**PROPOSAL TRACKING NUMBER:**

**TEXAS AIR RESEARCH CENTER FULL PROPOSAL COVER SHEET**

**PROPOSAL TITLE:** Urban flux measurements of Volatile Organic Compounds (VOCs) and other trace gases from a tall lattice tower near central Houston, TX

(Please copy this form and provide the following information for any additional researchers)

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PROJECT ABSTRACT

Urban meteorology and air quality are increasingly important issues as the population and size of urban areas continue to grow worldwide. Urban emissions can strongly affect atmospheric chemistry and are a significant component of global emission inventories used to understand chemistry at all spatial scales. We propose to install a sonic anemometer and gas inlets on a tall broadcast tower north of downtown Houston (approximate measurement height: 80 m) to carry out micro-meteorological flux measurements of energy (sensible and latent heat flux), carbon dioxide (CO₂), ozone (O₃), and selected volatile organic compounds (e.g. highly reactive (HR) alkenes and BTX compounds). Chemical analyzers will be installed at the bottom of the tower, and are proposed to operate for at least one year, starting in mid summer or fall 2007. Standard air quality analyzers will be used to monitor CO, NOₓ, and ozone from the same measurement height as the fluxes. In-situ, automated gas chromatography will monitor selected VOCs and their fluxes using a relaxed eddy accumulation technique. Additional grab sampling will be employed alongside a fast alkene analyzer to measure, and speciate, HRVOC fluxes. Aldehydes as major oxidation products of HRVOCs will also be measured. A new Lagrangian footprint model, using urban roughness parameters for all relevant wind directions, will be used to assign emission characteristics to the underlying surfaces inside the footprint. Measured emissions for these city “sectors” will ultimately be compared to a GIS model that can be developed from data which need to be gathered on traffic emissions, city (energy use) statistics, building structure heat flux and storage characteristics, and leaf area index of the city vegetation.
**Proposed Budget**

Requested from TARC

A. Salaries

I. Principal Investigator
   (one summer month) $6,592

II. Graduate Assistant
   (18 months at 50% FTE) $31,518
   Subtotal Salary $38,110

IV. Fringe Benefits on 1 through 3
   (34.2% of Salary) $13,032
   Total Salary $51,142

B. Travel
   (1 National Meeting, 1 TARC Meeting) $2,000

C. Equipment $0,000

D. Supplies (see text) $3,000

E. Other Expenses (Tuition, space rent) $11,936
   Total Costs $68,078

Total Project Cost is ~$92,054

Funding Requested from TARC is $68,078
Urban flux measurements of Volatile Organic Compounds (VOCs) and other trace gases from a tall lattice tower near central Houston, TX

A proposal to the Texas Air Research Center (TARC), Lamar University

June 2006

1 Problem Statement

1.1 Urban air quality concerns

Studies examining the influence of anthropogenic activities on urban air quality continue to be of a high priority in both the environmental and health sciences. In particular, anthropogenic emissions from transportation are dominant contributors to the environmental pollutants carbon monoxide (CO), nitrogen oxides \( \text{NO}_x = \text{NO} + \text{NO}_2 \), suspended particulate matter, and the secondary pollutant ozone \( \text{O}_3 \), all of which can create serious health affects when threshold concentrations are exceeded. Although very significant urban air quality improvements have been achieved through the introduction of catalytic converters in cars, some of that progress, in particular with regards to \( \text{NO}_x \), has been counteracted by continuing increases in car traffic. Houston air in particular is regularly violating the federal air quality 1-hour ozone standard of 120 ppb and the new 8-hour standard of 80 ppb ozone \([1, 2]\).

