Mobile measurements of ambient concentrations of formaldehyde and aerosol optical properties in Houston, TX.

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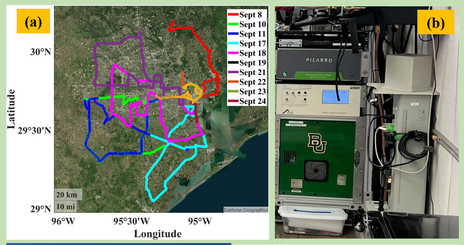
Abstract

Anthropogenic emissions from traffic and industrial activities and their impact on air quality are a major concern in urban areas. The concentration of the air pollutants from these sources is typically measured with stationary air quality monitors, which are often limited in number. In addition, these stationary measurements often prove inadequate in representing the emission scenarios of the entire city due to the large spatial variability of these pollutants in urban environments. On the other hand, using specialized mobile monitoring techniques helps to evaluate air quality by better capturing spatial variability of pollutants in different micro-environments throughout the city. This study focuses on mobile monitoring of ambient concentrations of HCHO and optical properties of $PM_{2.5}$ (particulate matter $\leq$ 2.5 µm) in different locations in Houston. The mobile measurements were conducted during the Mobile and OFFshore Measurements (MOFFS), in September 2023. The measurements to be discussed include Picarro for measuring HCHO and Methane, the Tricolor Absorption Photometer (TAP) for measuring aerosol absorption coefficient, and the Nephelometer for measuring scattering coefficient. Mobile measurements in this study will be used for the characterization of air quality in industrial areas, urban areas, and urban backgrounds, with the long-term goal of improving the spatial resolution of urban atmospheric chemistry and exposure assessment.

Objectives

- Identifying the hot spots for equivalent black carbon (eBC) and formaldehyde (HCHO) and characterizing spatial and temporal differences in concentration.
- Evaluating the potential sources of equivalent black carbon (eBC) and HCHO downwind of Houston.

Sampling Site and Instrumentation



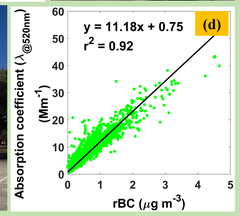


Figure 1. ***(a)*** *The mobile measurement routes in Houston, Texas.* ***(b)*** *Air quality instrument package inside the University of Houston mobile air quality lab (MAQL3).* ***(c)*** *MAQL3 during mobile measurements in Houston* ***(d)*** *Intercomparison between refractory black carbon (rBC) concentration measured by Single Particle Soot Photometer (SP2) and absorption coefficient at 520 nm measured by TAP at Aldine, Texas (2022).*

Instruments and methodology

- Picarro: formaldehyde (HCHO) and methane (CH_4)
- TAP (MAQL-3 and Aldine): Absorption coefficient (σ_{abs}) of $PM_{2.5}$ (λ = 640 nm, 520 nm, and 365 nm) and calculated absorption Ångström exponent (AAE)
- Nephelometer: Scattering coefficient (σ_{sct}) of $PM_{2.5}$ (λ = 700 nm, 550 nm, and 450 nm) and calculated scattering Ångström exponent (SAE)
- SP2 (Aldine): Refractory black carbon (rBC) measured in 2022.
- SP2 and TAP (Aldine): Mass absorption coefficient (MAC), 11.18 (Figure 1(b)).

$$eBC = \frac{\sigma_{abs}\ at\ 520\ nm}{MAC} \qquad AAE = -\frac{\log(\sigma_{abs}\ at\ \lambda_1)\ /\ \log(\sigma_{abs}\ at\ \lambda_2)}{\log(\lambda_1/\lambda_2)}$$

$$SAE = -\frac{\log(\sigma_{sct}\ at\ \lambda_1)\ /\ \log(\sigma_{sct}\ at\ \lambda_2)}{\log(\lambda_1/\lambda_2)}$$

$$eBC\ enhancement\ ratio = \frac{eBC}{average\ background\ eBC}$$

$$HCHO\ enhancement\ ratio = \frac{HCHO}{average\ background\ HCHO}$$

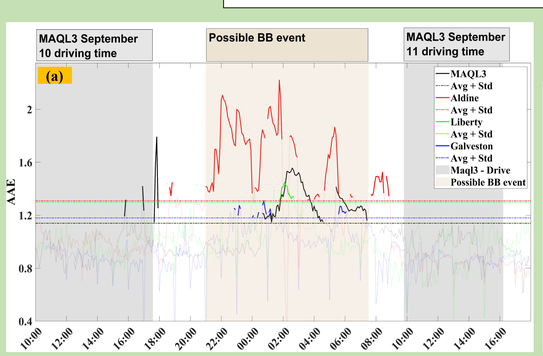
Note: Average background eBC and HCHO are calculated each day by removing peak areas in the mobile measurement period.

