

Rapid Science Synthesis

Question F: How do the mesoscale chemical environments (NO_x-sensitive ozone formation vs radical-sensitive ozone formation) vary spatially and temporally in Houston, Dallas and eastern Texas? Which mesoscale chemical environments are most closely associated with high ozone and aerosol?

Question K: How can observation and modeling approaches be used for determining:

- (i) the sensitivities of high ozone in the HGB non-attainment area to the precursor VOC and NO_x emissions, and
- (ii) the spatial/temporal variation of these sensitivities?

Ozone sensitivities to VOC and NO_x
emissions - Observation-based approach

HGB

David Parrish - NOAA ESRL

WP-3D Research Folks

Ronald H Brown Research Folks

This Presentation:

- Investigate ambient measurements of indicator species for VOC vs. NO_x sensitivity.
- Examine what 2000 measurements have told us.
- Examine what 2006 measurements have begun telling us.

Observation-based methods (OBMs) for analyzing urban/regional ozone production and Ozone-NO_x-VOC sensitivity.*

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*<http://www-personal.engin.umich.edu/~sillman/obm.htm>

Why Select this method?

- Integrated total O₃ production approach, not instantaneous O₃ production approach; i.e. designed to answer:
How does maximum O₃ respond to changes in VOC versus changes in NO_x emissions?
- Fits well with analysis that NOAA group has pioneered.
- Utilizes measurements NOAA WP-3D and Ronald Brown make very well.
- Most fully developed method.

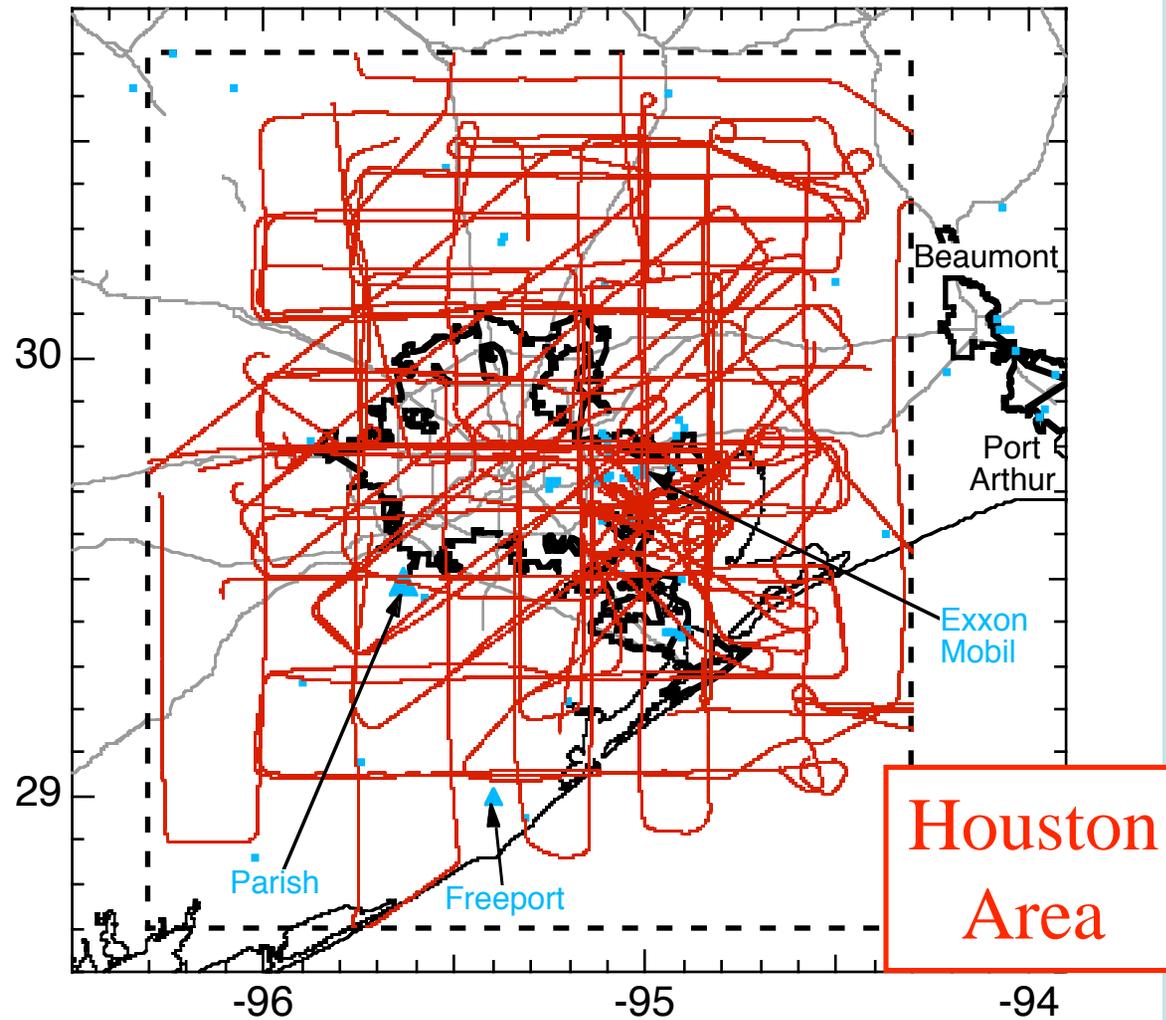
Observation-based methods (OBMs) for analyzing urban/regional ozone production and Ozone-NO_x-VOC sensitivity.

