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Measurement and analysis of atmospheric concentrations of isoprene and its reaction products in central Texas

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Abstract

A field experiment was conducted in August 1998 to investigate the concentrations of isoprene and isoprene reaction products in the surface and mixed layers of the atmosphere in Central Texas. Measured near ground-level concentrations of isoprene ranged from 0.3 (lower limit of detection – LLD) to 10.2 ppbv in rural regions and from 0.3 to 6.0 ppbv in the Austin urban area. Rural ambient formaldehyde levels ranged from 0.4 ppbv (LLD) to 20.0 ppbv for 160 rural samples collected, while the observed range was smaller at Austin (0.4–3.4 ppbv) for a smaller set of samples (37 urban samples collected). Methacrolein levels did not vary as widely, with rural measurements from 0.1 ppbv (LLD) to 3.7 ppbv and urban concentrations varying between 0.2 and 5.7 ppbv. Isoprene flux measurements, calculated using a simple box model and measured mixed-layer isoprene concentrations, were in reasonable agreement with emission estimates based on local ground cover data. Ozone formation attributable to biogenic hydrocarbon oxidation was also calculated. The calculations indicated that if the ozone formation occurred at low VOC/NO_x ratios, up to 20 ppbv of ozone formed could be attributable to biogenic photooxidation. In contrast, if the biogenic hydrocarbon reaction products were formed under low NO_x conditions, ozone production attributable to biogenics oxidation would be as low as 1 ppbv. This variability in ozone formation potentials implies that biogenic emissions in rural areas will not lead to peak ozone levels in the absence of transport of NO_x from urban centers or large rural NO_x sources. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Biogenic emissions; Isoprene; Isoprene reactions; Ozone formation; Texas

1. Introduction

Biogenic hydrocarbons, including isoprene (2-methyl-1,3-butadiene), participate in a variety of atmospheric reactions, including those involved in the production of tropospheric ozone. Guenther et al. (2000) estimate total annual emissions of isoprene for the United States to be 17–20 TgC yr^{-1} and a recent study (Wiedinmyer et al., 2000) has shown that isoprene emissions in the eastern half of Texas are substantial. Because of the large flux of isoprene into the atmosphere and its high reactivity, it is important to characterize the emissions of isoprene and the concentrations of its reaction products, particularly in regions such as the eastern half of Texas, where isoprene emissions are considerable.

The overall objective in the current study is to examine the role of biogenic emissions in the chemical reactions that govern ozone levels in Central Texas. Specifically, flux measurements are compared to emission models to validate current biogenic emission inventories. Incremental reactivity is used to quantify the O_3 attributable to
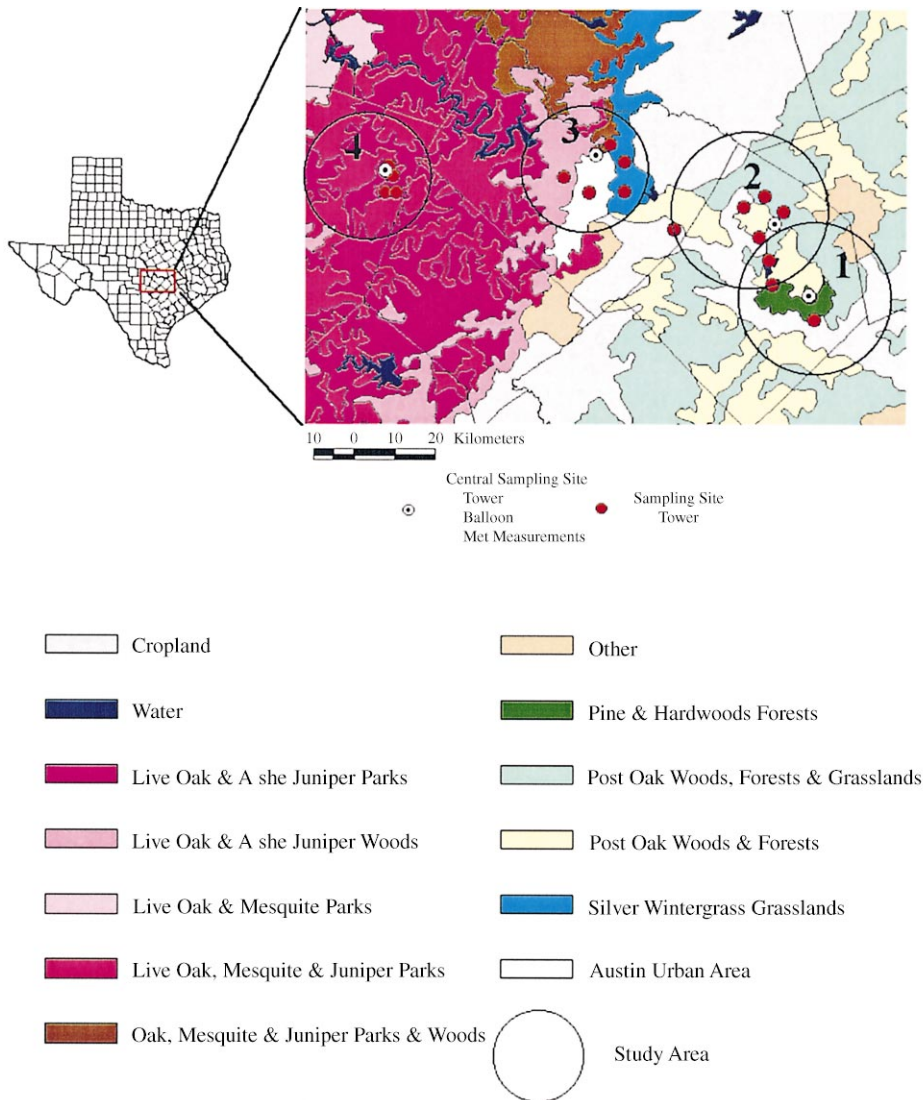
Fig. 1. Location of the study including vegetation types in the region.

photooxidation of isoprene and the O_3-forming potential of hydrocarbons in rural and urban Central Texas. The O_3 attributable to the photooxidation of hydrocarbons and the O_3-forming potentials of hydrocarbons at rural and urban sites in this study are calculated using both high and low VOC to NO_x ratios to indicate the relative importance of NO_x levels on O_3 formation in central Texas. This paper reports the results of this experiment, while individual details regarding study design, measurements and procedures are reported elsewhere (Allen et al., 2000).