Comparison with the BC2 network for biomass burning identification

The analysis of AAE and SAE is used to distinguish between dust, biomass burning (BB) (brown carbon, BrC), and urban aerosol in airborne in situ data[4].

AAE mobile (MAQL3): All the AAEs of the $PM_{2.5}$ aerosols on both days are < 1.31 (average ~ 1), and the SAE > 0.5 (average ~ 2.14). Except for the ~ 4 km of the section in Highway 225, where the average **AAE is above 1.31 (Figure 1c)**. This suggests the contribution of biomass burning or other light absorbing aerosol in this industrial corridor.

MOFFS Stationary (MAQL3 at Laporte) and BC2 monitoring network (Aldine): The possible BB event is identified at Laporte (from 9/11 at ~ 1:00 to 9/11 at ~ 7:30) and at Aldine (from 9/10 at ~ 21:00 to 9/11 at ~ 6:00). The SAE for these days is > 0.5. **Did this overnight smoke influence have a role in high BC and HCHO on the next day, 9/11?**



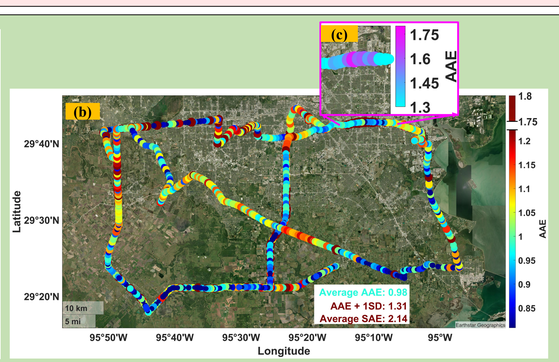


Figure 1*:* ***(a)*** *Five-minute average time series plot of calculated AAE from 9/10/2023 to 9/11/2023 at Laporte (MAQL3) and BC2 sites (Aldine, Liberty, and Galveston) in Houston.* ***(b)*** *MAQL3 path colored by calculated AAE of measured $PM_{2.5}$ aerosol in and around the Houston metropolitan area on Sept 10 and 11, respectively.* ***(c)*** *The section in Highway 225 with AAE above 1.31.*

Results and Discussion

September 10:
- **Maximum eBC concentration 2 µg m^{-3}**
- **Maximum HCHO mixing ratio 18 ppb**

September 11:
- **Maximum eBC concentration 60 µg m^{-3}**
- **Maximum HCHO mixing ratio 13 ppb**

eBC

- **Average eBC concentration of mobile measurement**: September 10 average: 0.38 µg m^{-3}, September 11 average: 1.49 µg m^{-3} (more than **3.5 times higher** than September 10).
- **Potential weekday-weekend effect:** September 10 was a Sunday, and September 11 was a Monday.
- The overnight smoke influence might have a role in the enhancement of BC concentration on the next day, September 11.
- **Wind direction**: September 10 - mostly from the northeast and relatively strong (Figure 3 (e, f, h, and i)), September 11 – differential sea breeze impacts in wind direction across the city (Figure 4 (b, c, e, and f)).
- **Downwind plume:** September 10- BC plume detected downwind of Houston (Figure 3 (b, c, and d)), September 11 - background concentration is mostly uniform throughout the measurement path (Figure 4 (a)).
- **BC hot spot:** Highway 225 - eBC enhancement ratios were as high as 6 and 78 times on September 10 (Figure 3 (g)) and 11 (Figure 4 (d)) respectively, which is a stark difference between the two days. The average background concentrations for September 10 and 11 are ~ 0.3 µg m^{-3} and ~ 0.8 µg m^{-3} (areas of peak concentration are removed to calculate the average background concentrations).

