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Citation for published version:
Wiedinmyer, C, Greenberg, J, Guenther, A, Hopkins, B, Baker, K, Geron, C, Palmer, PI, Long, BP, Turner, JR, Petron, G, Harley, P, Pierce, TE, Lamb, B, Westberg, H, Baugh, W, Koerber, M & Janssen, M 2005, 'Ozarks Isoprene Experiment (OZIE): Measurements and modeling of the "isoprene volcano"' Journal of Geophysical Research, vol 110, no. D18, D18307, pp. 1-17., 10.1029/2005JD005800

Digital Object Identifier (DOI):
10.1029/2005JD005800

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher final version (usually the publisher pdf)

Published In:
Journal of Geophysical Research

Publisher Rights Statement:
Published in the Journal of Geophysical Research: Atmospheres by the American Geophysical Union (2005)

OPEN ACCESS

Ozarks Isoprene Experiment (OZIE): Measurements and modeling of the "isoprene volcano"

Christine Wiedinmyer,[1] Jim Greenberg,[1] Alex Guenther,[1] Brian Hopkins,[2]
Kirk Baker,[3] Chris Geron,[4] Paul I. Palmer,[5] Bryan P. Long,[6,7] Jay R. Turner,[6]
Gabrielle Pétron,[1] Peter Harley,[1] Thomas E. Pierce,[4,8] Brian Lamb,[2] Hal Westberg,[2]
William Baugh,[1,9] Mike Koerber,[3] and Mark Janssen[3]

[1] The Ozarks Isoprene Experiment (OZIE) was conducted in July 1998 in Missouri, Illinois, Indiana, and Oklahoma. OZIE was designed to investigate the presumed strong isoprene emission rates from the Missouri Ozarks, where there is a high density of oak trees that are efficient isoprene emitters. Ground, balloon, and aircraft measurements were taken over a three-week study period; 0-D and 3-D chemical models were subsequently used to better understand the observed isoprene emissions from the Ozarks and to investigate their potential regional-scale impacts. Leaf-level measurements for two oak tree species yielded normalized average isoprene emission capacities of 66 mgC g^{-1} h^{-1}, in good agreement with values used in current biogenic emissions models. However, the emission capacities exhibited a temperature dependence that is not captured by commonly used biogenic emission models. Isoprene mixing ratios measured aloft from tethered balloon systems were used to estimate isoprene fluxes. These measurement-derived fluxes agreed with BEIS3 estimates within the relatively large uncertainties in the estimates. Ground-level isoprene mixing ratios exhibited substantial spatial heterogeneity, ranging from <1 to 35 ppbv. The agreement between measured isoprene mixing ratios and regional-scale chemical transport model estimates was improved upon averaging the ground-level isoprene data observed at several sites within a representative area. Ground-level formaldehyde (HCHO) mixing ratios were very high (up to 20 ppbv) and were consistently higher than mixing ratios predicted by a regional chemical transport model. The spatial distribution and magnitude of the elevated HCHO concentrations showed good agreement with GOME satellite column observations of HCHO.

1. Introduction

[2] Isoprene (C_5H_8) is emitted in significant amounts from terrestrial vegetation. The geographic focus of this paper is North America where the temperate forests of the central and eastern United States produce a large fraction of the total continental isoprene emissions. The role of isoprene chemistry in tropospheric ozone (O_3) production is well understood [e.g., *Fehsenfeld et al.*, 1992], but the magnitude and spatiotemporal variability of isoprene emissions are uncertain. Ambient concentrations of tropospheric O_3 have implications for oxidant chemistry in the troposphere, air quality, and climate. Formaldehyde (HCHO), a major product of isoprene oxidation, can affect the atmospheric HO_x balance and further contribute to the production of O_3. As a result of this chemistry, isoprene and its oxidation products impact regional and global air quality. On a regional scale, a better understanding and quantification of isoprene emissions will improve evaluations of O_3 abatement strategies for several regions throughout the United States [e.g., *Chameides et al.*, 1988].

[3] Current biogenic emissions models such as the Biogenic Emissions Inventory System (BEIS) [*Pierce and Waldruff*, 1991; *Lamb et al.*, 1993; *Pierce et al.*, 1998] predict particularly high isoprene emissions for the oak

[1]Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado, USA.
[2]Department of Civil and Environmental Engineering, Washington State University, Pullman, Washington, USA.
[3]Lake Michigan Air Directors Consortium, Des Plaines, Illinois, USA.
[4]U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, USA.
[5]Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA.
[6]Department of Chemical Engineering, Washington University, St. Louis, Missouri, USA.
[7]Now at U.S. Department of Defense, Washington, D. C., USA.
[8]Atmospheric Sciences Modeling Division, National Oceanic and Atmospheric Administration, Research Triangle Park, North Carolina, USA.
[9]Now at Hydrobio Consulting, Santa Fe, New Mexico, USA.
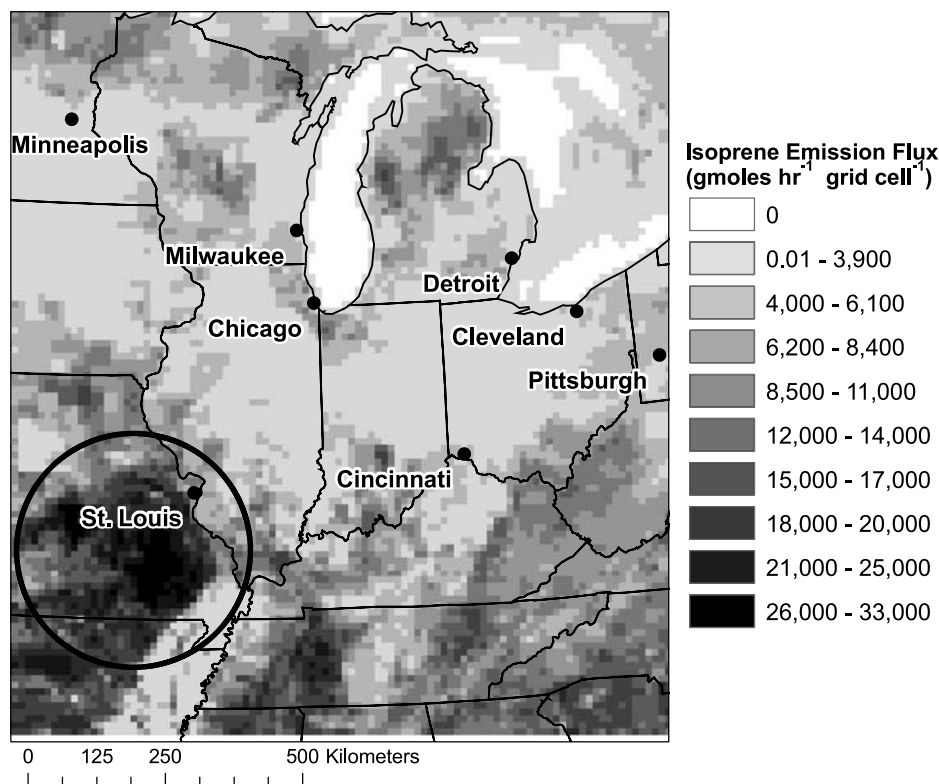
Figure 1. BEIS3-estimated isoprene emissions for 20 July 1998 at 14:00 CDT. The grid cell size is 12 km by 12 km. The oak forests of the Missouri Ozarks are predicted to be a zone of relatively high isoprene emissions (southwestern corner of map) (10,000 gmol h^{-1} grid cell^{-1} = 4.72 mg h^{-1} m^{-2}). See color version of this figure at back of this issue.

forests of the Ozarks in the central United States. The isoprene emission rates predicted by BEIS3 (http://www.epa.gov/asmdnerl/biogen.html) and using the BELD3 land use data set [*Kinnee et al.*, 1997, 2005] at a 12 km resolution for a model domain in the Midwestern United States are shown in Figure 1. The circled area in the southwest corner of the domain identifies the so-called "isoprene volcano," an area of elevated isoprene emissions that is predicted for the Missouri Ozarks. Initial model evaluations of these emissions predicted by BEIS2 suggested that these estimates were too high [*MoDNR*, 1999]. However, there were no previous measurements of isoprene emissions in this region with which to evaluate the model output.

[4] Although these Midwestern forests emit large amounts of isoprene, the region is characterized by relatively low emissions of oxides of nitrogen, or NO_x, and the local O_3 production from isoprene and NO_x chemistry is therefore expected to be small: there may even be a net loss of O_3 due to isoprene photochemistry. However, under typical summertime conditions, the emitted isoprene and its reaction products can be transported northward and eastward to more polluted urban areas such as St. Louis and Chicago. Simulations from a three-dimensional photochemical transport model that was used to investigate potential pollution control strategies for these urban areas suggested that the large isoprene emissions from the Ozarks may contribute to the O_3 burden in these populated areas (Figure 2). Additionally, HCHO is a high yield product of

isoprene oxidation and also a carcinogen included in the list of air toxics by the Clean Air Act. It has been shown to influence urban areas far downwind from isoprene sources due to its atmospheric lifetime. The GOME satellite has observed elevated HCHO columns over the central U.S. [*Palmer et al.*, 2003], and these observations have been largely attributed to isoprene oxidation.

[5] Understanding and quantifying the isoprene emissions from the Ozarks is important for predicting air quality in the central, and possibly, eastern United States. The Ozarks Isoprene Experiment (OZIE) was performed during July 1998 to address several uncertainties in the biogenic isoprene emission inventories in the central United States. The study spanned four states and investigated geographic regions with a variety of landscapes and isoprene emission potentials. Three different measurement platforms were employed for the study: ground, tethered balloon, and aircraft. The study was designed to address the following questions: (1) Can the isoprene emission capacity (determined at 30°C and incident photosynthetically active radiation (PAR) of 1000 μmol m^{-2} s^{-1}) of the dominant tree species in the Ozarks be considered constant on time scales of days to weeks, or does it change?, (2) What is the magnitude of biogenic isoprene emissions from the Ozarks?, and (3) How well do emission and chemistry models predict the observed isoprene emission rates and atmospheric mixing ratios of isoprene and its oxidation products? This paper presents data collected as part of the OZIE study, which can be used for validating isoprene
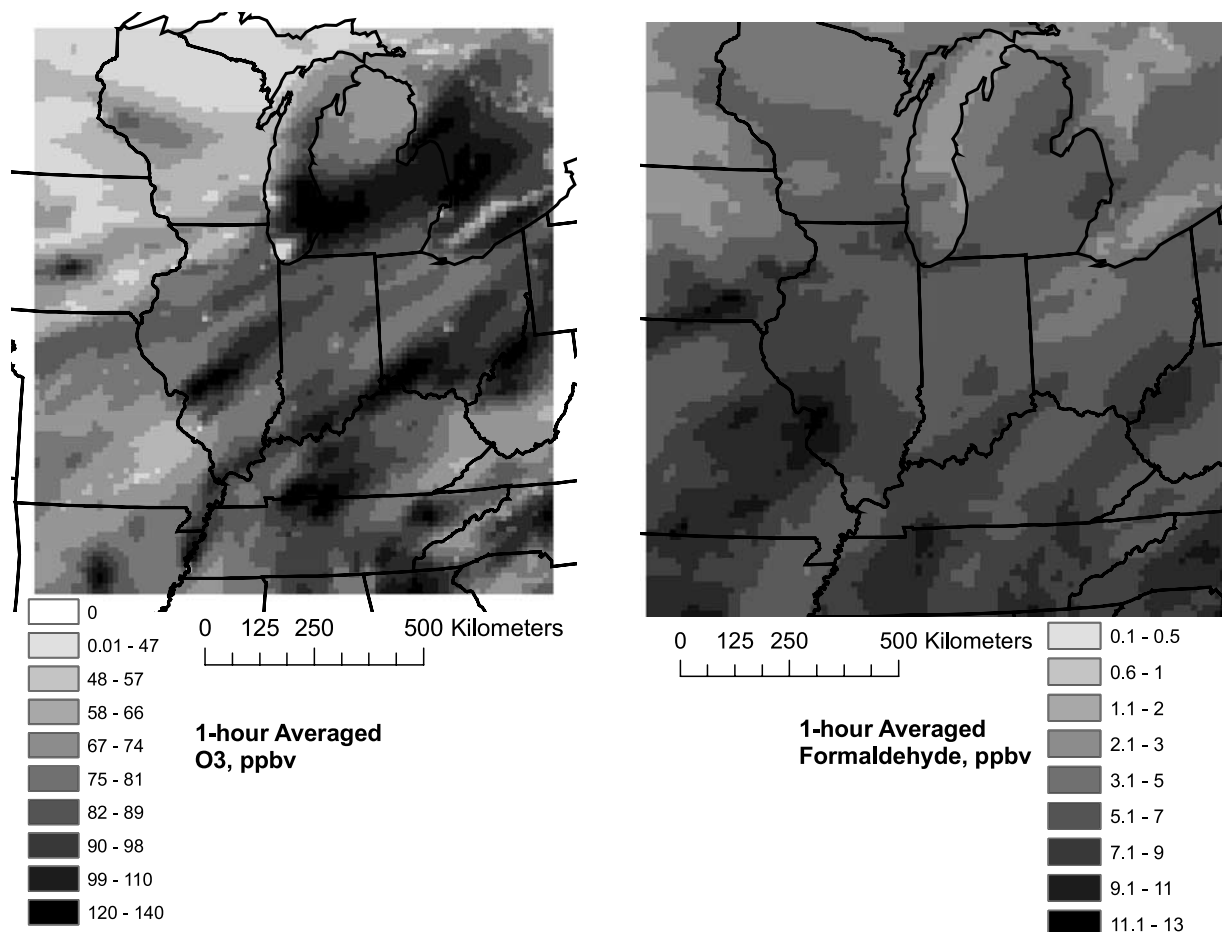
Figure 2. (left) Hourly averaged ozone (O$_3$) mixing ratios (ppbv) for 16:00 CDT on 21 July 1998, as simulated by the CAMx model. (right) Hourly averaged HCHO mixing ratios simulated by CAMx for 18:00 CDT on 21 July 1998. See color version of this figure at back of this issue.

emission and regional air quality models. Section 2 describes the study area and the measurements used to quantify isoprene and HCHO. Section 3 describes the biogenic emission and chemical transport models used to assess the impact of isoprene emanating from the Ozarks on regional air quality. Section 4 presents results from this study and also integrates results from the in situ field measurements and satellite observations with the photochemical model simulations.

