and August, and moderate emission rates for two MTs were found for all three months. Unfortunately, the SuperQ cartridge yielded poor identification of these two compounds in GC–MS analysis. Through retention time comparison, tentative identities of trans-ocimene and cis-ocimene have been assigned to these peaks. In August, Arizona ash also strongly emitted an additional MT, which was tentatively identified as allo-ocimene by retention time comparison. In May, trans-ocimene and cis-ocimene were light-dependent (reductions of 4% and 6% during the dark run). Loreto et al. (2000) found that *Pinus pinea* emits trans- β -ocimene in a light-dependent manner, while also emitting other stored MTs. Our tentative identifications are supported by the observation that ocimene is emitted in a light-dependent manner by other plant species. Regardless, Arizona ash produces a large source of reduced carbon to the atmosphere that was previously not accounted for.

3.1.4. Creosote bush and saltbush

Two species in this study, creosote bush and saltbush, were also measured by Geron et al. (2006) at a location approximately 100 km northwest of Las Vegas. Our current study and Geron et al. both found no significant isoprene emissions from these two species. For creosote bush, Geron et al. found that MTs totaled $2.0 \mu\text{gC m}^{-2} \text{h}^{-1}$, an amount which is larger than our results by a factor of six. Both studies detected at least five MTs, including significant levels of α -pinene, camphene, and limonene. We postulate that differences in phenology might explain the discrepancy in magnitude. We detected but did not quantify oxygenated monoterpenes (data not shown) in some creosote bush samples; Geron et al. also report a variety of oxygenated compounds. For *Atriplex* spp. (saltbush), our total monoterpene result, $0.347 \mu\text{gC m}^{-2} \text{h}^{-1}$, is very similar to Geron et al. ($0.31 \mu\text{gC m}^{-2} \text{h}^{-1}$). But while they found two major MTs, camphene and myrcene, we found a range of MTs, with the largest being p-cymene and allo-ocimene. We cannot explain this discrepancy, except to say that both studies have relatively small sample sizes and there could be differences in environmental conditions and/or phenological state.

3.1.5. Juniper and acacia

Juniper emitted four unique SQTs, and these were identified via SuperQ cartridges and GC–MS analysis. Juniper had the three highest individual emission factors for α -copaene, β -caryophyllene, and α -humulene. Juniper also emitted low amounts of several MTs, with higher amounts of α -pinene and 3- Δ -carene. Our results for total MT

emissions concur with a previous range estimate of Owen et al. (0.5 – $20 \mu\text{gC m}^{-2} \text{h}^{-1}$, 1998). Numerous species of juniper are present in Las Vegas, and although only one species was measured, the taxonomic technique for assigning BVOC emissions within genera and even families has proven successful (e.g., Benjamin et al., 1996; Harley et al., 2004). Our results for *Acacia* spp. (acacia) are low compared to the value from Guenther et al. (1994): 0.06 versus $3 \mu\text{gC m}^{-2} \text{h}^{-1}$, but this genus is widely dispersed throughout the world. This is a case where a location-specific emission factor is preferable to literature estimates derived from measurements performed in much different environmental conditions.

