

CRPAQS Data Analysis Task 2.7

When and Where Does High O₃ Correspond to High PM_{2.5}?
How Much PM_{2.5} Corresponds to Photochemical End Products?

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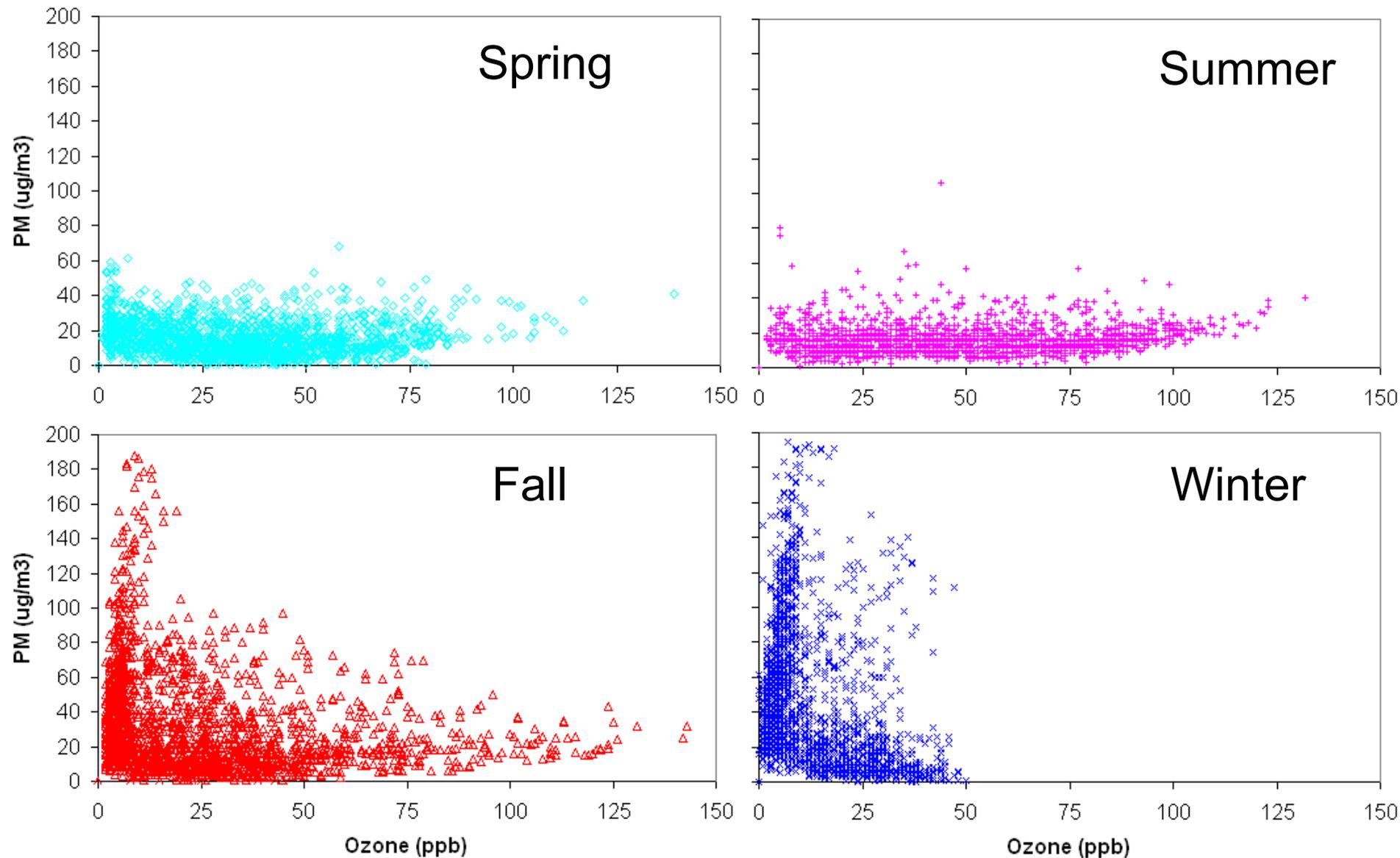
9 March 2003

Discerning O₃-PM Relationships Hypotheses

- Some relationship must exist between O₃ and PM_{2.5} because O₃ and key secondary PM_{2.5} components are governed by the same precursors (NO_x and VOC)
- Season-specific relationships: high O₃ predominantly occurs in summer, but high PM_{2.5} occurs in winter

Do High O_3 and $PM_{2.5}$ Occur Together?

