DISCOVER-AQ Houston as a case study for understanding spatial and temporal trends in urban particulate matter

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Introduction

- PM concentrations can display large spatial and temporal heterogeneity across urban areas

- Distinct temporal and spatial regimes in urban PM are expected for Houston

- Variable time resolution sampling at four Houston sites during DISCOVER-AQ was designed to capture these regimes (Sept 2013)
  - AQRP 12-032

Research Goal

- *The overall goal was to quantify the strength of PM formation and contributions of PM emission sources, including industrial sources, motor vehicle exhaust, biomass burning and biogenic emissions, across the Houston metropolitan area.*

Objectives

- Utilize molecular marker-CMB modeling, enhanced with radiocarbon source apportionment, to tightly constrain fossil and contemporary *sources including motor vehicle exhaust, biomass burning, and total biogenic contribution.*

- Utilize semi-quantitative tracers to characterize secondary organic aerosol (SOA) (i.e WSOC), local urban emissions (persistent organic pollutants; POPs) and rural impacts (pesticides).

Carbon Source Apportionment

Quantitative efforts include

- Radiocarbon
  - ^{14}C measurements, a definitive split between fossil and contemporary carbon

- Chemical Mass Balance (CMB) model
  - Organic and inorganic molecular and elemental markers
    - hopanes, steranes, PAHs, alkanes, levoglucosan and elemental tracers, EC and OC

Baylor Ground-Based Sites

Ground-based Sites

Moody Tower

Manvel Croix

La Porte

Conroe

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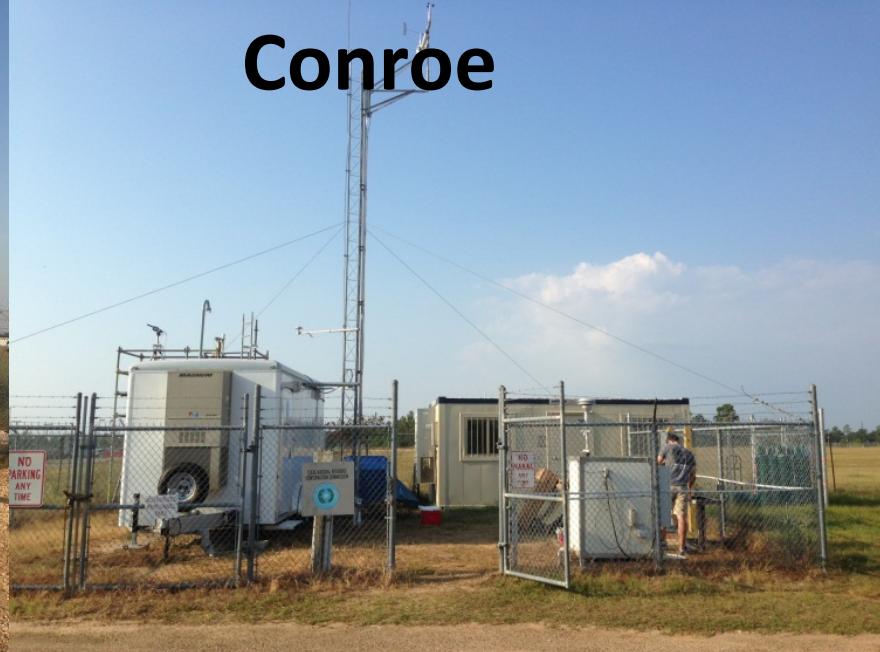
Particulate Matter Samples

Ground-based Sites	Sampler Type	Sampler Operator	Sampler Provider
Moody Tower	HVTSP	BU	BU
Moody Tower	MV2.5 *	BU	BU
Moody Tower	HV2.5	BU	EPA
Moody Tower	HVTSP	BU	UW
Moody Tower	Aethalometer	BU	BU
Manvel Croix	HVTSP	BU	BU
Manvel Croix	MV2.5	BU	BU
Manvel Croix	HV2.5	BU	EPA
Manvel Croix	PAX	BU	DMT
Conroe	HV2.5	UT	EPA
La Porte	HVTSP	EPA	UW

* Dual sample train with quartz fiber and Teflon filters
EPA denotes Environmental Protection Agency
BU denotes Baylor University
UW denotes University of Wisconsin-Madison
UT denotes University of Texas -Austin
DMT denotes Droplet Measurement Technologies

Particulate Matter Samples

Site	Filter Type	Potential Analysis	Total collected
Moody Tower	QFF	OCEC, WSOC, ^{14}C, organic contaminants and molecular markers	107
Moody Tower	Teflon	Trace metals	25
Moody Tower	Aluminum	OCEC, WSOC, ^{14}C, elemental and single particle analysis	35
Moody Tower/ Manvel Croix	PUF	Organic contaminants and molecular markers	9
Manvel Croix	QFF	OCEC, WSOC, ^{14}C, organic contaminants and molecular markers	74
Conroe	QFF	OCEC, WSOC, ^{14}C, organic contaminants and molecular markers	25
La Porte	QFF	OCEC, WSOC, ^{14}C, organic contaminants and molecular markers	25

Bulk carbon:
Elemental Carbon and Organic Carbon

Moody Tower HV2.5 Day
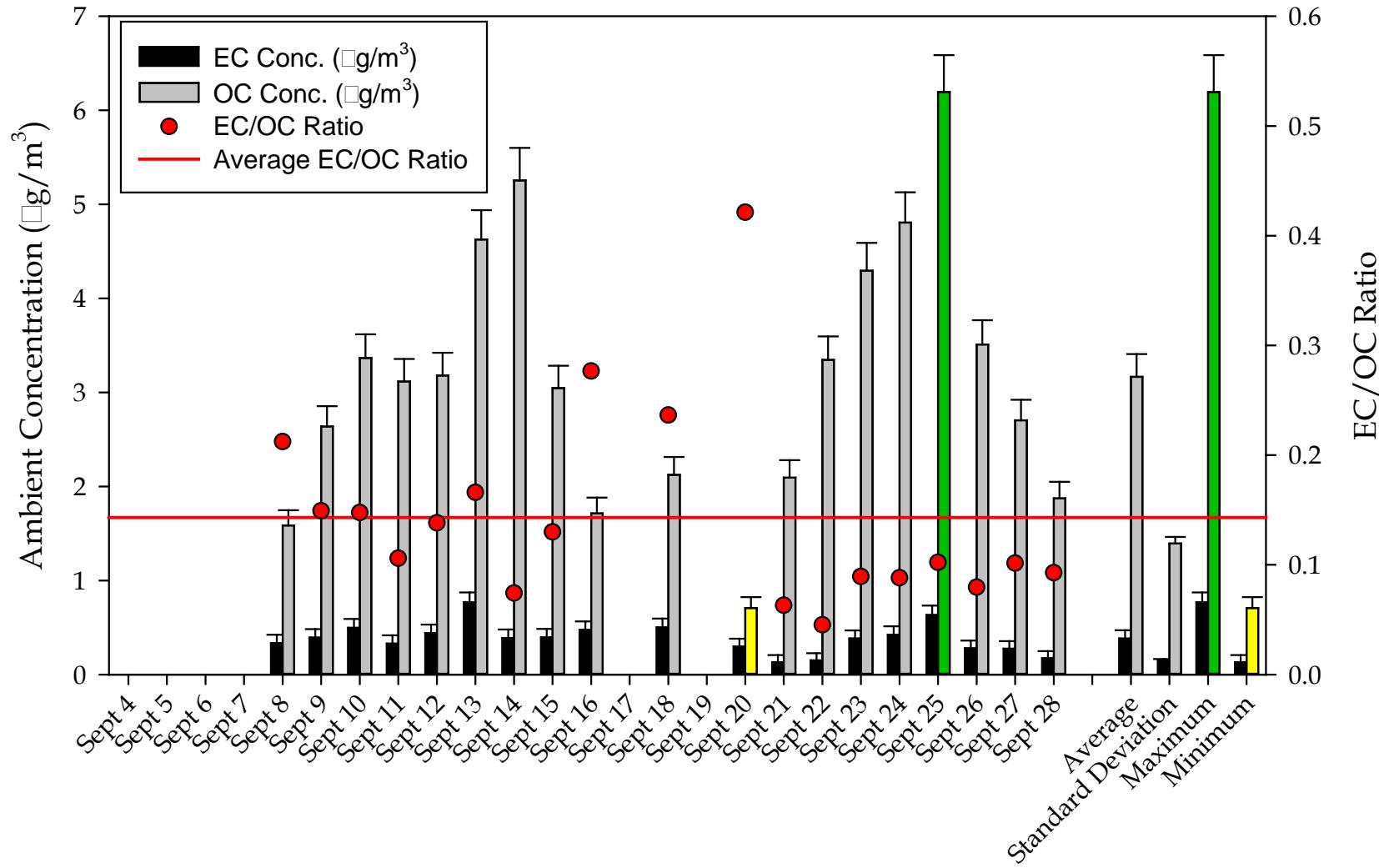
Bulk carbon:
Elemental Carbon and Organic Carbon