3.1.6. Mesquite, rosemary, barometer bush, mulberry, and oleander

For these species (except for rosemary), little or no information concerning monoterpene emissions currently exists in the literature. Mesquite species, including two native to the desert southwest, *Prosopis pubescens* (screwbean mesquite) and *Prosopis glandulosa* var. *torreyana* (honey mesquite), are often selected for landscaping projects in the Las Vegas area because of their low water needs. Behind only pine and palm species, mesquite is present in six urban land use classes. However, mesquite was found to emit only minor amounts of five MTs and one SQT. Mesquite could therefore be considered a 'good' species for landscaping in Las Vegas since it is native, has low water needs, and has low BVOC emissions. But a companion measurement made by Matsunaga et al. (2009) found much higher levels of SQT emissions ($0.793 \mu\text{gC gdw}^{-1} \text{h}^{-1}$) from mesquite, and this discrepancy is unexplained. We do not include this data from Matsunaga et al. in our emissions inventory. Rosemary and *Leucophyllum* spp. (barometer bush, also known commonly as Texas Sage and Texas Ranger) emitted small amounts of β -caryophyllene. Although barometer bush only emitted small amounts of a few MTs, rosemary emitted significant ($>0.1 \mu\text{gC gdw}^{-1} \text{h}^{-1}$) amounts of eight MTs. Rosemary and barometer bush are popular for landscaping in Las Vegas, and rosemary is often used in road medians and traffic corridors, which places emissions of BVOCs very near emissions of NO_x . Our total MT emissions for rosemary, $1.14 \mu\text{gC gdw}^{-1} \text{h}^{-1}$, is in reasonable agreement with a previous report of $2.2 \mu\text{gC gdw}^{-1} \text{h}^{-1}$ (Hansen et al., 1997). There are multiple barometer bush species and several different clones of each, but again we assumed a genus-level emission factor. To our knowledge, no studies have examined BVOC emissions from barometer bush or emissions from any other member in the family Scrophulariaceae. Also, *Morus alba* (mulberry) emitted significant amounts of limonene and *Nerium oleander* (oleander) emitted almost no MTs; again, there were no previous reports for MT emissions for these species in the literature.

3.1.7. Sesquiterpenes

SQTs were emitted by five of the 13 plant types measured in the Las Vegas metropolitan area. Our results are in line with other leaf-level chamber studies that show SQTs are emitted in amounts less than or equal to MTs and are not sufficient to account for the reactive terpenoid fluxes suggested by the ozone deposition and HO studies (Goldstein et al., 2004; Di Carlo et al., 2004).

3.2. Landscape modeling

Urban land use class emission factors for 16 BVOCs are shown in Table 5 and total BVOC emissions for each land use class in Fig. 4. Cis-ocimene has the highest emission factor for several classes, while isoprene has a high emission factor for each class. While isoprene emissions are expected to be high due to the presence of palms and cottonwoods, the high emissions of cis-ocimene were unexpected. Several plants emitted cis-ocimene, but pines with their large spatial coverage and moderate emission factor were the primary contributor. The selection of T_{max} introduces some uncertainty into our

Table 5
BVOC landscape emission factors by urban land use category.

BVOC	IND	LIND	SUB	URB	RUR	PARK	COM	MD	RoW
ISO	144.27	144.27	212.47	144.27	212.47	212.47	144.27	144.27	0.00
API	10.86	33.28	37.23	11.56	33.48	26.66	7.53	7.64	0.00
CAM	0.53	0.66	3.13	2.67	1.26	3.57	0.20	0.40	0.00
SAB	0.58	0.82	1.16	0.08	0.93	0.35	0.08	0.08	0.00
BPI	4.32	15.01	18.81	7.97	15.50	14.65	4.10	3.70	0.00
CAR	9.18	16.91	18.05	3.72	16.94	8.94	2.57	2.65	0.00
LIM	3.15	7.83	36.74	54.77	34.34	34.38	27.01	2.28	0.00
PCY	0.34	0.15	2.97	3.31	0.78	5.06	0.19	1.56	0.00
BTE	0.48	0.48	1.42	0.00	1.25	0.77	0.00	0.23	0.00
COC	69.73	274.02	289.76	99.76	286.71	222.12	81.17	68.63	0.00
AOC	4.27	11.57	15.73	12.56	14.96	14.03	6.71	3.20	0.00
Total MTs	103.49	360.76	425.37	197.03	406.52	330.88	129.90	90.41	0.00
BEL	0.03	0.10	0.12	0.04	0.10	0.09	0.03	0.03	0.00
ACO	0.64	0.64	0.64	0.00	0.64	0.00	0.00	0.00	0.00
BCA	0.52	0.99	0.99	0.22	0.96	0.53	0.16	0.16	0.00
AHU	0.66	0.66	0.66	0.00	0.66	0.00	0.00	0.00	0.00
AFA	0.16	0.16	0.14	0.15	0.11	0.02	0.02	0.00	0.00
Total SQTs	2.01	2.56	2.54	0.41	2.47	0.65	0.21	0.18	0.00
Total BVOC	249.73	507.55	640.02	341.08	621.10	543.65	274.04	234.83	0.00

Refer to Table 1 for species codes and Table 3 for land use codes. Landscape emission factors are in $\mu\text{gC m}^{-2} \text{h}^{-1}$.

predictions, but the effect is small for the spatial emissions inventory since measurement temperatures (32–38 °C) were close to the temperature selected for the spatial emissions inventory (37.8 °C). Changing T_{max} from 41 °C to 51 °C actually reduces the isoprene emission predictions, but by less than 8%.