Fresno, Hourly Data



Statistics at Fresno (January - December 2000)

	<u>Annual</u>	<u>Spring</u> ⁽¹⁾	<u>Summer</u> ⁽¹⁾	<u>Fall</u> ⁽¹⁾	<u>Winter</u> ⁽¹⁾
80 th perc. O ₃	50 ppb	52	74	41	24
80 th perc. PM _{2.5}	39 µg/m ³	22	21	50	77
Tot. # samples	8028	2112	1817	2081	2018
# samples w/ high ⁽²⁾ O ₃ & PM	68 (0.8%)	102 (4.8%)	113 (6.2%)	28 (1.3%)	36 (1.8%)
Conditional Probability ⁽³⁾	0.04	0.24	0.31	0.07	0.09

(1) Spring: Mar to May; Summer: Jun to Aug; Fall: Sep to Nov; Winter: Dec to Feb

(2) Defined as the top 20th percentile

(3) $P(\text{high O}_3 \text{ \& PM} \mid \text{high O}_3) = P(\text{high O}_3 \text{ \& PM} \mid \text{high PM})$

Statistics at Bakersfield (January - December 2000)

	<u>Annual</u>	<u>Spring</u> ⁽¹⁾	<u>Summer</u> ⁽¹⁾	<u>Fall</u> ⁽¹⁾	<u>Winter</u> ⁽¹⁾
80th perc. O₃	57 ppb	57	76	45	23
80th perc. PM_{2.5}	29 µg/m³	19	16	38	67
Tot. # samples	7080	1753	1982	1942	1368
# samples w/ high⁽²⁾ O₃ & PM	70 (1.0%)	63 (3.6%)	98 (4.9%)	34 (1.8%)	39 (2.9%)
Conditional Probability⁽³⁾	0.05	0.18	0.25	0.09	0.14

(1) Spring: Mar to May; Summer: Jun to Aug; Fall: Sep to Nov; Winter: Dec to Feb

(2) Defined as the top 20th percentile

(3) $P(\text{high O}_3 \text{ \& PM} \mid \text{high O}_3) = P(\text{high O}_3 \text{ \& PM} \mid \text{high PM})$

Statistics at Angiola (February 2000 - January 2001)

	<u>Annual</u>	<u>Spring</u> ⁽¹⁾	<u>Summer</u> ⁽¹⁾	<u>Fall</u> ⁽¹⁾	<u>Winter</u> ⁽¹⁾
80 th perc. O ₃	51 ppb	54	66	50	32
80 th perc. PM _{2.5}	27 µg/m ³	16	15	32	66
Tot. # samples	6717	1766	1565	1744	1639
# samples w/ high ⁽²⁾ O ₃ & PM	109 (1.6%)	99 (5.6%)	75 (4.8%)	47 (2.7%)	98 (6.0%)
Conditional Probability ⁽³⁾	0.08	0.28	0.24	0.13	0.30