Although a seasonally varying ozone background mixing ratio of up to 55 ppb \([1]\) contributes significantly to Houston’s ‘bad air’, much of its high ozone values are ‘homemade’ \([3]\). High urban emissions of volatile organic compounds (VOCs) and \( \text{NO}_x \) from the transportation sector, and significant VOC emissions from the local petrochemical industry in Houston’s ship channel combined with high photochemical activity especially during the summer months, results in efficient secondary ozone formation in the urban boundary layer (UBL) during daytime \([4]\). In general, ozone formation in urban environments, meaning close to the sources of anthropogenic VOC and \( \text{NO}_x \) emissions, is found to be ‘VOC-limited’, meaning that efficient ozone formation is suppressed by a rather low VOC to \( \text{NO}_x \) ratio and reducing
VOC (or NOx) emissions from car traffic or industry does not normally lead to efficient ozone mixing ratio reductions in the urban core [5]. As an air mass is transported away from the urban core, decreasing NOx emissions from less dense traffic and increasing VOC emissions from natural vegetation in suburban areas often reverse the situation of ozone formation from VOC- to ‘NOx-limited’, e.g. [6, 7] and references therein. In these areas, increased NOx emissions do lead to significant ozone enhancements, as can higher urban core NOx emissions if they are rapidly transported to rural environments. High biogenic VOC emissions lead to NOx-limited ozone formation in many suburban areas downwind of large urban centers [5]. Real-world ozone levels depend strongly on the urban VOC and NOx emissions mix, its day-to-day transport characteristics away from the urban core area, and the regional density of anthropogenic NOx and biogenic VOC emissions during transport. Only the simultaneous reduction of both precursor emissions ensures lower ozone formation rates in urban and rural areas downwind.

Ozone pollution in and downwind of Houston is more complicated, however, than the above summary suggests. Large emissions of highly reactive (HR) VOCs from the petrochemical industry concentrated along Houston’s ‘ship channel’ modify the urban VOC/NOx mix to create ratios that can lie between the extremes of VOC- and NOx-limited ozone formation, which can lead to highly efficient ozone formation in the UBL [3, 8]. During the first Texas Air Quality Study in 2000 (TexAQS 2000) a major effort was undertaken to investigate the Houston metropolitan area air pollution composition and variability, mostly during one month of intensive measurements, from both ground-based [9-19] and airborne platforms [8, 20-22]. Findings included

- High VOC and NOx mixing ratios that can be attributed to a mix of car traffic, petrochemical industry, and some biogenic emissions
- Transient, high HRVOC mixing ratios (in particular ethene and propene) likely related to petrochemical industry emissions, and irreconcilable differences between measured
ambient mixing ratios and expected abundances using existing emission inventories for many VOCs that can affect ozone formation, similar to an earlier result [23]

- Extreme local and regional ozone formation in air masses affected by emissions from the petrochemical industry in the ship-channel area, and parallel formation of very high oxidation product mixing ratios, especially formaldehyde and acetaldehyde from ethene and propene photochemical processing

While these findings can explain much of the observed variability and distribution of Houston’s urban smog, important questions remain with regards to the quantitative effects of anthropogenic traffic versus petrochemical emissions. Existing emissions data bases are difficult to verify from abundance measurements alone (or are suspect), and in-situ flux measurements, which could rectify this problem, are generally unavailable.

To support the decision making with regards to the doubtlessly required emissions reductions to bring Houston into compliance with the NAQS for ozone, our understanding of the real-world sources and dynamics of anthropogenic pollutants in urban areas, such as from car traffic, must be improved. For this, we propose to carry out direct flux measurements of emissions in-situ from an urban tower platform near Houston’s urban core.

1.2 Urban micrometeorology and flux measurements

As urban populations continue to expand, the need for urban meteorological and air quality observations also increases. The exchanges of heat, trace gases, and particles are substantially modified in the urban as compared to the rural environment. Scientists are called upon to supply such data and forecasts to citizens to aid in building and urban design, energy conservation, development and construction of transportation and communication infrastructure, and for monitoring air quality. Although meteorologists and the citizens they serve have a clear need for urban (micro-) meteorological flux measurements, relatively few such measurements have been carried out so far.
Reviews of micrometeorological measurements made in the UBL to date and a thorough description of the challenges associated with such measurements are given by Roth [24], Grimmond [25], and Oke [26]. Most urban micrometeorological measurements to date have focused on the phenomenon of the “urban heat island” and report measurement of quantities such as sensible and latent heat flux, and heat storage [27-32]. The latter is commonly high in cities and can dominate the heat budget as can be seen during the dry season in Mexico City [32]. Studies of mass fluxes (trace gases or particles) have so far been limited to a few cities and studies. Nemitz et al. [33] and Dorsey et al. [34] measured particle and CO₂ fluxes above the city of Edinburgh, UK, while Mårtensson et al. [35] measured aerosol but not CO₂ fluxes in Stockholm. Grimmond et al. [28] reviewed urban CO₂ measurements and reported their own measurements of CO₂ mixing ratios and fluxes in Chicago, USA, while Soegaard et al. [36] report measurements of CO₂ fluxes over the city of Copenhagen. Both CO₂ and volatile organic compound (VOC) flux measurements were carried out in Mexico City in 2003 by Velasco et al. [37, 38] and are also currently carried out and analyzed by Nemitz and co-workers (NCAR, Boulder, Colorado, USA; CEH, Edinburgh, UK)(David Fowler, pers. Comm. 2006). Extensive measurements during the Basel Urban Boundary Layer Experiment (BUBBLE) [39-41] have provided further detailed information on the structure of the UBL.