Based on 6 modeling studies throughout the US

Location	Photochemistry	Reference
Nashville	Modified Lurmann et al., 1986	Sillman et al., 1998
Lake Michigan	“	Sillman, 1995
Northeast Corridor	“	Sillman, 1995
Atlanta	CB4 (Gery et al., 1989)	Sillman et al., 1997
San Joaquin	“	Sillman et al., 2001
Los Angeles	“	Godowitch et al., 1994; Sillman et al., 1997

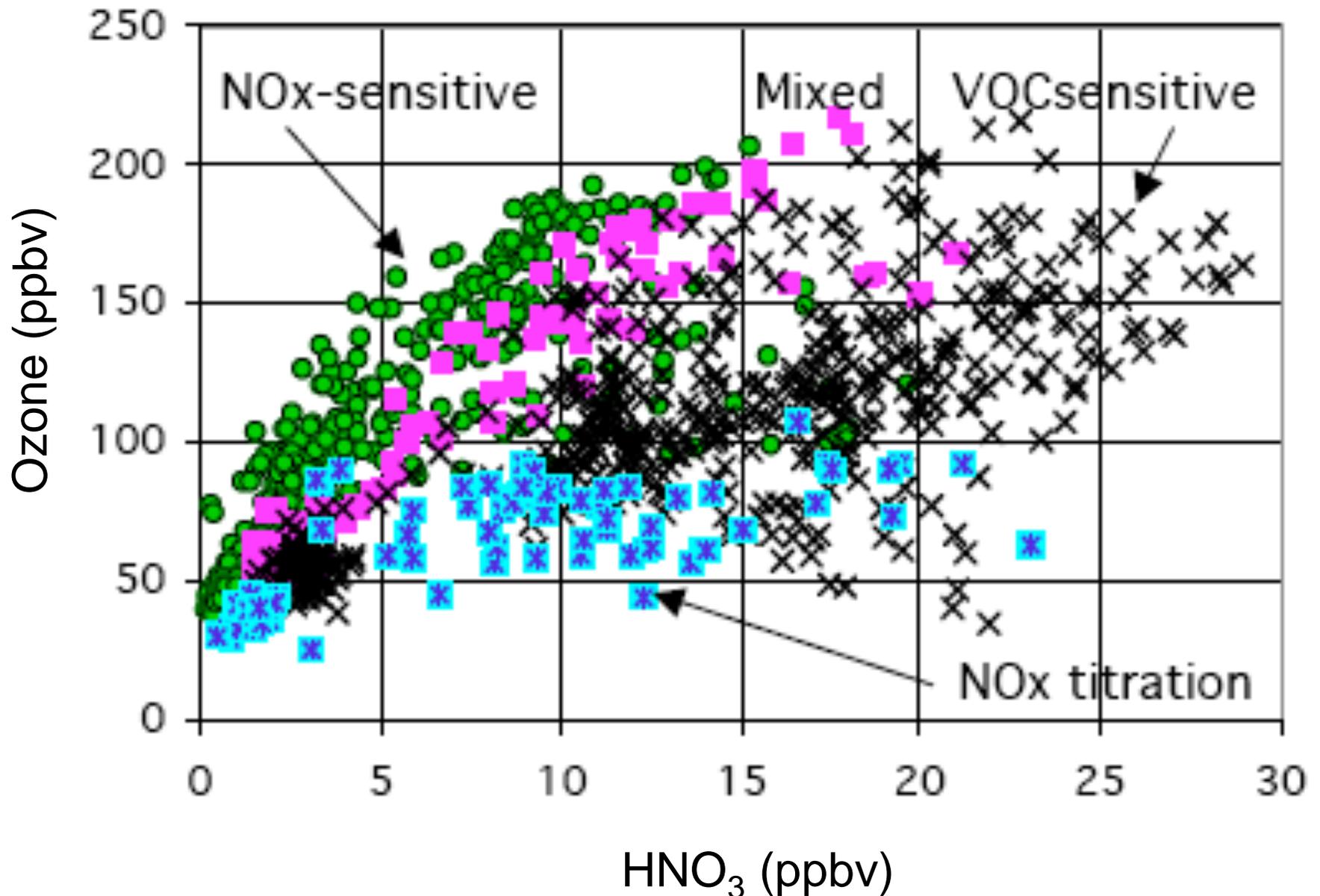
Caveat: Analysis focused on maximum O₃, not 8-hour average

What have 2000 measurements told us?