Manvel Croix HV2.5 Day
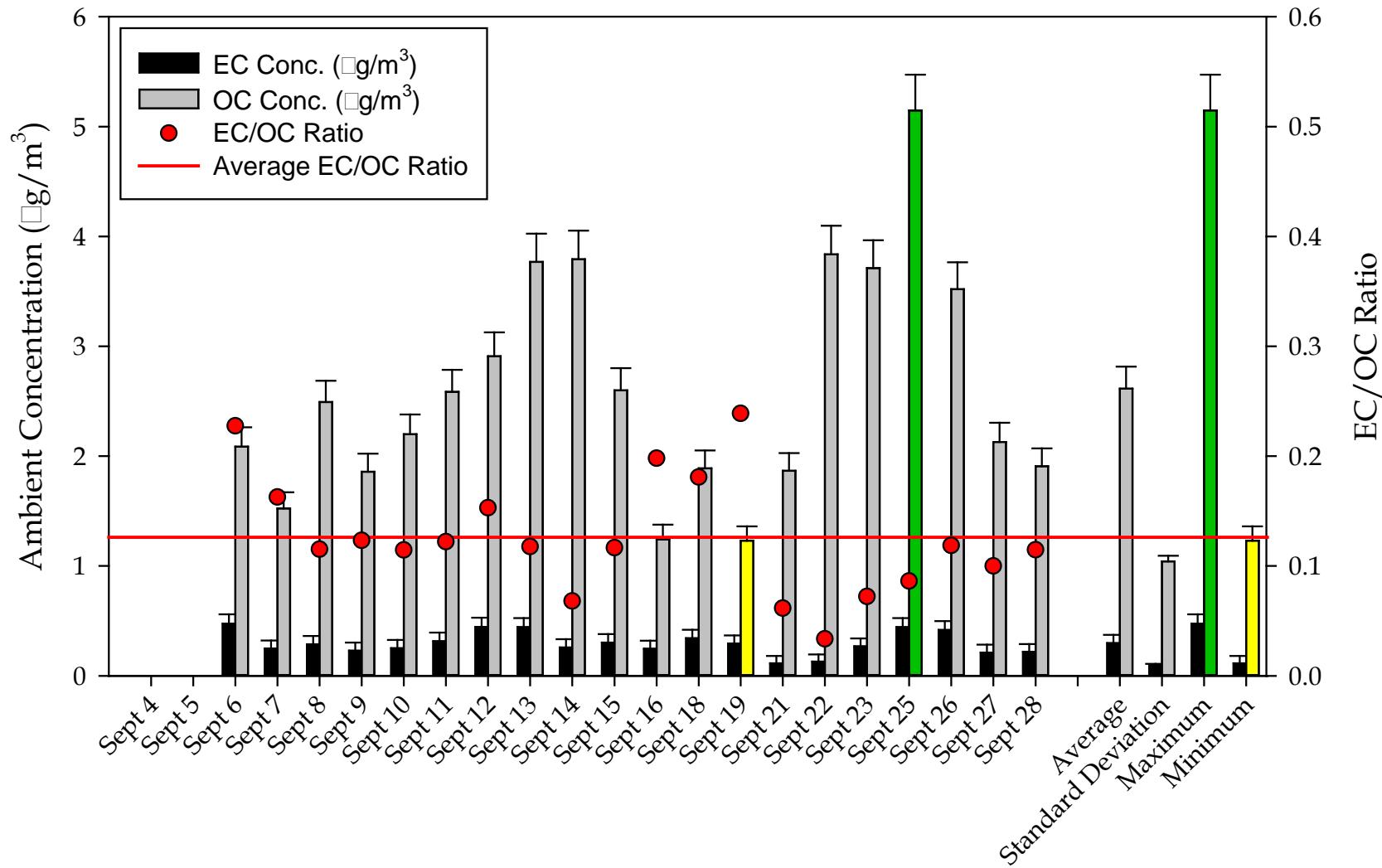
Bulk carbon:
Elemental Carbon and Organic Carbon

Conroe TSP September 4-28, 2013
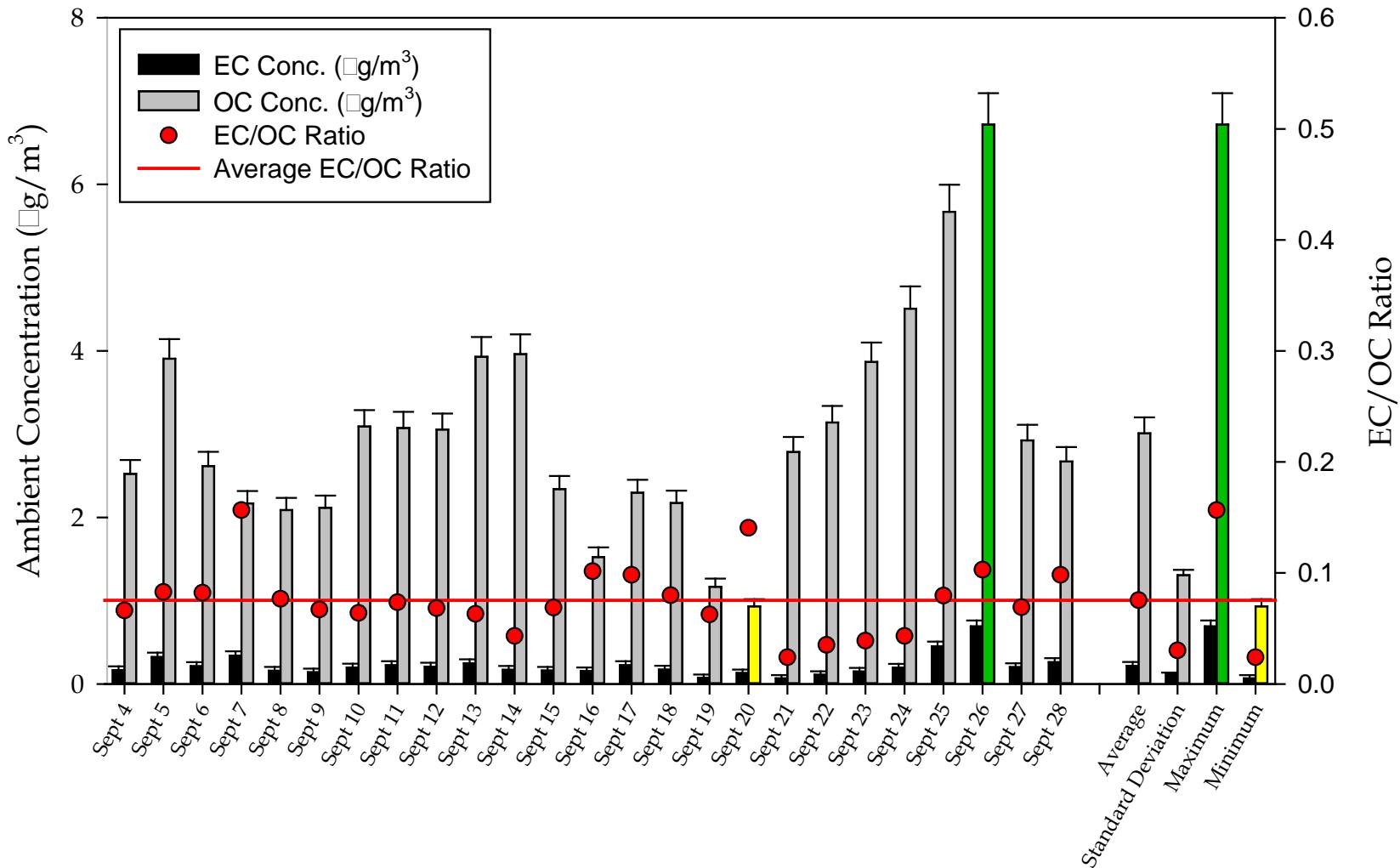
Bulk carbon:
# Elemental Carbon and Organic Carbon

La Porte TSP September 4-28, 2013

Elemental Carbon and Organic Carbon
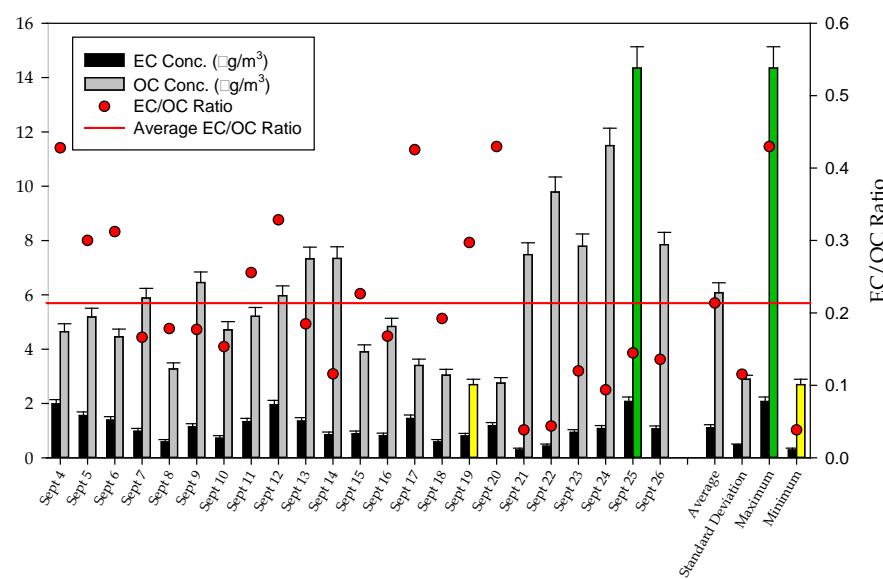
Bulk carbon:
# Water-soluble organic carbon