Urban micrometeorological measurements are complicated by the heterogeneity and roughness of the urban terrain. This has lead to the qualitative subdivision of the UBL into a number of sub-layers [26]. For example, in the roughness sub-layer (RSL), or the layer extending from within the urban “canopy” (i.e. the roughness elements such as buildings and foliage) to several times its height, the principle of flux constancy is not obeyed. Monin-Obukhov similarity theory, which applies to the boundary layer above more homogeneous surfaces and which provides a theoretical basis on which atmospheric parameters such as fluxes can be calculated, is not valid in the RSL. Data reviewed by Roth [24] and from the BUBBLE suggest that the RSL top (zs) may extend up to at least 1.5, more likely to 2-4
times the average roughness element (building) height ($z_{th}$) in a heterogeneous urban environment. Beyond this height, individual micrometeorological structures (“eddies”) caused by the surface elements are “blended” into a horizontally homogeneous flux field representative of the underlying surface. This is the beginning of what is called the constant flux layer (CFL). While fluxes measured from within the RSL are suspect, flux measurements in the CFL can be reliably carried out [42], i.e. the turbulent boundary layer properties appear to follow Monin-Obukhov similarity theory.

Deployment of instrumentation in the CFL is challenging. As roughness elements making up urban terrain such as buildings or trees can be tall, even taller towers are often needed to position instrumentation (or their inlets) in the CFL for measurements. Although existing buildings can be used, sensors must be mounted such that the building itself does not influence the local micrometeorology where measurements are made. In addition to difficulties in establishing a monitoring site, thorough characterization of urban morphology in a large radius around the measurement location is also necessary to ascertain the approximate height of various sub-layers, and to allow useful inter-comparison between urban studies in different locations incorporating different morphology. Furthermore, estimates of the roughness length ($z_0$, the height at which the logarithmic wind speed profile found within the CFL reaches 0) and the zero displacement height ($z_d$, the difference between $z=0$ m and $z_0$) are needed to calculate flux footprints, which are valuable for localizing specific sources or sinks within the urban area. With these complications in mind, we next review specific site characteristics that should be fulfilled in planning a city flux project.

1.2.1 Optimum site characteristics

Following Roth [24] and Oke [26], a (micro-) meteorological station in the urban boundary layer ought to fulfil the following requirements:

(I) *Fetch*: area surrounding the station should be flat, with a homogeneous surface morphology that extends up to 100 times the measurement height.
(II) Site surroundings: Distance between station and nearest buildings/roughness elements
must be large enough that no local effects from the structures are observed; support
structure for the station must minimally influence measurements (e.g., a lattice tower on
top of a building of representative height or an unobstructed, independent surface
setting); sensors need to measure integrated urban influence from within the CFL
(III) \(z_0\) and \(z_d\): credible measurements or estimates of both parameters are needed to
calculate the footprint and representativeness of a potential site
(IV) Instrumentation: Eddy Covariance or equivalent; minimum integration time 15 min,
longer for larger heights
(V) Documentation: Explicit and comprehensive description of all details of the site

There are a number of practical limitations to this list. First of all, the surface morphology in
most cities is often not uniform enough for extended fetches of several kilometres (I), a basic
limitation that cannot be overridden. Second, erecting a tall tower within a city has limitations
based on necessary stability, security, and permits, both in the case of ground or rooftop
installation. While rooftops may be safer, it is difficult to place a station such that it is not
influenced by the local micrometeorology of the building itself (II). However, independent
structures, such as tall broadcasting towers common in Texas, minimally influence local
airflow and can be made accessible for scientists for measurements. Though the ideal urban
flux measurement site does probably not exist, the two selected lattice towers north of
downtown Houston come close with respect to the goals of this project.