MTs were emitted in much greater quantities than were SQTs, and SQTs made up less than 1% of MT emissions across the Las Vegas metropolitan area. Total MT emissions were also higher than total isoprene emissions. This is interesting since isoprene emissions are 10% higher than MT and SQT emissions combined for North America (Guenther et al., 2000). *Quercus berberidifolia* (scrub oak) is the only other species present in the metropolitan area known to have high isoprene emissions. However, scrub oak is only present as 1% of the coverage for two land use categories which

together account for <15% of area and therefore scrub oak does not contribute greatly to overall isoprene emissions for the Las Vegas metro region. The low results for SQTs relative to total BVOCs are comparable to results reported by Sakulyanontvittaya et al. (2008), with the caveat that their study includes our dataset. Considering our sample size, the fact that SQT emissions vary widely (Helmig et al., 2007) and that the controls are less well understood compared to isoprene and MT, our results for landscape SQT emission rates must be considered tentative.

Total BVOC emissions were highest for the Suburban Residential, Rural Residential, Public Facilities and Parks, and Light Industrial/Office land use classes, while a second group (Major Development, Right of Way, Industrial, Commercial, and Urban) had much lower landscape emission factors (Fig. 4). MT and isoprene emission were highest in the Suburban and Rural Residential classes with MTs accounting for about two-thirds of the total emissions and isoprene comprising roughly one-third. SQT emissions also were near their highest levels in these two classes, but only contributed about $2.5 \mu\text{gC m}^{-2} \text{h}^{-1}$ for each class. Both of these classes include between 3 and 5% (of vegetated area) cover for Arizona ash, juniper, cottonwood, and palm and between 11 and 21% cover for pines. Pines and ash were the highest emitters of MTs, while cottonwood and palm were the highest emitters of isoprene. Rosemary also emits MTs at significant levels, and makes up 5% of the vegetated area in the Suburban class. Juniper and pines were the highest emitters of SQTs, and together, emissions of BVOCs from the aforementioned plant types contributed to the high total BVOC emissions from the Suburban and Rural Residential land use classes. Emissions of MTs and isoprene were lowest in the Major Development and Industrial land use classes with isoprene emissions making up roughly 60% of the total emissions and MTs comprising about 40%. SQT emissions were less than $0.25 \mu\text{gC m}^{-2} \text{h}^{-1}$ for each of these classes. Emissions of MTs, SQTs, and isoprene were lowest in the Major Development class due to a high percentage of barren ground and low BVOC-emitting plant types. The Industrial class had a very low percentage of vegetated area (13%) and only small coverages of plant types that emit higher quantities of BVOCs, such as pines, juniper, and palm, leading to low total BVOC emissions for this class.

The highest total BVOC emissions occurred in the northwestern and southwestern regions of the Las Vegas metropolitan area

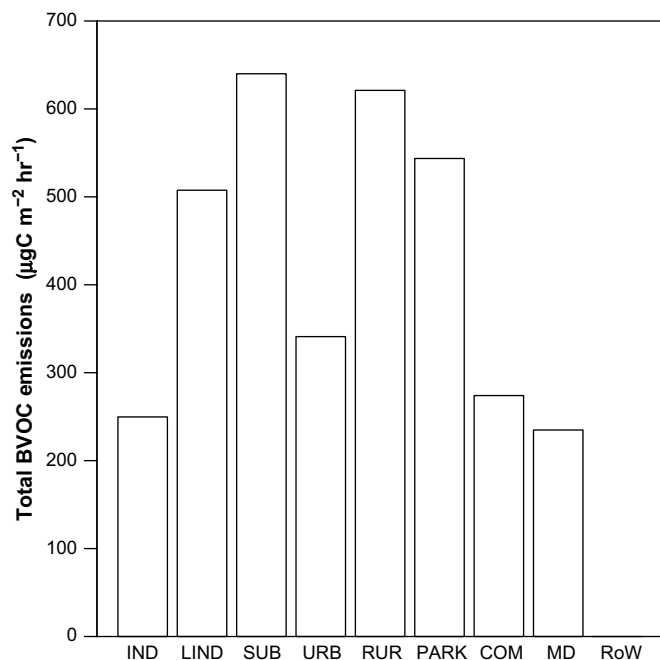


Fig. 4. Total BVOC emissions by urban land use category.

