LOCAL AND REGIONAL SECONDARY ORGANIC AEROSOL FORMATION:

INSIGHTS FROM A YEAR AT PITTSBURGH AND COMPARISONS WITH LOS ANGELES AND ATLANTA

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MOTIVATION

- Organic compounds comprise 20-70% of $PM_{2.5}$ in urban and rural areas of the U.S.
- Organic PM is emitted in particulate form (primary) and formed in the atmosphere from gas-phase emissions (secondary).
- Development of effective control strategies for $PM_{2.5}$ requires knowledge of:
  - Primary vs. secondary contributions.
  - Local vs. regional contributions.

HYPOTHESIS

- Regional transport coupled with secondary formation of sulfate is a dominant contributor to $PM_{2.5}$ in the eastern U.S.
- Homogeneous (gas-phase) photochemistry, surface reactions such as acid catalyzed oligomer formation, and in-cloud processes could all contribute to regional formation of secondary organic aerosol (SOA).
- We hypothesize that regional transport in the eastern U.S. results in dramatically larger SOA contributions to total OC in the east than in the southwestern U.S. (i.e. Los Angeles).

FIELD STUDIES

Southern Calif. Air Quality Study (SCAQS):

2 hr cycle	Claremont, CA	June-Aug. 1987
1-4 hr	Long Beach, CA	Nov. 1987

(No denuder; dynamic blank for each sample)

Atlanta Supersite Experiment:

2 hr	Atlanta GA	Aug. 1999

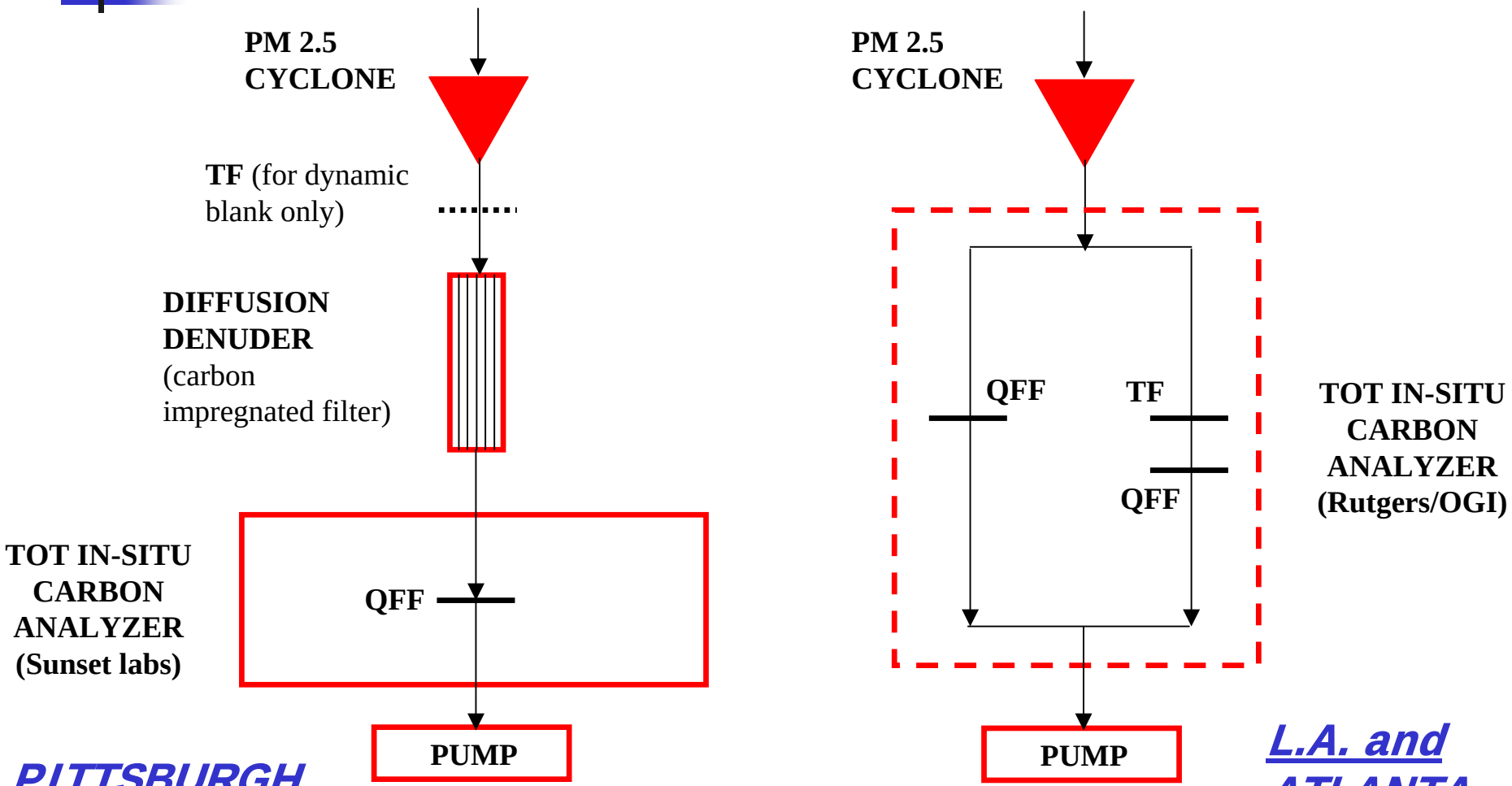
(No denuder; dynamic blank for each sample)