1.2.2 Pilot Corporation communications tower next to Interstate Highway 45

The Pilot Corporation, operating travel/truck care centers all over the US, owns a 158.5 m
tall triangular lattice tower on 4104 Fulton Street approximately 4 km north-northwest from
downtown Houston and just 100 m west of IH-45 at the Patton Street exit. The tower is
operated by Global Signal, a Florida based tower infrastructure provider, and has an air-
conditioned mobile container at its base. Plate 1 shows the immediate surroundings of the tower from a satellite picture on the backdrop of the Houston city map while Plate 2 shows a photograph of the tower itself.

**Plate 1:** Aerial view of the Fulton Street tower location. White bar shows 1 km length scale.

**Plate 2:** Bottom-up view of the Pilot Corp. lattice tower

There are no other tall structures surrounding the tower that could influence airflow within a 1 km radius. A sonic anemometer and gas inlets could be installed between 60 and 130 m height of the tower not currently occupied by antennas or any other equipment. Higher placement will increase the footprint area contributing to the flux measurement.
Too low placement risks installation in the RSL. Assuming that the roughness element heights in the surrounding parts of Houston are, on average, between 10 and 20 m, the micrometeorological sampling height would be at least $3z_{d}$ and would therefore likely reside above the RSL. - The tower’s own influence on the boundary layer turbulence, its “wake”, has to be avoided. Kaimal and Finnigan [42] and Roth [24] suggest that measurements be made at a distance at least 1.5 times the structure’s horizontal extent. At 0.1 m vertical beam width and <1 m horizontal extend, a horizontal beam extending at most ~2 m off the edge of the tower would be more than sufficient.

Note from plate 1 that the footprint areas of this tower encompass anthropogenic sources from a major highway (all western directions), typical residential areas (most western, northern, and eastern directions), and biogenically influenced areas, in particular Moody Park in the south-east. This site therefore allows observations of several typical urban surface source areas under different wind directions, with a strong influence of car traffic.

1.4.2 Greater Houston Transportation Co. communications tower

The Greater Houston Transportation Company owns and operates a triangular, 91 m tall lattice tower on its parking lot at 1406 Hays Street, approximately 4 km north of downtown Houston. Plate 3 shows an aerial view of this area on the Houston city map backdrop. The tower itself looks like that shown in Plate 2. Similar to the first tower, this structure has no other heights occupied by antennas or other equipment except its top, there are no other tall structures influencing airflow to the tower within a 1 km radius, and there is a dedicated, air-conditioned room at the end of a building at its base. A sonic anemometer and gas inlets could be installed at a height of up to 80 m in a similar fashion as described above.

The footprint areas of this tower are slightly different compared to the Fulton Street tower, which is just 1.7 km northwest of Hays Street. There is no major direct traffic influence in the form of a highway within 500 m of the tower. However, the site is surrounded by warehouses (light industry) and bordered by a larger industrial area in
all eastern directions (Plate 3). Moody Park is due west, and typical residential areas are
found in the south, south-west, and north. Hence, this site has similarly diverse surface source
areas contributing to the expected fluxes under different wind directions. Its major difference
to the Fulton Street tower is the “replacement” of the highway with a light industrial area.

1.3 Goals for establishing a new research site in Houston

Both companies have indicated their interest in providing us access to their towers for the
air quality measurements described below. Our mid-term intention is to establish at least one
of these structures as a long-term measurement platform for urban flux measurements and a
part of the growing urban fluxnet of energy and trace gas exchange sites (refer to
http://www.indiana.edu/~muhd/). We consider this area of Houston an ideal and
representative site for urban flux measurements, well worth continued research beyond the
limited funding requested in this proposal.
Our short-term goal is to establish a basic turbulence and trace gas flux measurement setup by the end of summer 2007, for which we are requesting a seed grant. For the initial 1-year measurement period our objectives are related to the above described immediate needs for research into HRVOC and related fluxes, photochemical transformations, and fate related to car traffic versus petrochemical industry emissions.

2. Objectives

The objectives of the research proposed here are

1. To set up urban, micrometeorological flux measurements of energy, CO$_2$, O$_3$, and selected VOCs from a tall lattice tower and observe fluxes for at least one year

2. a) Investigate $z_d$, $z_0$, and other turbulence parameters for this urban setting, which includes different surface regimes under different wind directions
   b) Input these data into a 2-dimensional flux footprint model with the goal to develop an emissions inventory for those parts of the city included in the footprint area

3. Focus on alkene-VOC fluxes and their speciation by measuring both the sum fluxes as well as the speciation of alkenes. Collaborate with Dr. Rappenglück from the University of Houston to simultaneously measure abundances and fluxes of the most common alkene oxidation products formaldehyde and acetaldehyde