2. Experimental Setup

2.1. Location of Study and Participants

[6] OZIE was carried out from 9 through 22 July 1998. More than ten investigation teams participated in the study, including academic institutions (Washington State University, Washington University in St. Louis, Purdue University), an NSF-sponsored non-profit research facility (National Center for Atmospheric Research [NCAR]), U.S. federal government agencies (U.S. Environmental Protection Agency [EPA] and the U.S. Army), state agencies (Illinois EPA, Indiana Department of Environmental Management), and non-profit regional planning organizations (Lake Michigan Air Directors Consortium). Field sites were established throughout Illinois, Indiana, Missouri, and

Oklahoma. Figure 3 shows a map of the locations of all the OZIE field sites overlaid on the fraction of oak crown area in the study domain [*Kinnee et al.*, 1997, 2005]. The oak area fraction is strongly correlated with the areal isoprene emission potential since oak trees are the dominant isoprene-emitting species in the region.

[7] Intensive field measurements were conducted at the U.S. Army base at Fort Leonard Wood, Missouri (37.631°N and −92.154°W). On the Fort Leonard Wood post (hereafter called FLW), a ground-level measurement site was set up next to the launching area of the large balloon (see description below) in a large clearing. Five additional ground-level sites were located 2.3 to 5.6 km south of this main site. Carbonyl and volatile organic compound (VOC) measurements were taken at 2 m above ground level (AGL) at all of these ground-level sites. Extensive leaf-level enclosure measurements were taken from the leaves of two isoprene-emitting trees in the vicinity of the large balloon launch area.

[8] VOCs were measured at additional field sites in Missouri, Indiana, and Illinois by the respective state agencies for the Indiana and Illinois sites, and by Washington State University (WSU) and Washington University in St. Louis (WUSTL) for the Missouri sites. Aircraft-based measurements of VOCs and carbonyls were conducted on a few of the study days by the Purdue University team; flight
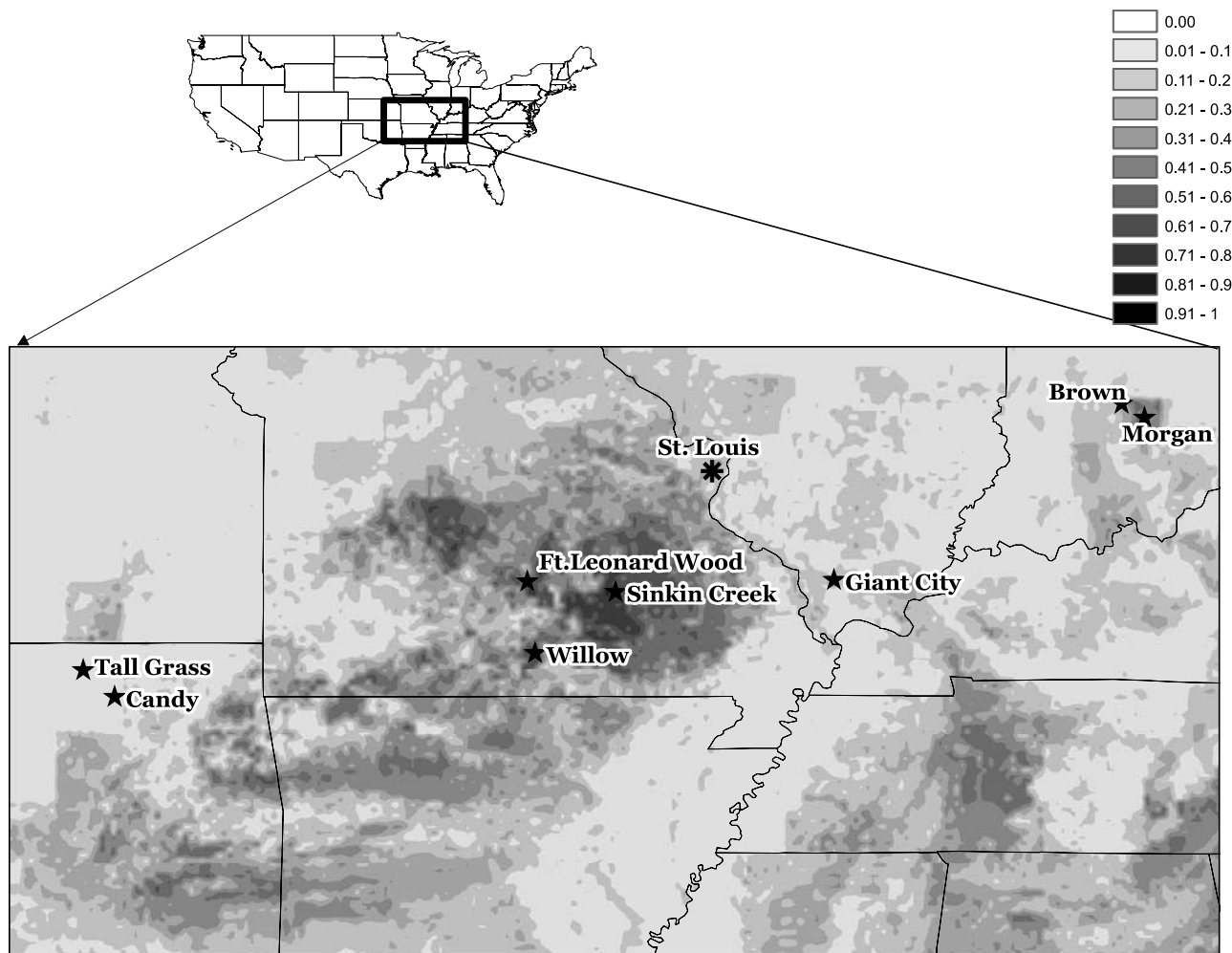
Figure 3. The locations of the field sites of the OZIE study. The fraction of forest oak crown area (color scale) from the BELD3 data set is shown for the study region. See color version of this figure at back of this issue.

Table 1. Summary of Measurement Platforms, Locations, and Data Collected During the OZIE Study[a]

				Site Name				
	Ft. Leonard Wood (Missouri)	Brown County Park (Indiana)	Morgan Monroe State Park (Illinois)	Giant City (Illinois)	Sinkin Creek (Missouri)	Candy WMA (Oklahoma)	Tall Grass (Oklahoma)	Willow Springs (Missouri)
Latitude	37.631	39.162	39.295	37.614	37.502	36.499	36.753	36.918
Longitude	−92.154	−86.221	−86.438	−89.180	−91.259	−96.035	−96.333	−92.028
YYYYMMDD								
19980708			V	V				
19980709	B, RB, M, V		V, AC, AV	V, AC, AV				
19980710	B, RB, M		V	V				
19980711	B, M		V					
19980712	B, M	RB, V	V	V				
19980713	B, M, V, C		RB, V, AC, AV	V, AC, AV				
19980714	B, M, V, C		V	RB, V				
19980715	B, RB, M		V	RB, V				
19980716	B, RB,M, V, C			V, AC, AV				
19980717	B, M					RB		
19980718	B, M, V, C		V, AC, AV	V, AC, AV			RB	
19980719	B, M, V, C		V, AC, AV	V, AC, AV				
19980720	B, M, V, C		V	V, AC, AV				
19980721	B, M		V, AC, AV	V, AC, AV				RB, C, V
19980722			V	V	RB, C, V			

[a]B, Big Balloon; RB, Roving Balloon; V, ground-level VOC sampling; C, ground-level carbonyl measurements; AC, aircraft carbonyl measurements; AV, aircraft VOC measurements; M, meteorological measurements.

patterns focused on areas over the ground-level sites. Table 1 summarizes the OZIE study locations and measurements. Only the balloon and ground-level observations are presented and discussed in this paper.

2.2. Balloon Measurements

[9] Two different tethered balloon systems were employed during the OZIE campaign. The *Large* balloon had a volume of 12 m^3 and flew at altitudes from a few meters to approximately 1000 m AGL. The *Roving* balloon had a volume of 3 m^3 and flew to approximately 250 m AGL. The large balloon was located at one site (FLW) for the entire experiment, while the roving balloon was transported to several sites during the study (Table 1).

[10] Sampling packages described by *Greenberg and Guenther* [2002] were attached at one-to-four points along the balloon's tether. Air samples were collected onto solid absorbent cartridges [2 stage: carbosieve S-III/carbotrap B (both from Supelco, Inc., Bellefonte, Pennsylvania)]. Thirty-minute integrated samples were collected at flow rates of 200 cm^3 sec^{-1} through the cartridges. The cartridges were stored at $-30°C$ and were subsequently transported back to the laboratory at NCAR for analysis. Analytes desorbed from each cartridge were cryogenically concentrated and analyzed using GC-MS (HP5890- HP5972, Hewlett-Packard, Palo Alto, California). The tethered balloon-based cartridge sampling approach has been applied successfully at many field sites; this technique and the laboratory analysis protocols are described in more detail by *Greenberg et al.* [1999]. The detection limit for isoprene using this methodology was 1 pptv; measurement precision for isoprene with atmospheric mixing ratios on the order of 1 ppbv was 0.05 ppbv. A variety of compounds was measured with this technique; only the isoprene mixing ratios are reported and discussed in this paper. Temperature, humidity, and pressure altitude were also measured by sensors on the tethered balloon sampling packages.

2.3. Ground-Level Measurements

[11] FLW ground-level measurements were conducted at the large balloon launching area and five additional sites in the so-called "footprint" of the large balloon for typical wind directions, wind speeds, and isoprene atmospheric lifetime. At each of these sites, carbonyl and VOC sampling systems were housed in weatherproof shelters. The hydrocarbon collection systems consisted of a pump (Teflon/aluminum head), flow restrictor to provide a constant fill rate, solenoid valve, and a stainless steel collection canister initially at vacuum. At the pre-selected sample start time, a programmable timer started the pump and opened the solenoid valve to allow flow into the canister for thirty minutes. After collection, canisters were recovered from the field and shipped to the WSU laboratory in Pullman, Washington, for gas chromatographic analysis. Analyses were performed with two separate Hewlett Packard 5890 systems (FID). One system was equipped with a 2m Carbonex 104 (Supelco) column for determination of the C_2 and C_3 hydrocarbons. The other system had a DB-1 fused silica capillary column (J & W Scientific) for the separation of higher molecular compounds (C_4-C_{12}). Both systems included a cryotrap (described below) for concentrating the organic compounds from the ambient samples

collected in the canisters. The Carbonex column was operated with a carrier gas (He) flow of 5 cm^3 min^{-1} and a temperature of 165°C. Hydrogen at 1 cm^3 min^{-1} was used as the carrier gas with the DB-1 fused silica capillary column system, and oven temperature was ramped from -50 to 150°C at 4° min^{-1}. In both systems, air from the canister was drawn through the cryogenic trap into an evacuated cylinder. The sample volume was monitored by measuring the pressure change in the cylinder. Normally, 500 ml of air was passed through the freeze-out trap, which was maintained at $-186°C$ (liquid oxygen). The trap consisted of a 3.18 mm × 15.24 cm stainless steel tube containing 60–80 mesh glass beads. The trap was attached to the gas chromatograph via a six-port gas sampling valve (Valco Inst. Co. Inc.). Peaks were identified by comparing retention times with known standards. Hydrocarbon concentrations were determined by the ratio of the FID response for each peak to the response recorded for a known concentration of 2,2-dimethylbutane. The concentration of the 2,2-dimethylbutane standard was assigned through comparison with a NIST-purchased propane standard reference material (SRM).