Pittsburgh Air Quality Study (PAQS):

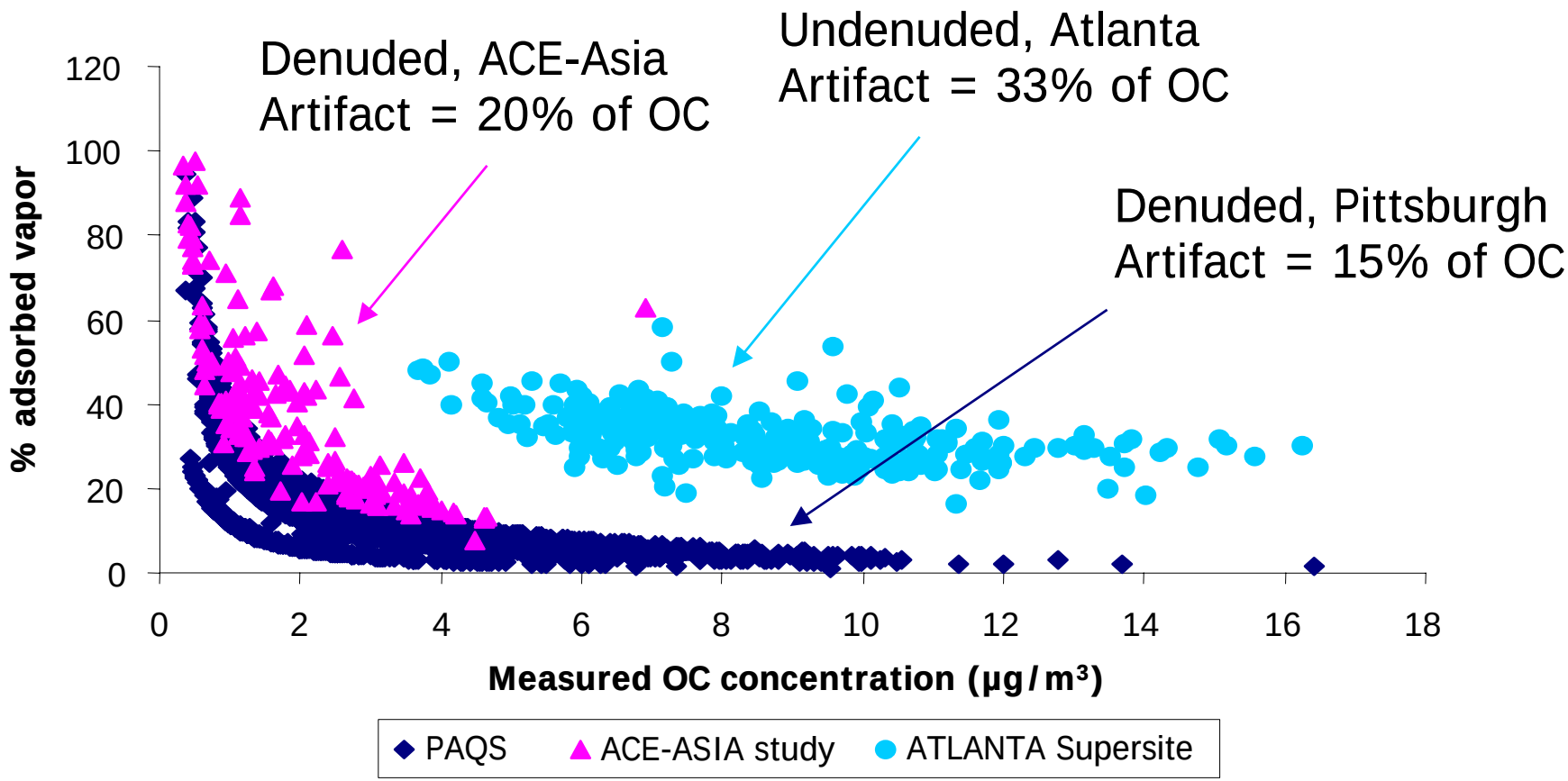
2-4 hr	Pittsburgh, PA	July 2001- August 2002