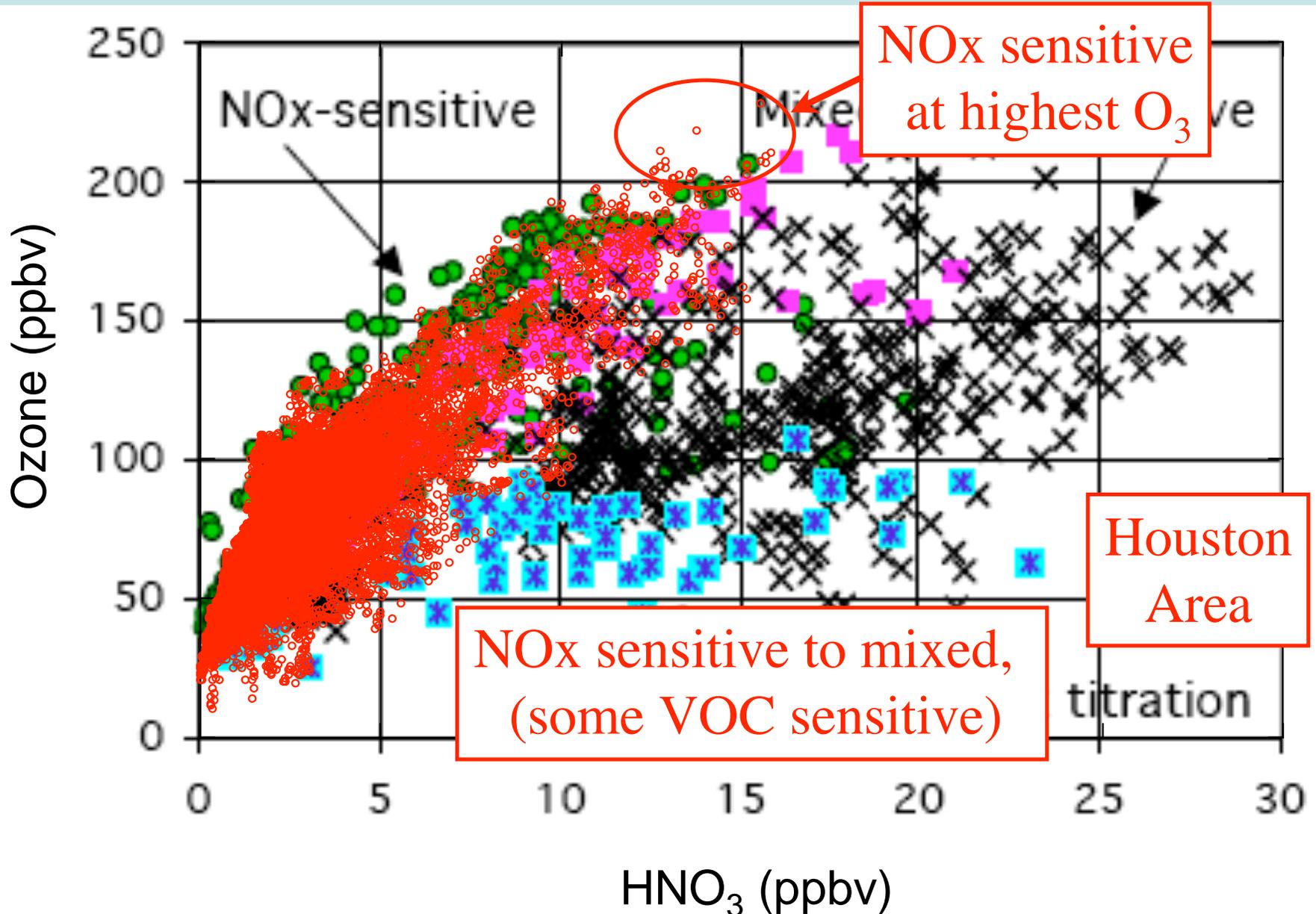


Examine all 5 sec avg data in PBL

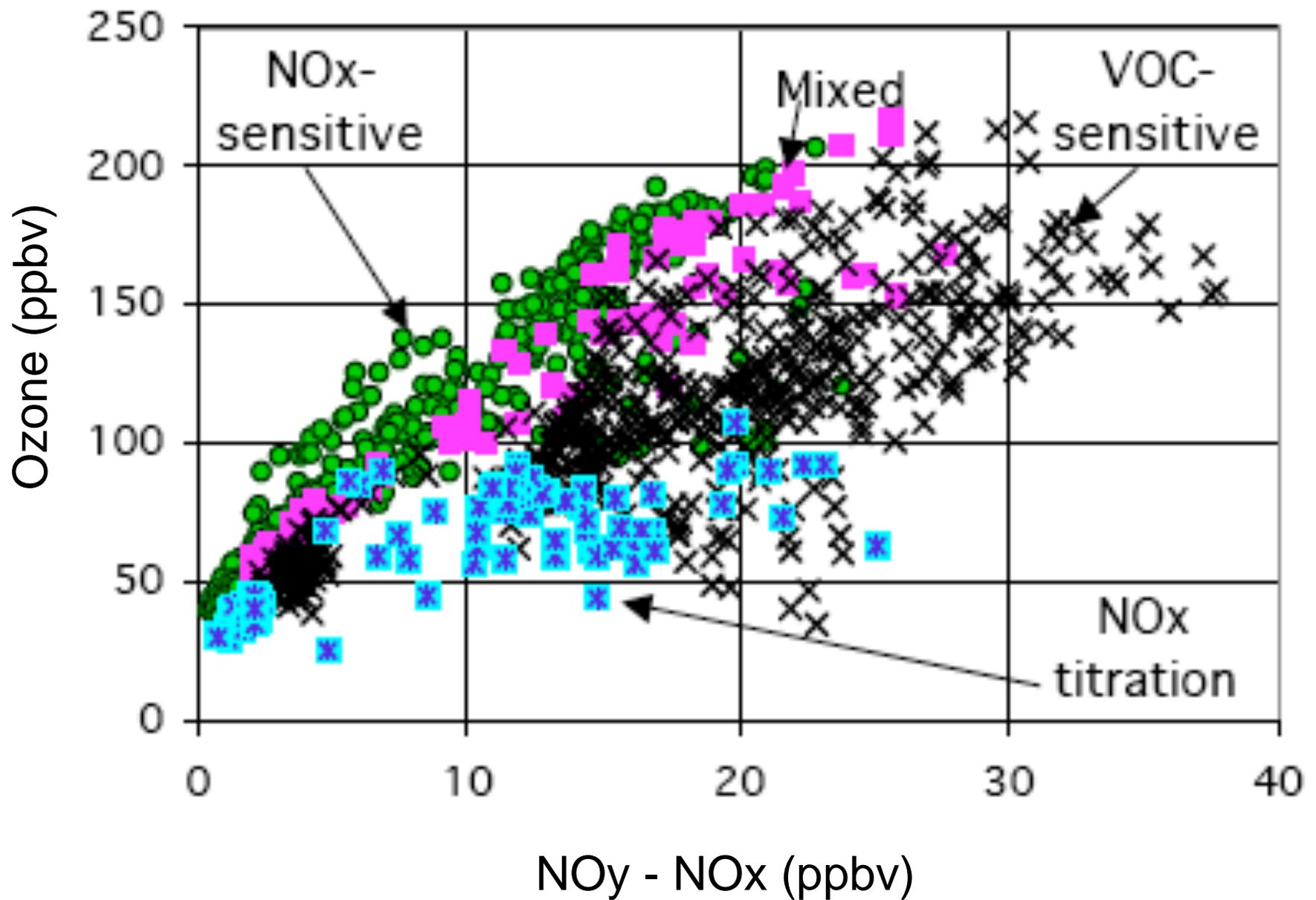
Sillman: Observation-based methods (OBMs)



