Ozone photochemistry trends in the Houston Ship Channel

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TEXAS COMMISSION ON ENVIRONMENTAL QUALITY

Introduction

- Due to transportation and industry dominating Houston's economy, local air quality is in non-compliance according to EPA NAAQS.
- Policy-makers and industries have worked together to decrease the reactive hydrocarbon and NOx emissions in order to bring the area into attainment of the ozone NAAQS (Figure 2).
- Decreased emissions have influenced the number of ozone NAAQS exceedance days (Figure 3).
- This study explores the changes in the photochemical environment in the **Houston Ship Channel** (3 sites listed in Figure 1) with a photochemical box model, as emissions have decreased since 2000.

Houston Ship Channel

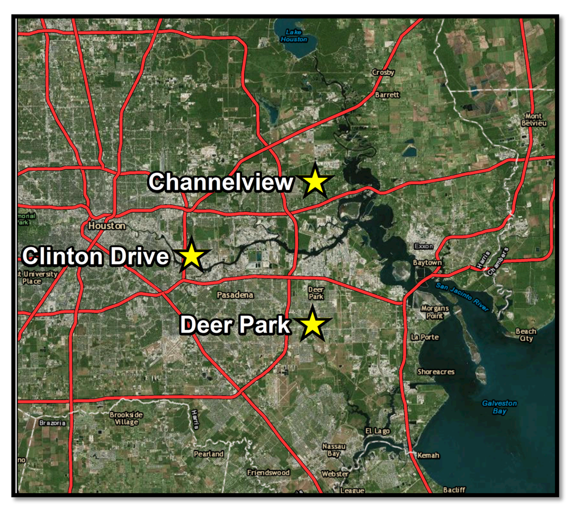
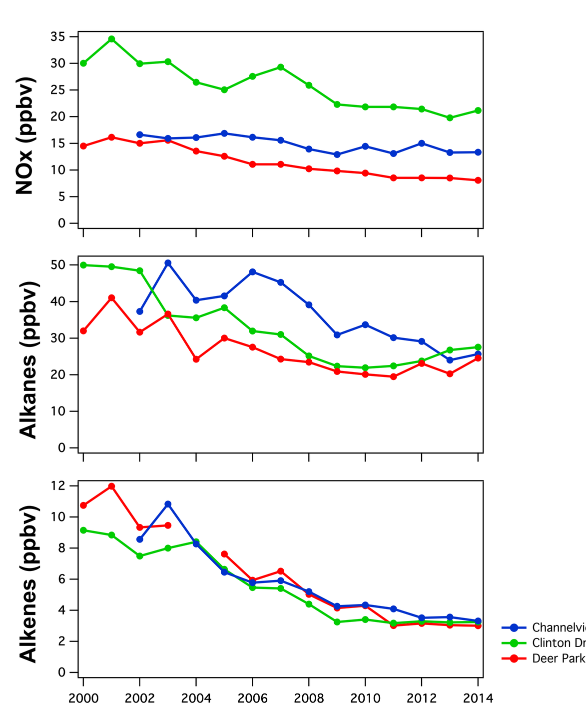


Figure 1: Modeled monitoring sites in the Ship Channel

- One of the busiest seaports in the US and home to numerous petrochemical facilities and other industries
- Emissions in the area have decreased since 2000 (Figure 2) and have been linked to the decreases ozone NAAQS exceedances in the Houston region (Figure 3).