4. Calculate the surface heat budget from energy balance considerations, and quantify the contribution of the investigated surface areas to the urban heat island effect

Continuous, half-hourly turbulent flux data will be computed from 10-Hz raw data from the sonic anemometer, a high precision closed-path NDIR CO$_2$/H$_2$O analyzer, a fast ozone analyzer, and a fast alkene analyzer. A relaxed eddy accumulation (REA) – gas chromatography system will be set up for automated, segregated, 30-min adsorbent sampling and subsequent analysis of VOCs with hourly flux data acquisition. Additional grab samples will be taken with an automated sampler using Summa® passivated stainless steel canisters to
identify C$_2$-C$_6$ alkenes by high-resolution gas chromatographic analysis. Routine air quality measurements of ozone, carbon monoxide and nitrogen oxides will also be carried out from the same height for comparisons to nearby air quality sites.

Most of the above instrumentation is currently set up at the PIs research site at Lick Creek Park, College Station, TX, as part of the TexAQS II, and we are testing the portable, automated, two-channel gas chromatograph (GC) with flame ionization detection (FID) in REA setup that is to be used in this study. After an engineering study of the lattice tower installation in spring 2007 and contract negotiations with the tower’s owner/operator, a field deployment is envisioned for July 2007, subsequently allowing for a whole year of measurements. The graduate student funded through this grant will be trained to operate, automate and interpret the standard micrometeorological instrumentation/measurements, with an approximately once every two weeks attendance during routine operations. The PI and a second graduate student, funded on another grant, will be responsible for all operating procedures of the automated VOC measurements including maintenance in the field. Routine data analysis will be carried out by the graduate students, under guidance from Dr. Schade, who will be responsible for graduate student training, proper preparations and field deployment including initial data acquisition methods, and setting up initial data analysis routines. Dr. Schade will also be partially responsible for contract negotiations. Should the company allow continued use of the site, we intend to maintain all monitoring for at least another season to improve statistics and avoid data misinterpretation in case the first year was climatologically or otherwise unusual. If all meteorological and air quality measurements operate successfully at least 50% of the total time period during 2007/2008, all objectives listed above can be met within the two years of funding requested.

3. Methodology

3.1 Standard air quality measurements
One inlet, a single Teflon PFA line for all the standard air quality measurements will be placed at the same level of the tower than the flux measurements inlet. A dedicated pump will deliver sample air to the foot of the tower inlet filter. Standard analyzers will be used for CO (Thermo Electron Corp. Model 48C-TLE), NOx (Electron Corp. Model 42C) and ozone (used Dasibi model 1008-RS), housed inside an air-conditioned instrument building/room at the foot of the tower. Averaging time for these three instruments will be <1-5 min based on the desired precision. Appropriate field calibration procedures for CO will include hourly measurements of (catalytically produced) zero air and periodic injections of a 500 ppb CO calibration gas. Field calibrations for the NO instrument will include daily to weekly measurements of zero air and a 0.1 ppm NO-standard at the instrument, and a dynamic dilution of a ppm-level NO₂ standard upstream the MOLY converter.

3.2 Micrometeorological measurements

Raw 3-D wind from a sonic anemometer, auxiliary micrometeorological measurements, and chemical analyzer data will be stored in binary format on a CR23X data logger (Campbell Sci., Logan, UT) and archived. Auxiliary micromet-sensors will include a net radiometer (NR-LITE, Kipp & Zonen), a wind speed/wind direction sensor (model 034B, MetOne), several wind speed (model 014A, MetOne) and T/RH (Vaisala CS500) sensors deployed at lower tower heights, and several surface heat flux and temperature sensors. They will be used for the calculation of surface heat budget contributors and an estimate of urban heat storage. The raw data will be processed by R-language based software to calculate turbulence data, mixing ratios, and fluxes for all quantities measured. Quality control will include de-spiking, rotating, and appropriate lagging of data, as well as, e.g., co-spectral analysis for necessary stationarity checks and flux corrections due to limited instrument response and/or “eddy-smearing” inside the tubing. All data will be archived both in raw and processed format. They are intended to be made available on the world-wide-web.
The inlets for the micrometeorological measurements will be placed as close as possible to the sonic anemometer (CSAT3, Campbell Sci.), which will extend from a horizontal beam that will be installed at approximately 80 m on the lattice tower. All fast acquisition (10 Hz) CO$_2$/H$_2$O (Licor 7000), ozone (LOZ-3F, Drummond Technology Inc.), and integrated alkene (Hills Scientific, Boulder, CO) instruments will be operated on the same 3/8” Teflon PFA line, which will be flow regulated (~20 L min$^{-1}$) for repeatable tubing delay times [43]. Another pump has been budgeted for this sampling line. The ozone measurement is based on fast photon-counting from the reaction of ozone with a dye (Eosin) to produce a chemiluminescent product. The instrument’s output can be calibrated for each half-hour measurement by comparing it to the UV-absorption based, slow ozone analyzer. The fast alkene analyzer measurement is described below.