[12] At each of the FLW ground sites, three-hour integrated carbonyl samples were collected on 2,4-di-nitrophenylhydrazine (DNPH) coated silica cartridges using a nominal sample flow rate of 1.0 standard l min^{-1} (slpm) generated by a downstream pump (Metal Bellows -151). This method has been used successfully at other field sites to measure ambient concentrations of formaldehyde, acetone, acetaldehyde, and propanal [e.g., *Wiedinmyer et al.*, 2001]. An ozone scrubber (granular KI) was attached to the inlet line to remove oxidants upstream of the cartridge. The collection system employed Clippard Minimatic ET-2-12VDC solenoid valves connected to timers; air flow data was acquired with the AALBORG GFM-17 mass flowmeters. The total volume of air passed through each cartridge was calculated from the flow rate data. Samples were shipped to WSU for analysis. Exposed cartridges were eluted with acetonitrile (ACN), the elutant was weighed, and the hydrazones in the eluted samples were quantified by a Hewlett Packard 1090 series II High Performance Liquid Chromatograph with a diode array detector (DAD) operated at 360 nm. Peak separation was accomplished with a 10 cm OD-MPS reverse phase column (Supelco) with a gradient elution ranging from 50:50 to 30:70 H_2O:ACN over the period from 5 to 17 minutes. A 20 mL sample loop was employed and the total solvent flow rate was 0.8 mL min^{-1}. Qualitative identification of the hydrazones was performed by matching the retention times with those of known standards. For quantification, pure carbonyl hydrazone derivatives were prepared. High concentration master standards were prepared for each carbonyl of interest (formaldehyde, acetaldehyde, acetone, and propanal), and these master standards were then used to prepare a set of working standards ranging from 0.2 to 5 mg ml^{-1}. A running calibration for relating peak areas to hydrazone concentrations was created by taking the running mean of the standard analyses (area counts for each analyte) over the time period that the analyses were conducted. Ambient carbonyl concentrations were calculated from the recorded peak area, elutant mass, and air volume sampled. Average field blank values from each site were subtracted from the ambient. Precision tests were performed by collo-

cating samplers both at WSU and at several field locations. From these tests, a precision for all the compounds of better than 15% was obtained. The collection efficiency, which limits the accuracy of the method, is estimated to be 95– 100% for the aldehydes and 90–95% for acetone [*Shepson and Sirju*, 1995].

2.4. Leaf-Level Measurements

[13] Repeated measurements were made to determine the isoprene emission capacity (defined here as the rate of isoprene emission at leaf temperature of 30°C and incident PAR of 1000 μmol m^{-2} s^{-1}) of sun-lit leaves from two species of oak, *Quercus marilandica* (blackjack oak) and *Q. stellata* (post oak). A 6 cm^2 portion of a leaf was enclosed in a light and temperature controlled cuvette (LI-6400, Li-Cor, Lincoln, Nebraska). Temperature was controlled thermoelectrically and incident light was provided using an accessory LED light source (LI-6400-2). Air entering the cuvette was scrubbed of isoprene using an activated charcoal filter (Supelco, Bellefonte, Pennsylvania) and flow rate was controlled to ~660 cm^3 min^{-1}. A portion of the air exiting the leaf enclosure was routed through the 1 cm^3 sample loop of the chromatograph where isoprene was separated isothermally (100°C) on a stainless steel column (2 mm i.d. and 2 m long) packed with Unibeads 3S, 60/80 mesh (Alltech Assoc., Deerfield, Illinois). Isoprene was quantified using a reduction gas detector (RGD2, Trace Analytical, Menlo Park, California) and peaks were integrated using a commercial integrator (Model 3396, Hewlett-Packard, Avondale, Pennsylvania). The analytical system was calibrated several times daily against a standard cylinder containing 24.1 ppbv isoprene referenced to a NIST propane standard. Details of the analytical system are given by *Greenberg et al.* [1993]. All emission capacity measurements were made with incident PAR of 1000 μmol m^{-2} s^{-1} and a leaf temperature of 30°C. Under these conditions, isoprene concentrations in the air exiting the enclosure were always greater than 10 ppbv, well above the system detection limit of approximately 0.5 ppbv. After measurements were completed, each leaf was oven-dried at 60°C for 48 hours and weighed to determine leaf dry mass, and reported rates are in units of μgC g^{-1} h^{-1}.

2.5. Ancillary Data

[14] Meteorological data were collected by the U.S. Army at five 10 m towers located on the Fort Leonard Wood base and provided additional temperature, winds, solar radiation, and humidity information.

3. Modeling

[15] Several models were used to support data interpretation and biogenic emissions model evaluation. Biogenic emissions fluxes were estimated with an existing model (BEIS3) and also with a 0-D box model driven by the field measurement data. Photochemical transport modeling was performed using the Comprehensive Air Quality Model with Extensions (CAMx) version 3.02.

3.1. Emissions Modeling

[16] To produce the necessary emissions for input to the three-dimensional chemical transport model, emissions data were processed and merged using EMS-2001 [e.g., *Wilkinson et al.*, 1994; *Hogrefe et al.*, 2003]. This model was selected for its ability to efficiently handle the large requirements of regional and seasonal or daily emissions processing. In addition to extensive quality assurance and control capabilities, EMS-2001 also performs basic emissions processes such as chemical speciation, spatial allocation, and temporal allocation. Outputs from EMS-2001 included a coordinate-based elevated point source file and gridded emission estimates for low-elevation point, area, motor vehicle, and biogenic sources. The anthropogenic emissions were based on the 1996 National Emission Inventory and were allocated to the modeling grids (described below) with EMS-2001. Anthropogenic emissions estimates were developed for summer weekday, Saturday, and Sunday.

[17] The hourly biogenic emissions for each day of the model episode were estimated within EMS-2001 [e.g., *Wilkinson et al.*, 1994; *Hogrefe et al.*, 2003], which used BEIS3 (http://www.epa.gov/asmdnerl/biogen.html) and the BELD3 land use data set [*Kinnee et al.*, 1997, 2005]. The BELD3 data set includes high resolution (1 km) mapping of tree species distributions throughout the U.S. and was developed from field data, including the U.S. Forest Inventory Analysis. Inputs to the biogenic emissions model included 15 m (AGL) temperature and PAR data. The temperature at 15 m was selected for this application because of its spatial representation of the tree canopy layer, and these estimates were obtained from output from Penn State University/NCAR Mesoscale Meteorological model 5 version 2 (MM5) (described below). The PAR inputs were based on gridded satellite estimates, which are available from the University of Maryland as part of the GEWEX Continental Scale International Project (GCIP) Surface Radiation Budget (SRB) [*Pinker and Laszlo*, 1992; *Frouin and Pinker*, 1995].

3.2. Three-Dimensional Photochemical Transport Model

[18] Photochemical transport modeling for the period from 16 through 22 July 1998 was performed using the Comprehensive Air Quality Model with Extensions (CAMx) version 3.02, a publicly available three-dimensional photochemistry and transport model (available at http://www.camx.com). The CAMx simulations used the Carbon Bond IV (CB4) gas-phase chemistry mechanism with isoprene chemistry updates [*Carter*, 1996]. This model has been used to simulate regional air quality and to support ozone control strategy development in several regions within the United States and throughout the world [e.g., *Nobel et al.*, 2002; *Tanaka et al.*, 2003; *Chen et al.*, 2003; *Morris et al.*, 2004].

[19] The CAMx model simulations used a 36 km coarse grid and a 12 km fine grid, with 1-way nesting (from the coarse grid to the fine grid). The coarse grid, which covered most of the Central and Eastern United States, was selected to reconcile boundary conditions for the fine grid that covered the Upper Midwest region (Figure 1). The coarse grid contained 78 cells in the X direction and 67 cells in the Y direction. The nested 12 km grid contained 101 cells in the X direction and 110 cells in the Y direction. Both grids were centered in the Lambert projection at (−90°W, 40°N), with true parallels at 30°N and 60°N. The atmosphere

between the surface and 4 km AGL was resolved with 12 vertical layers. This vertical structure was chosen to capture the diurnal variations in the boundary layer, where the tops of layers 1 through 9 were 31 m, 76 m, 138 m, 261 m, 387 m, 514 m, 642 m, 772 m, and 1071 m AGL.

[20] Meteorological input data for the photochemical model simulations were processed using the Penn State University/NCAR 5th generation Mesoscale Model (MM5) version 2 [*Dudhia*, 1993; *Grell et al.*, 1994]. Important MM5 parameterizations and physics options applied to each grid included the CCM2 radiation scheme, simple ice moisture, Grell cumulus algorithm, and the Blackadar boundary layer option. GCIP NCEP Eta model 3-D and surface analysis data (http://dss.ucar.edu/datasets/ds609.2/) were used to supply MM5 initial and boundary condition information. Surface and 3-D analysis nudging for temperature and moisture were only applied above the boundary layer; analysis nudging of the wind fields was applied above and below the boundary layer. The MM5 model simulations used the same projection and grid resolutions as the CAMx modeling domains described above and applied two-way nesting with feedbacks between the fine 12 km grid and the coarse 36 km grid. MM5 was configured with 26 vertical layers to resolve up to approximately 15 km AGL. Surface wind fields, rain fall, and pressure were compared to archived UNISYS surface data plots to ensure MM5 output captured important synoptic features in the Ozark region during the model episode (http://weather.unisys.com/archive/index.html).

4. Results and Discussion

[21] Measurements of meteorological conditions and the mixing ratios of isoprene and several carbonyl species were made at the surface and in the boundary layer from 9 through 22 July 1998. The OZIE study area spanned four states in the Midwestern United States, with a focus on the dense oak forests of the Missouri Ozarks (Table 1 and Figure 3). CAMx was run for a seven day period from 16 through 22 July 1998 with a nested 12 km domain (Figures 1 and 2). The data collected were used to evaluate the emission estimates and chemical-transport simulations of the region.

4.1. Meteorological Measurements

[22] Temperature, radiation, and other meteorological parameters were continuously measured at FLW. The conditions during the study were primarily sunny and humid, with cloudless or partly cloudy skies. Mid-day temperatures (2 m AGL) at this site ranged from 24.3°C to greater than 36°C. Nighttime lows ranged from 15.6°C to 24.3°C. Generally, the first part of the study (9–16 July 1998) was characterized by relatively cooler temperatures, followed by days (18–21 July 1998) with relatively warm temperatures (Figure 4a). July 14 was the coolest study day, with the mid-day temperature never rising above 26°C, low solar radiation intensity, and high relative humidity. During the final days of measurements (18–21 July 1998), afternoon temperatures were typically 3–4 degrees warmer than those observed during the earlier days of the study, with average afternoon temperatures close to 35°C. This period

also featured the highest solar radiation intensity and lowest relative humidity of the entire study period.

4.2. Enclosure Measurements

[23] Enclosure measurements were performed on leaves of two oak trees (*Quercus stellata* [post oak] and *Q. marilandica* [blackjack oak]) in the vicinity of the large balloon launch site at FLW. These species were chosen for study because they comprise a large fraction of the oak crown area in the region and are known to be strong emitters of isoprene. All of the measured leaves were located on the outer edge of the crown and were considered to be sun-lit leaves. The same nine leaves were measured each day at approximately the same time; four post oak leaves were measured in the morning between 10:00–12:00 CDT, while five blackjack oak leaves were measured in the afternoon window 12:30–18:00 CDT. The post oak leaves were not in full sunlight during their measurement period and this may have impacted the results.

[24] Each day, isoprene emission capacities were determined for each leaf from the enclosure measurements made at 30°C and 1000 μmol m^{-2} s^{-1}; for cases in which the LI-6400 was unable to maintain leaf temperature at 30°C during the measurement period, the observed emission rates were normalized to 30°C using the temperature algorithm of *Guenther et al.* [1993] (Figure 4b). The average normalized emission capacities observed in leaves of the post oak and blackjack oak were 65.6 ± 8.7 and 66.2 ± 10.4 μgC g^{-1} h^{-1}, respectively (Table 2). These values are in good agreement with the value of 70 μgC g^{-1} h^{-1} assigned to these and other North American oak species in current biogenic emission models [e.g., *Geron et al.*, 2001]. However, Figure 4b demonstrates substantial day-to-day variability in average normalized isoprene emission capacity over the nine days of observations, with values ranging from 56.4 to 86.5 μgC g^{-1} h^{-1} for the blackjack oak, and from 47.2 to 78.1 μgC g^{-1} h^{-1} for the post oak. This type of variability has been observed in other leaf-level studies [e.g., *Petron et al.*, 2001; *Geron et al.*, 2000] and introduces additional uncertainty into biogenic emission estimates based on leaf-level emission capacities. In those studies, it has been proposed that an isoprene emission capacity during a given measurement varies in relation to variation in temperature over the preceding hours or days.