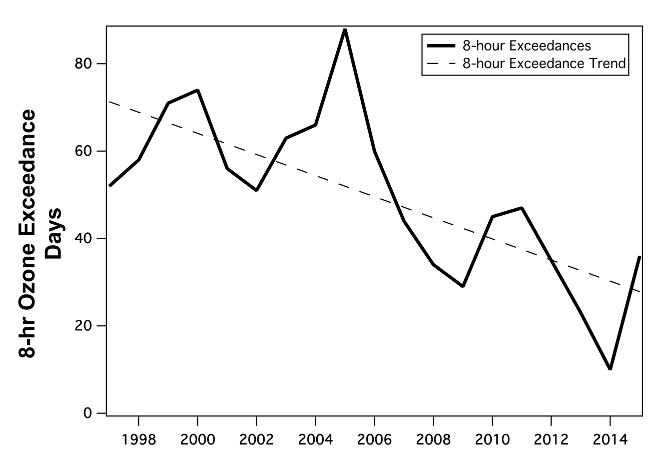


Figure 2 (left): Annual averages of NOx, Alkanes, and Alkenes for Channelview, Clinton Drive, and Deer Park

Figure 3 (above): Annual number of 8-hr ozone NAAQS exceedances

LaRC Model

- **0-D** photochemical box model ran in time dependent diurnal steady state to simultaneously solve 251 chemical reactions (Olson et al., 2006; Crawford et al., 1999).
  - Chemical reaction kinetics from Sander et al. (2006)
  - NMHC lumping scheme from Lurmann et al. (1986)
- First time used for long term monitoring in Houston (2000-2014)
  - Previous studies by Flynn (2013) and Ren et al. (2013) used LaRC in Houston during research campaigns: TRAMP 2006, SHARP 2009, and MT 2010.
- **Model Inputs:** O_3, NOx, CO, NMHCs, and basic meteorology
- **Model Output:** Components for O_3 production (PO_3) and individual reaction rates along with calculated species concentrations

Results

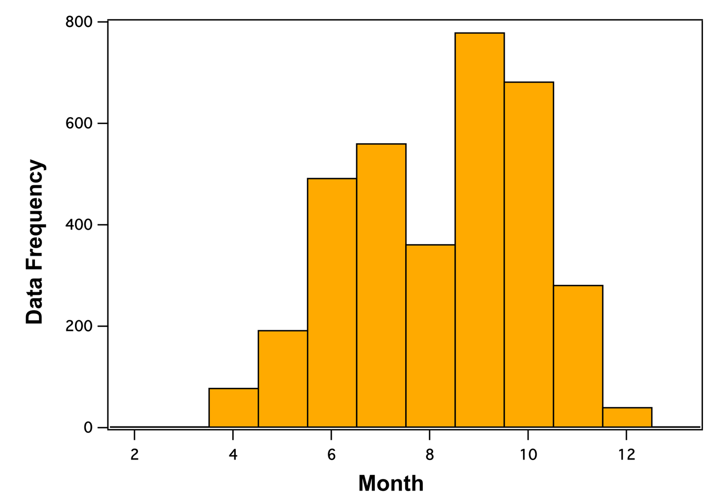


Figure 4: Histogram of the top 5% polluted days data points indicating when they occur during the year.

- Although emissions occur daily, ozone build up only occurs on days when meteorological conditions are prime.
  - Strong sunlight: visible with the summer peak in Figure 4
  - Calm wind conditions: often coinciding with post frontal conditions (Lefer et al., 2010)
- **Only data from the top 5% maximum daily average 8-hr ozone days are considered for this analysis.**