(Fig. 3). The northwestern area is composed mainly of Suburban and Rural Residential land use classes, while the southwest is mainly Rural Residential and Light Industrial/Office classes. As was noted above, these classes have high total BVOC emissions. Due to high isoprene and MT emissions, the Public Facilities and Parks class also had significant total BVOC emissions. Areas comprised of this class lie toward the outside of the metropolitan area and can be seen as broad swaths of light gray in Fig. 3.

3.2.1. BVOC emissions from the emission profile sites

Total SQT, MT, and isoprene emissions were higher at the Suburban location than at the Urban site (Fig. 5). SQT emissions were higher at the Suburban location due to the influence of pines and juniper. MT emissions were higher at the Suburban site because this location is composed of 72% rural residential land use and 17% suburban residential land use and these two land use classes have the highest total MT emissions, as noted above. Similarly, isoprene emissions were higher at the Suburban site because the rural residential and suburban residential land use classes have two of the three highest isoprene emission rates. When using $T_{\max} = 51$ °C, there is an increase in isoprene emissions from both sites. Air temperatures are lower at the Suburban site compared to the Urban site, so isoprene emissions increase 33% and 110% respectively, and overall isoprene emissions are then higher at the Urban site. β -caryophyllene was the SQT emitted in the largest quantity at both sites, which is in agreement with previous studies that found this compound to be the most abundant SQT (orange tree species in Spain, Ciccio et al., 1999; loblolly pine, Helmig et al., 2006; Scots pine, Hakola et al., 2006). Emissions of α -humulene and α -copaene were higher than those of β -elemene and α -farnesene at both sites.

3.3. Atmospheric chemistry modeling

The RACM2 simulations provided insight into the impacts of BVOC emissions on tropospheric chemistry at Urban and Suburban sites. Two basic assumptions of this box model system were that (1) everything was well mixed in the box and (2) transport into and out of the box did not occur. The second assumption is important to

note because transport of chemical species often contributes to the highest ozone levels measured in the Las Vegas Valley (T&B Systems, 2006b). Also, SQT emissions were not included in the atmospheric chemistry modeling since SQT emissions were always < 1% of isoprene and MT emissions. A separate effort to include SQT reactions in RACM2 revealed that these emissions would have an impact on ozone creation equal to 0.1% of the impact of isoprene and MTs acting together.

3.3.1. Patterns common to both sites

In every simulation, when BVOCs were emitted, NO_x was consumed more rapidly and more ozone and hydroxyl radicals were produced (Figs. 6 and 7). The levels of NO_x steadily decreased in the simulations without BVOC emissions as well, which agrees with the reaction cycles for NO_x in the troposphere (no NO_x source was included in the simulations, except as noted below). NO is converted to NO_2 through the VOC oxidation process, and then NO_2 either photo-dissociates, leading to the formation of ozone, or it reacts with HO radicals to form nitric acid, which does not undergo further chemistry in RACM2. NO_x was consumed faster in simulations with BVOCs because more NO was converted to NO_2 and subsequently lost as nitric acid. Hydroxyl radical production is higher in the BVOC simulations due to the elevated ozone produced and its subsequent photolysis.

BVOCs were only a small component of total ozone reactivity. Between the two emission profile sites, roughly 0.01–0.03% of the total ozone consumed was due to direct reaction with BVOCs. Of the ozone consumed by BVOCs, MT reactions consumed 83–92% and isoprene 8–17% for the two sites. Therefore, these compounds contribute more to ozone production (via NO_2 production) than to ozone consumption. The contributions from isoprene and MTs to ozone production were comparable in each of the simulations (see the sensitivity analysis below). The BVOC reactions also accounted for only a small amount of hydroxyl radical (HO) reactivity. Between the two emission profile sites, MTs contributed 0.7–5.5% and isoprene contributed 0.06–4.5%. The highest contributions to HO reactivity for all BVOCs at both sites came during the afternoon hours of 14:00 to 16:00.