[25] Figure 4a depicts the measured air temperatures (2 m AGL) at the FLW site over the course of this study. Superimposed on the instantaneous temperature readings are the average air temperatures from the 24 hours prior to the start of the measurement period (10:00 CDT for the post oak; 12:30 CDT for the blackjack oak). The isoprene emission capacities for both the post oak and blackjack oak leaves generally followed these variations in temperature and exhibited a minimum in the middle of the study, corresponding to the period of lowest midday temperatures (Figure 4). The overall trends suggest the emission capacities for both species increase with increasing midday ambient temperature. Other studies have shown that historical (lagged) temperature conditions can affect the isoprene emission capacity [*Geron et al.*, 2000; *Guenther et al.*, 1999; *Petron et al.*, 2001; *Sharkey et al.*, 1999]. The correlation between ambient temperatures observed during the leaf-level measurement periods and the average of all
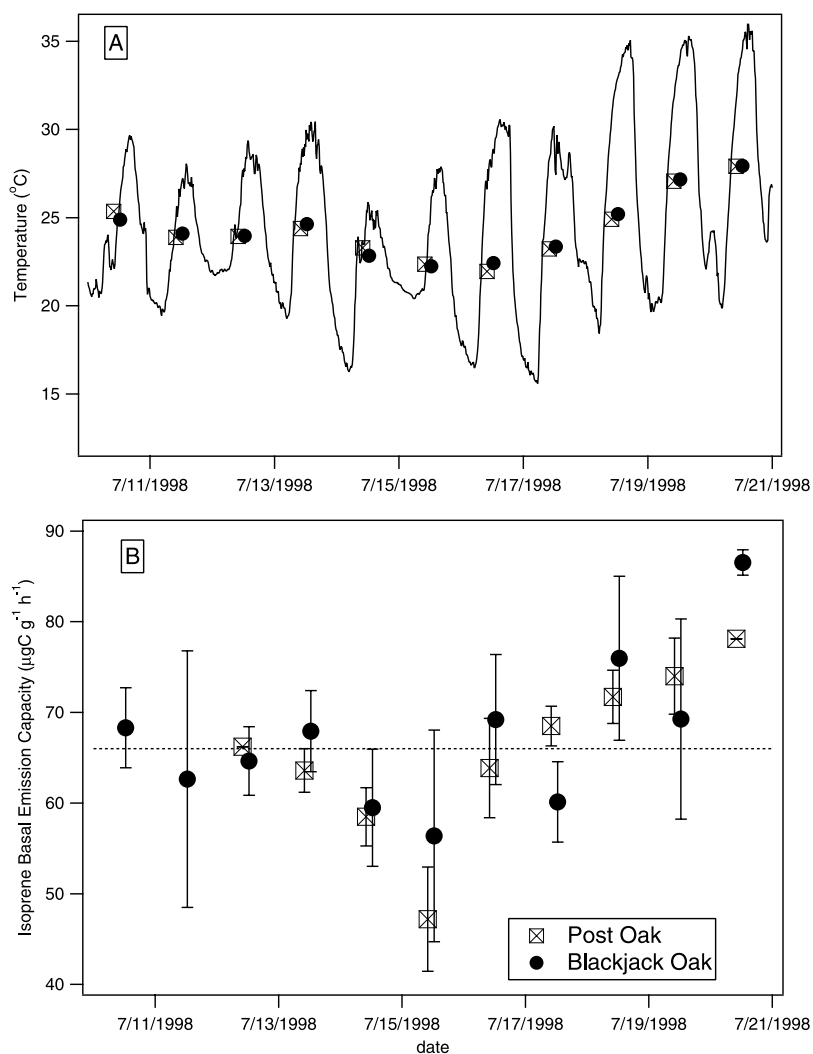
Figure 4. (a) Measured diurnal temperatures (2 m AGL) at the FLW site during the OZIE study. The markers represent the average temperature for the 24-hour period before sampling began on the post oak and blackjack oak leaves each day (10:00 CDT and 12:30 CDT, respectively). (b) Average calculated emission capacity (μgC g^{-1} h^{-1}), normalized to 30°C and 1000 μmol m^{-2} s^{-1}, for each of the two studied trees. The error bars represent the standard deviation of the daily measurements made from the leaves of each tree. The dashed line is the average measured emission capacity for all measurements: 66 μgC g^{-1} h^{-1}.

measured isoprene emission capacities was strong, with $r^2 = 0.64$ (Figure 5). We also investigated the influence of average temperature from the preceding 24 hours and found a strong correlation with the observed emission capacities ($r^2 = 0.58$). These data clearly show that there is a relationship between ambient temperature and isoprene emission capacity; however, isoprene emission capacity may potentially be affected by several other environmental variables (e.g., PAR, humidity, drought). This data set does not allow us to examine those factors. Nevertheless, the strong correlation between emission capacity and either the ambient temperature at the time of measurement or the average temperature over the preceding 24 hours strongly suggests the importance of temperature in explaining day-to-day variations. These data, with other leaf-level data, may be used to develop and evaluate algorithms that describe the influence of ambient temperatures on emission capacities. These relationships could be included in

future emissions models to more accurately estimate biogenic isoprene emissions for input to photochemical transport models.

4.3. Balloon Measurements

[26] Isoprene mixing ratios were measured from the large balloon at altitudes up to 1000 m AGL for 13 days in July 1998 at the FLW site (Table 1). Measured isoprene mixing ratios from the large balloon ranged from below

Table 2. Results From Leaf Enclosure Measurements[a]

	Isoprene Emission Capacities, μgC g^{-1} h^{-1}					
	Average	Median	Standard Deviation	Maximum	Minimum	N
Post Oak	65.6	66.7	8.7	78.3	43.1	20
Blackjack Oak	66.2	65.5	10.4	87.5	41.0	46

[a]The calculated emission capacities have been normalized to 30°C and 1000 μmol m^{-2} s^{-1} using algorithms in *Guenther et al.* [1993].
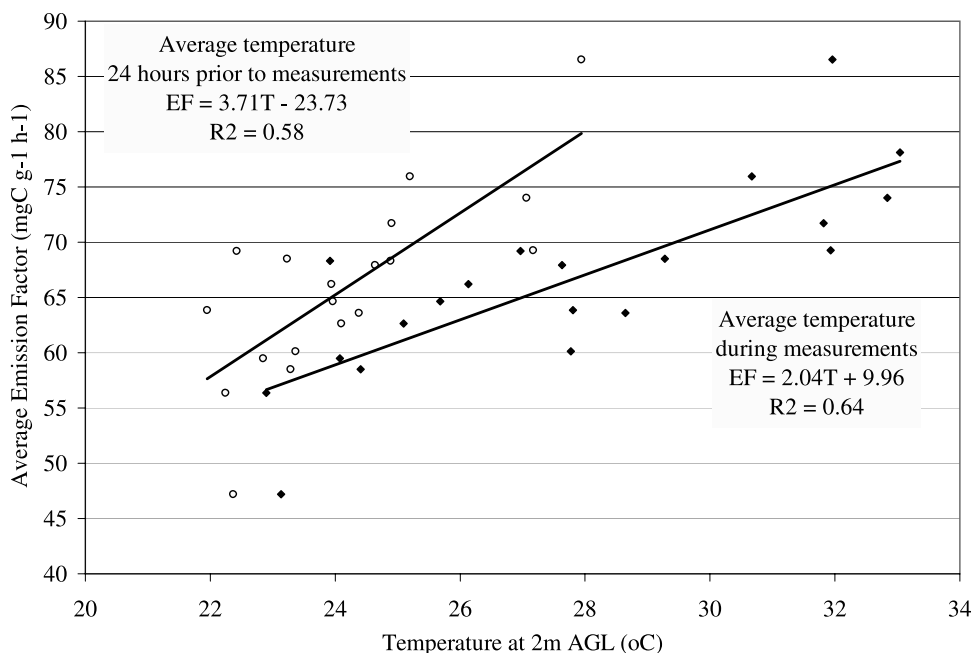
Figure 5. Correlations between average temperatures (°C) measured at 2 m AGL and the average measured isoprene emission capacities (EC; $\mu gC\ g^{-1}\ h^{-1}$) from both the blackjack and the post oak leaves. Two temperature correlations with the measured emission capacities are shown: (1) with the average temperature at 2 m AGL over the period when the measurements were made (solid diamonds), and (2) with the average temperature at 2 m AGL for the 24 hours before the measurements were made (open circles).

the detection limit (approximately 1 pptv) to over 5 ppbv, with daily maximum values observed closest to the surface (<300 m AGL) at early afternoon (from 12:00–16:00 CDT). The study-averaged isoprene mixing ratios (with their standard deviations) observed over different altitude ranges (50–300 m AGL, 300–500 m AGL, 500–700 m AGL, and 700–1000 m AGL) for various time-of-day intervals are shown in Figure 6. The measured isoprene mixing ratios were relatively low early in the day due to low emission rates. A strong vertical gradient in the isoprene mixing ratios was observed between the ground-level measurements (see next section) and the mixed layer measurements from the balloon. Higher isoprene mixing ratios were observed near the surface, closest to the emissions source. Daytime mixing ratios (~11:00–18:00 CDT) in the boundary layer at altitudes between 300 and 1000 m AGL showed small but significant gradients that reflected the strength of mixing in the mixed layer. These gradients ranged from approximately 0.5 ppb to 3 ppb between 100 and 950 m (0.6 to 3.5 ppt m^{-1}). As expected, concentrations decreased with height indicating a surface source.

[27] During the morning hours (between 6:00 and 9:00 CDT), low isoprene mixing ratios (<1 ppb) were observed at altitudes >400 m. The presence of isoprene at this altitude is likely due to isoprene emitted during the previous day remaining in the residual layer. The temperature and humidity profiles from the tethered balloon system indicated that the daytime boundary layer did not typically reach 400 m until later in the morning. The highest isoprene mixing ratios (Figure 6; orange markers) were observed in the newly formed nocturnal boundary layer (~200 m AGL)

in the late afternoons (17:00–20:00 CDT); light-dependent isoprene emissions continued until approximately 18:00; ozone reactions with isoprene in the nocturnal boundary layer would only slowly reduce nighttime isoprene concentrations.

[28] There were significant variations in the measured isoprene concentrations from day to day associated with varying meteorological conditions that affected boundary layer dynamics and emission rates. As noted in the previous section, ambient temperatures were relatively cool during the middle of the study, and the final days were characterized by relatively warm temperatures. Generally, emissions of isoprene were expected to be lowest during the cooler time period of the study and then to increase in the final, hotter days of the study [Guenther et al., 1993]. However, there was no apparent relation between measured isoprene mixing ratios aloft and ambient temperatures at the FLW site. This phenomenon occurs because an increase in temperature results in two offsetting effects, higher isoprene emissions and higher boundary layer height, which results in a nearly constant mixed layer isoprene mixing ratio.