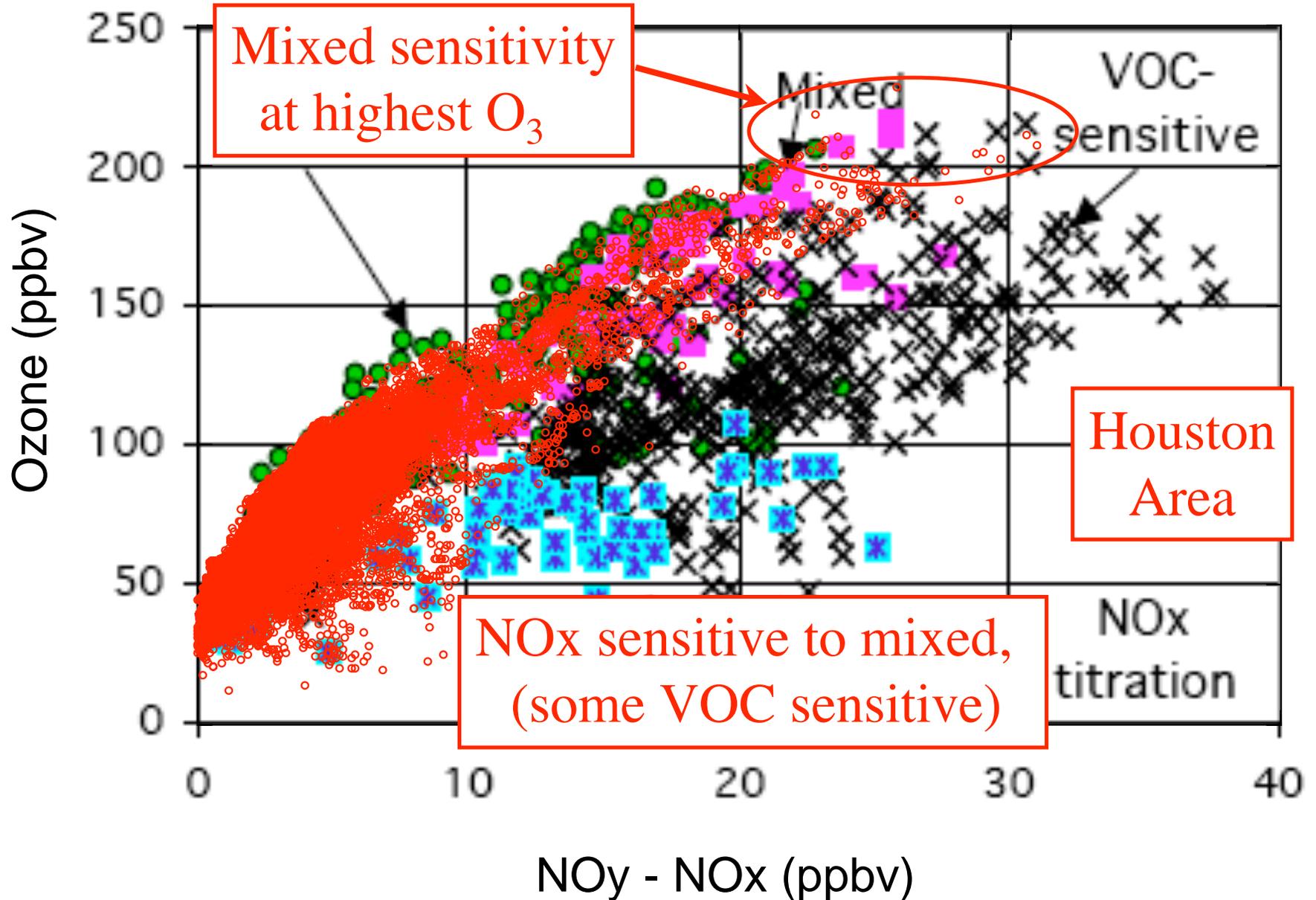
What have 2000 measurements told us?