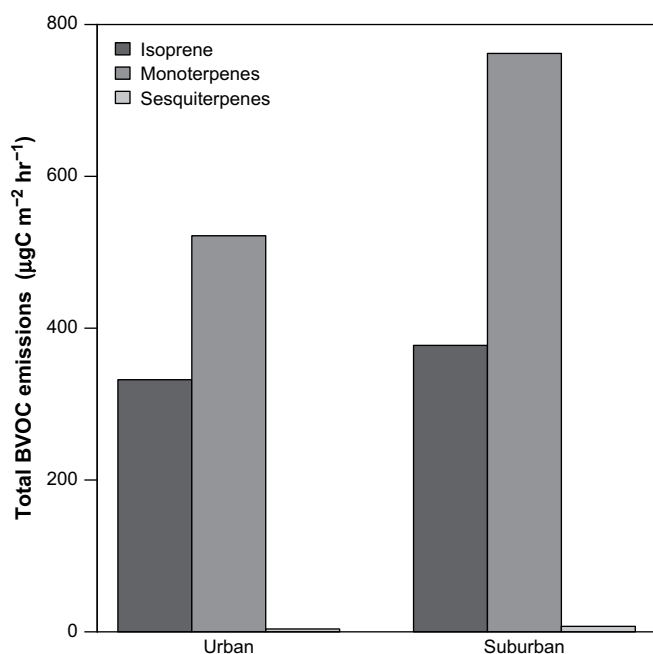


Fig. 5. Total BVOC emissions for emission profile sites.

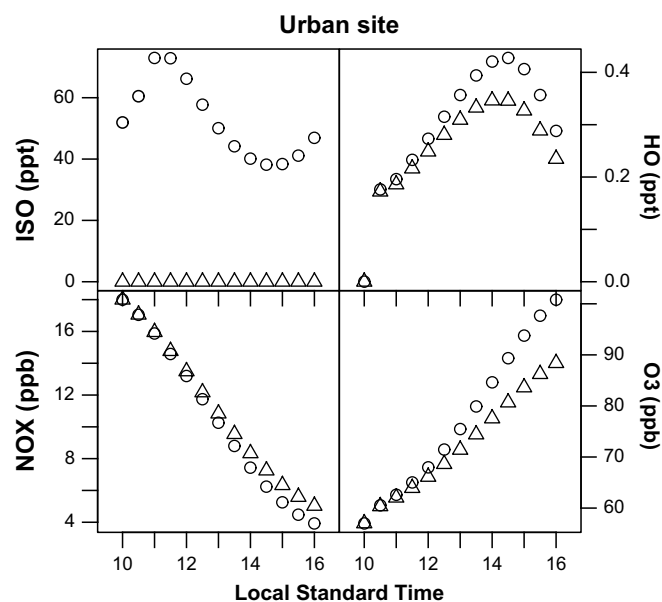


Fig. 6. SBOX output for the Urban Site. Levels of NO_x , ozone (O_3), and hydroxyl radical (HO) are shown with (circles) and without (triangles) the influence of BVOC emissions between 10:00 and 16:00. Levels of isoprene (ISO) are also shown.