[29] Isoprene was measured at elevations of 2 and 250 m AGL at six sites (in addition to FLW) on ten separate days using the roving balloon (Table 3). Observed isoprene mixing ratios ranged from <0.1 ppbv to greater than 9 ppbv. The highest isoprene mixing ratios were observed at the Sinkin Creek field site, while the lowest isoprene mixing ratios were measured at the Candy Wildlife Management Area (WMA). This trend corresponded well with the oak coverage in the BELD3 database that was used to estimate the isoprene emissions for the chemical transport modeling;
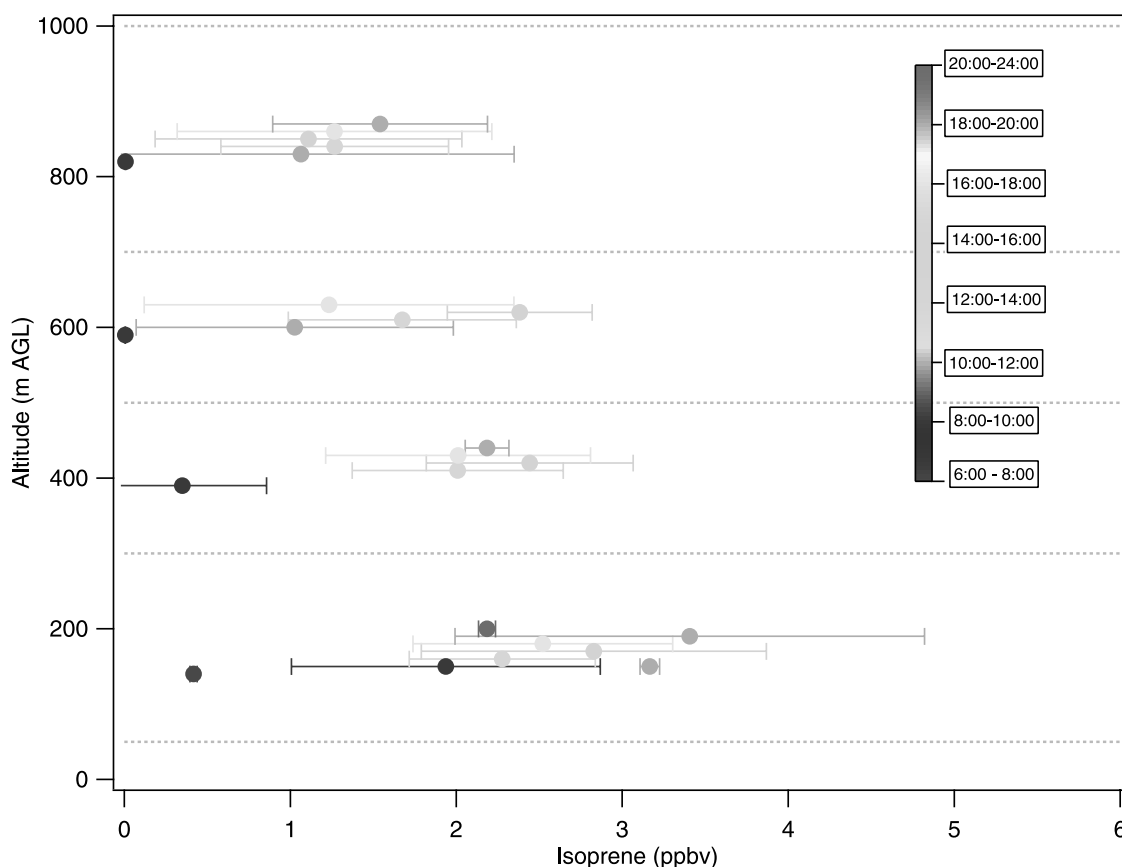
Figure 6. Summary of all large balloon measurements conducted during the OZIE study, showing variations with height and hour-of-day. Markers denote the study-average mixing ratios measured at the specified time (color scale) and within the altitudes denoted by the gray dotted lines above and below the markers (50–300 m AGL, 300–500 m AGL, 500–700 m AGL, and 700–1000 m AGL); error bars represent the standard deviations of those measurements over the course of the study. See color version of this figure at back of this issue.

BELD3 assigns 53% oak coverage at Sinkin Creek and less than 3% oak coverage at Candy WMA. Table 3 summarizes the daytime (primarily mid-day) mixing ratios of isoprene at ~250 m AGL and at ground level (<10 m AGL). As expected for a compound with a surface emission, both balloon data sets (large and roving) showed that isoprene mixing ratios were consistently lower at higher altitudes. This demonstrates that the surface mixing ratio cannot be assumed to be representative of the mixing ratio at 250 m. In addition, the large observed variation in this ratio for different sites and meteorological conditions indicates that assuming a constant ratio will introduce significant uncertainties in estimates of isoprene mixing ratios in the daytime mixed layer.

4.4. Ground-Level Carbonyl and VOC Measurements

[30] VOCs and carbonyls were measured at approximately 2 m AGL at five locations within FLW (in addition to the large balloon launching site). VOCs and carbonyls were also measured at other field sites on selected days (Table 1). The ground-level measurements of isoprene and selected carbonyls for the various OZIE study sites are summarized in Table 4. The highest single ground-level isoprene mixing ratio (35.8 ppbv) was observed at FLW (specifically, site FLW5) at 18:15 CDT on 20 July 1998. Indeed, all five

ground-level FLW sites exhibited high isoprene mixing ratios during this particular sampling day and time (26.3 ppbv average across the five sites). The environmental conditions corresponding to this sample period included temperatures greater than 36°C, with PAR ranging from 500 to 900 μmol m^{-2} s^{-1}. The elevated temperature, and

Table 3. Averaged Daily Concentrations of Isoprene Measured With Cartridges From Ground-Level and From the Roving Balloon, and the Ratio of Ground Concentration to the Concentration Measured at 250 m AGL[a]

| | | Isoprene, pptv | |
Date (YYYYMMDD)	Site Name	Ground	(250 m AGL)/ Ground
19980710	FLW (1)	3688	0.93
19980712	Brown Country Park	1206	0.93
19980713	Morgan Monroe	2004	0.62
19980714	Giant City	823	0.34
19980716	FLW (2)	1733	0.61
19980717	Candy WMA	218	0.85
19980718	Tall Grass	1158	0.51
19980721	Willow Springs	3597	0.78
19980722	Sinkin Creek	7494	0.43

[a]The two FLW sites are at different locations on the FLW army base.

Table 4. Isoprene and Carbonyl Mixing Ratios Measured at the Ground Sites During the OZIE Study

	Site Name				
	Giant City, Illinois	Morgan Monroe, Illinois	Ft. Leonard Wood, Missouri	Willow Springs, Missouri	Sinkin Creek, Missouri
Percent Oak	7	8	34	16	53
VOC:					
Dates Sampled	8−24 Jul	8−24 Jul	9−20 Jul	21 Jul	22 Jul
N	41	23	69	16	17
Isoprene					
Mean, ppbv	6.4	6.4	10.8	15	15
Range, ppbv	0.6−15.4	2.4−15.2	1.8−35.8	8.2−27.2	6.6−24.2
Carbonyls:					
Dates Sampled			13−20 Jul	21 Jul	22 Jul
N			45	8	7
Formaldehyde					
Mean, ppbv			11.4	14.0	10.5
Range, ppbv			5.4−20.2	9.1−16.3	6.1−13.3
Acetaldehyde					
Mean, ppbv			2.8	2.9	2.4
Range, ppbv			1.5−4.8	1.4−3.8	1.1−3.3
Acetone					
Mean, ppbv			1.7	1.7	2.2
Range, ppbv			0.5−3.1	1.1−2.4	1.3−2.8
Propanal					
Mean, ppbv			0.3	0.3	0.3
Range, ppbv			0.2−0.6	0.2−0.4	0.2−0.8

corresponding elevated isoprene emissions, could explain the high surface isoprene mixing ratios.
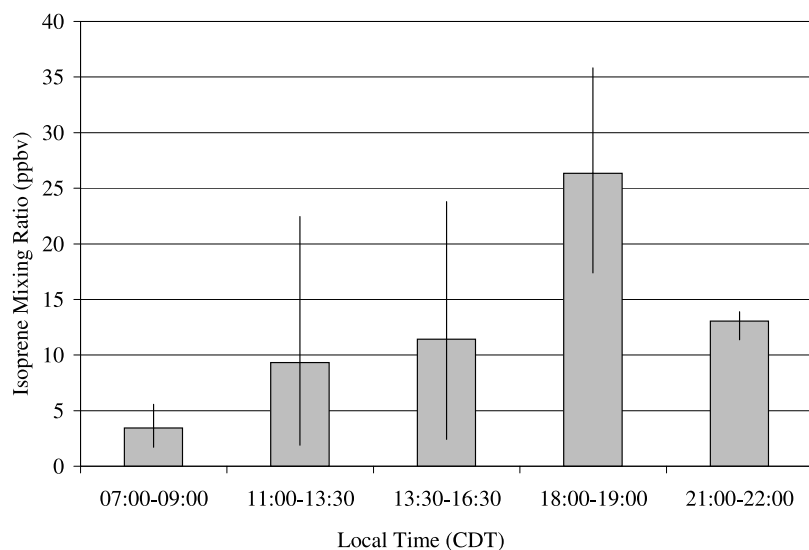
[31] The daytime isoprene mixing ratios measured at FLW were much higher than other reported values from within the United States. The mean isoprene mixing ratio from all daytime measurements made at the ground sites at FLW during OZIE was 10.8 ppbv. *Goldan et al.* [1995] observed an average mid-day isoprene mixing ratio of 6.3 ppbv for a forested site in southwestern Alabama during June and July. *Apel et al.* [2002] measured isoprene mixing ratios at a forested site in northern Michigan in July and

reported mean daytime isoprene mixing ratios to be 1.90 ± 0.43 ppbv (with daily maximum mixing ratios on the order of 10 ppbv). *Wiedinmyer et al.* [2001] measured mean isoprene mixing ratios ranging from 2.4 to 3.0 ppbv at 3 different sites in rural areas of central Texas. Although these other studies took place in forested areas with expected isoprene emissions, none of the reported isoprene mixing ratios had the same magnitude as the measurements made during OZIE.

[32] The study-average diurnal profile for ground-level isoprene mixing ratios (Figure 7) reveals that the maximum observed mixing ratios occurred between 18:00−19:00 CDT. There were large spatial and temporal variations in the FLW ground-level observations despite these sites being in close proximity (within a few kilometers; see *Long* [2003] for details). Three-dimensional photochemical transport model evaluations using ground-level point measurements from a single site must consider such variability in the measured concentrations. Indeed, due to local influences, a single point measurement may not be suitable for evaluating chemical transport model output that has a spatial resolution of several kilometers.

[33] Mixing ratios of formaldehyde, acetaldehyde, acetone, and propanal are also summarized in Table 4. At all three sites located in Missouri, mean acetaldehyde mixing ratios did not vary significantly, ranging from 2.4 to 2.9 ppbv. This was also the case with the observations of acetone and propanal, where the mean mixing ratios measured at FLW were 1.7 and 0.3 ppbv, respectively. Formaldehyde concentrations measured at the Missouri field sites were relatively high, ranging from 5.4 to 20 ppbv. These concentrations were close to values observed in polluted urban plumes in Houston, Texas.

[34] Satellite observations of HCHO columns from the Global Ozone Monitoring Experiment (GOME) [*Chance et al.*, 2000] have been shown in previous work to be consistent with in situ HCHO mixing ratio measurements [*Palmer et al.*, 2003]. In particular, they can be used to

Figure 7. Study-average isoprene mixing ratios averaged for ground-level measurements at FLW for different time periods. Bars denote the average mixing ratios for all days and all ground-level sites; error bars represent the maximum and minimum values of the observed mixing ratios.
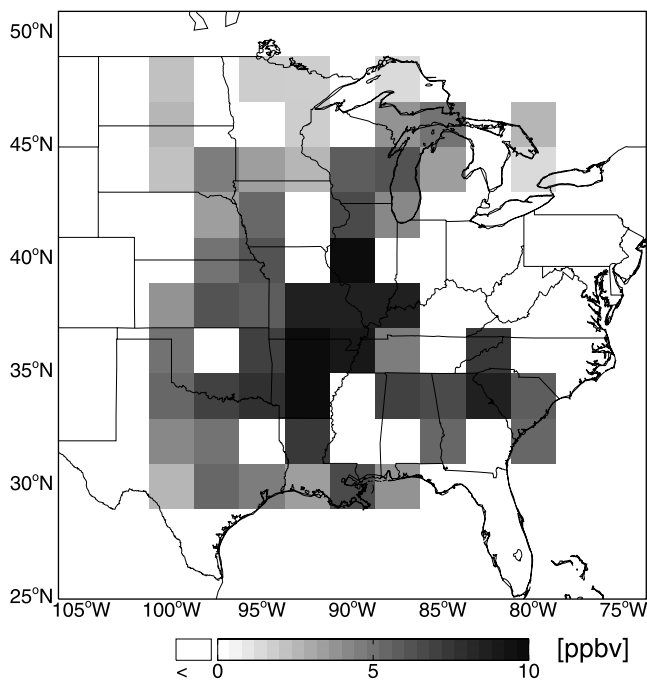
Figure 8. Surface HCHO concentrations (ppbv) calculated from HCHO column observations (molec cm^{-2}) from the GOME satellite instrument [*Chance et al.*, 2000] during 16–22 July 1998, assuming an exponentially decaying vertical profile of HCHO mixing ratio with a scale height of 1 km. Data are for 10–12 local time, averaged on a 2 × 2.5 degree grid, and for cloud cover <40%. See color version of this figure at back of this issue.

relate findings from in situ data to larger spatial scales. Figure 8 shows surface HCHO mixing ratios (16–22 July 1998) inferred from the GOME column data assuming an exponentially decaying vertical profile of HCHO mixing ratio with a scale height of 1 km. Under that assumption, the surface HCHO concentration is related linearly to the observed HCHO column and the scale height. The data are averaged on a 2 × 2.5 degree grid, a resolution comparable to the largest dimension of the GOME pixel (40 × 320 km^2) at mid-latitudes. GOME-derived HCHO mixing ratios at this spatial resolution are likely to correspond to greater mixing ratios at smaller scales. GOME shows elevated formaldehyde mixing ratios (up to 10 ppbv) over the Missouri Ozarks and the OZIE study domain, in good agreement with the in situ measured mixing ratios at ground-level. The study-averaged in situ daytime formaldehyde mixing ratios ranged from 11.4 ppbv (at FLW) to 14.0 ppbv (at Willow Springs, Missouri). The satellite observations also reveal that elevated HCHO mixing ratios persisted over a larger geographic region than one might have inferred from the spatially confined ground-level measurements.