What have 2000 measurements told us?



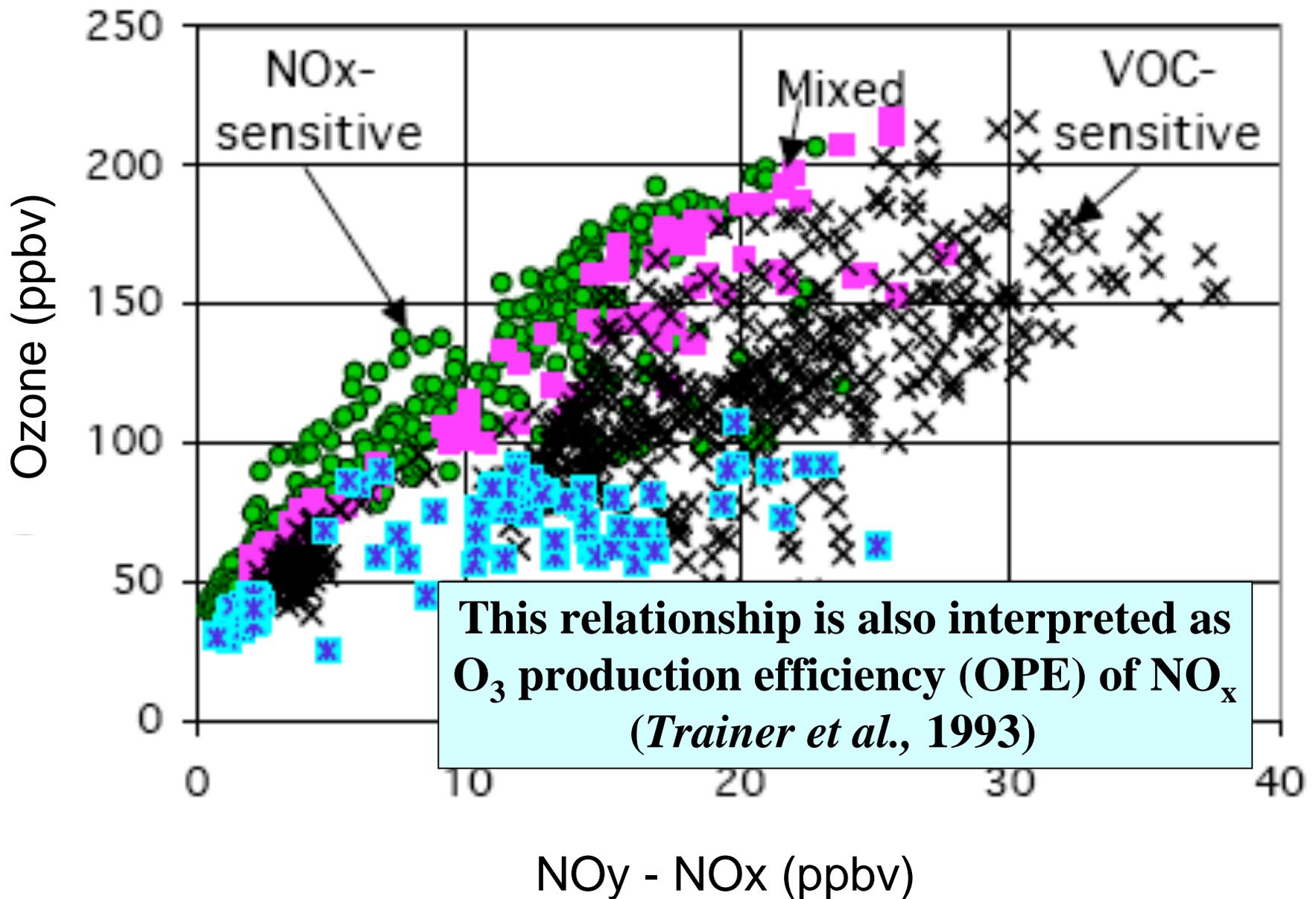
What have 2000 measurements told us?