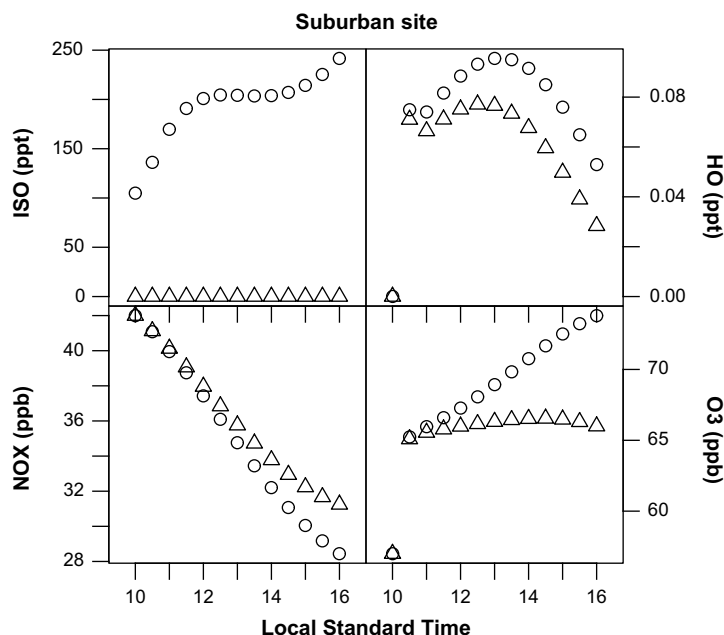


Fig. 7. SBOX output for the Suburban Site. Levels of NO_x , ozone (O_3), and hydroxyl radical (HO) are shown with (circles) and without (triangles) the influence of BVOC emissions between 10:00 and 16:00. Levels of isoprene (ISO) are also shown.

3.3.2. Urban site (JD Smith)

The effect of BVOC emission on ozone concentrations was observable at the Urban Site. Ozone concentrations reached 90 ppb by 16:00 without BVOCs, and went up to roughly 100 ppb with BVOC emissions (Fig. 6). Between 13:00 and 16:00, BVOC emissions increased the ozone growth rate by a factor of 1.5. Observed ozone levels for July 15, 2005 at JD Smith reached almost 90 ppb. These observed levels may be lower than those predicted by the model for the Urban site due to the low boundary layer height and lack of mixing in the model (see also the sensitivity tests below). In reality, ozone produced near the surface would be dispersed and diluted within nearly 4500 m of mixing height (in the summer months) assuming that ozone levels in the free troposphere were lower than those in urban air. Also, the model does not represent horizontal transport, which could bring clean air into the Las Vegas Valley.

3.3.3. Suburban site (Joe Neal)

The influence of BVOC emissions on ozone concentrations at the Suburban site was much greater than at the Urban site (Fig. 7). The Suburban site has the highest total BVOC emissions, and also the highest individual emissions of isoprene and MTs (Fig. 5). In the presence of BVOC emissions, ozone concentrations increased throughout the day, and growth rates of ozone close to 50 times greater than in the absence of BVOCs were modeled near 14:00.

Modeled ozone concentrations were lower at this site (65–80 ppb) than at the Urban site. However, due to the prevailing winds through the Las Vegas Valley from south to northwest, measured ozone concentrations are often highest in the northwestern region of the metropolitan area due to transport from urban areas upwind (T&B Systems, 2006a). Ozone levels recorded at the Joe Neal site were above 100 ppb on July 15, 2005, and winds were recorded at 3–13 km h^{-1} from the southeast, supporting the downwind character of this site. The discrepancy between modeled and observed ozone concentrations for this date is likely due to the transport noted above. Since the RACM2/SBOX system does not account for transport, pollutant input from upwind areas is missed when the model calculates ozone levels at the Suburban site. High NO_x concentrations were also observed at the Joe Neal site on this

date and could be due to transport and/or to emissions from high NO_x -emitting vehicles in the area. The low modeled ozone concentrations at the Suburban site in the absence of BVOCs could also be due in part to these high NO_x concentrations because NO effectively titrates ozone (Finlayson-Pitts and Pitts, 2000).

The Suburban site experiences a VOC-limiting regime due to high measured NO_x concentrations and has a low VOC/ NO_x ratio. The optimal VOC/ NO_x ratio for ozone production is between 6:1 and 9:1 (<http://www.bayareamonitor.org/may00/air3.html>), and the ratio measured at the Suburban site without BVOCs is roughly 3.5:1 (T&B Systems, 2006b). As a result, low ozone growth rates are observed in the absence of BVOCs because there are few anthropogenic VOCs available for reaction. Since this Suburban system is strongly VOC-limited, the addition of BVOCs explains the considerable increases in the rate of modeled ozone production. However, ozone concentration growth rates with BVOC emissions are 2–5 times slower compared to the Urban site because the VOC/ NO_x ratio remains low. The VOC/ NO_x ratio at the Urban site without BVOC influence is roughly 5:1 (T&B Systems, 2006b). The smaller VOC/ NO_x ratio at the Suburban compared to the Urban site explains the increase in the modeled impact of BVOC emissions on ozone production. Measured isoprene concentrations were higher at the Suburban site compared to the Urban site, and these concentrations only decrease slightly in the afternoon. This pattern is due, in part, to the lower concentration of ozone modeled at this site. As noted above, these low ozone concentrations are probably related to ozone titration by NO.