4.5. Modeling Results and Evaluation

[35] The data collected during the OZIE study were used to estimate biogenic isoprene fluxes to the atmosphere. These estimates were then compared to the fluxes predicted by the BEIS3 biogenic emissions model. Finally, observed isoprene and formaldehyde mixing ratios were compared to values predicted by photochemical transport model simulations.

[36] The balloon measurements were used to estimate the isoprene fluxes from the surface vegetation using a simple chemical box model [*Guenther et al.*, 1996], which assumed that isoprene is removed only through reactions with O_3 and OH. These calculations also assumed the average boundary layer ozone mixing ratio in the region during the day was 40 ppbv (measured at the Fort Leonard Wood airport), the OH concentration was 4×10^6 molecules cm^{-3} (as is recommended by *Chameides et al.* [1992] and *Guenther et al.* [1996]), and an assumed diurnal profile for the boundary layer height with a maximum height of 1500 m at 12:00–14:00 CDT. The vertical profiles of isoprene mixing ratios observed with the large balloon system were used to estimate the mixed-layer average isoprene mixing ratio. The roving balloon system provides mixed-layer observations only at 250 m. The roving balloon observations of isoprene mixing ratio at 250 m were related to the mixed-layer average mixing ratio using the average vertical profile observed with the large balloon system. This methodology has been applied for previous research efforts to reconstruct isoprene fluxes from boundary layer mixing ratio measurements [e.g., *Guenther et al.*, 1996; *Wiedinmyer et al.*, 2001]. The uncertainty associated with the applied OH mixing ratio was assumed to be 50% [*Guenther et al.*, 1996]. Further uncertainties in the box model flux estimates were due to uncertainties in the applied O_3 concentration, the assumed boundary layer height, and the assumption that the balloon measurements were representative of concentrations in a well-mixed boundary layer.

[37] The BEIS3 isoprene fluxes tended to over-predict the isoprene fluxes reconstructed from the field measurements using the box model (Figure 9). An uncertainty of 50% on both flux estimates are represented by the error bars in Figure 9. Each isoprene flux estimate reconstructed from a single balloon measurement is shown in Figure 9, including those estimated with measurements made when the boundary layer may not have been well-mixed. The roving balloon flew to altitudes of 250 m and only one measurement within the boundary layer was made. Measurements from this balloon may not always represent mixing ratios from a well-mixed boundary layer, and the single measurement prevents an assessment of when the boundary layer was well-mixed. Additionally, the roving balloon system was operated at eight locations between 36.499° and 39.295° latitude and 86.221° to 96.333° longitude. BEIS3 underestimated isoprene emissions at 3 sites and overestimated at 3 sites relative to the balloon estimates. BEIS3 estimated a much larger variability in isoprene emission between sites in comparison to the balloon system. A more quantitative comparison is prevented due to the uncertainties associated with the box model estimates (e.g., OH and O_3 concentrations and boundary layer height) and the difference in spatial resolutions between the two estimates. The BEIS3 flux estimates were area-averaged values for a grid cell with 12 km horizontal resolution, whereas the estimated fluxes from the balloon measurements were made from single points with different footprints. Direct measurements of isoprene fluxes, rather than relying on reconstructed fluxes from observed mixing ratios and a box
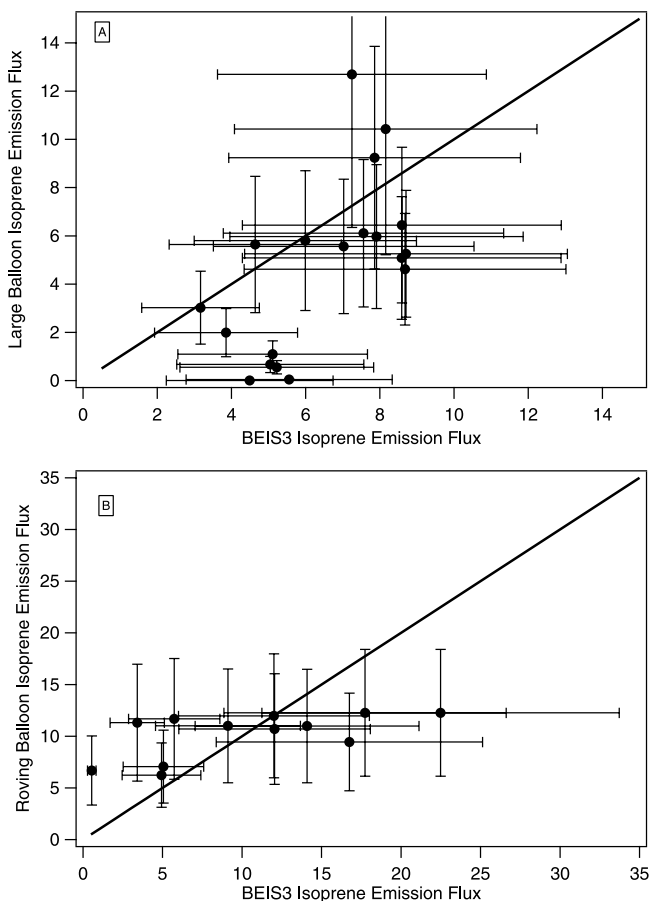
Figure 9. Isoprene fluxes (mg m^{-2} h^{-1}) reconstructed from observed isoprene mixing ratios versus BEIS3-estimated isoprene emission fluxes: (a) large balloon measurements at FLW; and (b) roving balloon measurements at various sites. The error bars represent a 50% uncertainty in all sets of estimates.

model, would enable a better evaluation of the biogenic emissions model and are recommended for future field studies.

[38] Biogenic emissions were estimated using the BEIS3 model algorithms and satellite-derived PAR. These values were used as inputs to the CAMx model for a 7-day simulation for 16–22 July 1998. The isoprene emission estimates for 14:00 CDT on 20 July 1998 are shown in Figure 1. Large emissions of isoprene were predicted in the Missouri Ozarks, particularly where the FLW and other Missouri study sites were located.

[39] The chemistry and transport simulated with CAMx were evaluated with comparisons between measured isoprene mixing ratios to those predicted by the chemical transport model. Four of the FLW ground sites were located within an area encompassed by a single CAMx grid cell. Figure 10 shows the surface mixing ratio of the isoprene modeled by CAMx for that particular grid cell (line) and the average of the ground-level isoprene mixing ratios measured at the four FLW sites located within the model grid cell area (circles). All of the four FLW ground-level measurements for a given time period have been averaged, and the standard deviations in these measurements are

shown by the error bars. The correlation between the average of the measured ground isoprene mixing ratios and the modeled isoprene mixing ratios had an $r^2 = 0.53$. A stronger correlation is not observed due, in part, to the fact that we are comparing simulated concentrations from a model with 12 km horizontal resolution (in which each grid is assumed to be well-mixed) to the average of several single point measurements that were each influenced by local phenomena. The discrepancies between the modeled and measured isoprene mixing ratios may also be the result of uncertainties in the simulated meteorology, boundary layer processes, emissions, and chemistry. However, the comparison showed that the model did a reasonable job at reproducing the ground-level measurements and their diurnal variations, suggesting the surface isoprene mixing ratios simulated by this modeling procedure (emissions estimated by BEIS3, and subsequent mixing ratios simulated by CAMx) was reliable but contains uncertainties. A comparison of the model output with data from a single site, rather than averaging over all appropriate sites, resulted in a much weaker correlation ($r^2 = 0.35$).

[40] A comparison of the measured and modeled vertical profiles of isoprene mixing ratios produced a similar result. Figure 11 shows the average of all isoprene mixing ratios measured within the first nine vertical model layers (up to 1071 m AGL) and the average of the corresponding modeled mixing ratios for the same times and location. The average modeled mixing ratios are from the horizontal grid cell encompassing the area where the four FLW sites (used in the above discussion) were located. The average measured mixing ratio in Layer 1 (up to 31 m AGL) is an average of all canister and cartridge measurements made within the area of the model grid cell, and the average measured mixing ratios within Layers 2–9 are from the large balloon. The error bars represent the standard deviation of the mixing ratios at each layer.

[41] The modeled and measured mixing ratios show a similar vertical structure; however, the results suggest that the model may overestimate isoprene mixing ratios at lower elevations (∼<500 m AGL). Possible explanations for the measurement-model differences could be an overestimate of surface-layer isoprene emissions at that site and inaccurate vertical mixing within the model. Uncertainties associated with this comparison exist as the result of differences in the temporal resolutions of the model and measurements. Additionally, the model output represents the average over an entire vertical layer, whereas the balloon measurement represents one point at a particular altitude.

[42] Although the differences in the spatial and temporal resolutions of the GOME satellite estimates of boundary layer HCHO mixing ratios (Figure 8) and the simulated surface concentrations of HCHO from CAMx (Figure 2b) prevent a quantitative comparison, a qualitative analysis of the two estimates suggests good agreement. Both outputs showed elevated formaldehyde mixing ratios above and downwind of the Missouri Ozarks. The elevated HCHO mixing ratios were observed over large geographic expanses. Figure 2b shows the CAMx-modeled formaldehyde for the late afternoon on 21 July when winds were from the south south-west. This formaldehyde, presumably from the oxidation of isoprene emitted in the Missouri Ozarks, was also observed in the GOME data. The satellite
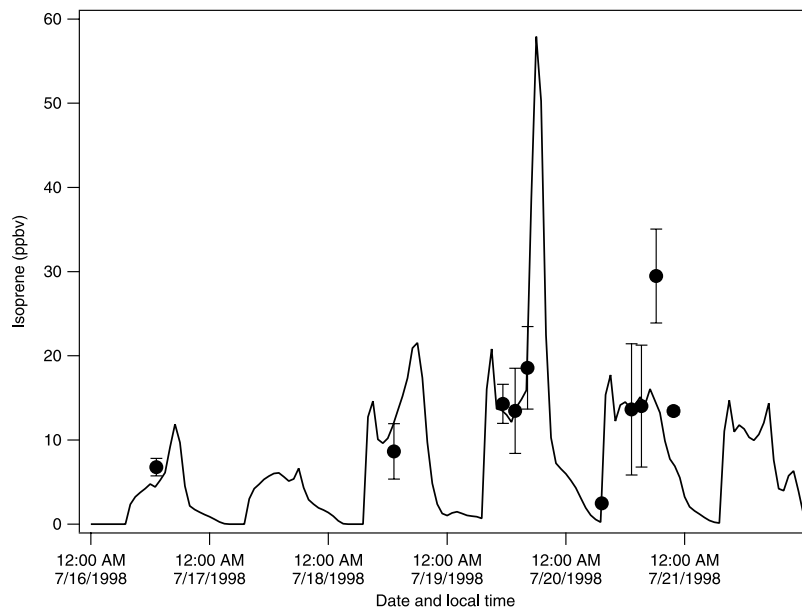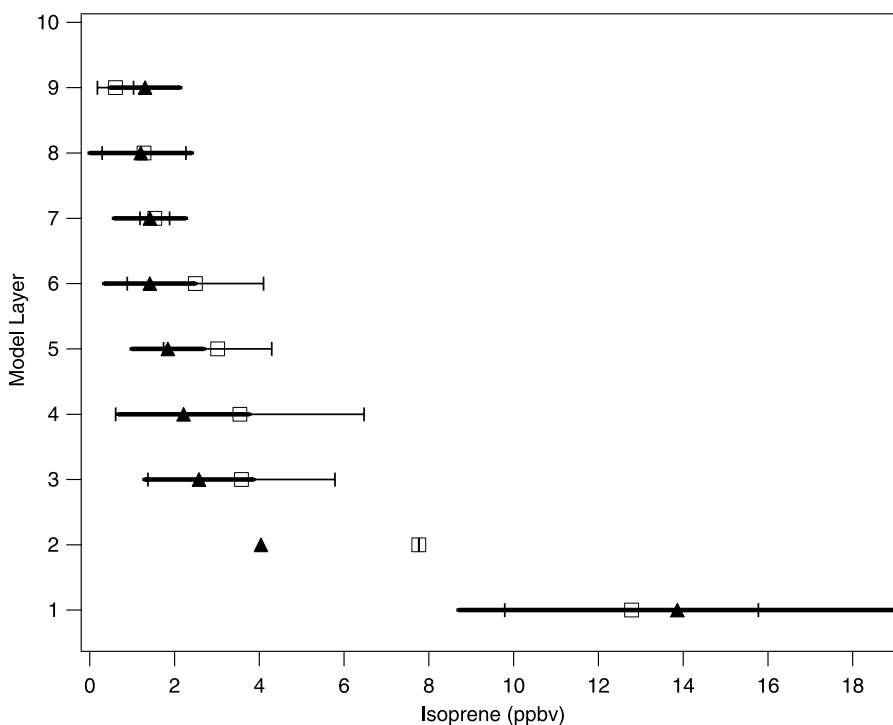
Figure 10. Measured (markers) and CAMx-modeled (line) isoprene mixing ratios during the OZIE study. Measured mixing ratios are reported as the average of all ground-level sites operated at FLW with error bars representing the standard deviation of these measurements.
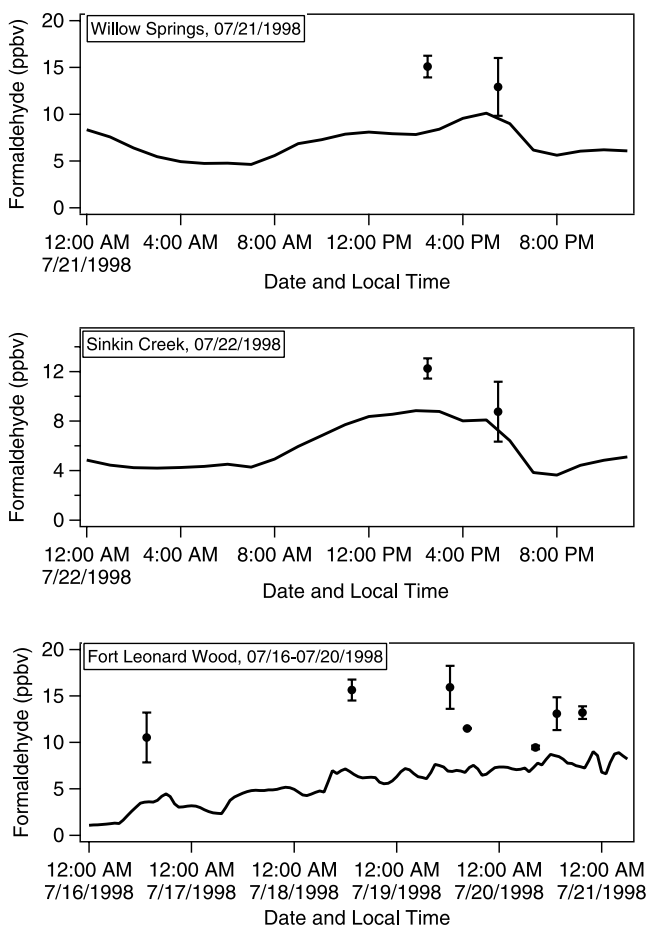
showed very high mixing ratios of HCHO throughout much of Illinois.

