Quantitative Comparison of VOC:NO_x Ratios in DFW

February 18, 2005

Data Analysis Fernando Mercado

Objective

- Use VOC:NOx ratio method to report limitation ratios for all available observed data.
- Compare limitation ratios among all available data, including CAMx modeling.
- Report which areas of DFW region are NOx, Transitional or VOC limited.

Data Types

1. **MCAN** – Specific 1-hour canister data sampling four times per day at different times of the day. Sampling dependent on ozone forecast and on site, (1999-2004, 52 days, 208 samples).

2. **CATMN** – 24-hour canister data. Sampling every 5th day (1997-2004, 405 samples).

3. **CAMx Modeling** – Specific to modeling episode; 10 days only (Aug 13 – 22, 1999).

4. **Aircraft** – Limited to 1 day at ~780 meters during 16-18:00 (8/30/2002)

5. **Auto GC** – 1-Hour samples for Hinton site (1997-2004) and Northwest Fort Worth (2003-2004).

VOC:NOx Background

- **There is no one standard method of calculating a VOC:NOx ratio.**
- The components that comprise a VOC vary depending on the available data and what the analyst believes which VOC species are significant. Different components that comprise a VOC can have a significant change to the ratio.
- Comparison of modeled to observed ratios are not equivalent, since the have different VOC components.
- Comparison of 24-hour to 1-hour canisters are not comparable, since the sampling periods are not of the same length.
- Comparison of the 10 day modeling period to 8 year period are not comparable due to the variation of the data.
- If the depth of the mixing layer is assumed to be well mixed, aircraft sample ratios can be considered similar to ground samples, provided there were more equal number of samples.

Methodology

- Compare the average of ratios. The averages is a better predictor.
- For observed data, Total Non Methane Organic Carbon (TNMOC) was used for analysis. TNMOC is comprised of all species that can be sampled.
- CAMx modeled VOCs contained the following 8 species:

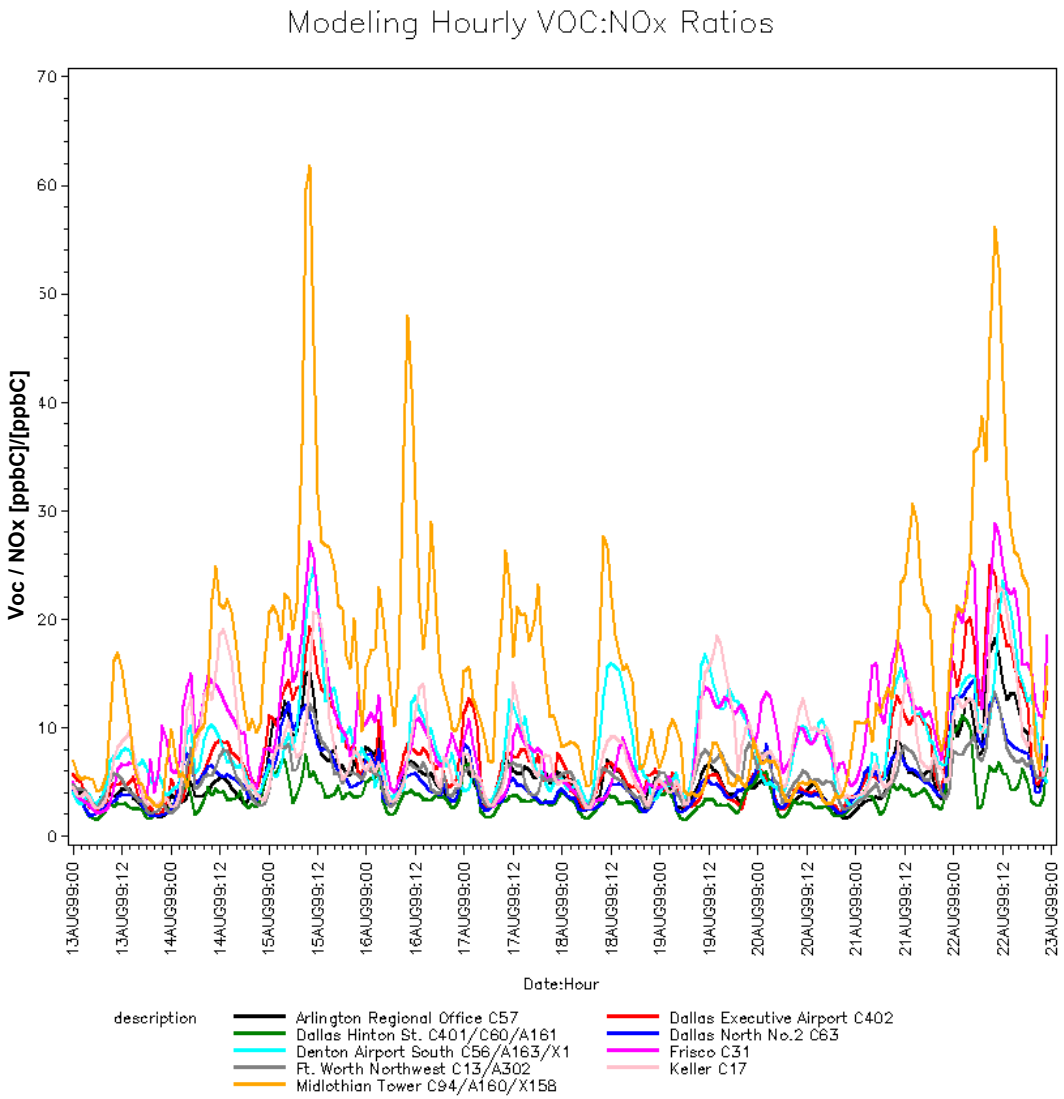
VOC[ppbC]	=	paraffin	+	2 * olefins
	+	7 * toluene	+	8 * xylene
	+	2 * aldehyde2	+	2 * ethylene
	+	5 * isoprene	+	formaldehyde