(Denuder at inlet; periodic dynamic blanks)

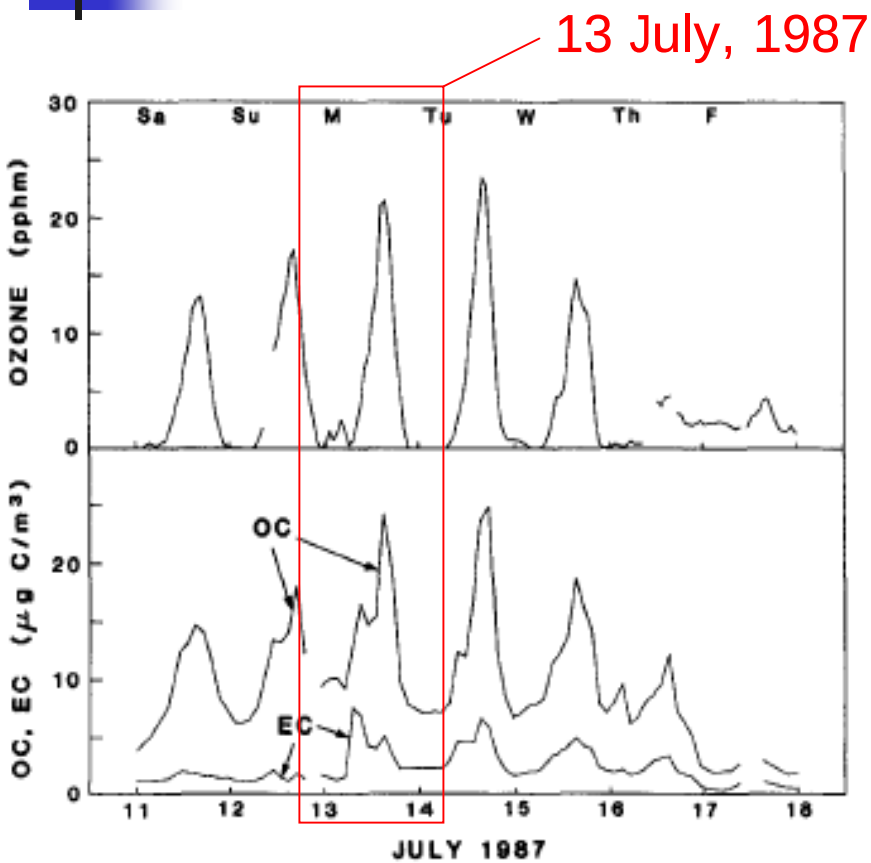
SEMI-CONTINUOUS THERMAL-OPTICAL CARBON ANALYSIS