O_3 Production

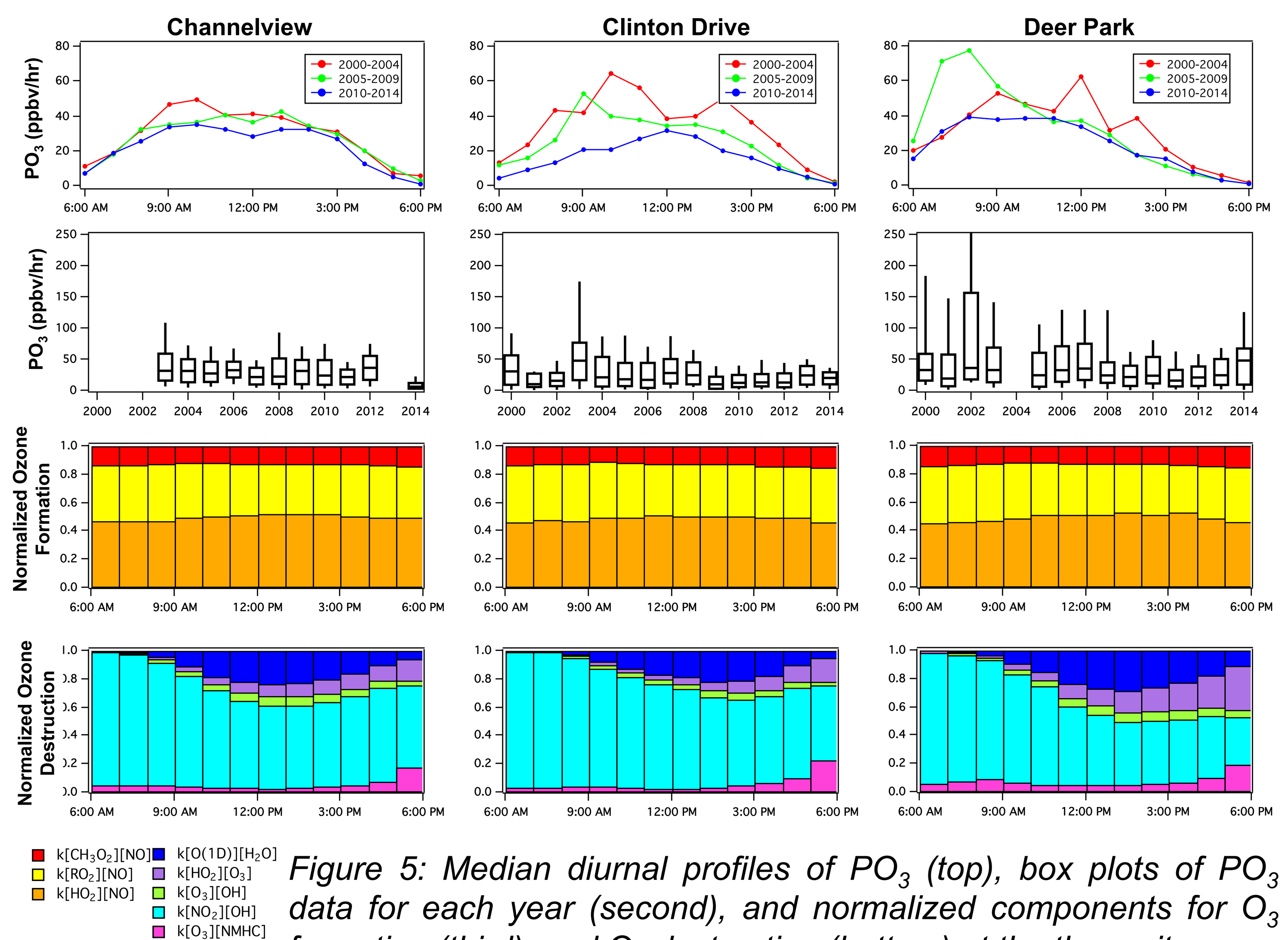


Figure 5: Median diurnal profiles of PO_3 (top), box plots of PO_3 data for each year (second), and normalized components for O_3 formation (third), and O_3 destruction (bottom) at the three sites.

- Ozone production peaks diurnally around solar noon for Channelview and Clinton Drive, but earlier in the day at Deer Park.
- Ozone production has decreased at all sites since 2000.
- The biggest contributor for O_3 formation is the creation of NO_2 from HO_2 and NO. The percent contribution for O_3 formation is consistent throughout the day.
- The biggest destructor of O_3 is the formation of HNO_3, however the percent contribution of this reaction decreases throughout the day with ozone reactions becoming a larger contributor.