Moody Tower HV2.5 Day
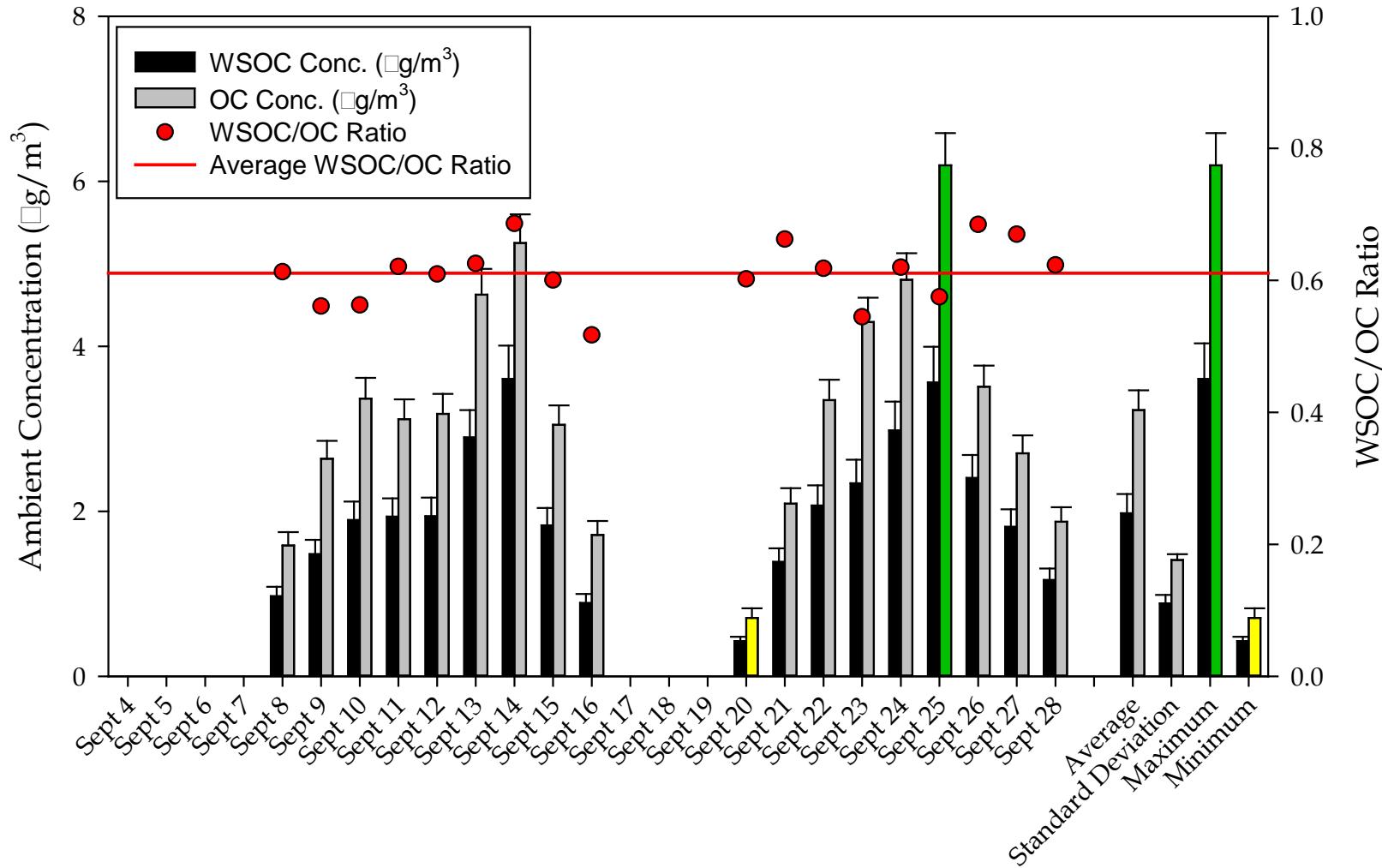
Bulk carbon:
Water-soluble organic carbon

Manvel Croix HV2.5 Day
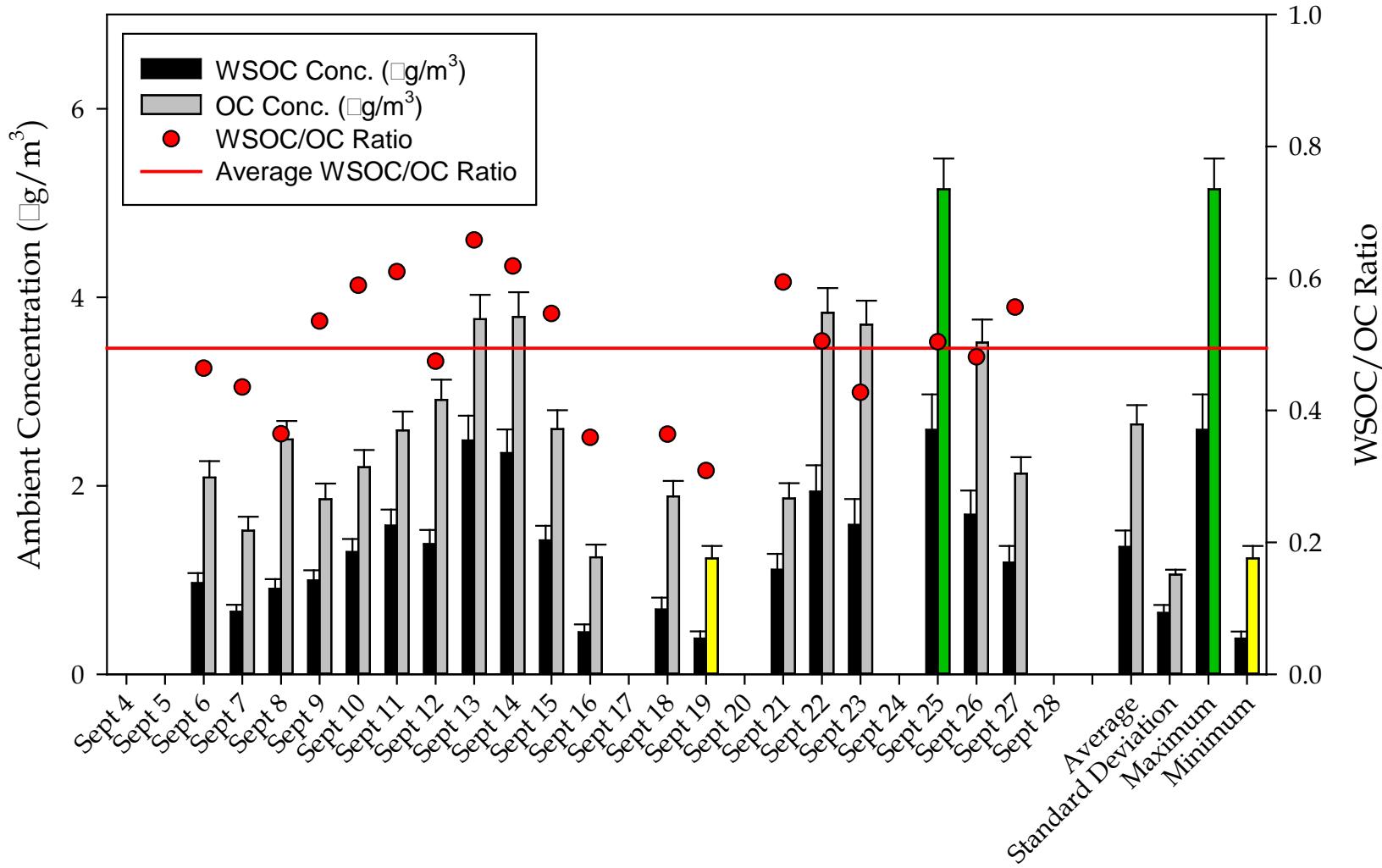
# Bulk carbon:
# Water-soluble organic carbon