ADSORPTION ARTIFACT



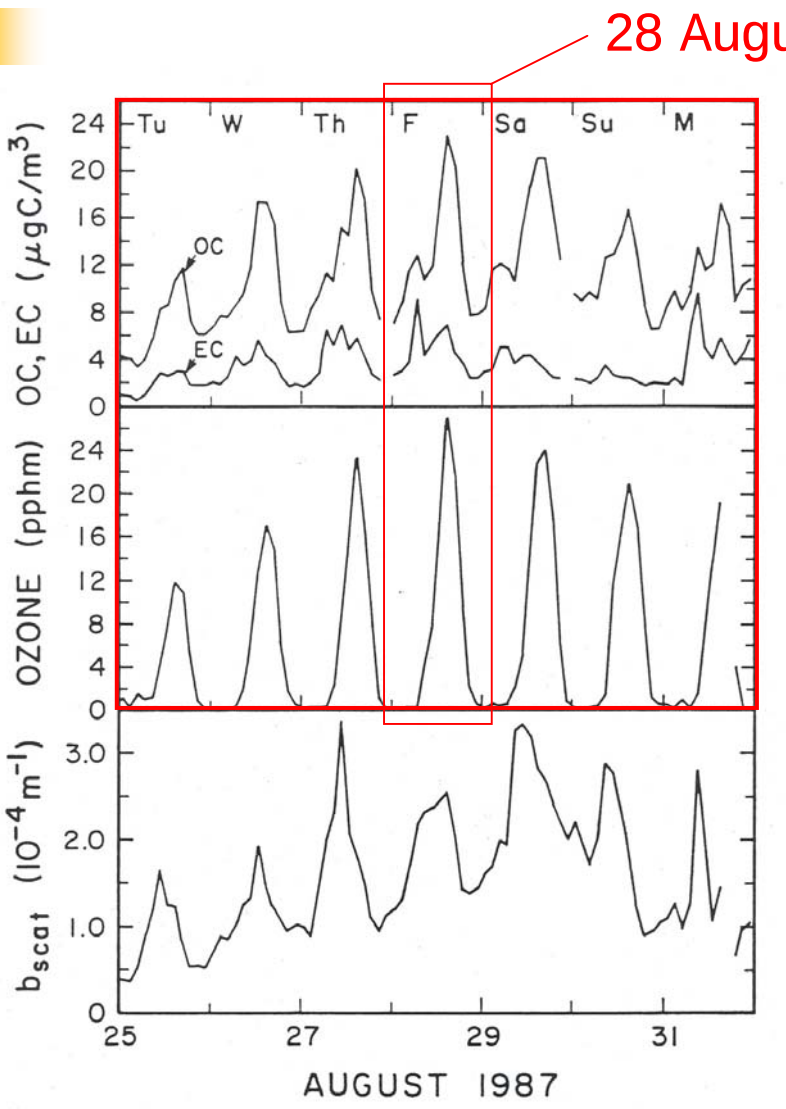
SCAQS - Claremont



***Turpin and Huntzicker*, 1995**

- EC was used as a tracer for primary combustion-generated OC.
- Typically, the afternoon OC peaks (e.g. 13 July) occurred with or just after the O_3 peaks, and cannot be explained by common origin with the EC.
- Afternoon OC peaks are likely to be produced locally (SOA).