2. Experimental description

The experiment was performed from 11 to 21 August 1998, in rural and urban areas of Central Texas as shown in Fig. 1. Measurements were made in four areas within the study region that were selected based on the local vegetation types. Extensive ground-level characterization of vegetation species distributions and biomass densities has been completed for the Central Texas region and these data were used in the site selection process.

Table 1
Leaf biomass densities assigned to land use classifications in Central Texas

Landuse description	Total leaf biomass density ($g\,m^{-2}$)	Oak leaf biomass density ($g\,m^{-2}$)
Live Oak & Ashe Juniper Parks	153	9
Live Oak & Ashe Juniper Woods	339	44
Live Oak & Mesquite Parks	285	75
Live Oak, Mesquite & Juniper Parks	326	63
Oak, Mesquite & Juniper Parks & Woods	326	63
Other	165	52
Pine & Hardwood Forests	556	70
Post Oak Woods, Forests & Grasslands	165	52
Post Oak Woods & Forests	290	152
Silver-Bluestem-Texas Wintergrass Grasslands	63	54
Water	0	0

2.1. Land cover and land use characteristics

Leaf biomass densities and species distributions for each land cover classification assigned to the Central Texas region have previously been estimated (Wiedinmyer et al., 2000). The Oak and total leaf biomass densities for each land cover classification in the region are reported in Table 1, and the spatial distributions of each of these land covers are shown in Fig. 1. Based on these leaf biomass densities, relative isoprene emissions from each land cover category can be estimated. Because isoprene emissions are dependent upon the vegetation density and the amount of isoprene emitting species (particularly *Quercus* (oak) for this region), higher isoprene concentrations are expected in wooded areas compared to regions dominated by grasslands or croplands (Lamb et al., 1993).

2.2. Sampling

A central location was selected at each of the four study areas. A $3\,m^3$ tethered balloon was flown at elevations up to 250 m above ground level (AGL) at the central location. Air samples were collected on adsorbent tubes filled with a combination of Carbosieve SIII and Carbotrap (Supelco Inc., Bellefonte, PA) for 30 min using automated air samplers. The tethered balloon sampling technique is explained in detail in Greenberg et al. (1999). The hydrocarbons collected with the cartridges were concentrated using cryo-focusing techniques and analyzed on a gas chromatograph with flame ionization detectors (GC/FID). Temperature, pressure, humidity, wind speed and direction, and photosynthetically active radiation (PAR) were also measured at approximately 2 m AGL at this central location.

For each of the four central sampling sites, four additional ground sampling sites were chosen within a 20 km radius. The locations of all of the peripheral sampling sites are also shown Fig. 1. A 3 m tower was erected at the central and the peripheral ground locations. All sampling equipment was placed at 3 m AGL to reduce sample loss through excess tubing. Near-surface air samples were collected simultaneously on hourly intervals at the central and peripheral sampling sites.

2.3. Isoprene measurements

At each near-surface site (3 m AGL), whole air samples were collected in 6 l electropolished, stainless-steel canisters (Meriter, model X56l-4MCG). A critical orifice was attached to the inlet of each canister to ensure a constant flow rate over the 1-h sampling period. The flow rates of the inlets were calibrated every 3–4 days during the field study. Canister samples were analyzed on the day they were collected. Hydrocarbons in the air samples were quantified using a GC/FID and identifications were confirmed by GC/MS. Seventy-six hydrocarbon species were identified during the analysis of the canisters; however, only isoprene concentrations are presented in this paper. The method detection limit was determined to be 0.3 ppbv for isoprene.

2.4. Carbonyl measurements

Concentrations of formaldehyde and methacrolein were determined using samples collected on 2,4-dinitrophenylhydrazine (DNPH) impregnated cartridges. Waters SepPak C_{18} cartridges were coated with a DNPH solution one to three days prior to their use in the field, according to the method of Trapp and de Serves (1995). Samples were collected at a nominal flow rate of $1.2 l\,min^{-1}$. One field blank was taken at each tower per day for most of the days by placing an impregnated

cartridge at the top of the tower, with the cartridge wrapped in foil, during a sampling hour. Cartridges were stored in the dark at 10°C until they were to be extracted and analyzed using liquid chromatography. Standards and samples were run through a Waters Nova-Pak C_8 guard column and Waters Nova-Pak C_8 3.9×150 mm column with a 45/55 (v/v) Milli-Q water/acetonitrile eluent on a Hewlett-Packard 1100 High Pressure Liquid Chromatograph equipped with a diode array detector, using a method adapted from Grosjean and Grosjean (1995).

Field blanks were collected throughout the two-week period and were variable as others have found when using the DNPH method (Sirju and Shepson, 1995; Tanner et al., 1996). The average and standard deviation of the blank areas were calculated, where the standard deviation determined the lower limit of detection (LLD). The atmospheric concentration for each compound was calculated after subtracting the average blank value from the sample peak area. Average hourly and site concentrations were calculated using all values, where concentrations that were below the LLD were given the value of the LLD.

A total of 194 canister samples, 190 carbonyl cartridges, 29 cartridge blanks, and 34 balloon cartridges were collected during the experiment. An average of 20 canisters, 20 carbonyl cartridges, and 4 balloon cartridges were collected daily. The measurements were taken during the midday hours, primarily between 1200 and 1600 CDT, although on some days measurements were taken earlier in the day.

3. Analytical approach

3.1. Modeled and observed isoprene flux calculations for Central Texas

Isoprene flux from surface vegetation can be estimated using any of several different methods, depending on the type of data collected in the field (Fuentes et al., 1996; Guenther et al., 1996a, b; Davis et al., 1994; Bowling et al., 1999). For the data collected in this field study, a simple box model was the most appropriate tool for calculating fluxes. This model and its parameters are explained in detail by Guenther et al. (1996a). Rate constants for the reactions of isoprene with the hydroxyl radical and with ozone were taken from Chameides et al. (1992) and Atkinson (1990), respectively. Ozone concentrations were assumed to be the same as those concentrations recorded at the nearest ozone monitoring site to the site of study. For all of the sites, the hydroxyl radical concentration was assumed to be 4×10^6 molecules cm^{-3}, as is recommended by Chameides et al. (1992) and Guenther et al. (1996b). An uncertainty of 50% is assigned to the estimation of OH concentration for the box model flux

predictions (Guenther et al., 1996a). The mixing height of the boundary layer was estimated from vertical wind and temperature data collected by Sonoma Technology, Inc. in San Antonio during the time of the study. These data contain hourly virtual temperature and wind speed and direction measurements at heights up to 4400 m.