Conroe HV2.5 Day
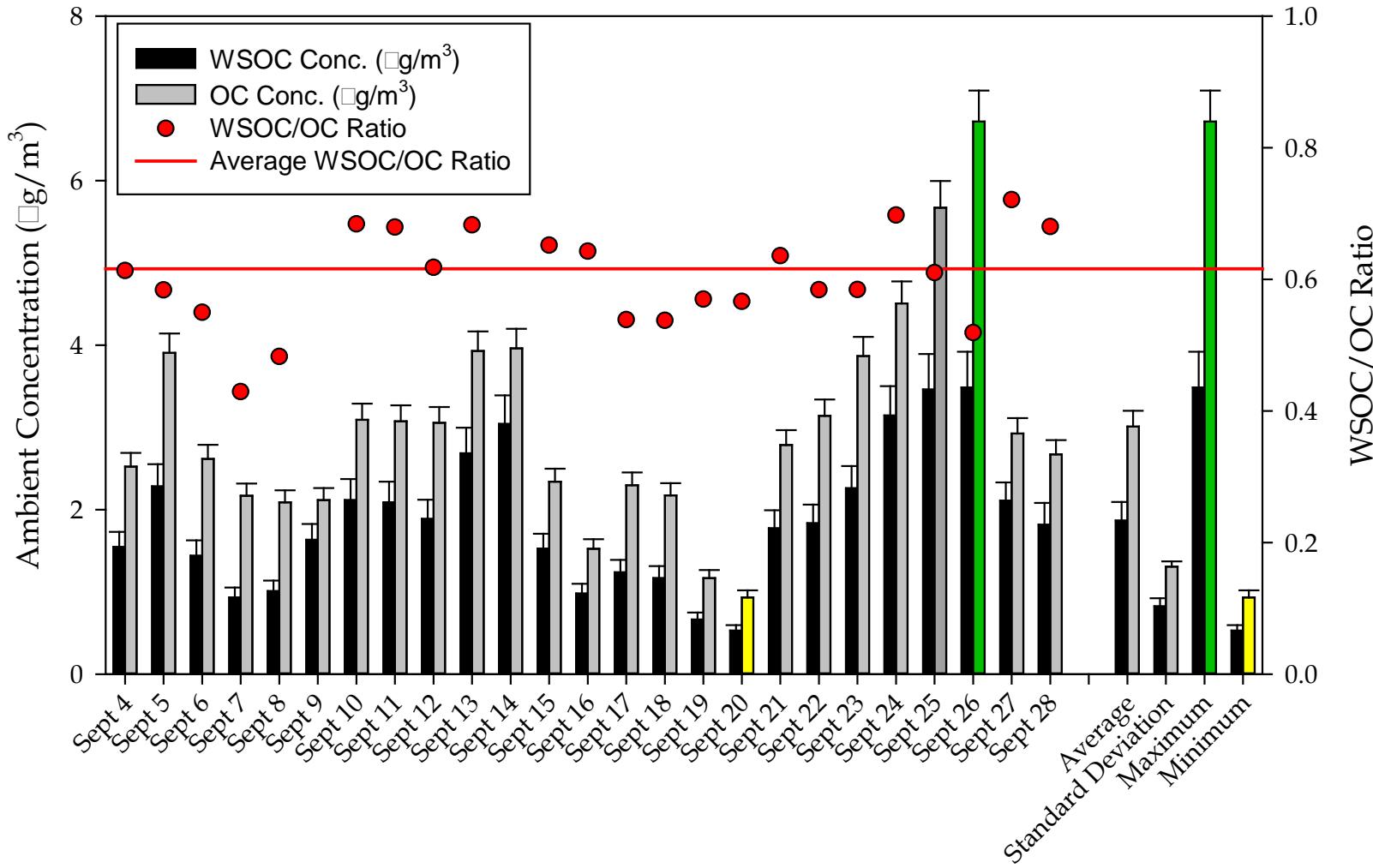
Bulk carbon:
# Water-soluble organic carbon
La Porte TSP
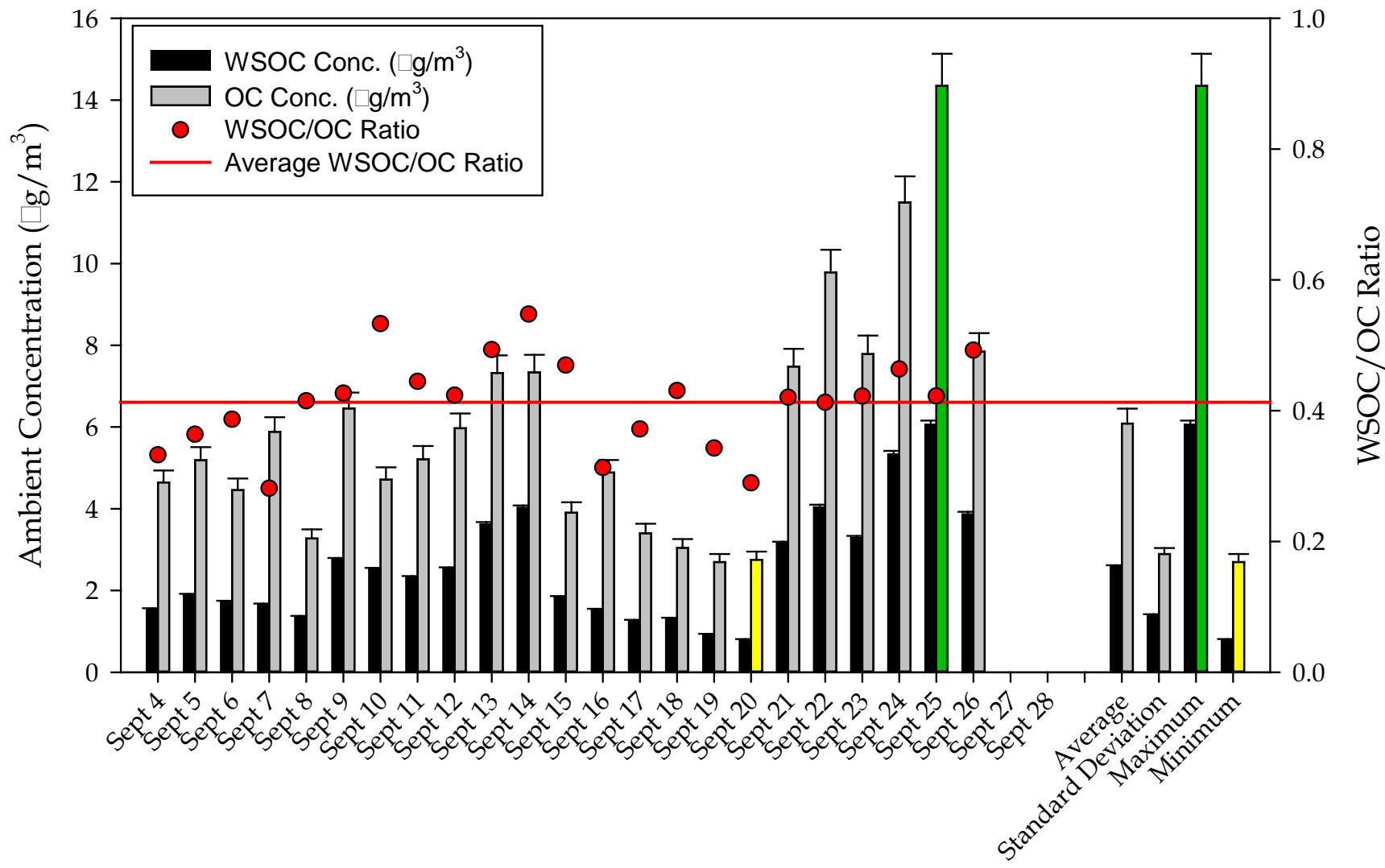
# Water-soluble organic carbon
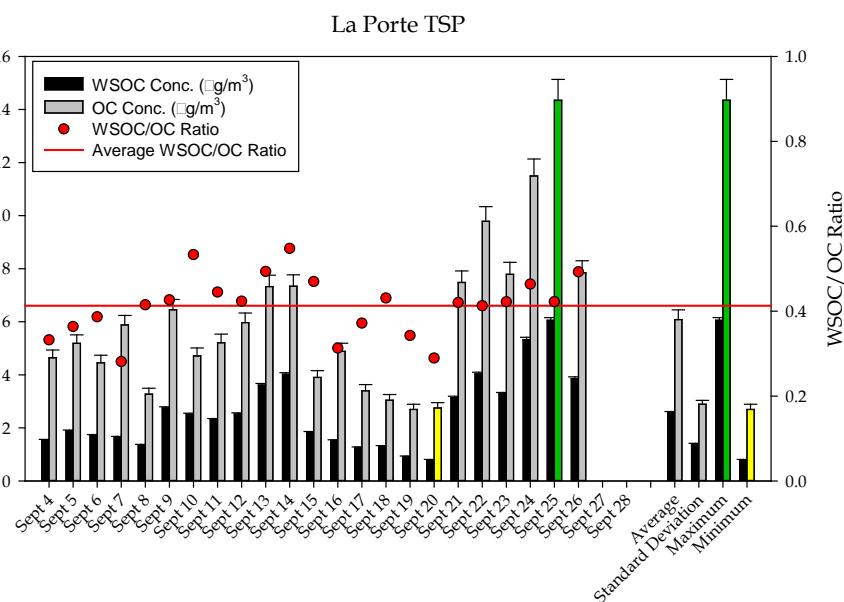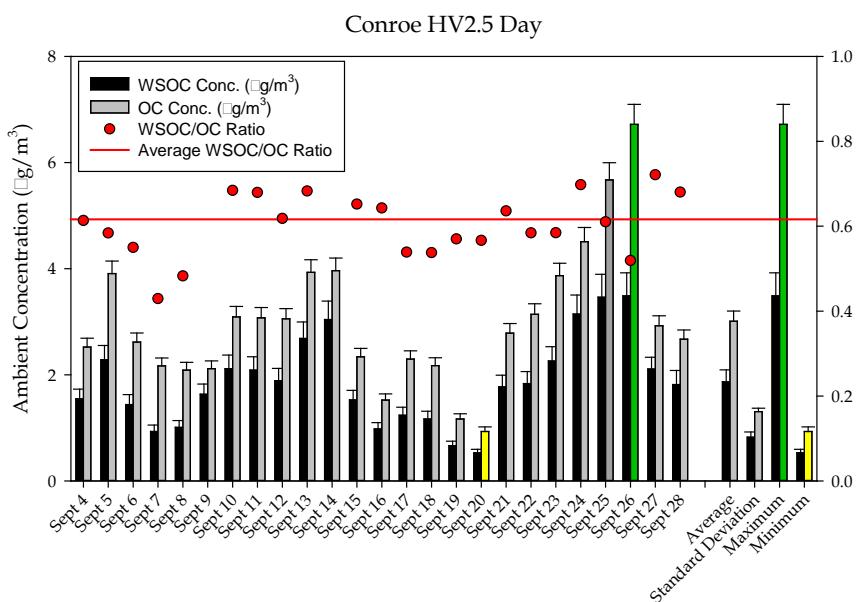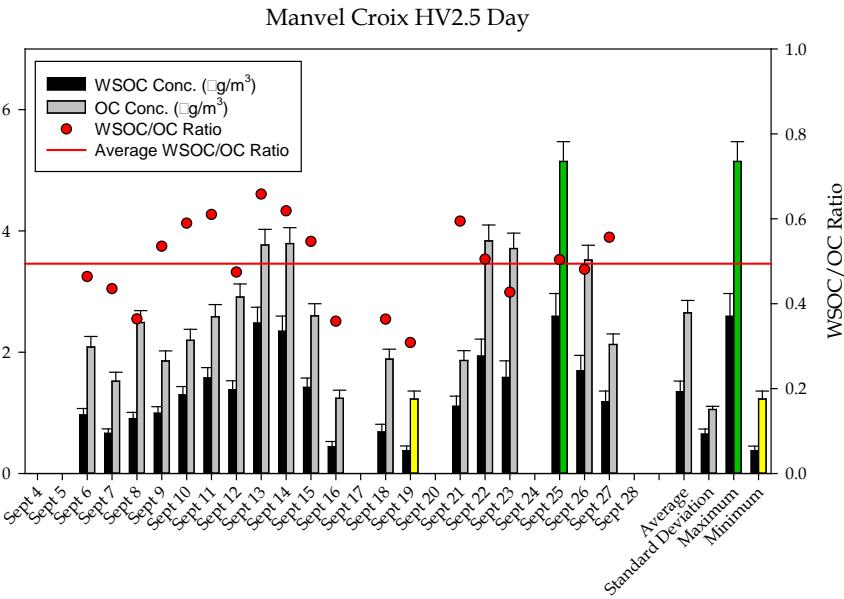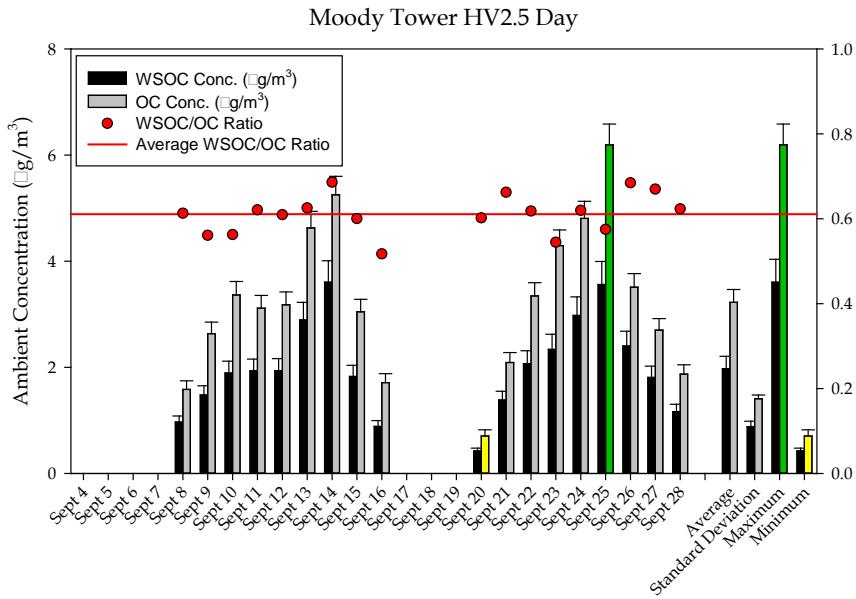
PM$_{2.5}$ speciation at Moody Tower