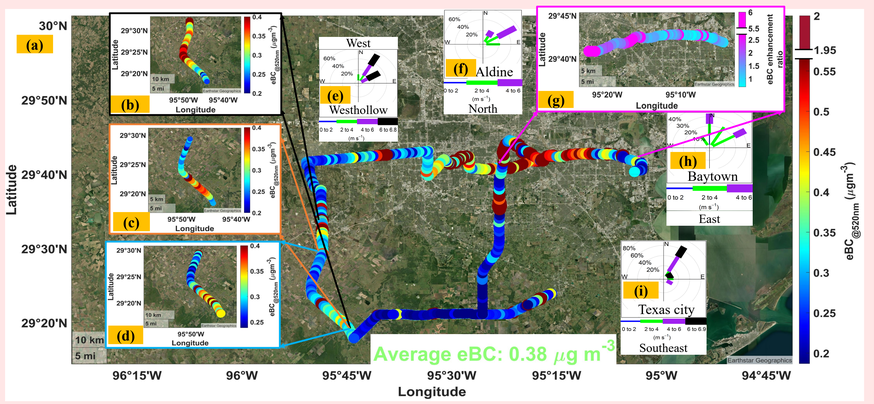


Figure 3: ***(a)*** *MAQL3 route colored by the concentration of calculated eBC during the air quality mobile measurement in Houston on September 10, 2023.* ***(b), (c), and (d)*** *The first, second, and third traverse made through the eBC plume detected downwind of the Houston urban area, respectively.* ***(e) and (f)*** *Windrose plots at the west (Westhollow) and north (Aldine) of Houston, respectively.* ***(g)*** *eBC enhancement ratio plot at Highway 225.* ***(h) and (i)*** *Windrose plots at the east (Baytown) and southeast (Texas city) of Houston, respectively.* ***Note:*** *All Windrose plots are placed at their respective geographic locations.*

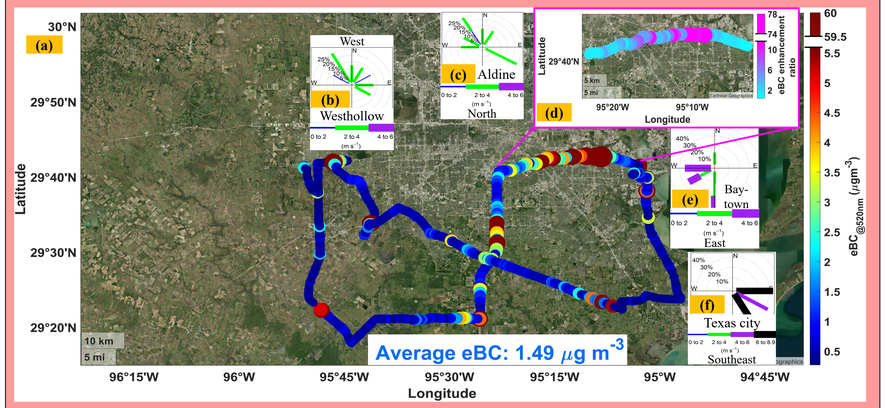


Figure 4: ***(a)*** *MAQL3 route colored by the concentration of calculated eBC during the air quality mobile measurement in Houston on September 11, 2023.* ***(b) and (c)*** *Windrose plots at the west (Westhollow) and the north (Aldine) of Houston, respectively.* ***(d)*** *eBC enhancement ratio plot at Highway 225.* ***(e) and (f)*** *Windrose plots at the east (Baytown) and the southeast (Texas city) of Houston, respectively. Note: All Windrose plots are placed at their respective geographic locations.*

HCHO:

- **Average HCHO mixing ratio:** Unlike BC, HCHO is slightly higher on September 10 (4.6 ppb) than on September 11 (4.19 ppb).
- Regardless of weekday or weekend, the average HCHO concentration is **similar** for both days.
- **Possible reasons for this similarity**: **1)** Its dependence on photochemical production[5] **2)** Different emission sources than BC.
- **Downwind plume: 1)** In contrast to the BC plume (Figures 3 (b, c, d)) on September 10, a stronger HCHO plume of up to 7 ppb was detected downwind of the Houston urban area (Figures 5 (b, c, d)). **2)** On September 11, contrary to BC emission, there was a detection of HCHO plume of 5 ppb on the Alvin-Sugarland Highway (as shown by the red ellipse in Figure 6 (a)), which might indicate enhanced photochemical production associated with circulating wind patterns in the larger Houston metropolitan region (Figure 4) and possible overnight smoke influence.
- **HCHO hot spot:** Highway 225 - HCHO enhancement ratios were as high as 4.2 times and 3.5 times on September 10 (Figure 5 (e)) and 11 (Figure 6 (b)) respectively. Although this is the same location as the eBC hot spot, the HCHO enhancement ratios were similar on these two days. The average background concentrations for September 10 and 11 are ~ 4.3 and ~ 3.7 ppb (areas of peak concentration are removed to calculate the average background concentrations).
- The reported background and average urban (Houston) concentration of HCHO are ~ 0.5 ppb[5] and ~3.6 ppb[6]. However, the average concentrations for both days are well above the background level and notably above the average urban level**.**
- **Emission Sources:** There are several high HCHO emission sources directly northeast of Highway 225 (Figure 6 (c)). The emission rate ranges from 0.8 to 4.82 Routine Tons of HCHO per year (Texas Commission on Environmental Quality, TCEQ, 2019). These may contribute to the peak HCHO measured along this route and the consistency of that location as HCHO hot spot.