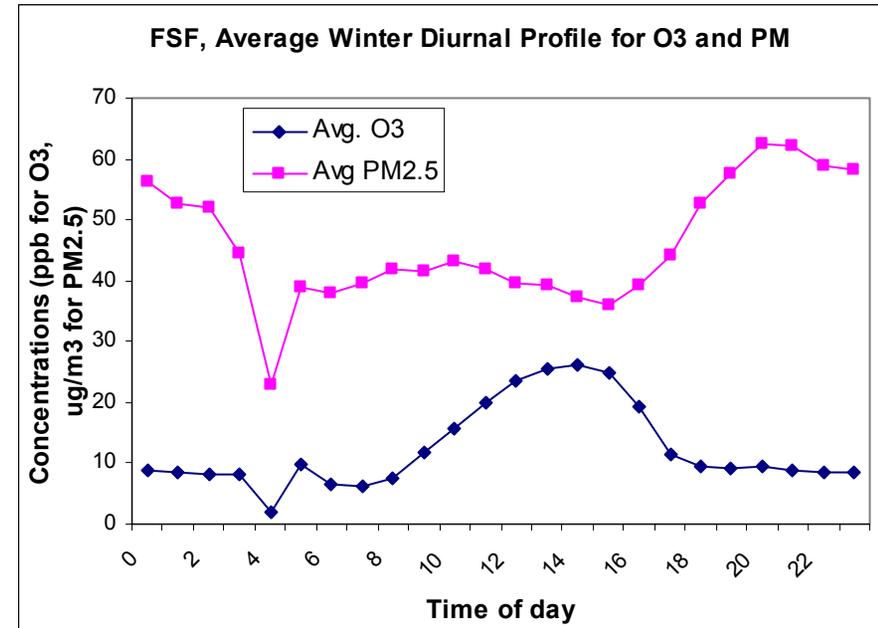
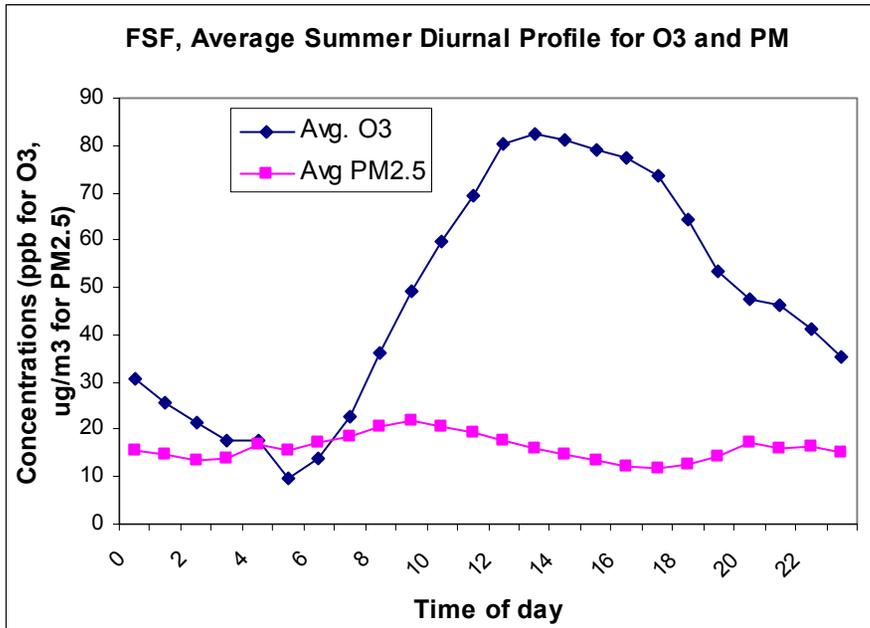
(1) Spring: Mar to May; Summer: Jun to Aug; Fall: Sep to Nov; Winter: Dec to Feb

(2) Defined as the top 20th percentile

(3) $P(\text{high O}_3 \text{ \& \; PM} \mid \text{high O}_3) = P(\text{high O}_3 \text{ \& \; PM} \mid \text{high PM})$

High Hourly O₃ & PM Do Not Frequently Occur Together

- Seasonality: O₃ high in summer, PM high in winter
 - At all three sites, joint high O₃ and PM on an annual basis most frequently recorded in October
- Diurnal profile:



Spatial Differences in the O₃-PM Relationship

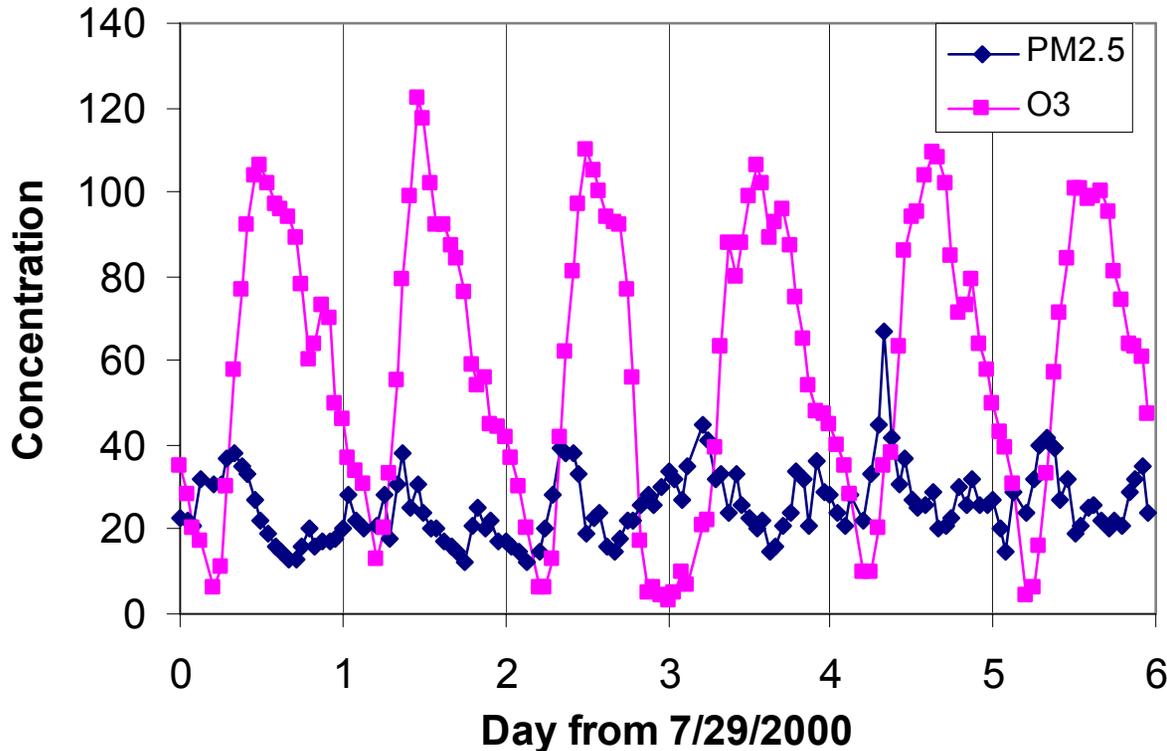
- Angiola: rural site
 - Winter > Spring > Summer > Fall > Annual
- Bakersfield and Fresno: urban sites
 - Summer > Spring > Winter > Fall > Annual
- High O₃ and PM occur together more frequently in Angiola than at Bakersfield and Fresno except during summer

Summer O₃-PM Relationship in Fresno

- Hypothesis: high O₃ and high PM both due to active day-time photochemistry
 - SOA formation accelerated due to availability of O₃ and other oxidants
 - Gas-phase HNO₃ formation increases due to availability of OH
- Expectation: Diurnal profile of both O₃ and PM show peak concentrations in the late afternoon when high O₃ and PM occur together