The slow standard air quality measurements, the fast eddy covariance (EC) measurements, and the fast REA valves (see below) will all be controlled and recorded by the data logger. It will be downloaded once to twice a week using a satellite link for remote access to the site, which also allows for regular daily quality checks.

Half-hourly momentum/friction velocity, sensible heat, CO$_2$, and H$_2$O (latent heat) EC measurements will provide necessary reference parameters for the chemical flux measurements. Additionally, our half-hourly sensible and latent heat, and ozone EC flux measurements will establish typical urban heat island emissions, Bowen ratios, and ozone loss characteristics to several representative urban surfaces depending on wind direction. These data and processes need to be modeled accurately to predict urban temperature and ozone in air quality models, and are currently parameterized without adequate validation data for those surfaces. We strive to collaborate with our colleague Daewon Byun from the University of Houston to input data from this study into his air quality modeling.

3.3 VOC flux measurements
For the VOC mixing ratio and flux measurements we will sub-sample the flow-regulated EC gas stream and route a small flow (~0.5 L min\(^{-1}\)) into “updraft”, “downdraft”, and “deadband” valves in order to carry out air sampling and flux determination based on relaxed eddy accumulation (REA)\(^1\). The REA system is intended to be set up similarly to the systems described in [44] and [45]. Air will be sampled by a Teflon membrane pump and pushed at a regulated flow rate via Teflon PFA tubing into either one of two Teflon bag reservoirs or dumped. A continuous sample flow (~100 mL min\(^{-1}\)) out of the reservoir will be ozone-scrubbed [43] and pre-concentrated onto carbon-based adsorption cartridges. Contrary to the [44] design, exhaust air will not be recirculated to the reservoir. The two main sampling lines will only be filled with ambient air when either the REA “updraft” or “downdraft” valve behind the main line pump is activated based on the sign of the vertical wind speed and its history [43], Figure 1. The much larger fill- (~1 L min\(^{-1}\)) than sub-sampling flow (<100 mL min\(^{-1}\)) will allow the choice of a large REA b factor, i.e. most sample air will be routed to the deadband (middle valve in Fig. 1) while maximizing the up- to downdraft difference.

The preconcentration unit is an integral part of the SRI Instruments GC that we operate. It consists of two ⅛” OD adsorbent cartridges that are connected to 12-port Valco valves via \(^{\frac{1}{16}}\) OD Silcosteel\(^{\text{©}}\) tubing. The cartridges are imbedded in heater blocks for fast thermal desorption after sampling is completed. The system is automated via the chromatography software, which (i) acquires the sample via valve switching and sample pump operation for one half hour, (ii) purges oxygen from the cartridges for several seconds, and (iii) heats and injects the sample into two identical GC separation columns with retention gaps.

We intend to use an intermediate polarity column (such as a DB-624) during most of the year-long monitoring effort, because it will allow us to measure both anthropogenic and biogenic VOCs. For shorter time periods, we will alter the sub-sampling path to scrub air of water and CO\(_2\), and install two PLOT-Alumina columns for high-resolution C\(_2\)-C\(_6\) non-

\(^1\) REA flux determination is based on the semi-empirical formula \(F_{\text{VOC}} = b \times ([\text{VOC}]_{\text{up}} - [\text{VOC}]_{\text{down}})\)
methane hydrocarbon (NMHC) analysis [46]. This will enable a more detailed analysis of local anthropogenic NHMC emissions, while still allowing flux measurements of biogenically emitted isoprene.

**Figure 1**: Schematic design for the REA field setup (not to scale)

VOC identification will be based on retention time, quantification will be based on a compound’s uniform carbon response on the FID [46], periodically compared to calibration gas injections. The VOC analysis system will be calibrated by alternately opening the REA valves to the main flow while diluting calibration gases in the ppm range into either one of
the lines (Figure 1). Channel intercomparisons will be performed similarly but without
injecting calibration gas, and field ‘blanks’ will be performed by sampling zero air injected in
front of the pump through the system.