Moody Tower HV PM$_{2.5}$
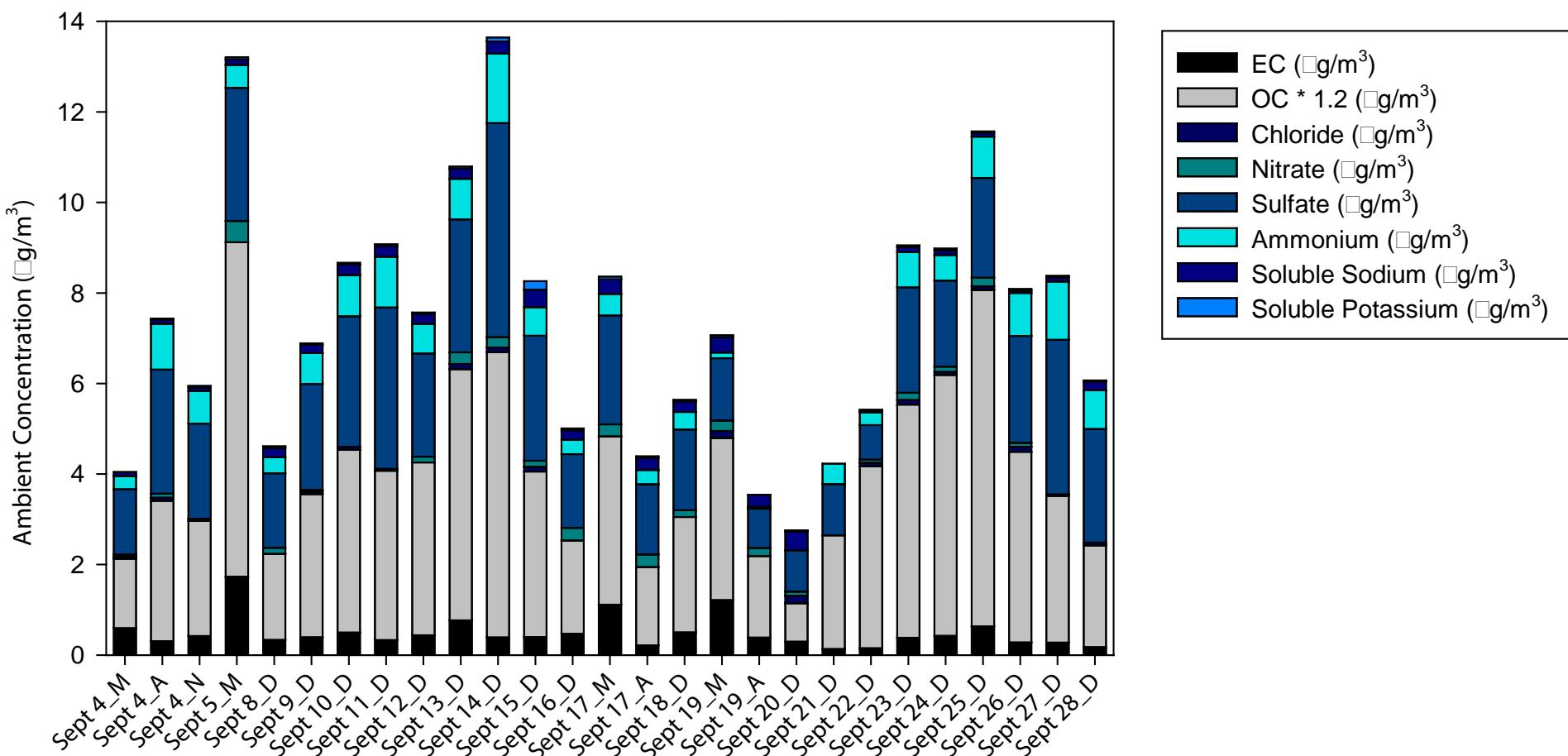
# PM$_{2.5}$ speciation at Conroe