SCAQS - Claremont



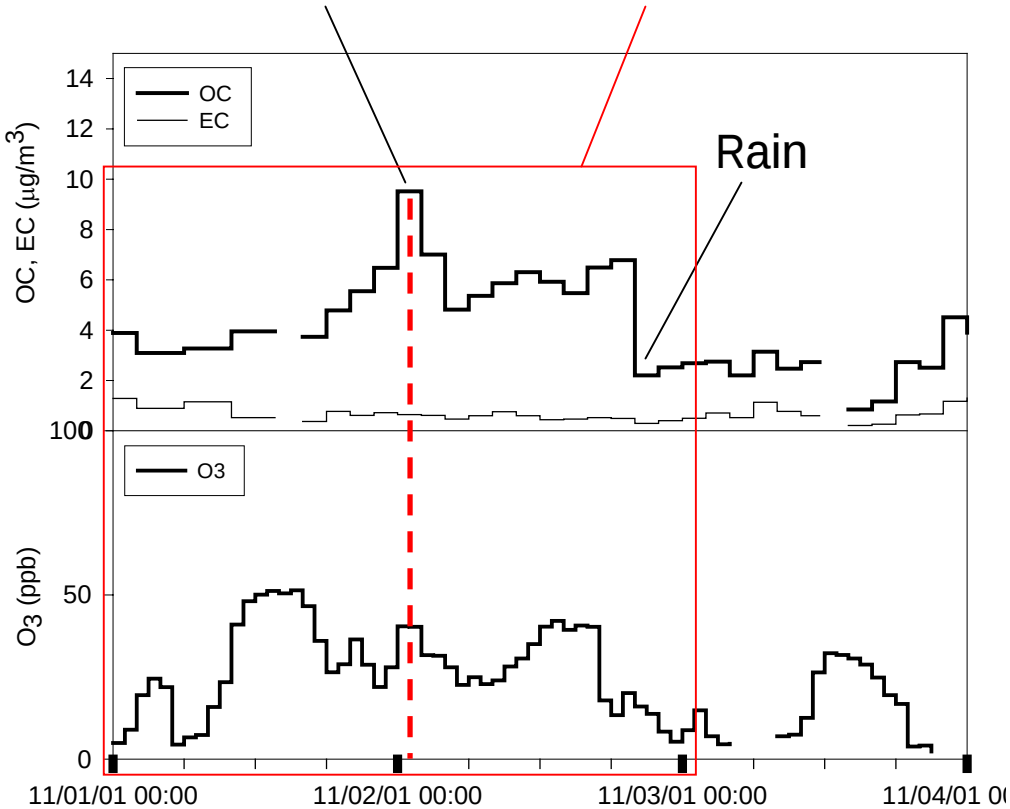
***Turpin and Huntzicker*, 1991**

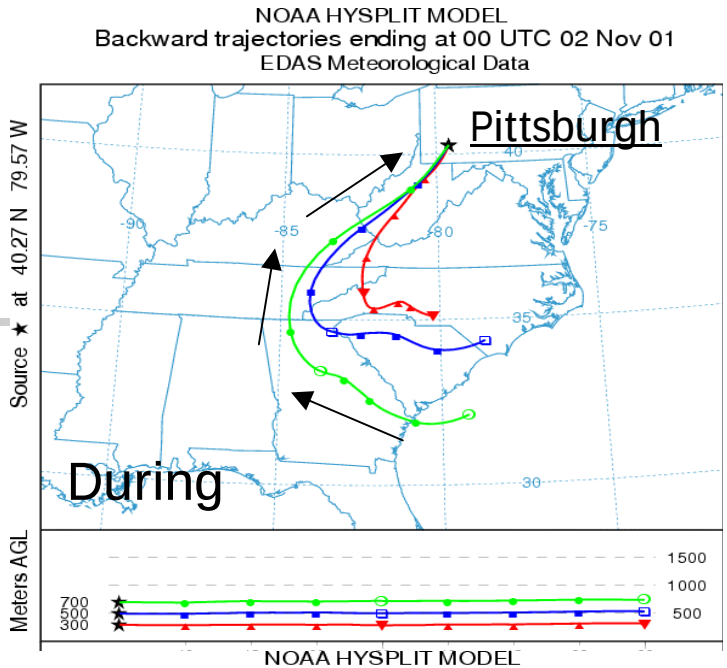
- The afternoon OC peak rises and falls with the O_3 episode.
- The strong diurnal variation of OC suggests that SOA is dominated by material generated that afternoon.