Direct EC fluxes of the reactive alkenes will be measured with a fast alkene analyzer
(Hills Scientific). The instrument uses photon-counting of the chemiluminescence produced
by the reaction of excess ozone with the alkenes. The instrument response is determined by
the air velocity and the reactivity of the individual alkenes with ozone. Stronger responses are
observed for alkenes that have short lifetimes with respect to reaction with ozone [47, 48].
The instrument will be calibrated daily by diluting a ppm-level propene standard into the
sampling stream of the instrument. Hence, ambient alkene levels will be reported in propene-
equivalents with respect to reaction with ozone. Those C<sub>2</sub>-C<sub>6</sub> alkenes contributing to the
signal will be identified through high-resolution gas chromatographic (HRGC) analysis of
grab samples collected with an automated sampler from the main sampling stream during the
flux measurements [49]. Fluxes of the individual alkenes will be determined from the HRGC
results and alkene sensitivities of the fast alkene sensor reported by Guenther and Hills [47].

Canisters provided by Paul Doskey of Argonne National Laboratory will be shipped to and
analyzed at Argonne within one week of sampling for non-methane hydrocarbons, with the
C<sub>2</sub>-C<sub>6</sub> alkenes as the major target analytes.

For the alkene oxidation product measurements, dominantly form- and acetaldehyde,
established cartridge methods would be employed [50-53], which can later be integrated into
another REA setup to determine fluxes. Dr. Rappenglück will also provide continuous in-situ
measurements of formaldehyde (Aero Laser Model 4021).

Data transfer to TAMU will be accomplished either remotely, or via regular site visits by
one of the personnel involved. A field site visit protocol will be developed to assure
uninterrupted operation, respectively procedures to return to it. All data analysis will be
carried out with a partially automated R-language based routine.
3.4 Footprint analysis

We calculated preliminary crosswind integrated footprint distributions for an assumed measurement height of 80 m under a variety of stability conditions using the parameterised footprint model of Kljun et al. [54]. The results of this analysis are tabulated in Table 1. For this analysis, roughness length extremes of 0.5 and 1.5 m were chosen, a typical range for urban areas studied by Grimmond and Oke [55]. The results in Table 1 show the expected functionality, where shorter footprints correlate with increased turbulence ($u^*$). They also limit the common footprint lengths to less than 1 km for the maximum flux footprint impact ($x_{\text{max}}$) and less than 3 km for the 90% level. Houston’s wind direction climatology shows that south-easterly wind directions dominate, followed by southerly and northerly directions, but all directions can be expected to contribute significantly to year-long observations. North- and north-easterly flows contribute stronger during the winter months, while southerly and south-easterly flows contribute stronger during the summer months. South-easterlies will carry significant hydrocarbon emissions from the ship-channel to the tower site, allowing for crucial summertime analysis of petrochemical industry contributions. Note also that for many wind directions, the major highway (IH-45, Plate 1) immediately to the west of the tower, will contribute to the measured fluxes. Results of the desired flux measurements are expected to be representative of real-world highway and urban traffic emissions, the most important contributor to anthropogenic air pollution parameters in most cities worldwide.

We intend to implement the above footprint model [56-58] into our data analysis software within the second year of this project, when all major wind directions have been sampled for an accurate estimate of $z_0$ and $z_D$. The model can identify the quantitative contributions of individual surface areas within the footprint to the total flux for each half-hour measurement period. A future comparison to bottom-up, GIS-based emission inventories for heat and trace gases will then allow a direct, quantitative as opposed to the currently more common qualitative assessment of urban emissions.
Table 1: Results from a parameterised footprint model for an 80 m measurement height

<table>
<thead>
<tr>
<th>Stability</th>
<th>$u^* \text{ (m s}^{-1}\text{)}$</th>
<th>$\sigma_w \text{ (m s}^{-1}\text{)}$</th>
<th>$z_0 \text{ (m)}$</th>
<th>$x_{\text{max}} \text{ (m)}^2$</th>
<th>$x_{90} \text{ (m)}^2$</th>
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1 lapse rate criterion; unstable: daytime convective condition, neutral: frequent urban nighttime condition
2 location (horizontal distance) of the maximum contribution to the flux
3 horizontal distances at which 90% of all flux contributions are accounted for

4. Personnel and Costs, Timetable

Personnel for this project include the PI, Dr. Schade, and a graduate student. Funding is sought for a graduate student for an 18-month period, and one summer salary month for the PI. In addition, TAMU policy requires the inclusion of tuition for the graduate student. The PI will finance the second graduate student for ½ year out of TAMU startup funding.