The contrasting NO_x concentrations also affected the production of HO and therefore isoprene concentrations. At the Urban site, low NO_x levels lead to less HO titration to nitric acid and higher HO concentrations. In turn, the higher OH shortens the lifetime of isoprene, especially during the mid-afternoon hours (14:00–15:00). At the Suburban site, the higher NO_x concentrations lead to lower HO concentrations, which causes relatively longer lifetimes of isoprene. At the Urban site, oxidation by HO outpaces emissions during the afternoon hours, which leads to a decrease in isoprene concentrations. In contrast, isoprene concentrations hit an equilibrium between emissions and oxidation, and levels are unchanged during the same period of the afternoon.

3.3.4. Sensitivity analyses

We performed three additional sets of model simulations (Fig. 8). The first tested the impact of adding only isoprene or MT emissions. The results demonstrate that the impact of these BVOCs on ozone production is approximately proportional to their mass.

The second tested the effect of using a higher T_{\max} value: 51 °C as opposed to the standard 41 °C. Qualitatively, all the conclusions drawn from the original runs are still valid. Ozone production does increase in the Urban scenario; the roughly doubled isoprene emissions lead to an ozone production increase of 40%. For the Suburban site with 33% higher isoprene emissions, ozone production increases 10%. The third set of model simulations focused on a more realistic treatment of boundary layer dynamics and NO_x emissions. This had a significant impact on all the simulations: ozone concentrations decreased under all scenarios. The decrease is directly related to the dilution, since there is no ozone source in the model. Measured ozone concentrations at both sites increase throughout the day (T&B Systems, 2006a), so this addition to the model does not improve our forecast ability. For our boundary layer growth model to be more representative of reality, we would need additional information concerning the free tropospheric concentrations and the

horizontal advection of all species. Because we lack this information and this would require a complex model with atmospheric dynamics, our modeling results without an expanding boundary layer and without NO_x emissions provide a qualitative understanding of the impact of biogenic emissions on ozone growth rates, and should not be considered an air quality forecast.

4. Conclusion

Landscape emissions of isoprene and MTs were significant in the Las Vegas region. High emissions led to the high total BVOC emissions at the Urban and Suburban emission profile sites. Ozone growth rates were significantly higher in the presence of isoprene and MTs at both emission profile sites, and these growth rates strongly depended on the VOC/NO_x ratio at each site. These findings highlight that total BVOCs should be considered as sources contributing to background ozone pollution when air quality experts are determining pollution control strategies. Accurate BVOC emission factors for plant species in the Las Vegas area represent the most basic and most important aspect of a biogenic emissions inventory. Knowledge of plant species with high BVOC emissions is important to urban planners as they devise regulation for new development in the area. As all new development is required to utilize xeriscaping practices, it could also be recommended that high BVOC-emitting vegetation not be planted.

The northwestern region of the metropolitan area had the highest SQT and MT emissions since this location is a residential area that is heavily landscaped. Total isoprene emissions were also lower than MT emissions, which is interesting since isoprene emissions are roughly 10% higher than MT and SQT emissions combined for North America (Guenther et al., 2000). This finding has important indications for air quality since many MTs are more reactive with HO and ozone than isoprene. For example, cisocimene, the BVOC emitted in the greatest quantities, is 2.5 times more reactive with HO than isoprene, and is over 40 times more reactive with ozone than isoprene.

The effect of BVOCs on ozone production was significant at both emission profile sites, but was the greatest at the Suburban site due to this location having the highest isoprene and total MT emissions and the lowest VOC/NO_x ratio between the sites. Ozone growth rates in the presence of BVOCs at the Suburban site are almost 50 times greater than those without BVOCs in the mid-afternoon. Both sites experience a VOC-limiting regime (low VOC/NO_x ratios), although the Suburban site is the most strongly VOC-limited. With this strong limitation, the addition of BVOCs greatly increases the rate of ozone production. These modeling simulations predict that isoprene and MT emissions have a significant impact on ozone pollution in the Las Vegas metropolitan area.