- Auto GC includes up to 50+ species.
- **These differences make ratios difficult to compare, since were are comparing 'apples to oranges'.**

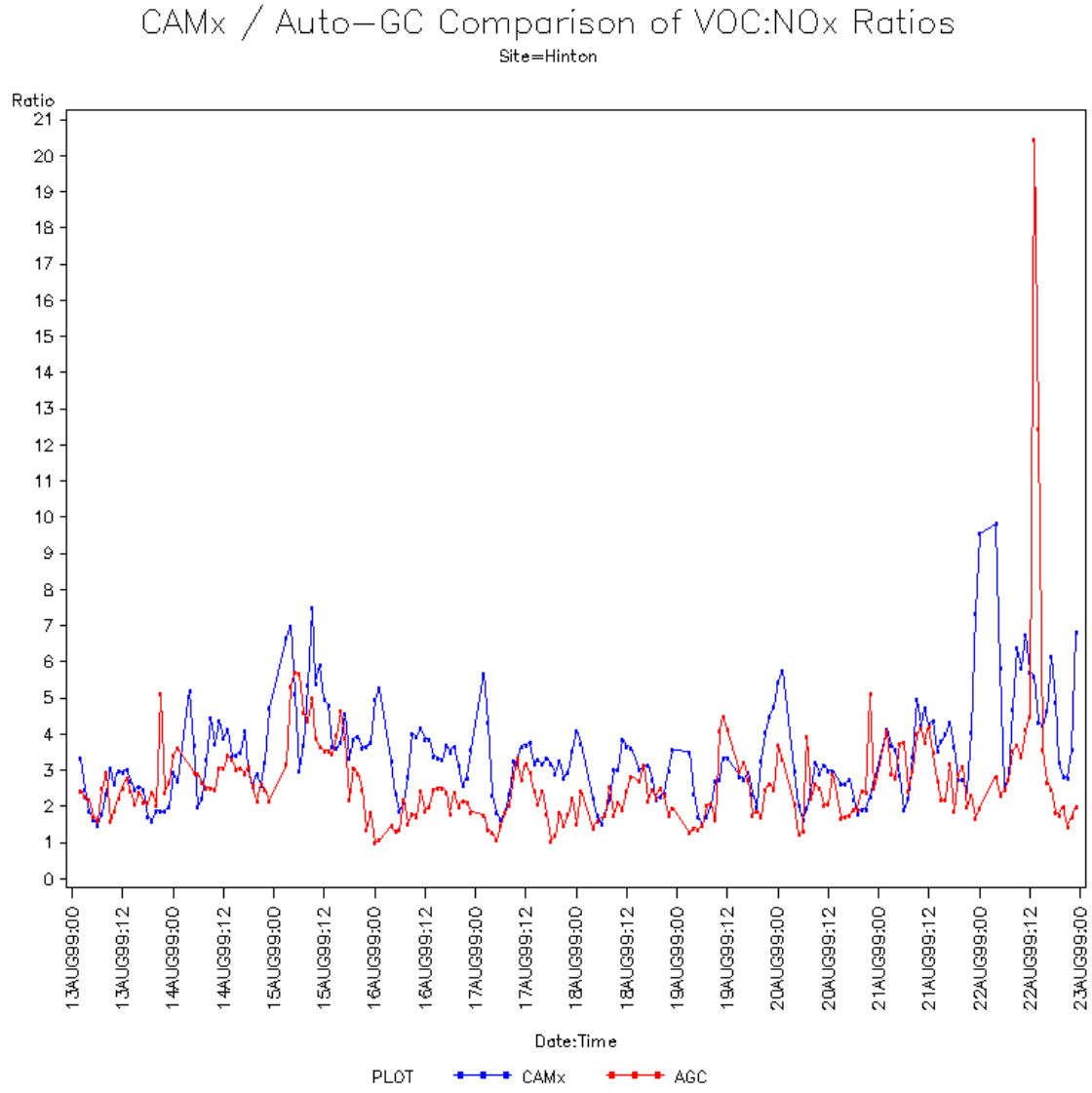
Definitions

- A VOC:NO_x ratio is simply, $\varphi = VOC_{[ppbC]}/NO_{x[ppbV]}$.
- **VOC limited** $\varphi < 5$: Low ratios mean that variations in NOx do not significantly influence ozone formation.
- **NO_x limited** $\varphi > 15$: Ozone formation limited by availability of NOx rather than VOCs.
- **Transitional** $5 \leq \varphi \leq 15$: Both NOx and VOC controls may be effective.