Inorganic Conroe HV PM$_{2.5}$
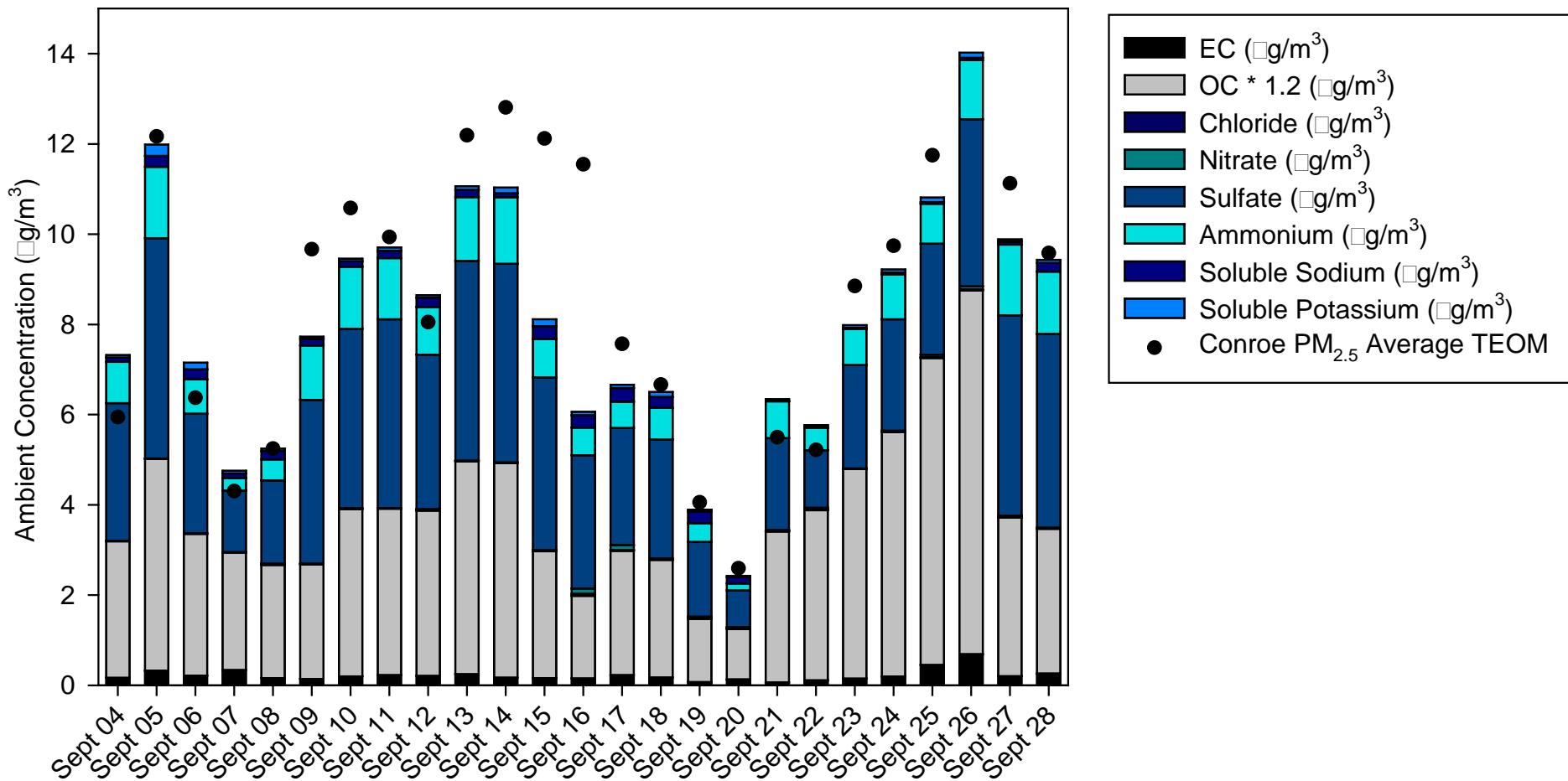
Chemical Mass Balance Modeling
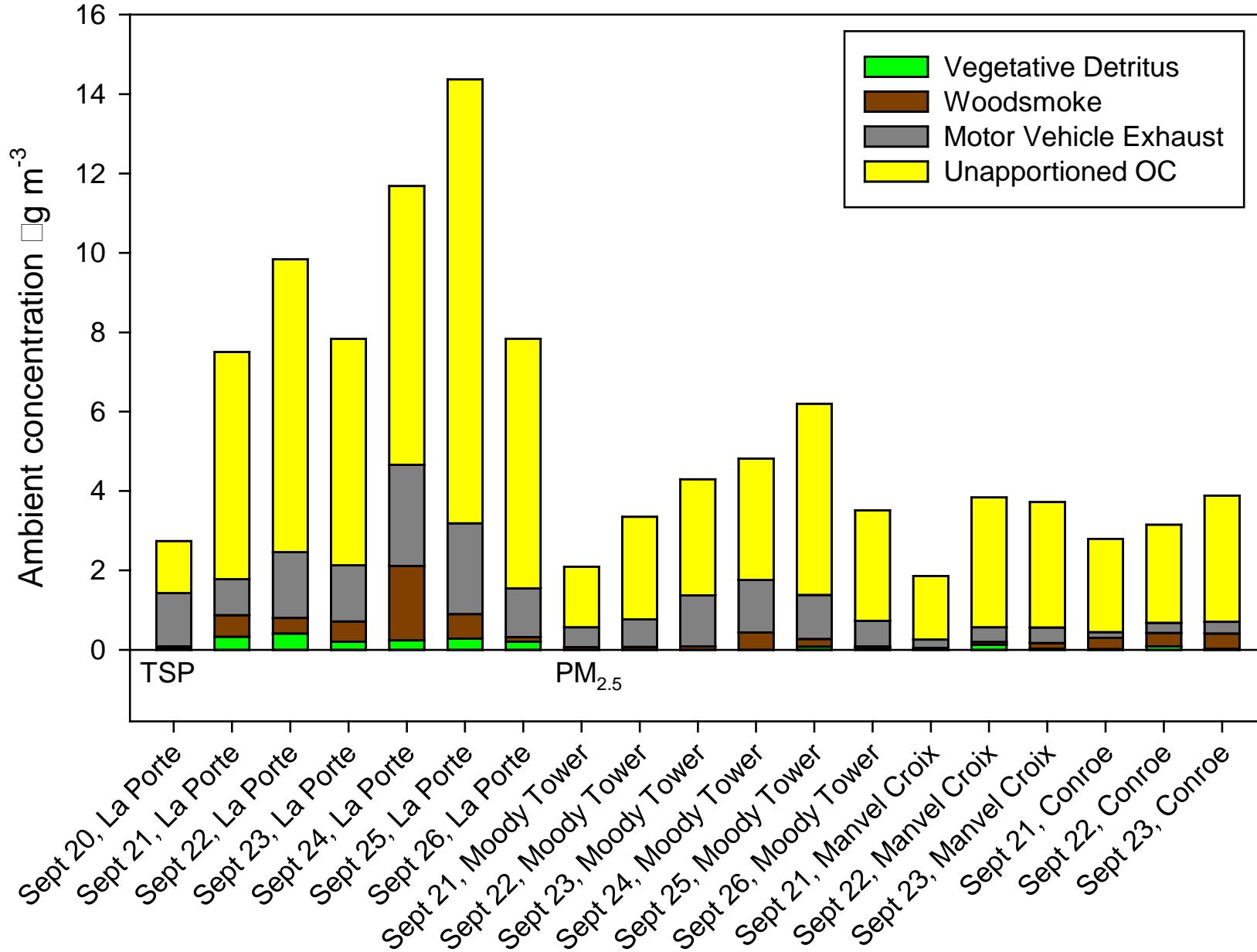
Organophosphate Ester (PM-TSP) Flame Retardants and Plasticizers
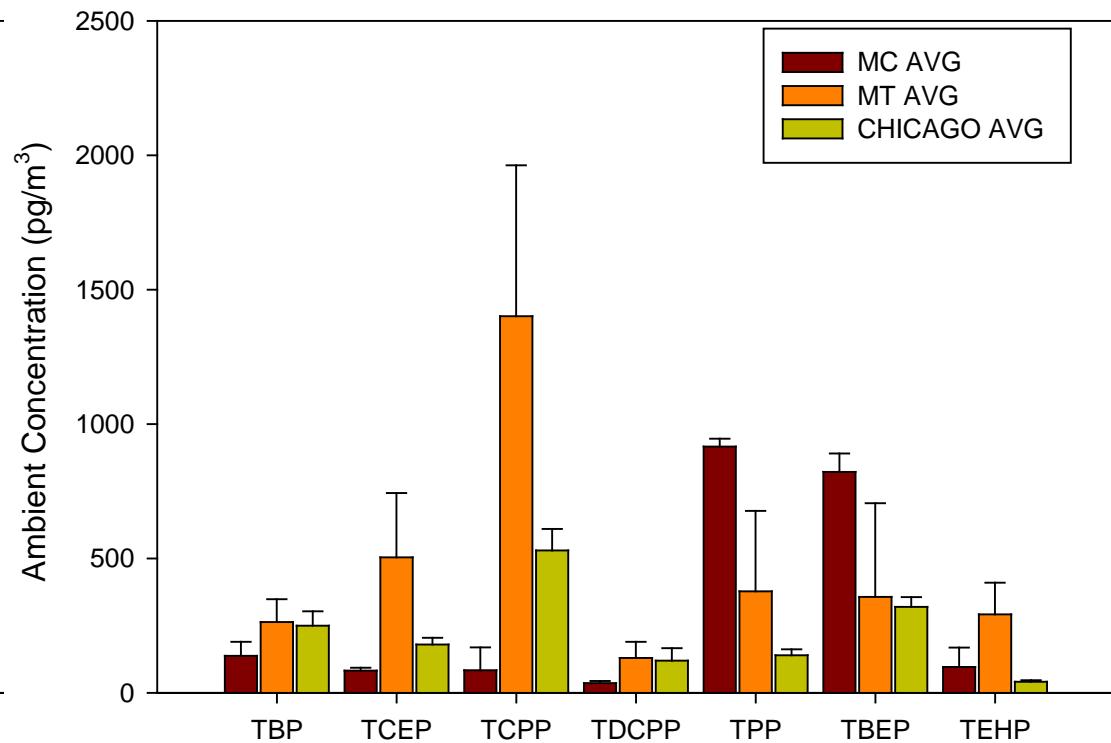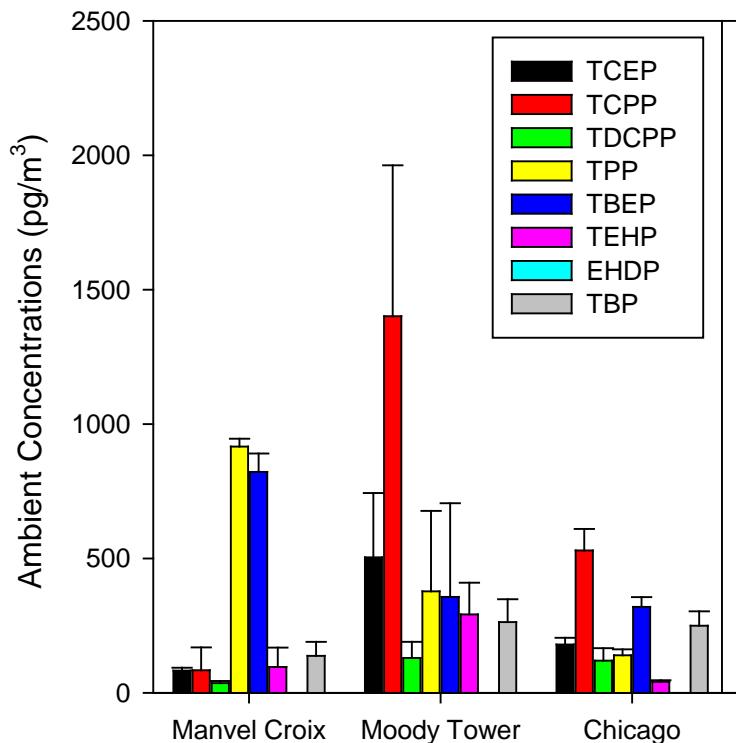