3.2. Ozone formation from hydrocarbon photooxidation

To develop effective control strategies for O_3 reduction, it is necessary to predict the effects of VOC and NO_x emission reductions given the variable VOC components of the atmosphere (Cardelino and Chameides, 1990; Milford et al., 1994; Carter, 1995; Simpson, 1995). The effect of VOC emission reductions on O_3 concentration is theoretically determined using the incremental reactivity (IR) characteristic to that VOC. Incremental reactivity is defined as the amount of O_3 formed per quantity of VOC added to the VOC mixture of a given air parcel (Carter and Atkinson, 1987; Bowman and Seinfeld, 1994; Carter, 1995; Seinfeld and Pandis, 1998), or

$$IR_i = \frac{\Delta_i O_3}{\Delta[VOC_i]}, \tag{1}$$

where $\Delta_i O_3$ is the change in maximum concentration of O_3 (ppb) that occurs from the presence of organic species i, and $\Delta[VOC_i]$ is the incremental change in concentration (ppb C) of organic species i. Although the impact and importance of biogenic VOCs on O_3 formation has been an ongoing discussion and debate (e.g., Isaksen et al., 1978; Lloyd et al., 1983; Trainer et al., 1987; Chameides et al., 1988; Logan, 1989; Bottenheim and Sirois, 1996), the implementation of an 8-h average National Ambient Air Quality Standard (NAAQS) for O_3 provides motivation for investigating biogenic VOCs' influence on O_3 concentrations in both rural and urban regions to assure compliance (Chameides et al., 1997; Holland et al., 1999).

Numerous studies have independently reported isoprene's reaction products (Miyoshi et al., 1994; Tuazon and Atkinson, 1990; Paulson and Seinfeld, 1992). Using the measured methacrolein data at each tower at each site (Allen et al., 2000) and a methacrolein formation yield of 0.22 from the photooxidation of isoprene, the concentration of *reacted* isoprene was determined, termed Δisoprene (ppb C). Using calculated reacted isoprene values and isoprene's incremental reactivity, ΔO_3 – i.e., ozone produced from isoprene photooxidation – was calculated according to Eq. (1).

3.3. ΔVOC_i calculations

While measurements of methacrolein could be used to assess the extent of isoprene reaction, similar molecular

tracers of photooxidation reactions are not available for other VOCs. Therefore, an alternative approach is required to assess the extent of photooxidation for the mix of VOCs detected during the field study. The approach assumes that relative source strengths of the reacting VOCs are constant in the immediate area surrounding the site. If this is the case, then the extent of reaction of a selected VOC can be estimated based on the extent of reaction of isoprene by multiplying the extent of isoprene reaction by the ratio of VOC to isoprene (to account for differences in emission rate) and the ratio of hydroxyl radical rate constants (to account for differences in reactivity). The value of ΔVOC_i, the concentration of reacted VOC_i, is then

$$\Delta VOC_i = \Delta \text{isoprene} \frac{k_{OH}^{VOC_i}}{k_{OH}^{\text{isoprene}}} \frac{[VOC_i]}{[\text{isoprene}]}, \qquad (2)$$

where $k_{OH}^{VOC_i}$ and k_{OH}^{isoprene} are the rate constants for reaction between the hydroxyl radical and VOC_i (Atkinson, 1990), and $[VOC_i]$ and $[\text{isoprene}]$ are the measured concentrations of VOC_i and isoprene (ppb C). If the isoprene measurement was below detection, usually with urban samples, the concentration was assigned a value of 1.7 ppb C, the lower limit of detection for isoprene. As with Δisoprene, the values of ΔVOC_i were used individually to calculate the O_3 formed by the addition of each VOC to the atmospheric mixture from Eq. (1).

While over 70 compounds were measured during the sampling period and are used to quantify total VOC concentrations, a subset of 15 compounds was used to determine the O_3 produced from photooxidation of VOCs and the O_3-forming capacity of the atmosphere, including isoprene, formaldehyde, propane, *n*-butane, *n*-hexane, toluene, *o*-xylene, *m*-xylene, *p*-xylene, *o*-ethyltoluene, *m*-ethyltoluene, *p*-ethyltoluene, *n*-propylbenzene, 1,3,5-trimethylbenzene, and 1-butene. These compounds were commonly quantified among the highest concentrations of VOCs and were selected to include a wide range of reaction rates with the hydroxyl radical and a variety of classes, including carbonyls, paraffins, olefins, and aromatics. This subset of compounds was used as a representative sample to approximate the actual atmospheric composition.

3.4. Incremental reactivity

Incremental reactivities for urban ($VOC/NO_x = 8.2$ ppb C ppb^{-1}) and rural ($VOC/NO_x = 20$ ppb C ppb^{-1}) scenarios are reported by Bowman and Seinfeld (1994) for 15 classes of compounds. Incremental reactivity is determined by adding a small amount of a compound to a base mixture of hydrocarbons and NO_x. For this work, which focuses on isoprene, a highly reactive compound, it is assumed that this incremental addition undergoes complete photooxidation in the

atmosphere. This assumption may lead to underestimations of O_3 formation (Benjamin and Winer, 1998). To estimate ozone formation due to compounds other than isoprene, the same approximation of complete reaction of incremental addition is made; while for isoprene this assumption is reasonable, it is less accurate for alkanes and aromatics. Nevertheless, these estimates of ozone production, which will be based on a weighted average of the individual VOC incremental reactivities (IR_{MIX}), provide some sense of the significance of ozone formation due to the reactions of isoprene and those due to the reactions of other compounds.

3.5. Predicted formaldehyde concentrations

The predicted concentration of formaldehyde was also calculated at each sampling event for the three rural sites as a further measure of the extent of oxidation of the atmosphere. Predicted HCHO concentrations were calculated from reacted isoprene, adjusted by a factor that accounts for the expected HCHO product. Thus,

$$[HCHO]_{\text{predicted}} = \Delta \text{isoprene} f_{HCHO}, \qquad (3)$$

where the quantity Δisoprene represents the concentration of reacted isoprene (ppbv) and f_{HCHO} is 0.63, the total fractional yield of HCHO from isoprene as reported by Carter and Atkinson (1996).