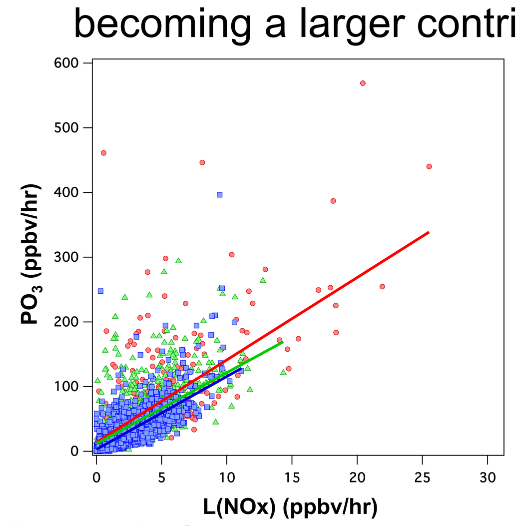


Figure 6: Scatter plot showing the comparisons between PO_3 and L(NOx) and their linear best fits (OPE) colored by year at all sites. Statistics are found in the table above.

Ozone production efficiency (OPE) is a measure of how many ozone molecules are produced per NOx molecule before NOx is taken out of the system
$OPE = PO_3/L(NOx)$

- OPE decreases are seen at Channelview and Clinton Drive since 2000.
- Deer Park has seen an increase in OPE in the last 5 years.

	OPE (r^2)		
	2000-2004	**2005-2009**	**2010-2014**
Channelview	13.1(0.61)	10.8(0.53)	10.9(0.63)
Clinton Drive	13.5(0.58)	11.3(0.60)	9.4(0.63)
Deer Park	11.0(0.14)	11.7(0.29)	13.7(0.48)
All Sites	**12.7(0.39)**	**11.0(0.39)**	**11.3(0.52)**