Tentative Findings

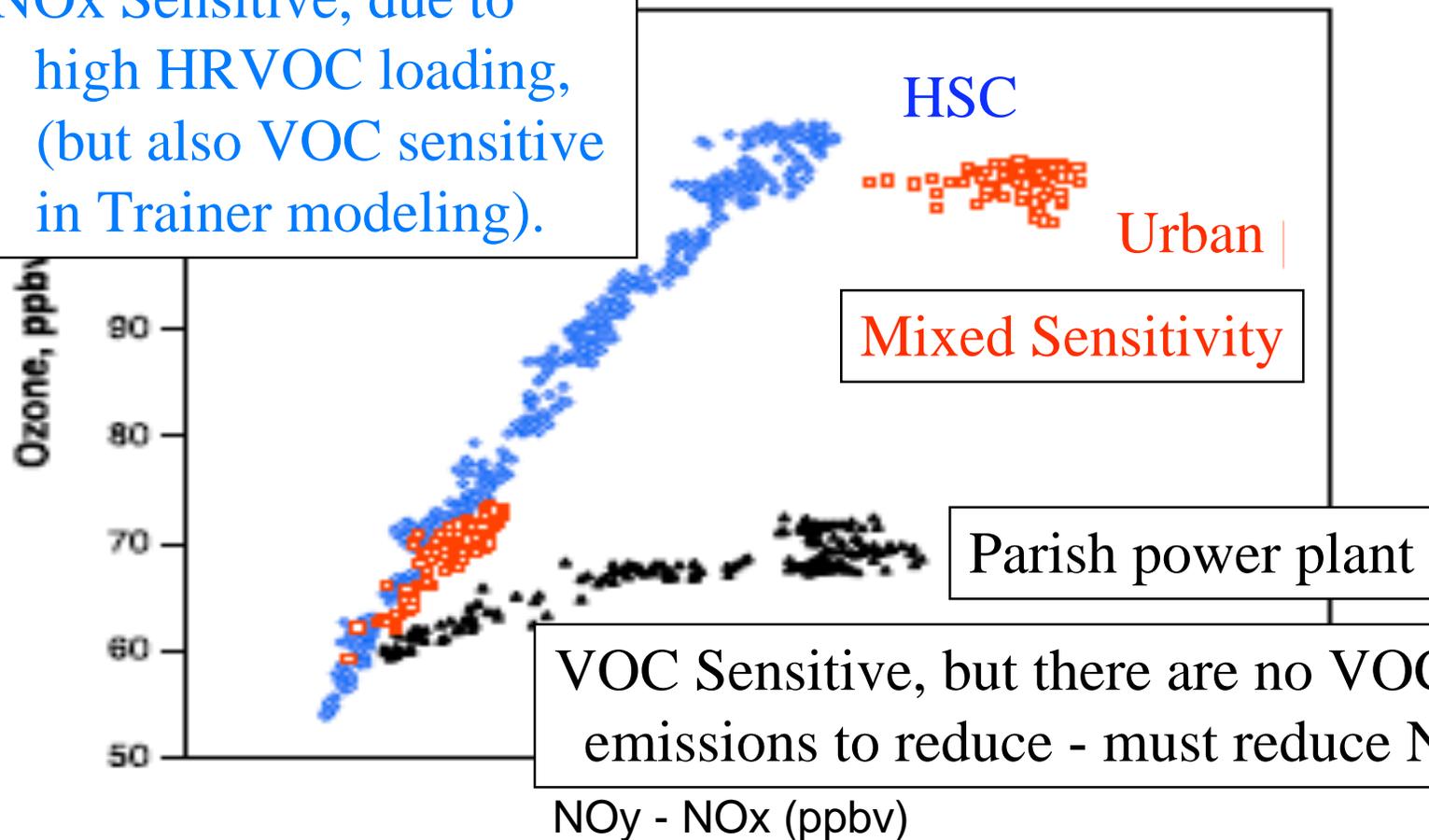
- 1) Caution: Indicator species are not fool-proof. They can give ambiguous results.**

What have 2000 measurements told us?



What have 2000 measurements told us?

NO_x Sensitive, due to high HRVOC loading, (but also VOC sensitive in Trainer modeling).



Ryerson et al., 2003

Effect of petrochemical industrial emissions of reactive alkenes and NO_x on tropospheric ozone formation in Houston, Texas

How can NO_x sensitive also be VOC sensitive???

1) OPE and rate of O₃ production are both important, especially for highest O₃ episodes in Houston (THOEs).

2) Plumes that produce THOEs are concentrated in both NO_x and HRVOC, and relatively compact.

3) HRVOC loading is high enough that OPE is maximized - Therefore NO_x sensitive according to indicator species.

4) The higher the HRVOC loading, the faster the rate of O₃ production, thus higher O₃ levels are reached before plume has chance to dilute and disperse.

5) Meteorological conditions in Houston help to slow dilution and dispersion.

Tentative Findings

1) Caution: Indicator species are not fool-proof. They can give ambiguous results.

2) Indicator Species Approach does not necessarily give useful and reliable answers.