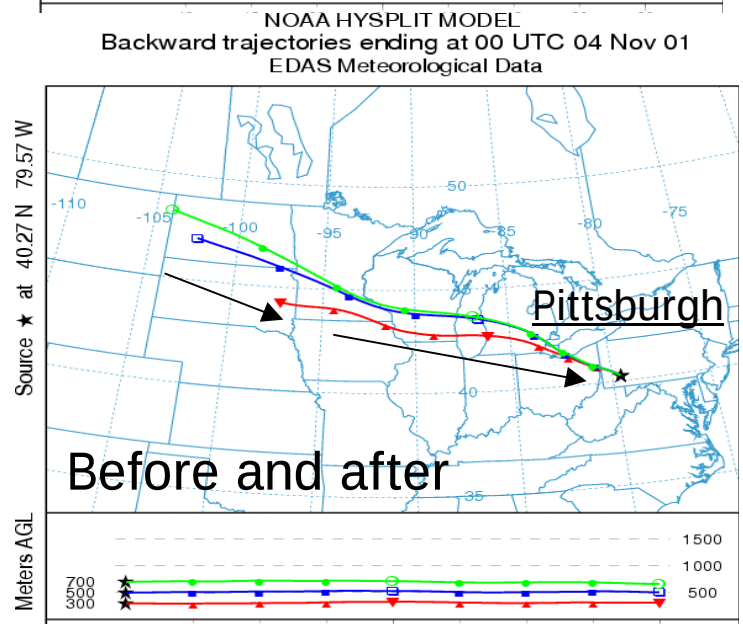
PAQS - Pittsburgh

SOA = 8.04 µg/m^3
(85% measured OC)