Diurnal Profiles of O₃ and PM

Fresno, Ozone and PM Time Series



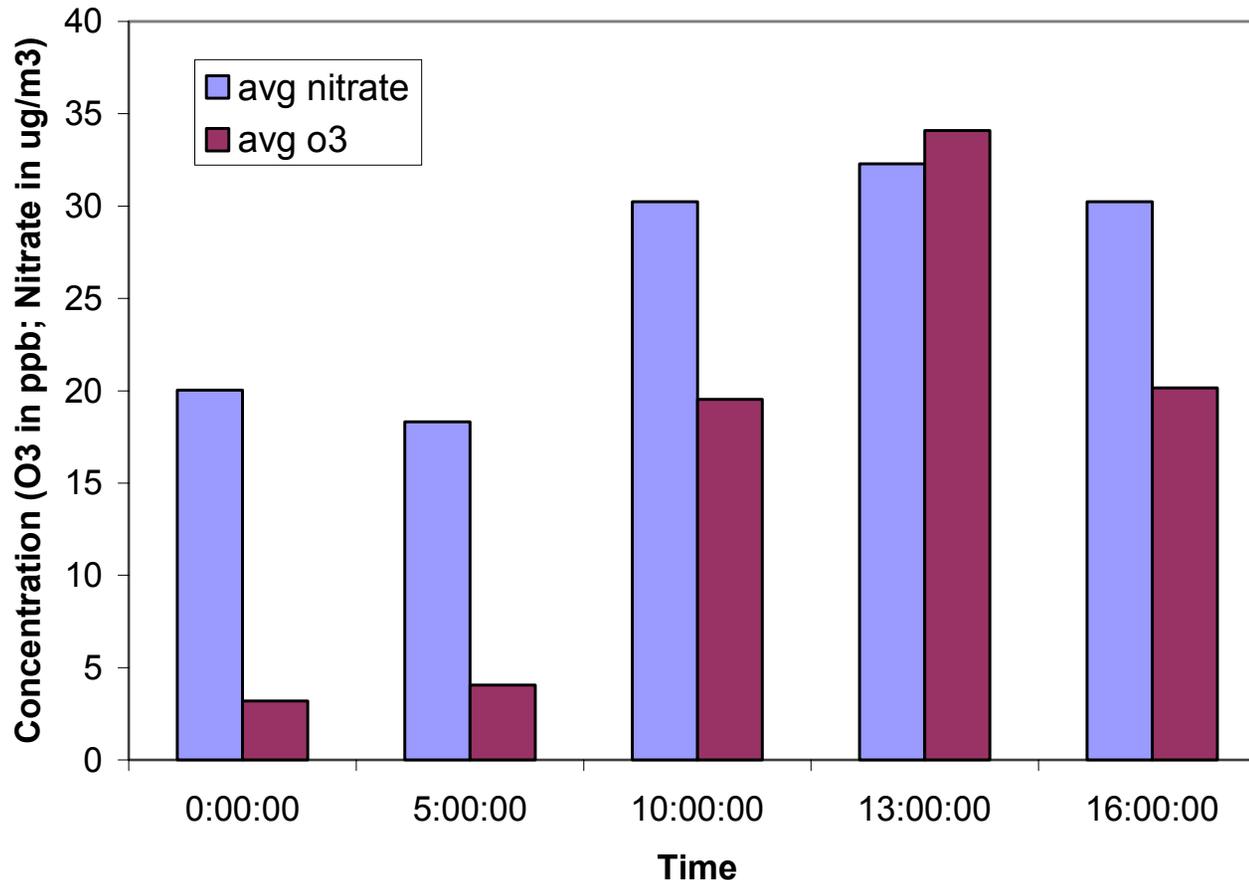
- PM concentrations peak during mid morning on days that record high O₃ and PM
- Afternoon PM typically lower

Diurnal profile inconsistent with hypothesis:
Factor(s) other than local photochemical production drive high PM concentrations

Winter O₃-PM Relationship in Angiola

- Hypothesis 1: high O₃ and high PM nitrate both due to active day-time photochemistry
- Hypothesis 2: high nighttime PM nitrate formation due to leftover high daytime O₃
- Expectation: For Hypothesis 1: diurnal profile of both O₃ and PM show peak concentrations in the late afternoon. For Hypothesis 2, out-of-phase diurnal profile.