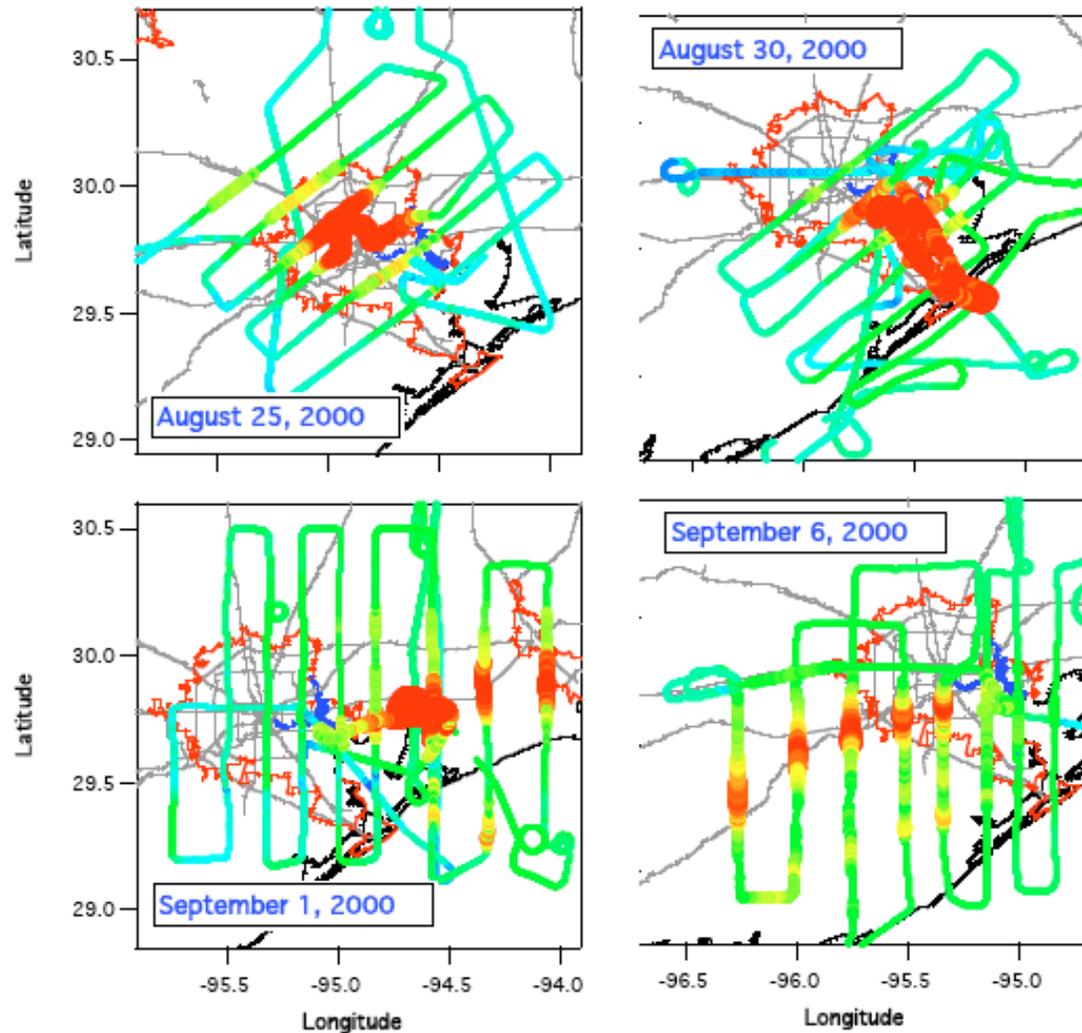
Chemical and meteorological influences on extreme (>150 ppbv) ozone exceedances in the Houston metropolitan area

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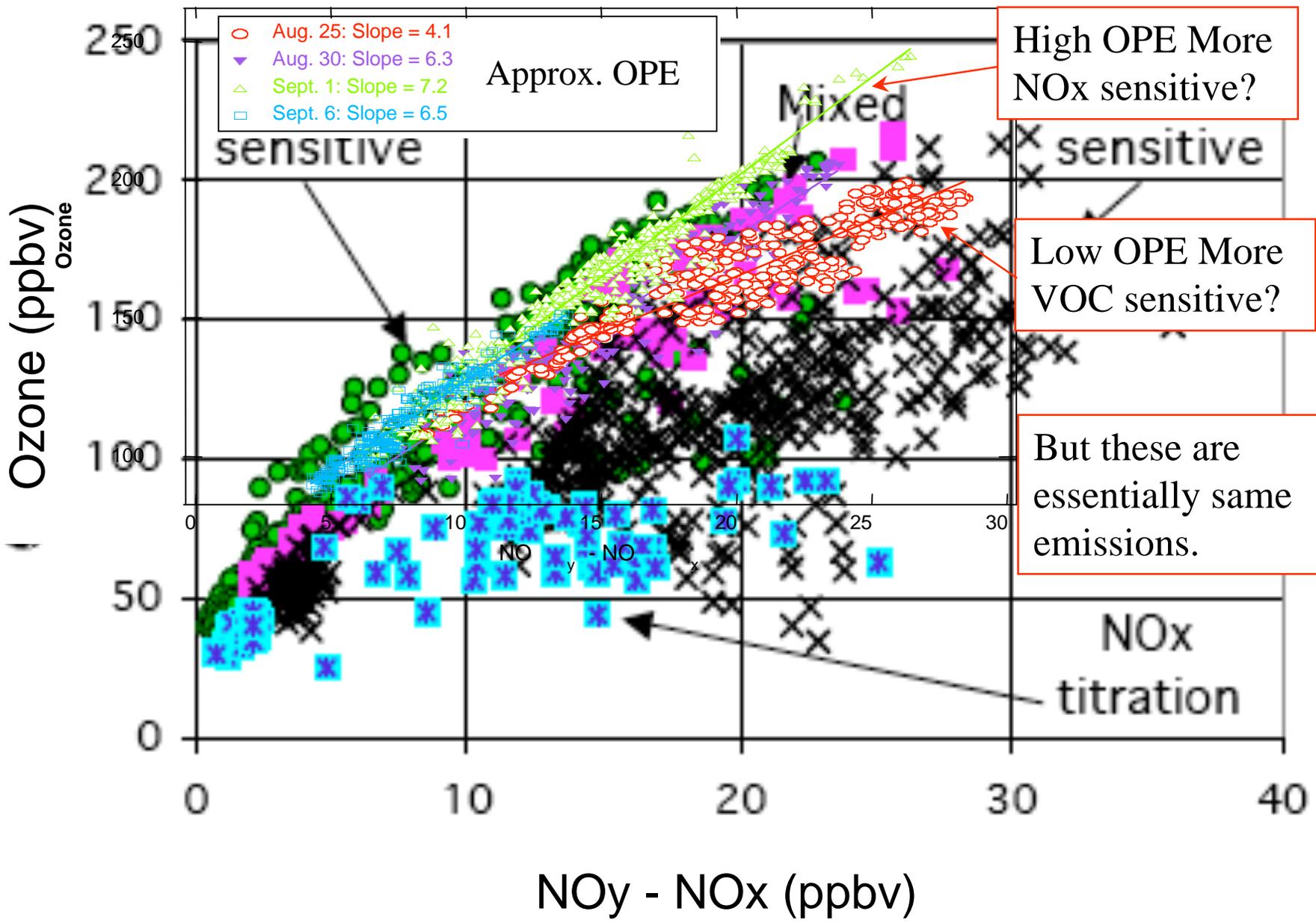
Draft report