[43] For three different locations in Missouri (Sinkin Creek, FLW, and Willow Springs), HCHO mixing ratios measured at multiple, nearby ground-level sites were averaged and compared to the model predictions (Figure 12).

In all cases, the observed HCHO mixing ratios were greater than the modeled surface layer concentrations. Site-specific variations in the HCHO mixing ratios did not appear to reconcile the differences between the model estimates and the observations, and the model consistently underpredicted the HCHO mixing ratios in these geographic areas

Figure 11. Average measured (triangles) and modeled (squares) isoprene mixing ratios for the vertical model layers up to ~1000 m AGL. The error bars represent the standard deviation of the mixing ratios within each model layer for the compared times.

Figure 12. Measured (markers) and CAMx-modeled (line) formaldehyde mixing ratios at three locations during the OZIE study. Measured mixing ratios represent the average over all ground-level sites within the modeled grid cell with error bars representing the standard deviation of these measurements.

CAMx model framework. Future study of the mixing ratios and fluxes of HCHO in the OZIE study area, and in the surrounding regions, would be useful for constraining the regional chemical transport models.

[44] The under-prediction of HCHO could have important implications in the regional chemical transport modeling of the central United States. The CAMx model output predicted large ozone mixing ratios in the urban areas of St. Louis and Chicago, and these results suggested that, for certain meteorological conditions, reaction products including HCHO from the oxidation of isoprene emanating from the Missouri Ozarks contributed to the ozone-forming chemistry (e.g., Figure 2). The results of this study showed that this is a possibility, but further measurements in both the rural and urban areas of the region should be made to better constrain the influence of isoprene and its oxidation products on the regional ozone chemistry.

5. Conclusions

[45] A field campaign designed to investigate the biogenic emissions from oak forests of the Missouri Ozarks and their role in regional oxidant chemistry was conducted in the summer of 1998. Measurements of VOCs, including isoprene and carbonyls, were made from the surface and within the boundary layer. These measurements were used to evaluate the isoprene emission estimates by the BEIS3 model. The measurements were also used to evaluate a regional photochemical transport model that is used to assess regional atmospheric chemistry and provide guidance for designing pollution control strategies in the urban areas of the region.

[46] Measured isoprene emission capacities of two predominant oak tree species showed that current emission capacities applied in biogenic emissions models are appropriate. However, it appeared that ambient temperatures may control isoprene emission capacities in ways that are not currently quantified. New algorithms to describe these processes need to be developed and included in future emissions models.

[47] The ground and balloon ambient measurements showed relatively high mixing ratios of isoprene, corresponding to large biogenic fluxes. The measurements showed reasonable agreement with the biogenic emissions model and chemical transport model output, which predict an "isoprene volcano" from the Missouri Ozarks. A comparison with other field measurements of isoprene demonstrate that the oak forests of the Missouri Ozarks are high emitters of isoprene and indeed are much higher than most other regions throughout the country, confirming that the BEIS3 estimates for this region are correct in predicting elevated isoprene emissions compared to other sites in the continental United States. The agreement between measured isoprene mixing ratios and regional-scale chemical transport model estimates was improved upon averaging the ground-level isoprene data observed at several sites within a representative area.

[48] Formaldehyde, a high yield isoprene oxidation product, was observed in the studied region at high mixing ratios. Satellite observations of HCHO agreed well with these ground-level measurements and showed elevated mixing ratios on a regional scale, suggesting significant

of elevated isoprene emissions. Due to the many sources of uncertainties associated with the model simulations, we only speculate the reason why the model did not compare well with the measurements. In addition to the uncertainties in the simulated meteorology and boundary layer processes, the model under-prediction could potentially be explained by inaccurate HCHO and other VOC emissions in the simulations or underestimation of HCHO transported into the model domain from other regions. Since HCHO is produced not only via isoprene oxidation but also from the oxidation of many other VOCs, it is possible that incorrect VOC emissions input to the simulation could have led to underestimated HCHO mixing ratios. Direct biogenic HCHO emissions could have also contributed to the elevated HCHO mixing ratios in this region; however, HCHO exchange between plants and the atmosphere appears to be dependent on ambient HCHO concentrations [e.g., *Rottenberger et al.*, 2004] and given the high ambient HCHO concentrations, HCHO deposition would be more likely than emission in this region. HCHO could have been transported into the study region from elsewhere, and this transport may not have been simulated correctly within the

transport of isoprene oxidation products northward and eastward toward urban centers such as St. Louis and Chicago where high levels of anthropogenic NO_x will affect the production of tropospheric O_3. A photochemical transport model appeared to predict this episode of elevated HCHO, but underpredicted the magnitude of the HCHO mixing ratios in rural regions. This underestimation could potentially lead to incorrect chemistry simulations within the urban centers of the region. Therefore, it is recommended that further measurements be made in the Midwestern urban centers to identify the accuracy of the model predictions for HCHO and the impact of the isoprene emitted from the Ozarks. Furthermore, biogenic emissions and their reaction products need to be considered more critically when evaluating the atmospheric chemistry in the urban centers of the Midwest towards determining optimal O_3 control strategies.

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K. Baker, M. Janssen, and M. Koerber, Lake Michigan Air Directors Consortium, Des Plaines, IL 60018, USA.

W. Baugh, Hydrobio Consulting, 1220 Cerro Gordo Rd., Santa Fe, NM 87501, USA.

C. Geron, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, USA.

J. Greenberg, A. Guenther, P. Harley, G. Pétron, and C. Wiedinmyer, Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO 80303, USA. (christin@ucar.edu)

B. Hopkins, B. Lamb, and H. Westberg, Department of Civil and Environmental Engineering, Washington State University, Pullman, WA 99164-5702, USA.

B. P. Long, U.S. Department of Defense, Washington, DC 20015, USA.

P. I. Palmer, Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA.

T. E. Pierce, Atmospheric Sciences Modeling Division, National Oceanic and Atmospheric Administration, Research Triangle Park, NC 27711-0001, USA.