4. Results

4.1. Near-surface concentrations

Complete meteorological and concentration data taken during the study are available (Allen et al., 2000). Measured near-surface isoprene concentrations (measured 3 m AGL) ranged from 0.3 (LLD) to 10.2 ppbv in the rural atmospheres, and from 0.3 (LLD) to 6.0 ppbv in the Austin urban area. Rural ambient, near-surface formaldehyde levels ranged from 0.4 ppbv (LLD) to 20.0 ppbv, while the observed range was smaller (0.4–3.4 ppbv) in Austin. Methacrolein levels did not show as much variation between rural and urban locales, where the rural observations ranged from 0.1 ppbv (LLD) to 3.7 ppbv and urban concentrations were between 0.2 and 5.7 ppbv.

The mean concentration of isoprene for the three rural sites is consistent, at 2.4, 2.5, and 3.0 ppbv for Bastrop, Pedernales, and Elgin, respectively. The mean isoprene concentration at Austin is lower, at 1.2 ppbv. The mean values were calculated by averaging all of the tower concentrations for all hours at each site. The mean concentrations of rural formaldehyde were 2.4 ppbv in Bastrop, 1.4 ppbv in Pedernales and 1.0 ppbv in Elgin, while in Austin the mean concentration was 1.2 ppbv. The

mean methacrolein concentrations at the rural sites were 1.1, 0.4, and 0.3 ppbv for Bastrop, Pedernales, and Elgin, respectively, while in Austin, the mean methacrolein concentration was 0.8 ppbv.

Isoprene and methacrolein concentrations are expected to be proportional (Montzka et al., 1995) as methacrolein is a reaction product of isoprene. This proportionality, however, is limited because of transport and reaction of isoprene in the atmosphere. The average Austin methacrolein concentration is over double the averages measured at Pedernales Falls and Elgin, and approximately the same concentrations observed in Bastrop. The ratio of methacrolein to isoprene should be greatest in Austin, since urban areas are expected to have a lower isoprene source strength and isoprene transported from surrounding rural regions undergoes chemical reactions during transport to yield higher methacrolein concentrations. As expected, the calculated methacrolein-to-isoprene ratio at Austin is 0.7, while at Bastrop, Pedernales, and Elgin the ratio is 0.5, 0.2, and 0.1, respectively.

4.2. Diurnal variations

The temporal distribution of isoprene concentrations indicates that the isoprene concentrations observed were from biogenic sources, and not from anthropogenic sources, such as automobile exhaust. The isoprene concentrations followed characteristic patterns throughout the day, as shown in Fig. 2. This pattern is expected, as isoprene emissions are both light (PAR) and temperature dependent. The concentrations rise during the afternoon as temperature and PAR increase. The last hour shows a decrease in isoprene concentrations as a result of a decrease in PAR.

4.3. Rural versus urban concentrations

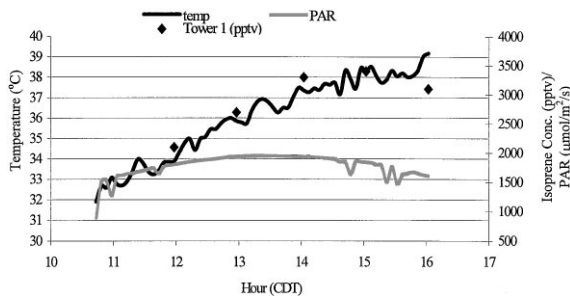The separation of cities from large rural sources of isoprene allows for mixing, dilution and reaction of

isoprene during transport, and thus there typically are lower levels of isoprene and higher concentrations of its oxidation products in urban areas (Montzka et al., 1995). Urban atmospheres contain increased levels of hydroxyl radicals, ozone, and NO_x that are available for reaction with isoprene, also leading to lower isoprene concentrations.

Fig. 3 shows the ratio (formaldehyde + methacrolein) to isoprene at each site. This ratio in Austin is greater than that at Bastrop, and it is higher by a factor of approximately two and four than at Pedernales and Elgin, respectively. This ratio and the methacrolein to isoprene ratio discussed earlier suggest that Bastrop is influenced by transport from urban areas, as predicted by its geographical location between the urban areas of Houston (to the Southeast), and San Antonio (to the Southwest). Although Elgin is similarly located between these urban areas, the wind patterns on the sampling days in Elgin were from the Northeast where only rural sources exist. Sampling in Bastrop occurred on days in which winds were from the Southeast (downwind of Houston) and Southwest (downwind of San Antonio).

4.4. Spatial variations between towers

Isoprene concentrations varied significantly from one tower to another. For example, the average isoprene concentrations measured for each tower at Bastrop (12 August) ranged from 0.8 to 4.7 ppbv. This variation is primarily due to the placement of the monitor with respect to the immediate surrounding vegetation. Monitors located in close proximity to isoprene emitting trees (within 1–2 m) measure greater isoprene concentrations than monitors located in an area with many isoprene-emitting trees, but placed a long distance from them (over 20 m from any trees).

The relationship of the monitor location to surrounding vegetation is not well understood, and more detailed site data are needed to characterize the monitor sites. A common trend was seen where central site locations (where large clearings were needed for balloon launches) reported lower isoprene concentrations as show in Fig. 4.

Fig. 2. Isoprene, temperature, and PAR measurements for measurements made at one tower location (3 m AGL) at the Bastrop site on 11 August 1998.
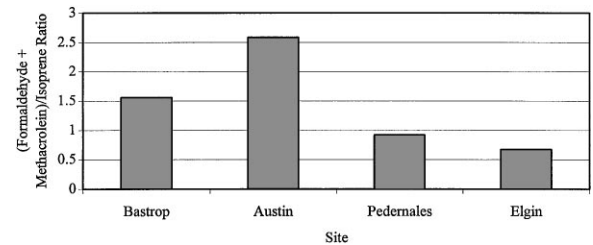

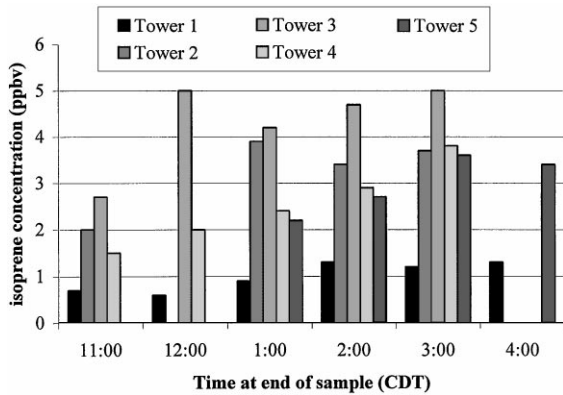Fig. 3. Ratio (formaldehyde + methacrolein) to isoprene at each site.