All major equipment for this study is already available, including the standard air quality analyzers, a portable GC-FID system for VOC measurements, and all eddy covariance and micrometeorological equipment. Funding is sought for one sampling pump ($500) and all Teflon PFA tubing ($500) to bring air from an elevation of 80 m down to the ground. Further funding is sought to cover consumables (tower rent to owner, standard calibration and GC operational gases, filters, energy costs, etc.; $3.5k), shipping costs for the stainless steel canisters ($500), and travel to and from the site and one meeting ($2k).

The table below sketches the envisioned timetable for the project.
As outlined above, the quality of the measured air quality parameters will be assessed via periodic blank and calibration gas measurements. The PI is familiar with setting up and operating field instrumentation of the kind described in this proposal and will develop routine ‘standard operating procedures’ (SOPs) for the students to follow each field site visit. Site visit duties will be rotated and proper logs will be kept on both routine and unusual events. Raw data will be backed up onto CDs as soon as possible after download and copies will be stored outside the PIs office and laboratory space. Processed data will also be copied to at least one other electronic location, and samples will be posted to the web page. Biweekly meetings or conference calls will be held of all personnel involved with the field measurements, and both students planned to be involved in this project will report directly to the PI. External input on site operations will be provided by Drs. Don Collins and John Nielsen-Gammon from within the Department of Atmospheric Sciences. Analytical procedures at Argonne National Laboratory will be carried out or directed and quality-controlled by Dr. Doskey. He also has several years of experience with the fast alkene analyzer and will train personnel at TAMU in operating and maintaining the instrument.

A detailed QA/QC plan especially with regard to the VOC measurements will be submitted after award of the project.
6. Qualifications

Dr. Gunnar Schade has been measuring trace gas fluxes with different techniques since 1992. He is using micrometeorological methods since his postdoctoral time at UC Berkeley in 1998 and has since been performing VOC measurements, including fluxes, from natural and agricultural areas. Dr. Schade has partially operated and managed three research sites since 1998, including a walk-tower with air quality and flux measurement equipment in College Station, where his new VOC flux setup, later to be deployed for the proposed project in Houston will be tested this summer.

Dr. Paul Doskey is a senior researcher at Argonne National Laboratory, Illinois, who has been involved with VOC measurements for almost three decades. He is a co-author of several studies of urban VOC chemistry in Houston carried out during TexAQS 2000. Among others, he pioneered research into oxygenated VOCs, their fluxes, and there importance in the atmosphere. Dr. Doskey’s long-term experience with VOC measurements using various methods is an asset to this project. Dr. Doskey is also an expert on micrometeorological trace gas flux measurement techniques, and will be able to provide assistance with field site setup and flux data interpretation beyond the VOCs.

7. Conclusions and Outlook

The activities proposed in this project will provide a unique urban data set of turbulence and chemical flux measurements above a heterogeneous surface. The data analysis will reveal when current understanding of surface layer micrometeorology over rough surfaces is sufficient for flux interpretation and when not. It will provide much needed data for further in-depth study. The measurements will also close a significant gap in urban air quality measurements, because so far they rely on bottom-up emission inventories and in-situ concentration, but not direct flux measurements. This study is intended to provide a look at
whether emissions inventories that are usually based on older input data can account for the real-world fluxes, such as from traffic emissions.

The funding time covers a 1 ½ to 2-year seed period and, insofar, is designed to (I) set up and test existing flux measurement equipment of the PI for a novel application, (II) expand micrometeorological expertise and education at the Department of Atmospheric Sciences at TAMU, (III) seed-fund a new graduate student with boundary layer meteorological background, and (IV) establish a lasting collaboration between TAMU and UH, and TAMU and Argonne air quality researchers. Further research of urban micrometeorology and its connection to air quality and greenhouse gas emissions dynamics is desired at this tower site for several years beyond the requested seed-fund. Based on location, the objectives can be extended to include monitoring or flux measurements of a variety of species relevant for air quality and atmospheric chemistry, as well as urban greenhouse gas budgets.
References