Hydrocarbon Reactivity

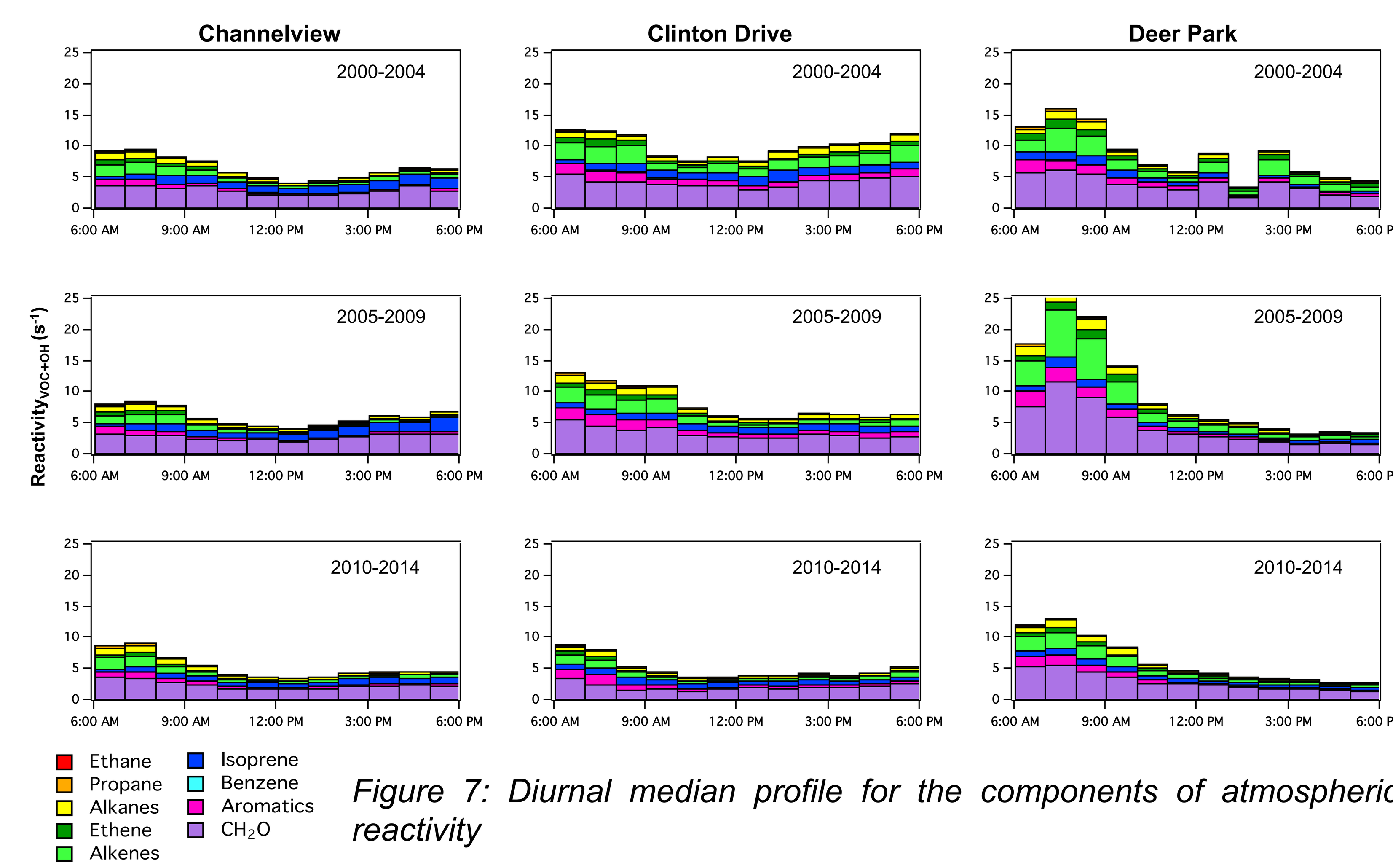


Figure 7: Diurnal median profile for the components of atmospheric reactivity

- Deer Park appears to be most influenced by fresh VOC emissions out of the three sites.
- CH_2O exhibits the largest contribution to hydrocarbon reactivity.
  - Formation linked to HRVOCs in Houston (Parrish et al., 2012)
  - CH_2O is not measured at these monitoring sites.
- Alkenes, including HRVOCs, have had a marked decrease in the last 5 years.
  - ✧ HRVOC rule for decreased emissions (30 TAC Chapter 115) adopted in 2004 as a strategy to combat ozone

HRVOCs: ethene, propene, 1,3-butadiene, & butenes

Ln/Q quantifies NOx/VOC sensitivity by comparing the loss of NOx to HNO_3 and PAN (Ln) to the production of free radical (Q).