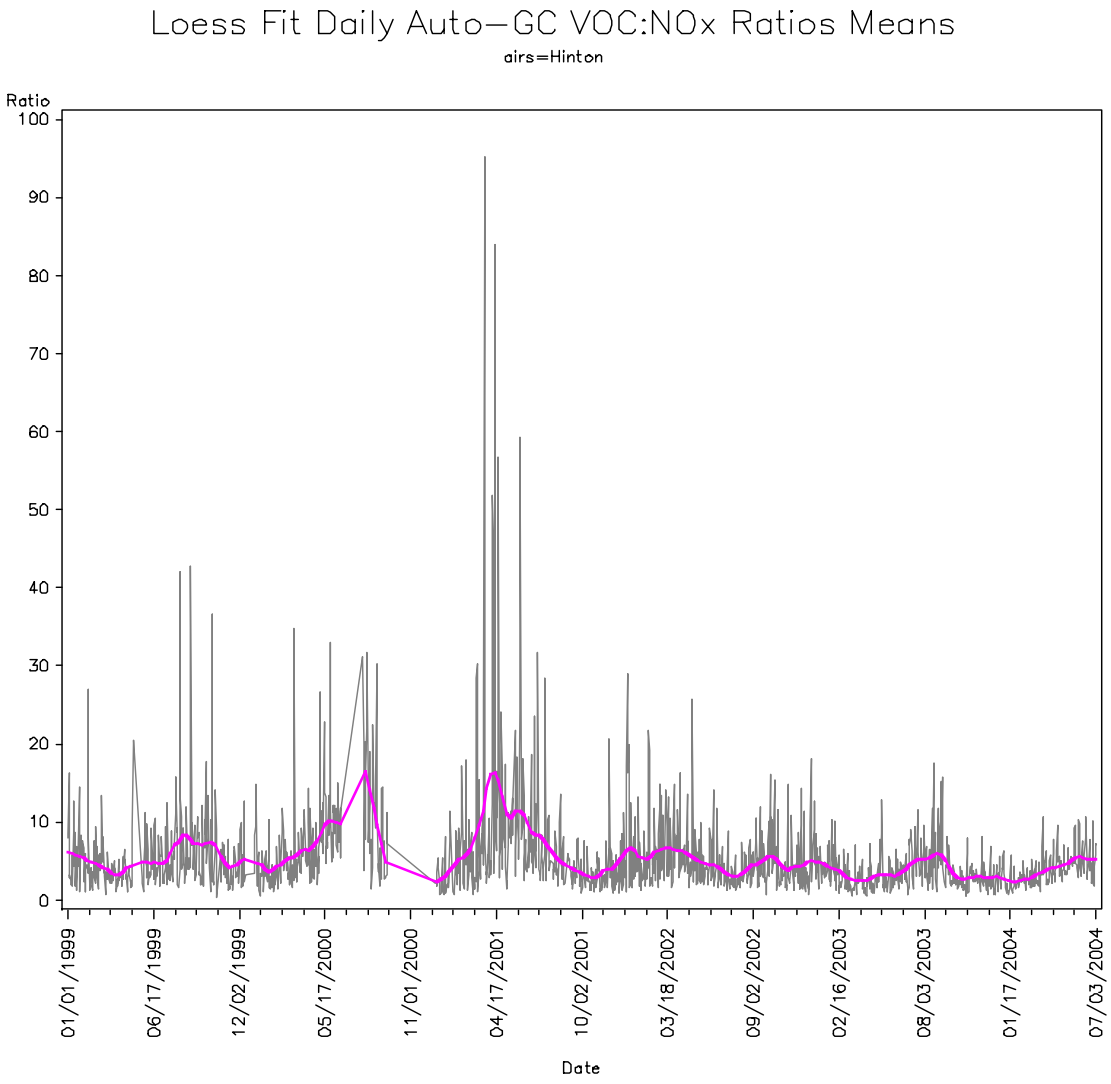
CAMx Comparison of Ratios Among Sites