Fig. 4. Isoprene concentrations (ppbv) measured at the five 3 m towers at Pedernales Falls State Park on 19 August. All towers were located within vegetation classified as Live Oak and Ashe Juniper Parks bordered by areas of Live Oak, Mesquite and Ashe Juniper Parks.

This trend has significance in evaluating isoprene concentrations at regulatory monitoring sites. These regulatory sites are usually placed in areas removed from forested areas and therefore may record isoprene concentrations that are biased low. These low measurements may play a role in the discrepancies between biogenic emissions models and recorded isoprene concentrations.

The variation in ground-level isoprene concentrations, regardless of the general vegetation class in which the monitor is placed, is more dependent on the vegetation in the immediate vicinity of the monitor than on the general land cover. Thus, a general description of an area's vegetation with a spatial resolution on the order of 1 km, as in Central Texas, is too coarse to provide accurate emission model-based prediction of a single-monitor

reading. In measurements from the Pedernales sampling location (with the most uniform land use distribution), the isoprene concentrations are also variable as seen from Fig. 4. Although all towers were located within the same land cover classification and within approximately 5 km of one another, the isoprene concentrations varied between towers. The coefficient of variation of hourly measurements is 40–90% of the average isoprene concentration for that hour. The vegetation surrounding these towers and the relative location of the monitors to this vegetation greatly affect the isoprene concentrations measured.

4.5. Aloft measurements

Fig. 5 shows a representative report of the isoprene concentrations observed from the balloon sampling aloft at the Perdernales site. Isoprene concentrations seen at 250 m ranged from 0.1 to 3.7 ppbv at the rural sites, and from 0.1 to 0.2 ppbv in north Austin. (Note that the LLD for the balloon samples was lower than for the canister samples.) The measurements taken in the mixed layer are generally much lower than those measured at 3 m, as expected, since isoprene reacts and diffuses throughout vertical transport in the atmosphere. Mixed-layer concentrations of isoprene were higher than ground-level measurements for only two sampling hours of the two-week period. Only one ground-level measurement was taken during these 2 h and was most likely not as representative of the region as when five concurrent measurements were taken.

Isoprene flux values (mg $C m^{-2} h^{-1}$) calculated with the mixed-layer isoprene measurements by the box model are reported in Table 2, and will be referred to as the observed flux values. The observed isoprene flux values ranged from 0.01 to 10.58 mg $C m^{-2} h^{-1}$ with an average isoprene flux over all samples as 1.15 ± 1.85 mg

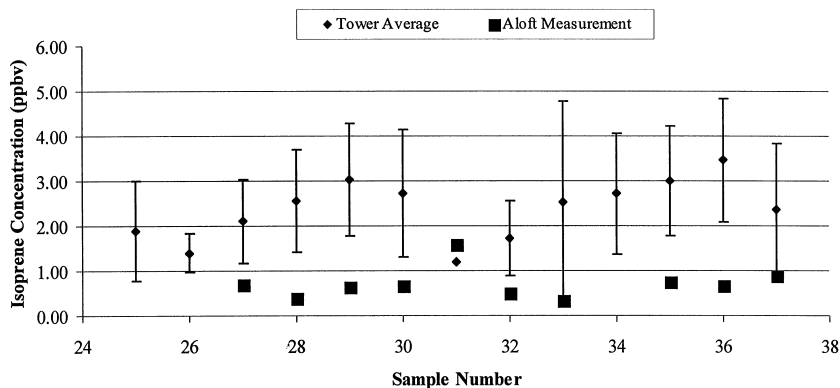Fig. 5. Average isoprene concentrations measured at 3 m AGL and aloft (∼ 250 m AGL) on 17–19 August at Pedernales Falls State Park. The error bars are the standard deviation between the 5 different tower site measurements. Sample number 31 only had one near surface (3 m AGL) measurement.

Table 2
Estimated isoprene flux calculations using (1) A simple BEIS2 model, and (2) the box model estimate

Sample no.	Date	Hour	Altitude (m)	Isoprene flux estimated using BEIS2 model $(mg\,C\,m^{-2}\,h^{-1})$	Isoprene flux estimated using box model $(mg\,C\,m^{-2}\,h^{-1})$	Difference (BEIS2-Box model Flux)
Stengle: Predominant vegetation class = Pine & Hardwood Forests						
8	8/11/98	12:15	250	1.34	10.58	− 9.24
1	8/11/98	13:15	250	1.27	2.50	− 1.22
2	8/11/98	14:15	250	1.61	3.21	− 1.60
3	8/11/98	15:15	250	1.13	2.15	− 1.02
4	8/12/98	12:30	250	1.23	0.09	1.14
5	8/12/98	13:30	250	1.23	2.17	− 0.94
6	8/12/98	14:30	250	1.21	1.76	− 0.55
7	8/12/98	15:30	250	0.93	2.19	− 1.26
Austin: Predominant vegetation class = Austin Urban Average						
9	8/15/98	12:30	150	0.80	0.48	0.32
10	8/15/98	13:30	200	0.78	0.31	0.48
12	8/15/98	14:30	200	0.86	0.11	0.75
13	8/15/98	15:30	200	0.71	0.20	0.51
14	8/16/98	12:30	200	0.86	0.13	0.73
15	8/16/98	13:30	200	1.10	0.20	0.91
Elgin: Predominant vegetation class = Post Oak Woods, Forests & Grasslands						
17	8/20/98	12:30	250	0.94	1.16	− 0.22
18	8/20/98	13:30	250	1.12	2.76	− 1.64
19	8/20/98	14:30	250	1.11	1.42	− 0.31
20	8/20/98	15:30	250	1.04	2.16	− 1.13
21	8/21/98	9:45	250	0.89	0.05	0.85
22	8/21/98	10:30	250	0.61	0.01	0.60
23	8/21/98	11:30	250	0.74	0.01	0.73
Pedernales Falls State Park: Predominant vegetation class = Live Oak & Ashe Juniper Parks						
24	8/17/98	11:40	200	0.11	0.91	− 0.80
25	8/18/98	10:30	200	0.10	1.11	− 1.01
26	8/18/98	11:30	250	0.12	0.78	− 0.66
27	8/18/98	12:30	200	0.13	0.91	− 0.78
28	8/18/98	13:30	200	0.13	1.83	− 1.71
29	8/18/98	14:30	200	0.13	1.18	− 1.05
30	8/18/98	15:30	50	0.11	2.03	− 1.92
31	8/19/98	11:30	250	0.13	1.51	− 1.38
32	8/19/98	13:30	250	0.12	1.83	− 1.70
33	8/19/98	14:30	250	0.12	1.55	− 1.42
34	8/19/98	15:30	250	0.15	1.52	− 1.37