1-3 November, 2001



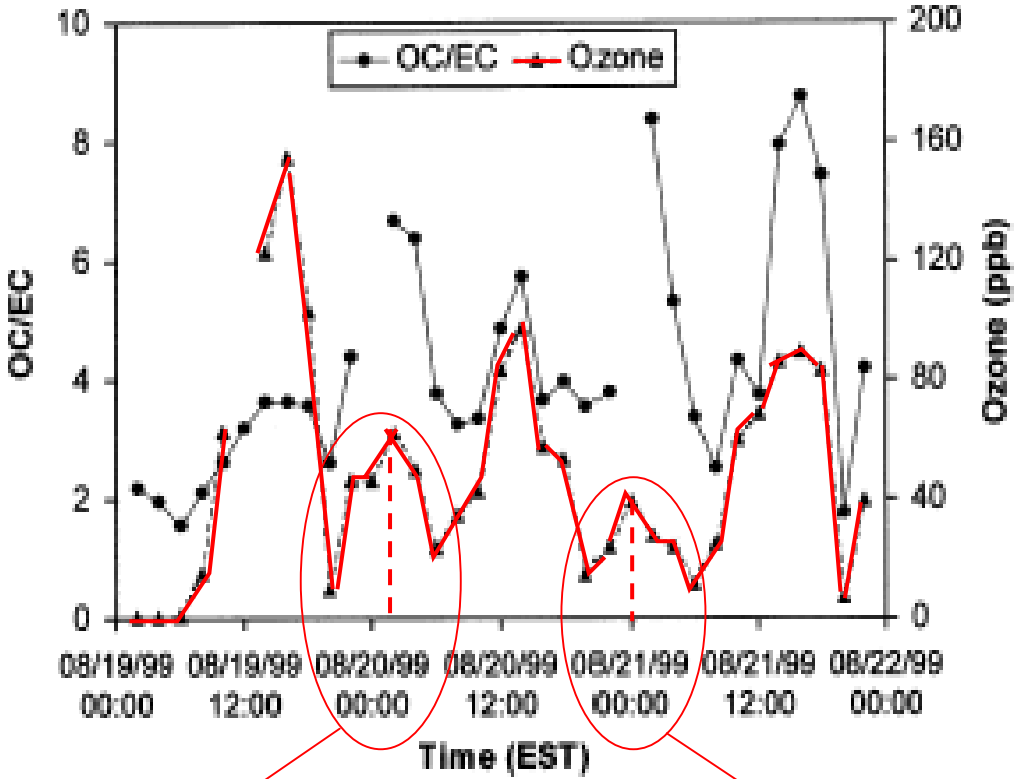




Polidori et al., in preparation

NIGHTTIME O_3 AND SOA PEAKS

***Lim and Turpin,* 2002**

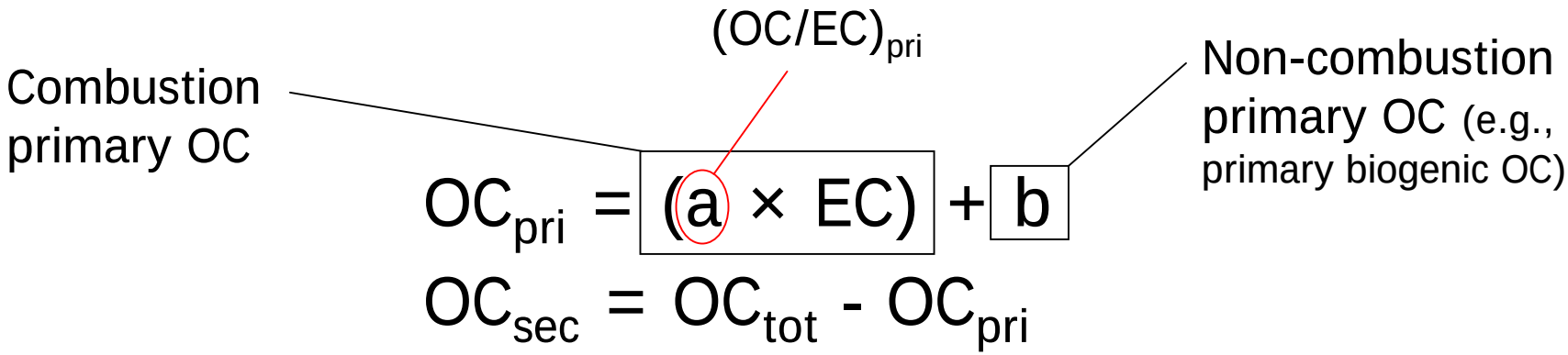


20 August, 1999

21 August, 1999

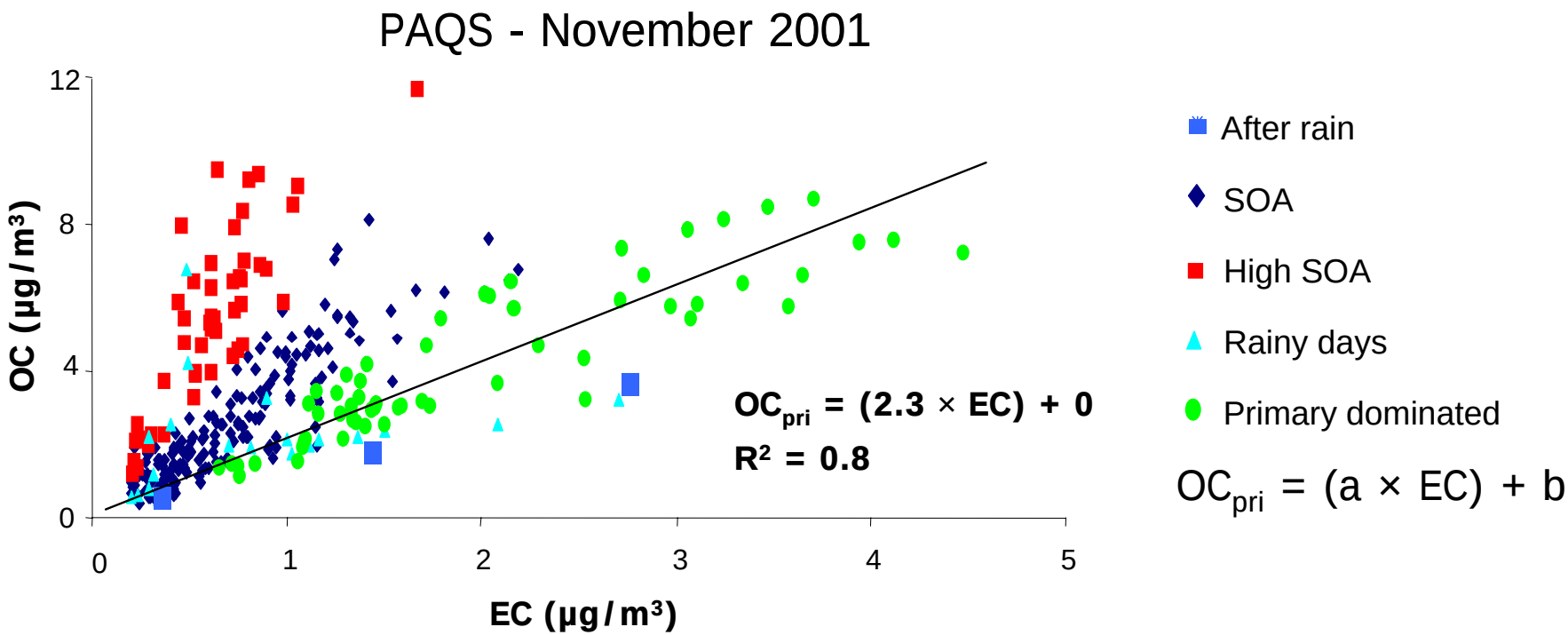
- Concurrent nighttime peaks of O_3 and SOA where measured both in Atlanta and in Pittsburgh.
- Vertical transport of O_3 and SOA from aloft through mechanical turbulence generated by a low-level jet (*Corsmeier et al.,* 1997).
- Particles aloft can be transported for long distances and exposed to conditions quite conductive to photochemistry.

THE EC TRACER METHOD OF SOA ESTIMATION



- Periods dominated by primary emissions: 1-hr [CO] and [NO] > corresponding monthly averages + 1-hr [O_3] and [NOx]/[NO] < corresponding monthly averages.
- Sampling periods affected by rain and storms were not used in the determination of $(OC/EC)_{pri}$.

THE EC TRACER METHOD OF SOA ESTIMATION



- For each month, the slope (a) and the intercept (b) were calculated by regressing OC on EC, using only data dominated by primary emissions (green circles). A Deming linear least-squares regression was used.

CONCLUSIONS: WEST vs EAST

- **Los Angeles Basin:**
  - In Claremont, summertime [SOA] exceeded 40% of the daily [OC] only during five afternoon photochemical smog episodes.
  - SOA is a minor contributor to the annual average particulate OC.
  - SOA is important when planning to reduce acute effects of PM due to peak exposures (i.e. cardiovascular effects), but not a major consideration for meeting annual average NAAQS.
- **Pittsburgh / Atlanta:**
  - SOA accounted 30-40% of monthly average OC from June to November in Pittsburgh, and 44% in Atlanta in August.
  - SOA is a substantial contributor to measured [OC] in the East. This is probably because of multi-day formation during regional transport.
  - SOA has to be considered for meeting annual average NAAQS in eastern U.S.

CONCLUSIONS: EAST COAST

- Regional transport is known to increase substantially the aerosol mass, and to dramatically enhance the hygroscopicity of atmospheric PM in the northeastern U.S. because of the oxidation of SO_2 to particulate sulfate.
- This work suggests that regional transport and, to some extent, vertical transport from aloft, also contributes substantially to ground level [SOA] in the northeastern U.S.

AKNOWLEDGEMENTS

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