In order to further clarify the effects of BVOCs on air pollution in Las Vegas, additional studies are necessary. Future studies should address the phenology of BVOC emissions, especially those of MTs and SQTs as these compounds have been shown in other studies to be influenced by seasonality (Hakola et al., 2006; Vuorinen et al., 2005). Higher emissions of SQTs during the early fall might explain, in part, the discrepancy between the SQT emissions found in this study and those calculated for loblolly pine (Helmig et al., 2006). These studies would help air quality specialists determine which times of year BVOCs would have their highest contributions to air pollution. Also unknown are the effects of landscape management practices, such as irrigation and fertilization, on BVOC emissions in this environment. Finally, it will be important to study the differences in BVOC emissions from normal landscape plants and xeriscape and native plants as requirements for xeriscaping are enforced in newer developments. Certain drought-tolerant plants, such as ephedra, have very high BVOC emissions, while others, such

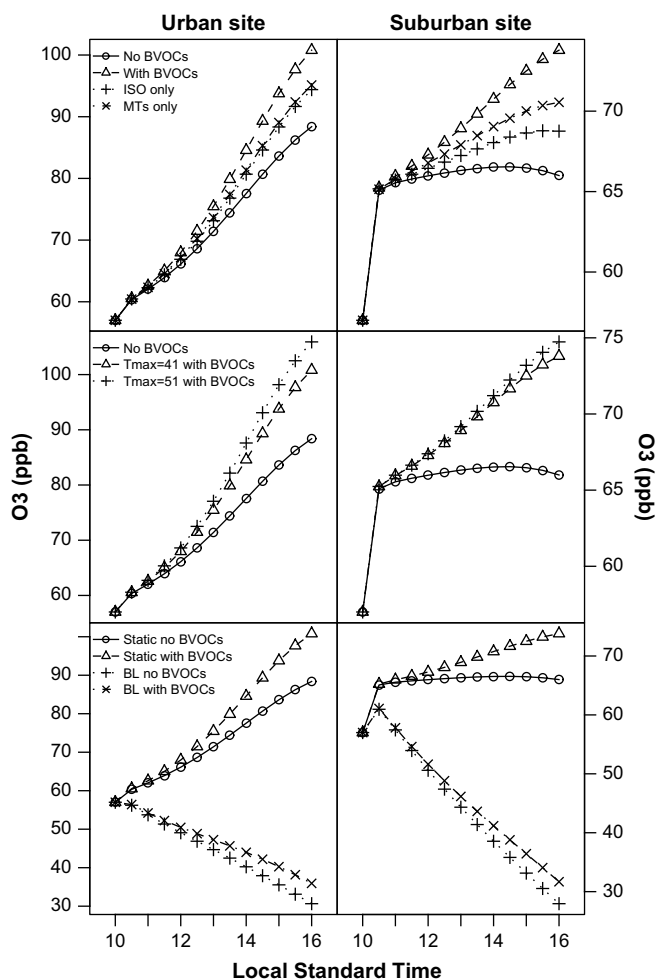


Fig. 8. The impact of three sets of model sensitivity tests on ozone concentrations (O_3) at both the Suburban and Urban sites. Note that the vertical scale is always ppb of ozone, and that the scale is different for each panel. The top two panels show the effect of running the model with no BVOCs (circles), with only isoprene emissions (crosses), with only MT emissions (stars), and with both isoprene and MT emissions (triangles). The middle two panels show output for two different T_{\max} parameterizations. Output for running the model with and without an expanding boundary level and NO_x emissions is displayed in the bottom two panels.

as creosote bush, do not (Geron et al., 2006). As the metropolitan area expands and native vegetation is replaced with buildings, asphalt, automobiles, and different plant species, the effect of BVOC emissions on air quality will change. Continually updating this research will be critical to air quality managers as they work to find the best air pollution control strategies for this rapidly expanding metropolitan area.

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