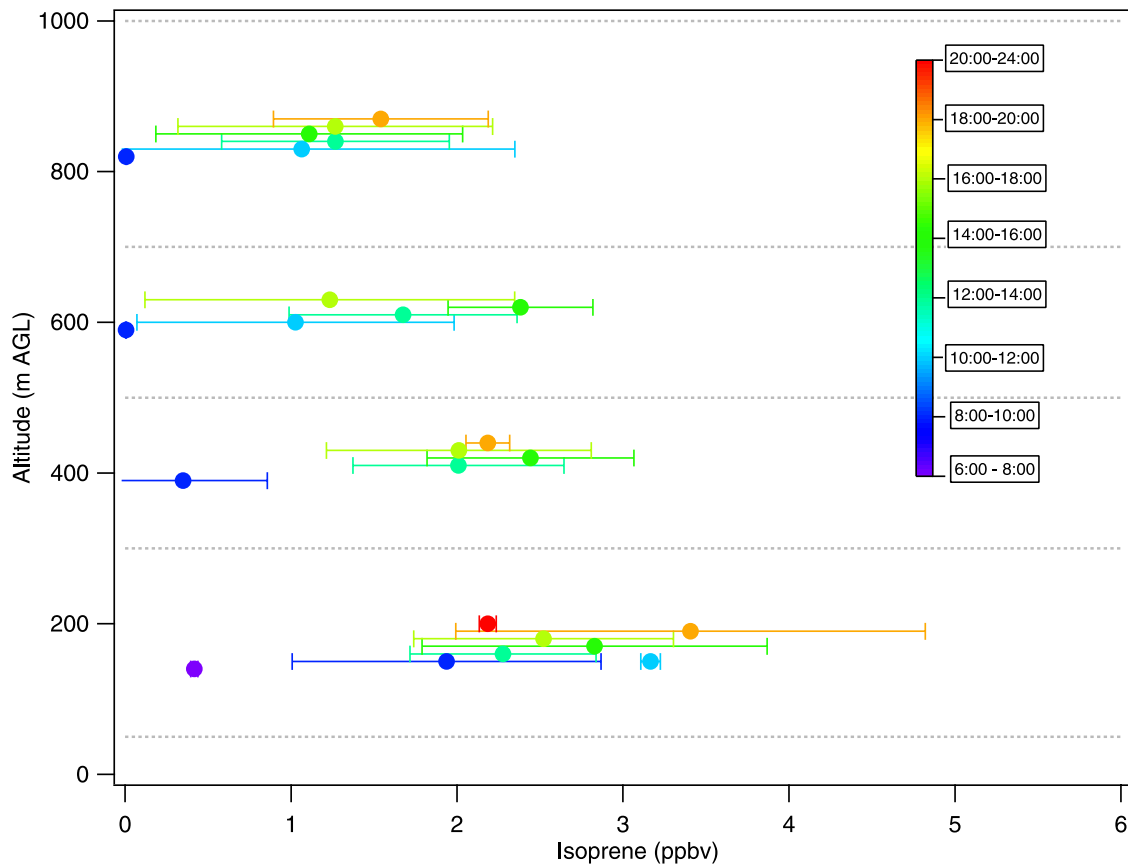J. R. Turner, Department of Chemical Engineering, Washington University, St. Louis, MO 63130, USA.
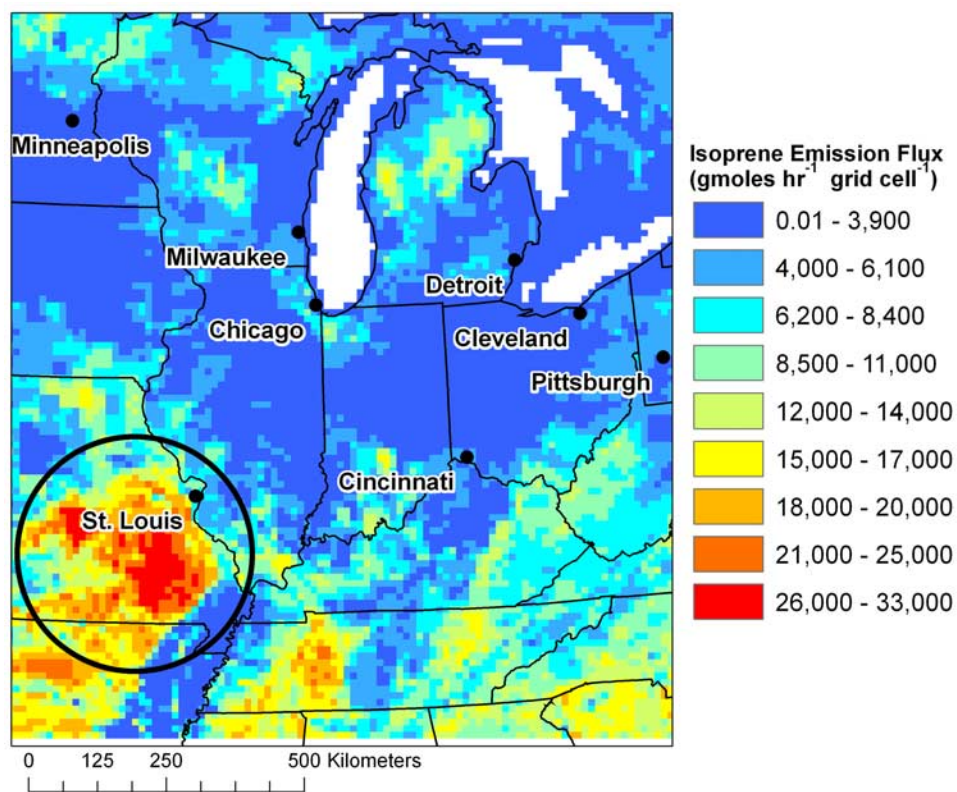
Figure 1. BEIS3-estimated isoprene emissions for 20 July 1998 at 14:00 CDT. The grid cell size is 12 km by 12 km. The oak forests of the Missouri Ozarks are predicted to be a zone of relatively high isoprene emissions (southwestern corner of map) (10,000 gmol h^{-1} grid $cell^{-1}$ = 4.72 mg h^{-1} m^{-2}).
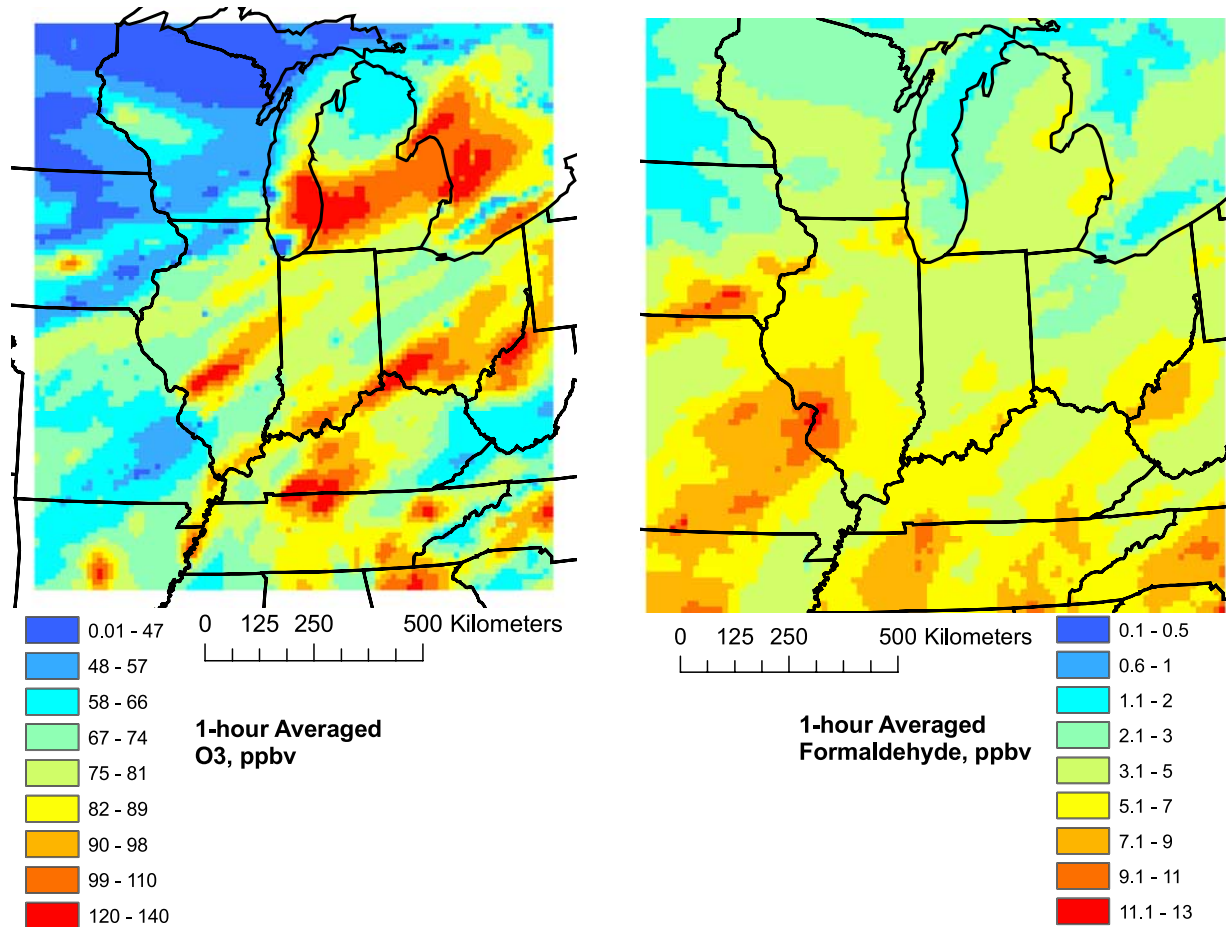
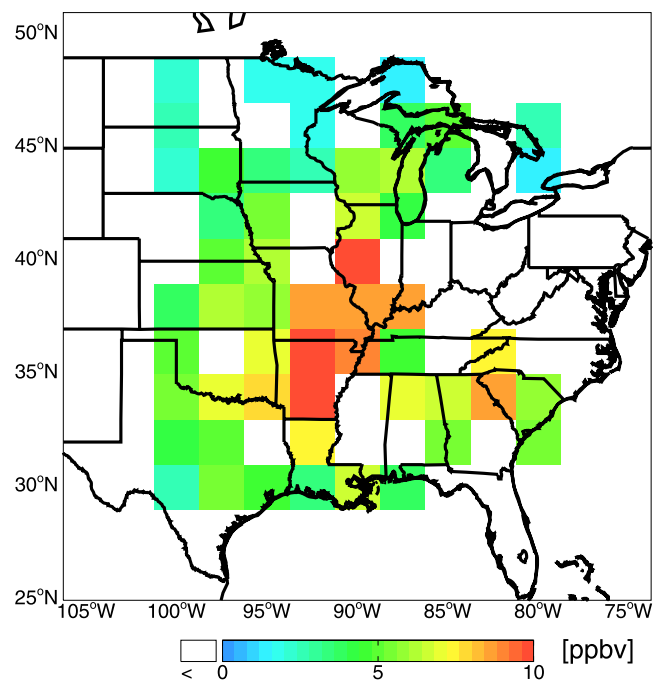**Figure 2.** (left) Hourly averaged ozone (O₃) mixing ratios (ppbv) for 16:00 CDT on 21 July 1998, as simulated by the CAMx model. (right) Hourly averaged HCHO mixing ratios simulated by CAMx for 18:00 CDT on 21 July 1998.
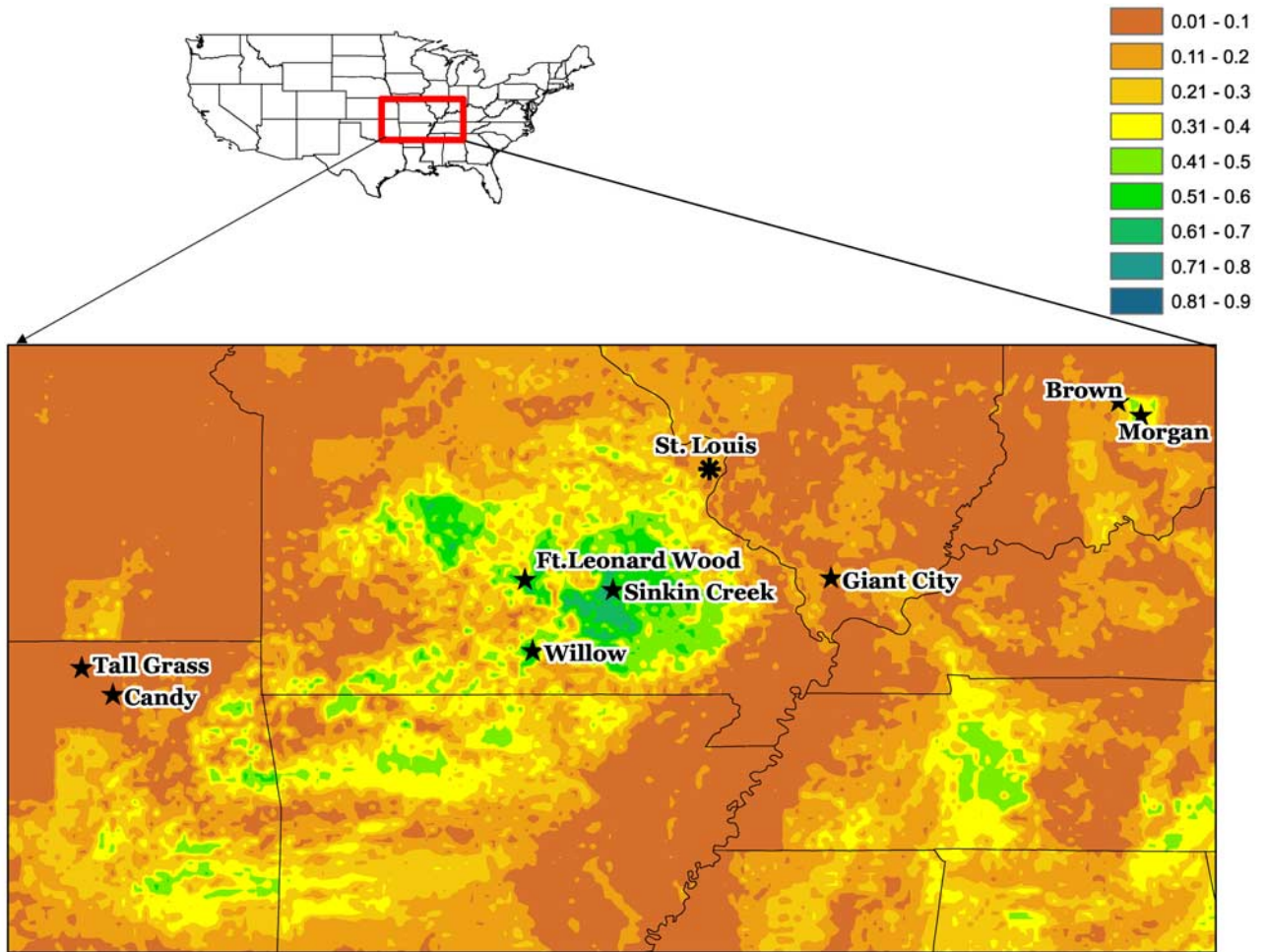
Figure 3. The locations of the field sites of the OZIE study. The fraction of forest oak crown area (color scale) from the BELD3 data set is shown for the study region.

Figure 6. Summary of all large balloon measurements conducted during the OZIE study, showing variations with height and hour-of-day. Markers denote the study-average mixing ratios measured at the specified time (color scale) and within the altitudes denoted by the gray dotted lines above and below the markers ($50-300$ m AGL, $300-500$ m AGL, $500-700$ m AGL, and $700-1000$ m AGL); error bars represent the standard deviations of those measurements over the course of the study.

Figure 8. Surface HCHO concentrations (ppbv) calculated from HCHO column observations (molec cm^{-2}) from the GOME satellite instrument [*Chance et al.*, 2000] during 16–22 July 1998, assuming an exponentially decaying vertical profile of HCHO mixing ratio with a scale height of 1 km. Data are for 10–12 local time, averaged on a 2 × 2.5 degree grid, and for cloud cover <40%.