$C\,m^{-2}\,h^{-1}$. The uncertainty bounds correspond to the standard deviation of the observed fluxes dependant on uncertainties in input parameters.

The observed isoprene flux values calculated with the box model were used to assess the accuracy of BEIS isoprene emission estimates for the study areas. Isoprene flux values were predicted for the sampling hours and meteorological conditions using the GLOBEIS model (Guenther et al., 2000) with emission factors and algorithms that were identical to the BEIS2 model (Pierce et al., 1998). This version of the GLOBEIS model is dependent only on the area fraction of oak trees and does not take into account the entire forest species distribution and density. Since oak trees are the primary tree genera that emit isoprene in the study region, the assumption that oak trees are the only producers of isoprene in the study region is reasonable. A BEIS2 isoprene flux estimate was calculated for each sampling period, using the area fraction of oak for the vegetation classification in which the balloon sample was taken and the meteorological data collected during the sampling period, reported in Allen et al. (2000).

The BEIS2 model predicted lower flux values than the observed results for 22 of 32 samples. For all of the measurements made at the Pedernales site and all but one sample hour at Stengle, the BEIS2 model predicted lower values for isoprene flux than the box model. The BEIS2 flux estimates were greater than the observed values for all sampling hours at the Austin (urban) site. The results for the Elgin site were mixed, but during the early morning hours, the BEIS2 model predicted fluxes greater than the observed values.

The disparity between the flux estimates using the BEIS2 model and the box model may be the result of the many sources of uncertainty in both models. A critical element in the uncertainty of the BEIS2 flux estimates is the uncertainty of the land use data.

For all of the rural sites, the balloon was located within homogeneous vegetation. But the measurements could have been influenced by isoprene emissions from other, nearby vegetation classifications. To account for the various vegetation types that may have affected the balloon measurements, BEIS2 flux estimates were re-calculated using the oak area fractions of each near-by classification. For example, the BEIS2 flux estimates were calculated for the Pedernales site with the oak area fraction of the Live Oak and Ashe Juniper classification (in which the balloon measurements were taken). Additionally, the flux values for the Pedernales site were also estimated with the oak area fraction of the Live Oak, Mesquite and Juniper Parks classification.

Average isoprene flux values from all of the BEIS2 flux estimates, based on the various land cover data, were calculated. The standard deviation of these average flux values was also calculated, as shown in Fig. 6. This standard deviation is a function of the variability in percent oak in the influencing land use classes.

At the Stengle site, the box model flux estimates and the BEIS2 flux estimates follow similar trends. The box model flux results fall within one standard deviation of the BEIS2 average estimate for 6 of the 8 samples. There is relatively good agreement between these two estimates, except for the last sample shown (Sample #8).

At the Elgin site, the flux estimates calculated with the minimum mixing height are within one standard deviation of the BEIS2 flux estimate for 4 of the 7 samples. For the last three samples, the observed isoprene flux values approach zero, whereas the BEIS2 model estimates range between 1 and 2 mg C m^{-2} h^{-1}. These three samples were taken in the morning hours, when mixing heights were lower than in the afternoon.

At the Pedernales site, the observed isoprene flux values are larger than the BEIS2 model predictions. The BEIS2 model may have been underpredicting the isoprene emissions in that area because of an underestimation of oak trees.

The uncertainties in both models are large enough to account for the discrepancy between the BEIS2 and the box model predictions; 66% of the observed flux values for the Stengle and Elgin sites were within one standard deviation of the predicted values.

4.6. VOC/NO$_x$ measurements

Total VOC concentrations (ppb C) were analyzed from the stainless-steel canisters, where over 70 organic compounds were identified. At the rural sites, total VOCs ranged from 72 to 372 ppb C at Bastrop; 43 to 246 ppb C at Pedernales; and 50 to 217 ppb C at Elgin. A similar but slightly smaller range was found at Austin (39–182 ppb C). The mean concentrations of VOCs were similar for all four sites: 132, 120, 90, and 116 ppb C at Bastrop, Austin, Pedernales, and Elgin, respectively.

Information regarding rural NO$_x$ data included two sites used to quantify regional transport of air pollutants in Central Texas. These include monitoring locations in San Marcos and Fayetteville, TX (Allen et al., 1999) which reported mean NO$_x$ values during the experiment of 4.7 and 10.5 ppbv, respectively. Using meteorological data collected during the experiment, it was determined that San Marcos was approximately upwind of Pedernales, while air parcels arriving at Bastrop originated from both the San Marcos area and the Fayetteville area. No monitoring locations were in the upwind direction from the Elgin sampling location. Using San Marcos NO$_x$ levels to estimate Pedernales and an average of Fayetteville and San Marcos to approximate NO$_x$ levels at Bastrop, the rural VOC/NO$_x$ ratios are calculated as 19.1 and 19.2, respectively. Therefore, the VOC to NO$_x$ ratio for rural areas was taken to be 20.

NO$_x$ data in Austin were not available on the sampling days. Summary data on the VOC/NO$_x$ ratio for various eastern United States cities were collected by Wolff and Korsog (1992), and it is assumed that the ratio in Austin is similar only for purposes of predicting the potential for ozone formation.