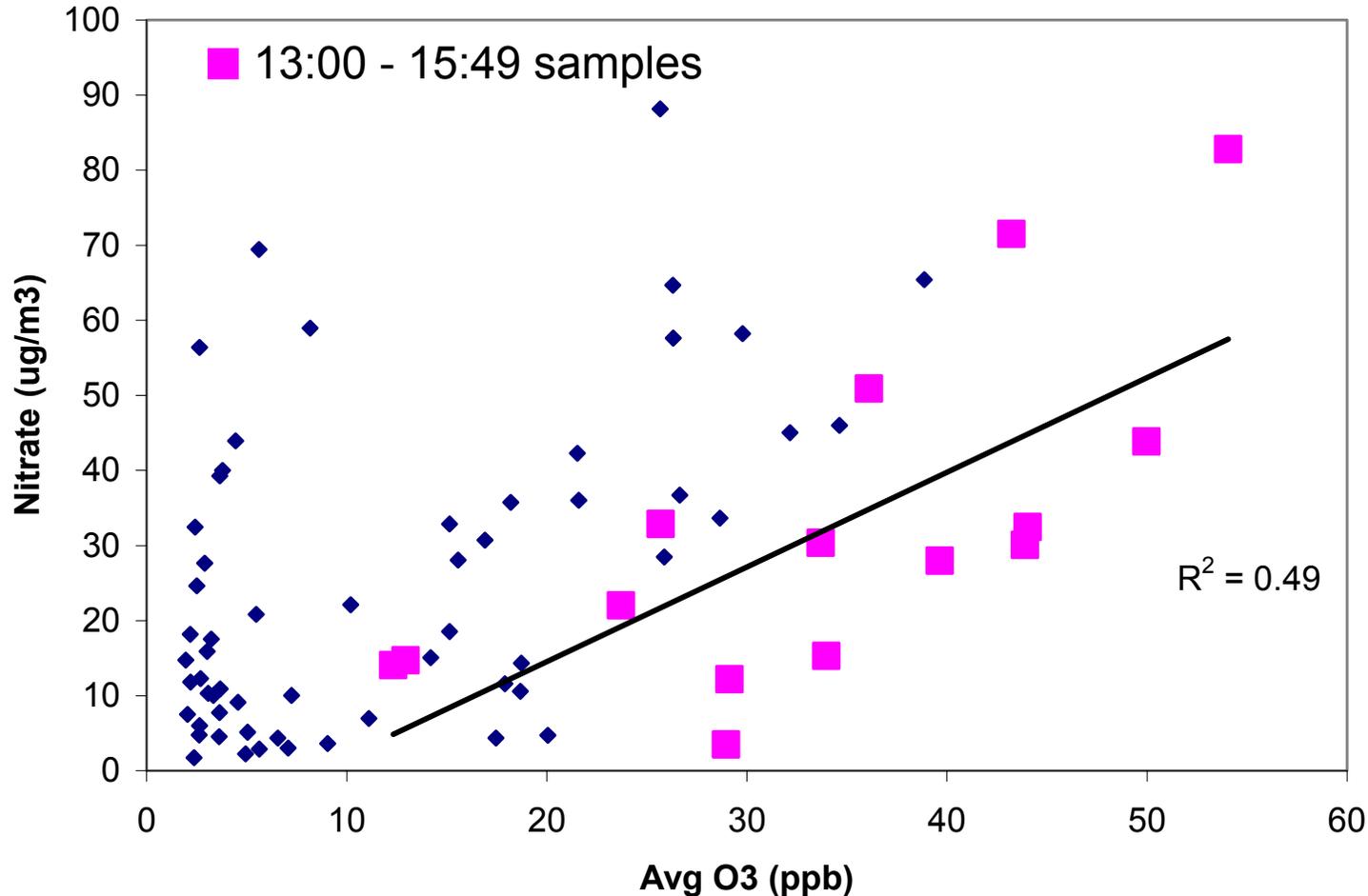
Diurnal Profile of O₃ and Nitrate Angiola, 15 Episode Days



Diurnal profile consistent with daytime nitrate formation hypothesis.

Formation may be local or regional

Do High O₃ Correlate with High Nitrate Formation in Angiola?



Correlation between Peak NO₃ and O₃ significant.
 Correlation via OH or NO₂ + O₃ reaction?

- Obtain PM composition data for summer
- Analyze the relationship of individual secondary component with respect to ozone during fog episodes