Ln/Q < 0.5 → NOx limited
Ln/Q > 0.5 → VOC limited

NOx/VOC Sensitivity

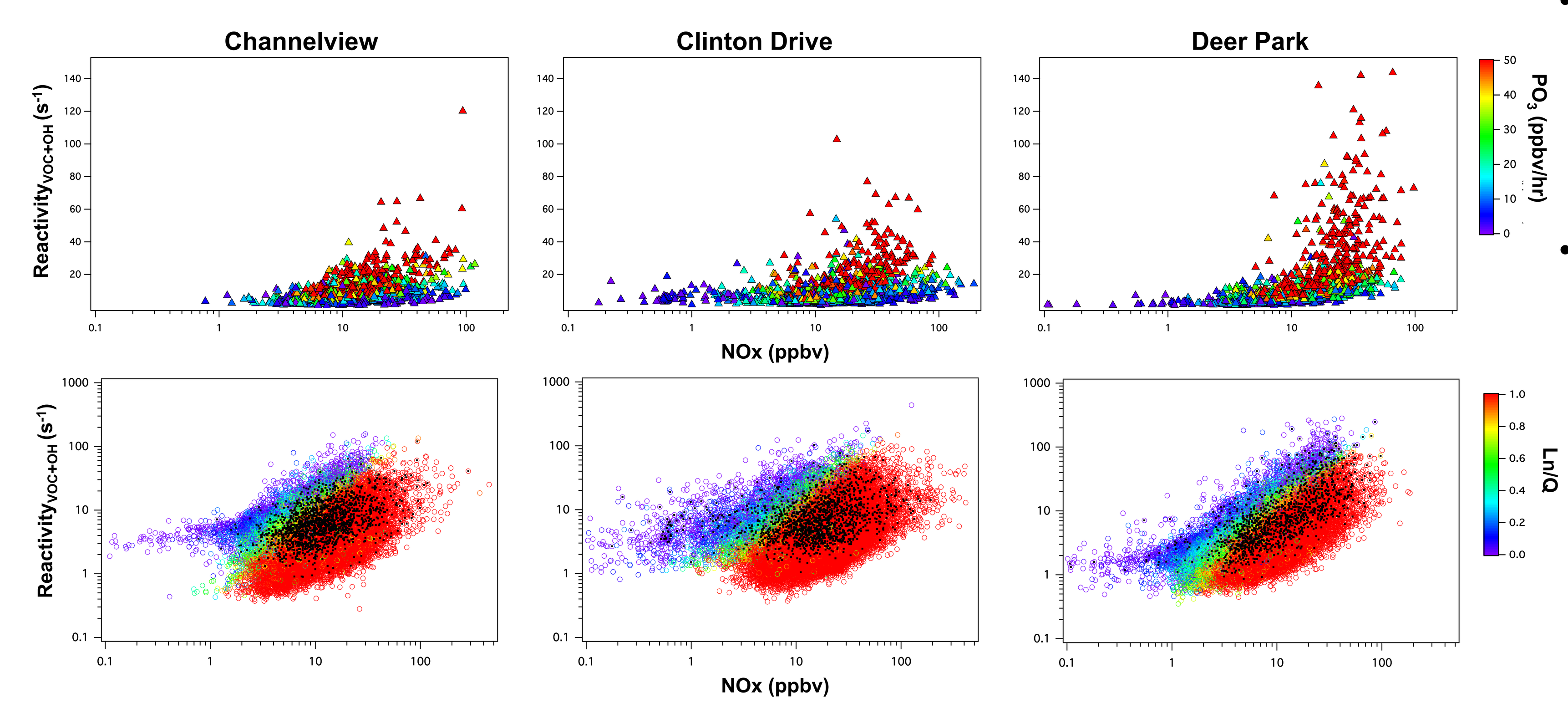


Figure 8: Hydrocarbon Reactivity (s^{-1}) vs. NOx (ppbv) for the three sites colored by net ozone production on polluted days (top) and Ln/Q on the bottom for all days (bottom). The black dots indicate the location of the data on polluted days.

- Determining whether an environment is NOx or VOC sensitive for ozone production is important step in determining actions needed to combat ozone.
- Figure 8 suggests that on polluted days, the ship channel is NOx saturated/VOC limited.
  - High ozone production spans a large NOx range and suggests decreasing VOCs would decrease ozone production rates.
  - The majority of days (polluted and non-polluted) have a Ln/Q greater than 0.5. On polluted days, Ln/Q is often 1 or larger. This supports the result of VOC sensitivity in the ship channel.

Conclusions

- Decreases in emissions have lead to decreased ozone production, ozone production efficiency, and hydrocarbon reactivity since 2000 in the Houston Ship Channel.
- Ozone production is sensitive to VOCs in the ship channel. This suggests additional VOC emission controls, particularly HRVOCs, as a more effective strategy to further reduce ozone production rather than targeting NOx reductions.
- CH_2O measurements would also greatly improve the ability to constrain ozone modeling in the Houston region.

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Disclaimer: These results have not been subject to TCEQ or NASA's scientific and policy review and therefore do not necessarily reflect the views of these agencies and no official endorsement should be inferred.

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