There are few studies of OPEs. Moody Tower has a similar profile to other urban source regions. Manvel Croix shows a similar profile to remote sites. This data suggests significant processing over the urban gradient.

# Current-Use Pesticides (PM TSP)
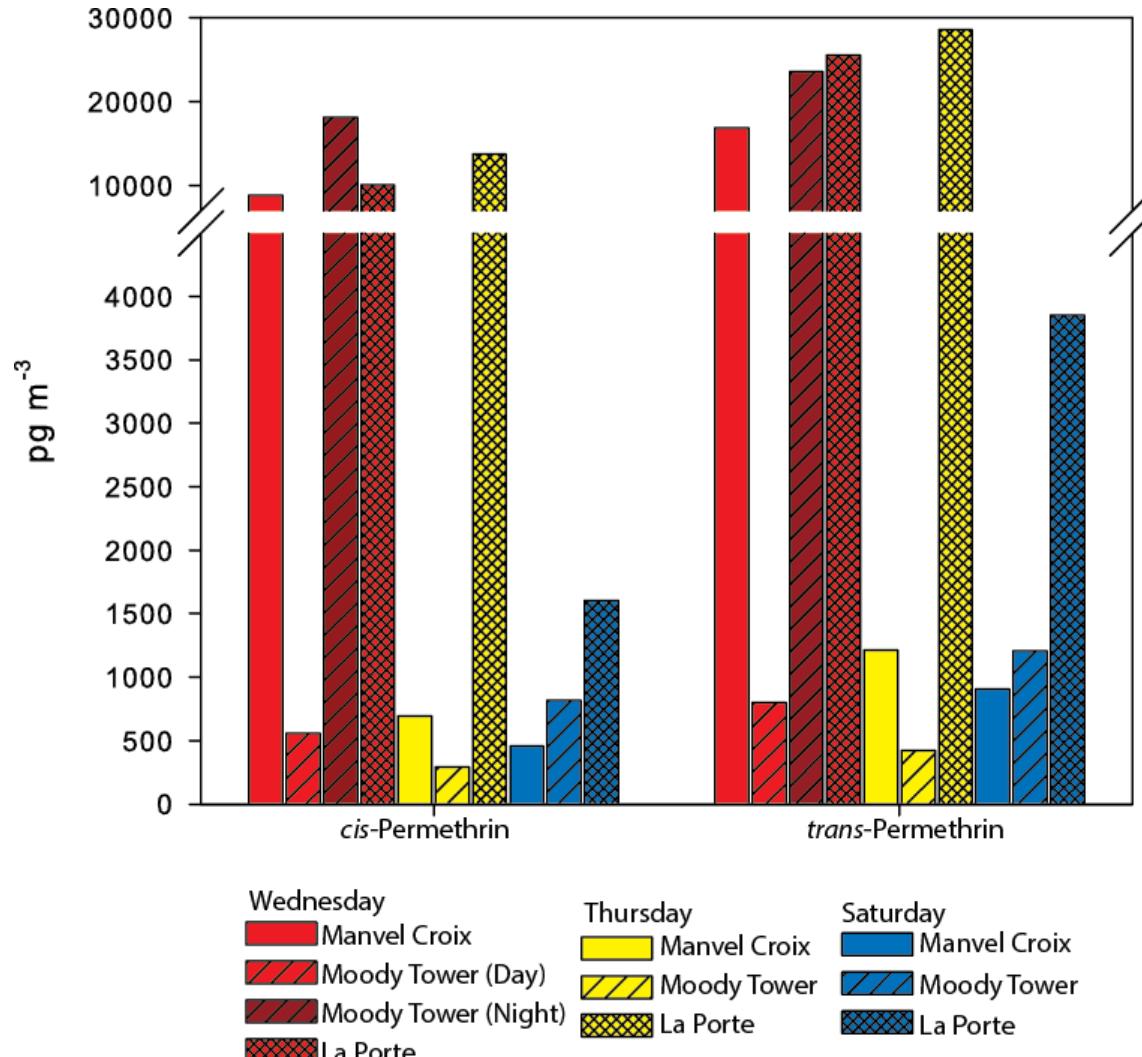
Permethrin and malathion are applied mosquito adulticides with known county application programs (location and time). They are easily measured in Houston $PM_{2.5}$ at all sites. The application and measurement presents an unique opportunity for the investigation of atmospheric transport and oxidation pathways in Houston.