4.7. Ozone concentrations attributable to photooxidation of measured VOCs

Reacted isoprene values (Δisoprene) were used to calculate ΔO_3 according to Eq. (1), and subsequently ΔVOC concentrations were calculated for all 15 compounds considered, according to Eq. (2). The sum of these individual compounds' ΔVOC, or $\sum_{i=1}^{15} \Delta VOC_i$, was then used with the weighted average value for the incremental reactivity (IR$_{MIX}$) to determine the ozone concentrations attributable to VOC photooxidation for the mixture of compounds. This calculation was made for each tower and each hour of sampling using both the MIX IR for urban (VOC/NO$_x$ = 8.2) and rural (VOC/NO$_x$ = 20) scenarios, and defined by Bowman and Seinfeld (1994). The average ozone concentrations produced from VOC reaction at the four sampling sites is shown in Fig. 7. The
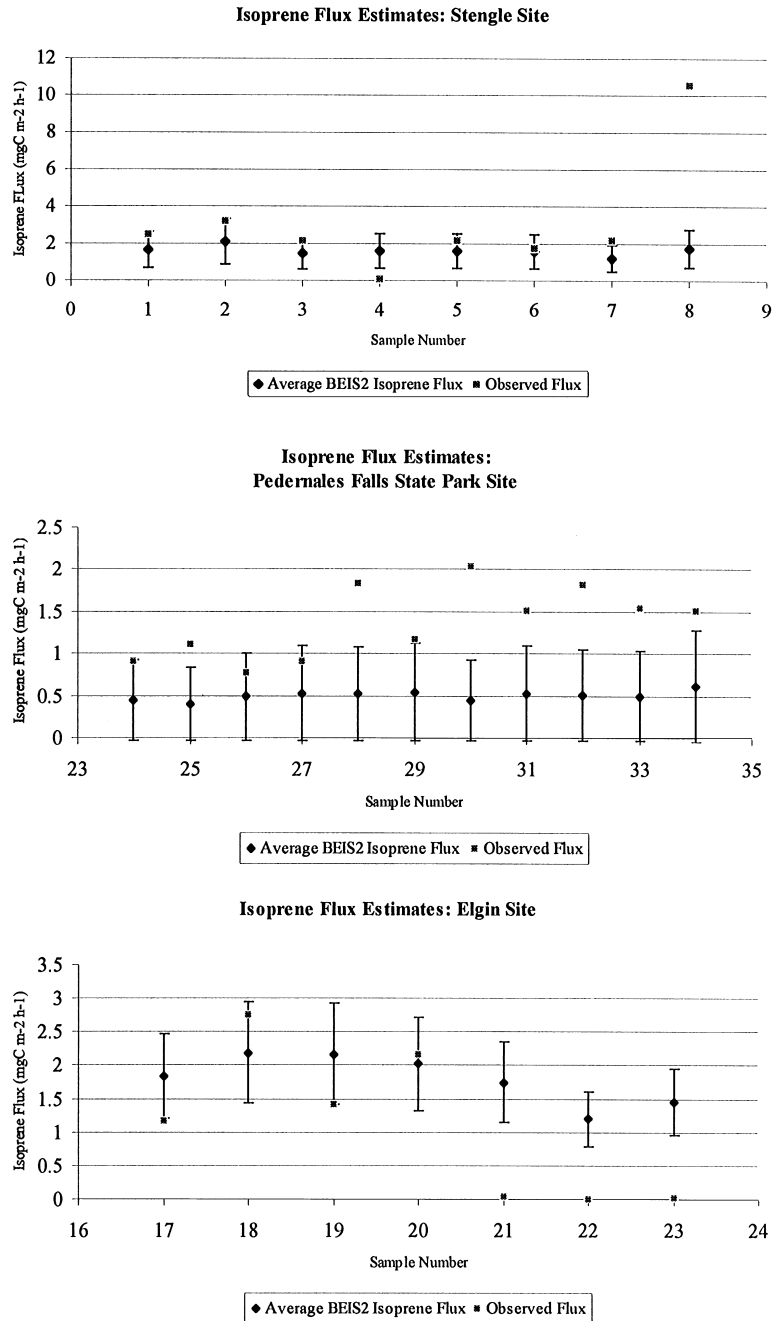
Fig. 6. BEIS2 model estimates using an average oak density for the Stengle Site, the Elgin Site and the Pedernales Falls State Park. The error bars represent the standard deviation of the BEIS2 flux estimate, based on average oak density. The flux estimates of the box model calculations at each sample hour are also shown.

averages for each site were determined using only values above detection limits; error bars indicate one standard deviation from the mean. The first bar for each site in Fig. 7 is divided into ozone that is attributable to isoprene photooxidation, and ozone attributable to photooxidation of the remaining hydrocarbons. The figure illustrates that between 50 and 100% of ozone attributed to VOC mixture photooxidation is in fact due to isoprene oxidation. This high fraction is due to the high incremental reactivity of isoprene.
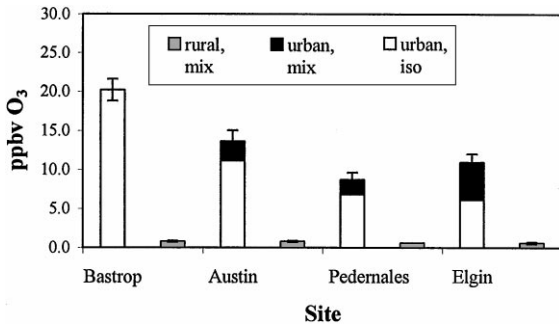
Fig. 7. Average ozone concentrations (ppbv) attributable to photooxidation of VOCs at the sampling sites using the incremental reactivity of a mixture of components in the atmosphere. All averages comprise those values calculated when methacrolein levels were above the lower limit of detection. Error bars represent one standard deviation. For each site, two values are calculated: ozone formed in the presence of urban NO_x conditions (divided into *urban,mix* and *urban,iso*) and rural NO_x conditions (*rural,mix*).
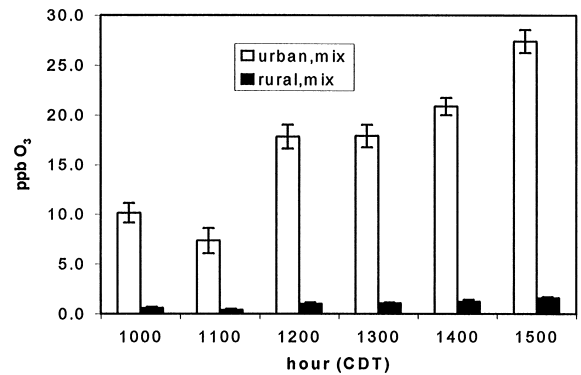

Fig. 8. Hourly average ozone concentrations (ppbv) attributable to photooxidation of VOCs at the three rural sampling sites (Bastrop, Pedernales, and Elgin). All averages comprise those values calculated when methacrolein levels were above the lower limit of detection. Error bars represent one standard deviation.