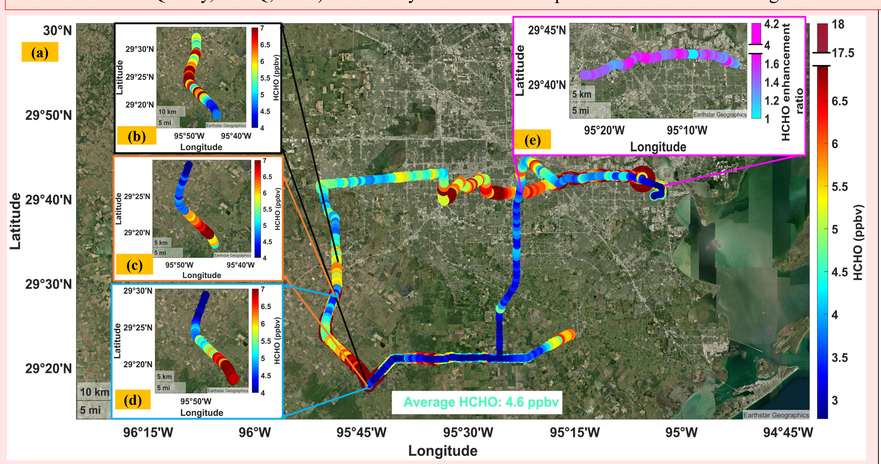


Figure 5: ***(a)*** *MAQL3 route colored by the concentration of HCHO during the air quality mobile measurement in Houston on September 10, 2023.* ***(b), (c), and (d)*** *The first, second, and third traverse made through the HCHO plume detected downwind of the Houston urban area, respectively.* ***(e)*** *HCHO enhancement ratio plot at Highway 225.*

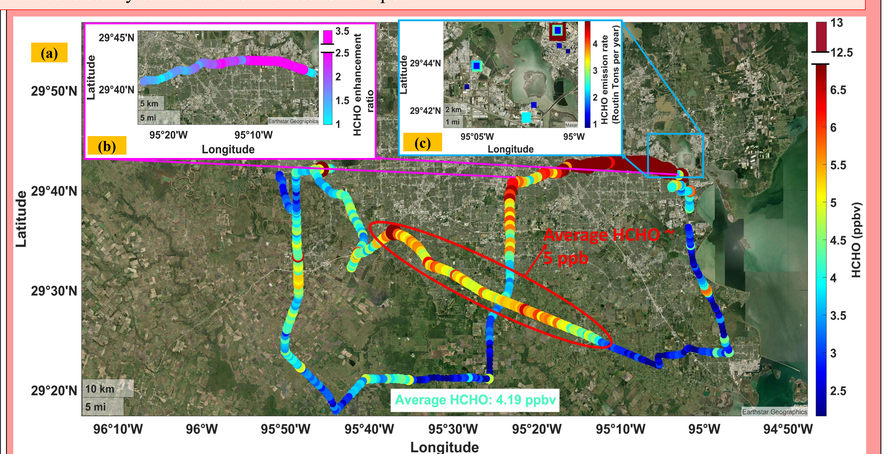


Figure 6: ***(a)*** *MAQL3 route colored by the concentration of HCHO during the air quality mobile measurement in Houston on September 11, 2023.* ***(b)*** *HCHO enhancement ratio plot at Highway 225.* ***(c)*** *Top 20 HCHO emission sources for Harris County based on the 2019 TCEQ emissions inventory.*

Future Work

- Evaluation of the impact of transport and processing on key pollutants (e.g. aerosol, CO, NO_X, SO_2 and O_3, and VOCs) in the Houston metropolitan area.

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