Radiocarbon Data
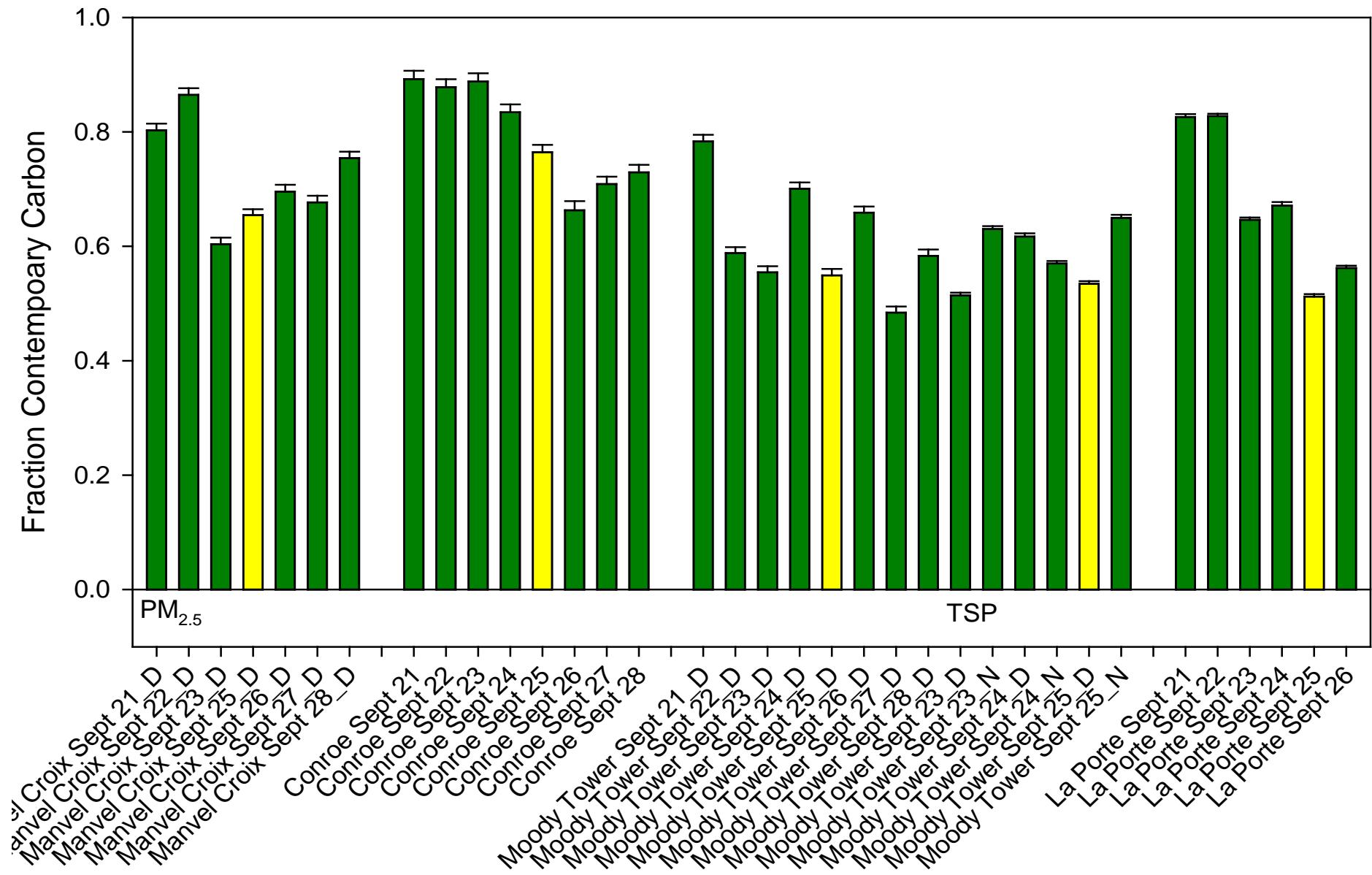
Moody Tower: Contemporary OC
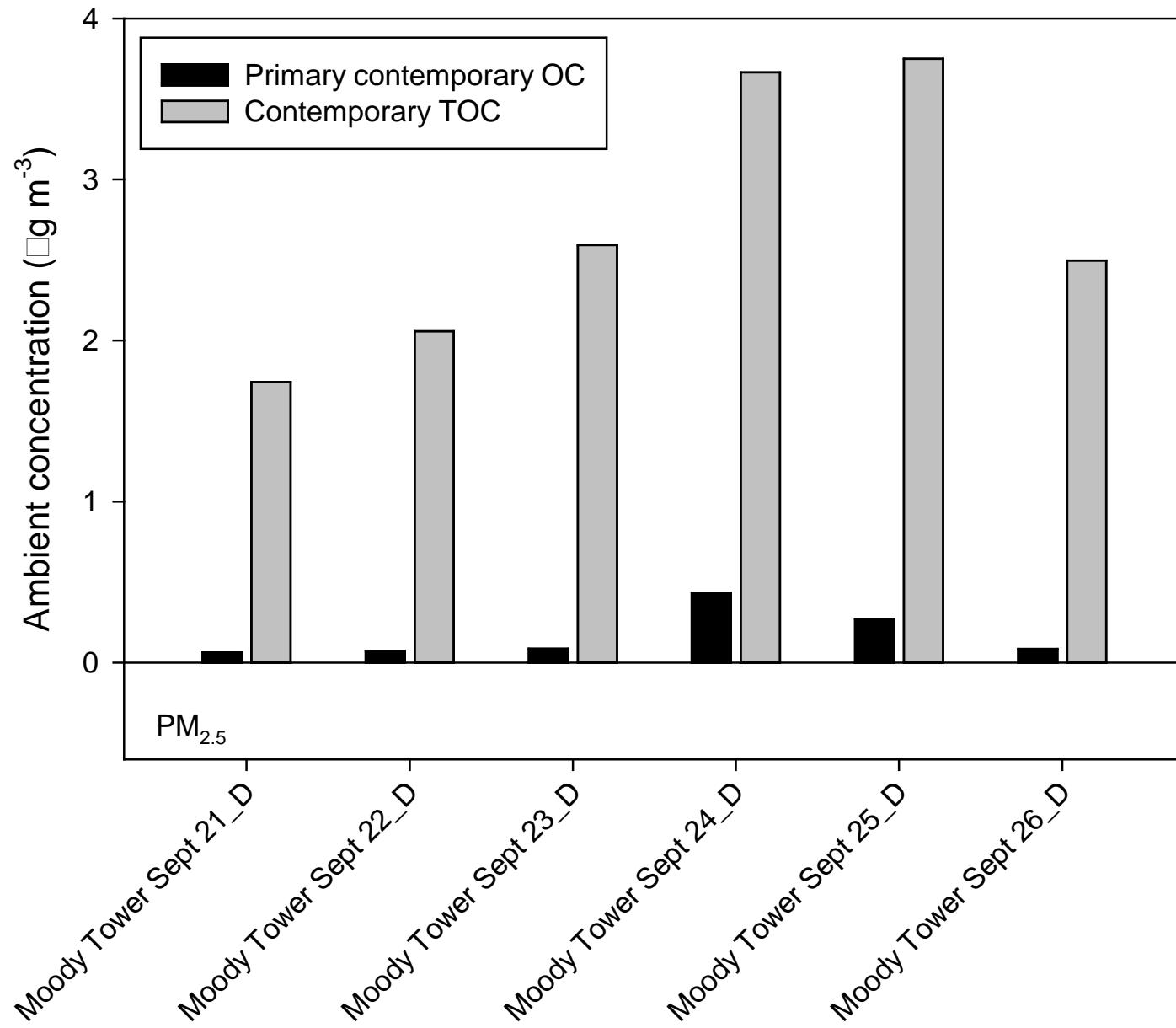
Moody Tower: Fossil OC
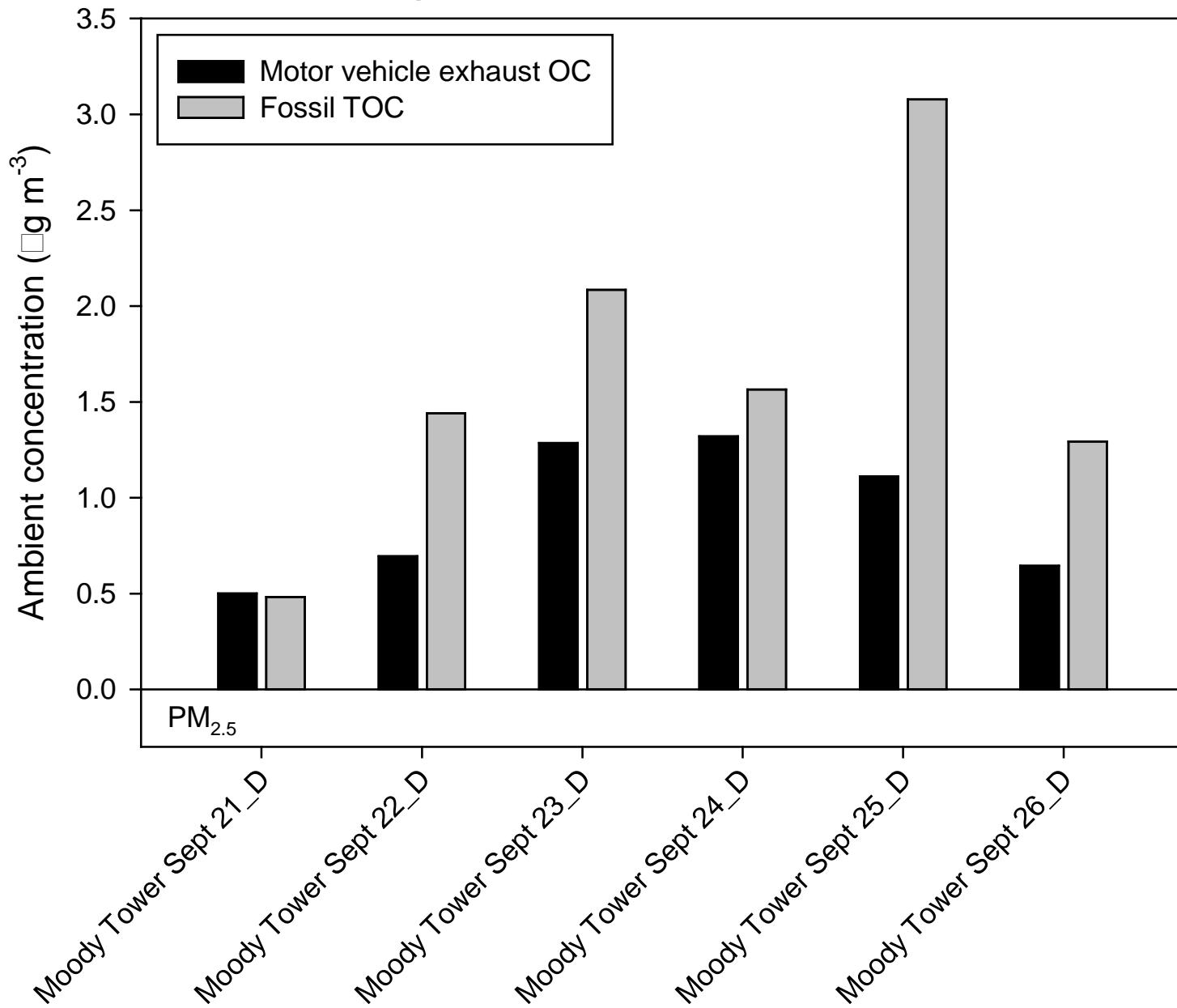
Future questions

- Investigate sources of semi-volatile OC using radiocarbon
- Extend detailed source analysis during DISCOVER-AQ
  - high ship emission events in Houston
  - Early Sept, high primary pollution regime
- Examine processing of particle phase organics with ozone
  - Potential impacts during peak ozone, NOx events
- Seasonal variability of primary vs secondary organic aerosol
  - Radiocarbon and organic tracers
  - Mobile Sampling Trailer: outfitted with PM (TSP and 2.5) NOx, Ozone, Aethalometer, and PTR-MS (VOCs)

Acknowledgements

- Funding – Texas AQRP
- University of Houston – Site Access and Site Modification
- TCEQ – Site Access and Site Modification
- USEPA – Samplers
- University of Wisconsin-Madison – Samplers
- Droplet Measurement Technologies
- USEPA – Filter Collection
- University of Texas, Austin – Filter Collection

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