As seen in Fig. 7, ozone levels attributed to VOC reaction at the sites under typical rural VOC/NO_x conditions (rural, mix) are much lower than if formed under a higher NO_x setting. While the ozone production using a rural IR_{MIX} is 0.6 ppbv at Pedernales and Elgin and 0.8 ppbv at Bastrop and Austin, the range and values of ozone concentrations using urban incremental reactivity data are much greater, from 8.7 ppbv at Pedernales to 20.0 ppbv at Bastrop.

The ozone attributable to VOC photooxidation also follows a strong diurnal pattern with higher levels in the afternoon hours as shown in Fig. 8. This is as expected as elevated isoprene emissions, higher temperatures and increased solar radiation all lead to elevated afternoon ozone levels.

4.8. Ozone formation potential from isoprene measurements

Another method for assessing the ozone formation potential of biogenic hydrocarbons is to multiply incremental ozone formation potential for isoprene by the isoprene concentration. This calculation assesses the additional ozone that might be formed, under high and low NO_x conditions, if all of the measured isoprene reacted. Ozone predictions based solely on isoprene considerations were made for incremental reactivities of urban (VOC/$NO_x = 8.2$) and rural (VOC/$NO_x = 20$) conditions, termed *urban,iso* and *rural,iso*, respectively (Fig. 9). The O_3-formation potential – comparing *urban,iso* O_3 concentrations – is highest at the three rural sites and lowest in Austin. The O_3 formation calculations are a direct product of the measured isoprene concentrations and the incremental ozone formation potential for
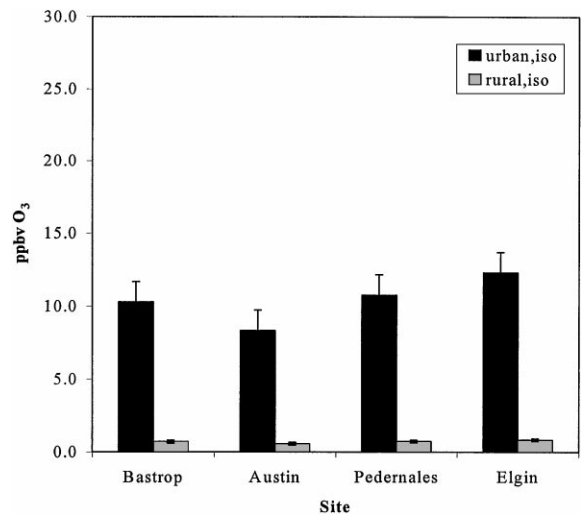

Fig. 9. Average potential ozone formation (ppbv) at the TEXIE sampling sites where calculations were made from the incremental reactivity of isoprene and measured isoprene concentrations only. Error bars represent one standard deviation.

isoprene. Therefore, the O_3 formation potential is expected to be highest nearer the source strength of isoprene emissions and concentrations, namely in rural locations. This potential does not necessarily imply that these rural areas have a higher capacity for O_3 formation than Austin; rather, the predicted concentrations are an indication of isoprene-induced O_3 formation when NO_x is transported to these rural areas. When VOC/NO_x is 20, the potential for O_3 formation is small (at around 1 ppbv), but is a persistent concentration, irrespective of NO_x levels.

Predicted O_3 formation potentials concentrations indicate that in rural regions that are influenced by NO_x

sources, the potential exists for relatively high ozone concentrations of 10–20 ppbv.

4.9. Predicted formaldehyde concentrations

Formaldehyde (HCHO) in rural areas is dominated by secondary formation from isoprene photooxidation, as well as a relative lack of anthropogenic emissions. Urban centers such as Austin, however, are expected to contain HCHO from both primary and secondary sources. Predicted HCHO concentrations from the photooxidation of isoprene were calculated using Eq. (3) to compare with ambient measured HCHO concentrations.

Calculations to predict HCHO were made to compare urban and rural differences during this study using Bastrop as a representative rural area and Austin (urban site). The mean predicted HCHO concentration in Bastrop is 3.1 ppbv, while the mean measured concentration is 2.4 ppbv. This difference implies that there are no (or few) primary sources of HCHO in Bastrop; there are no other hydrocarbon sources of HCHO; and HCHO formed from photooxidation of isoprene reacts more rapidly than methacrolein (as the measured HCHO is less than predicted).

In Austin, it is expected that primary sources exist in addition to the secondary formation of HCHO, and thus the observed levels of HCHO should be higher than predicted based on biogenic formation. The mean measured concentration of HCHO in Austin is 1.3 ppbv, while the mean predicted HCHO concentration from isoprene oxidation, however, is 2.1 ppbv. Although this result is contrary to expectation, it should be noted that sampling in Austin occurred during a weekend, where significant reductions in vehicular emissions and hence anthropogenic sources of HCHO are expected. Furthermore, observed concentrations are in fact higher than predicted levels at four of the five towers. Anomalous methacrolein concentrations were recorded at one location (an average of 2.7 ppbv), thus skewing the predicted HCHO concentrations in Austin.

5. Conclusions

Isoprene and isoprene reaction product measurements were made at several locations throughout Central Texas in August 1998, and provide data that can be used in evaluating biogenic emissions models and urban airshed model predictions. Isoprene, formaldehyde and methacrolein concentrations are reported. The spatial variation of isoprene and its reaction products' concentrations in the surface layer are strong functions of the immediate ($\sim$20 m) landcover surrounding the sampling sites. Mixed-layer concentrations of isoprene were lower than the surface layer concentrations as expected, and flux estimates based on mixed-layer concentrations were in reasonable agreement with flux estimates based on current emission models and local land cover data described by Wiedinmyer et al. (2000). Both ozone attributable to biogenic hydrocarbon oxidation and ozone formation potential are predicted to be insignificant under high VOC/NO$_x$ ratios typical of rural areas, but may be important under conditions where NO$_x$ levels are elevated.

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