Ryerson et al. report examines 4 highest O₃ days in 2000 studied by Electra

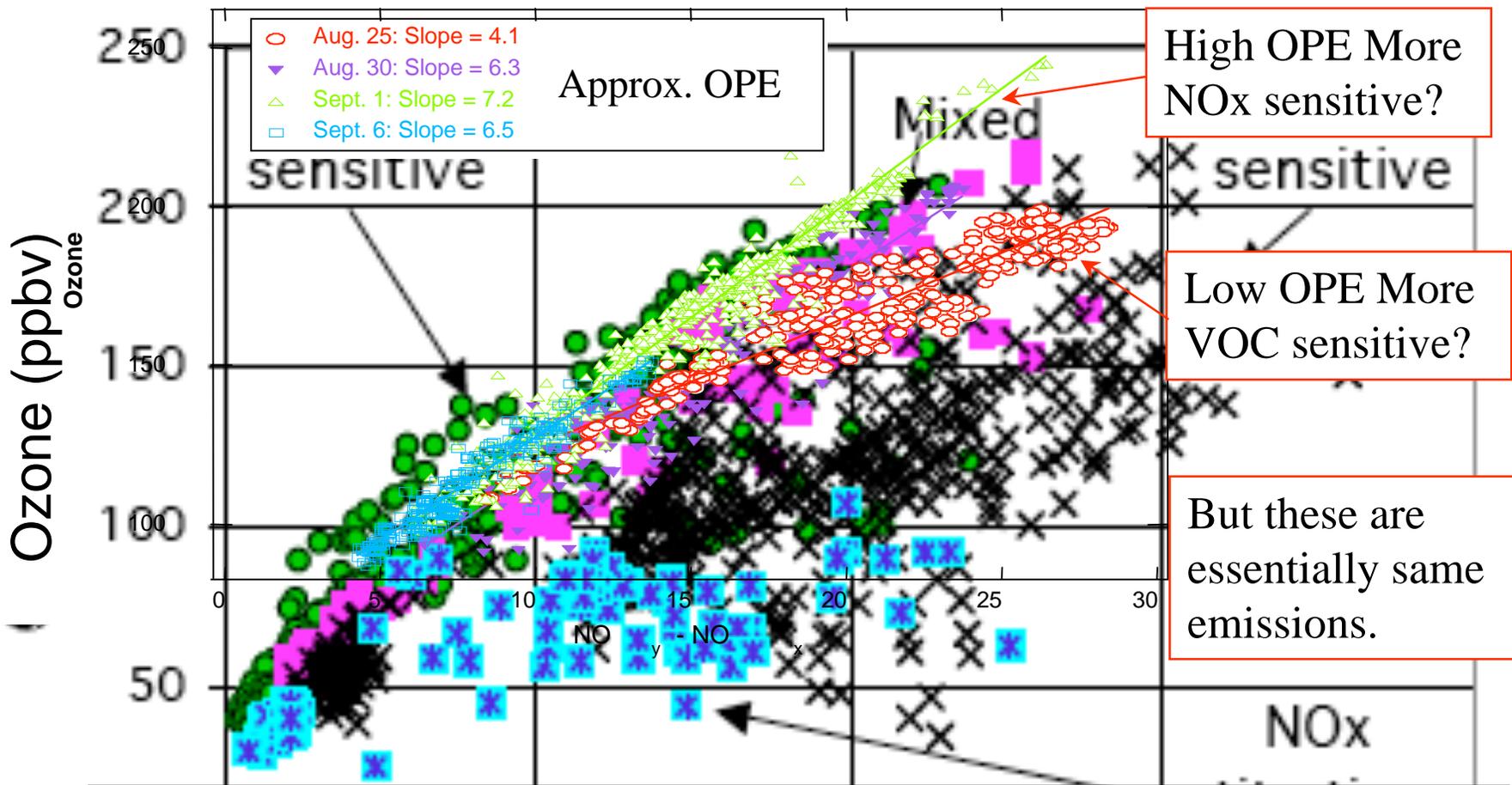
**All primarily due to emissions of HRVOC and NO_x from the Houston Ship Channel area
Differ in meteorology**



What are measurements telling us?



What are measurements telling us?



3) Same emissions under different transport (i.e. meteorological conditions) can affect OPE, and thus VOC vs. NOx sensitivity as given by indicator species.

NOy - NOx (ppbv)

SIP Relevant Findings

Question F & K: Determination of the sensitivities of high ozone to the precursor VOC and NO_x emissions

Ozone sensitivities to VOC and NO_x emissions - Observation-based approach

Use of indicator species:

- Can give ambiguous results, depending on choice of species.
- Does not necessarily give useful and reliable answers.
- Does not account for effect of rate of O₃ formation.
- Same emissions under different transport (i.e. meteorological conditions) can affect OPE, and thus VOC vs. NO_x sensitivity as given by indicator species.

Assertion: Best use of indicator relationships is as test of models:
Can model reproduce observed relationships? (Work in progress)