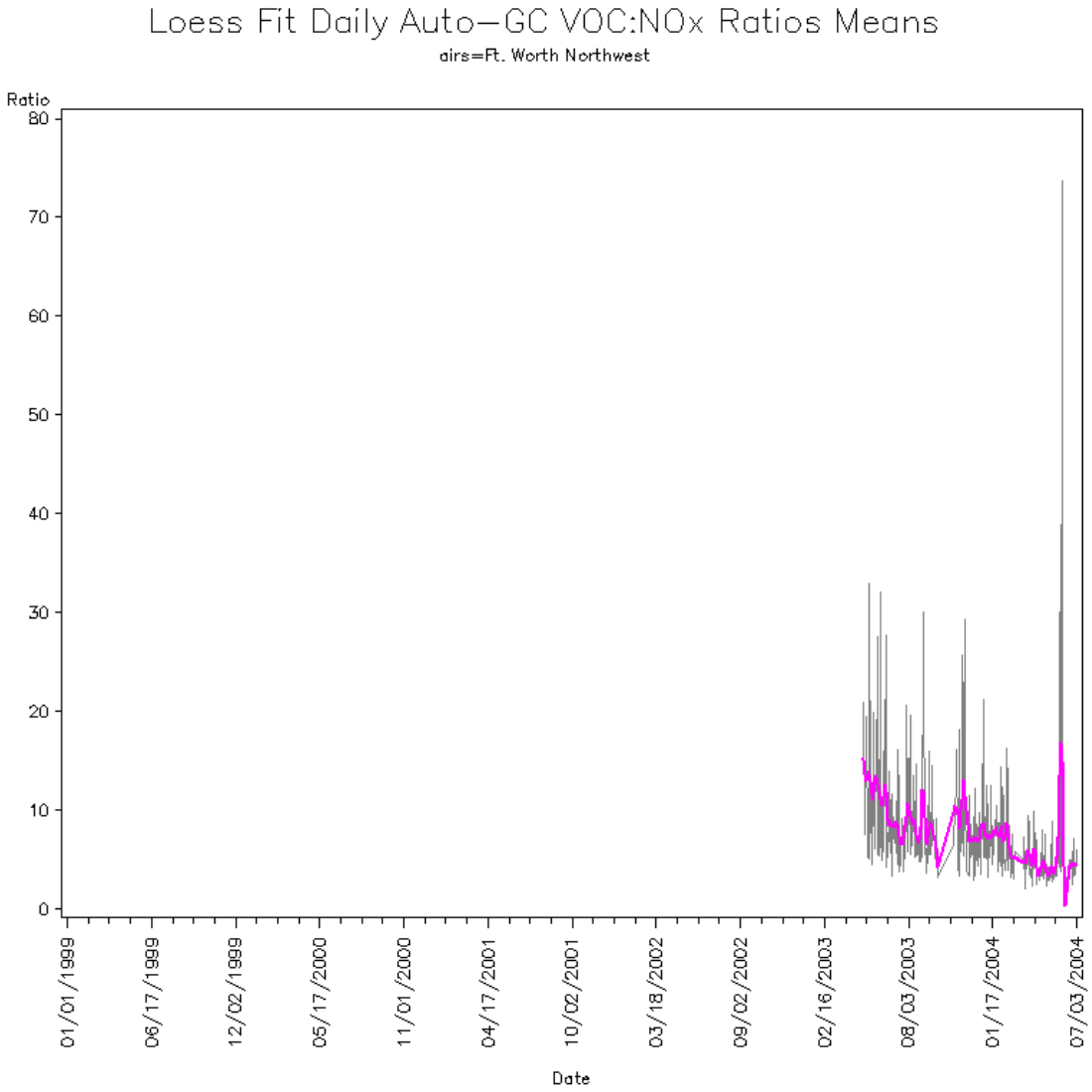
Comparison of CAMx & AGC



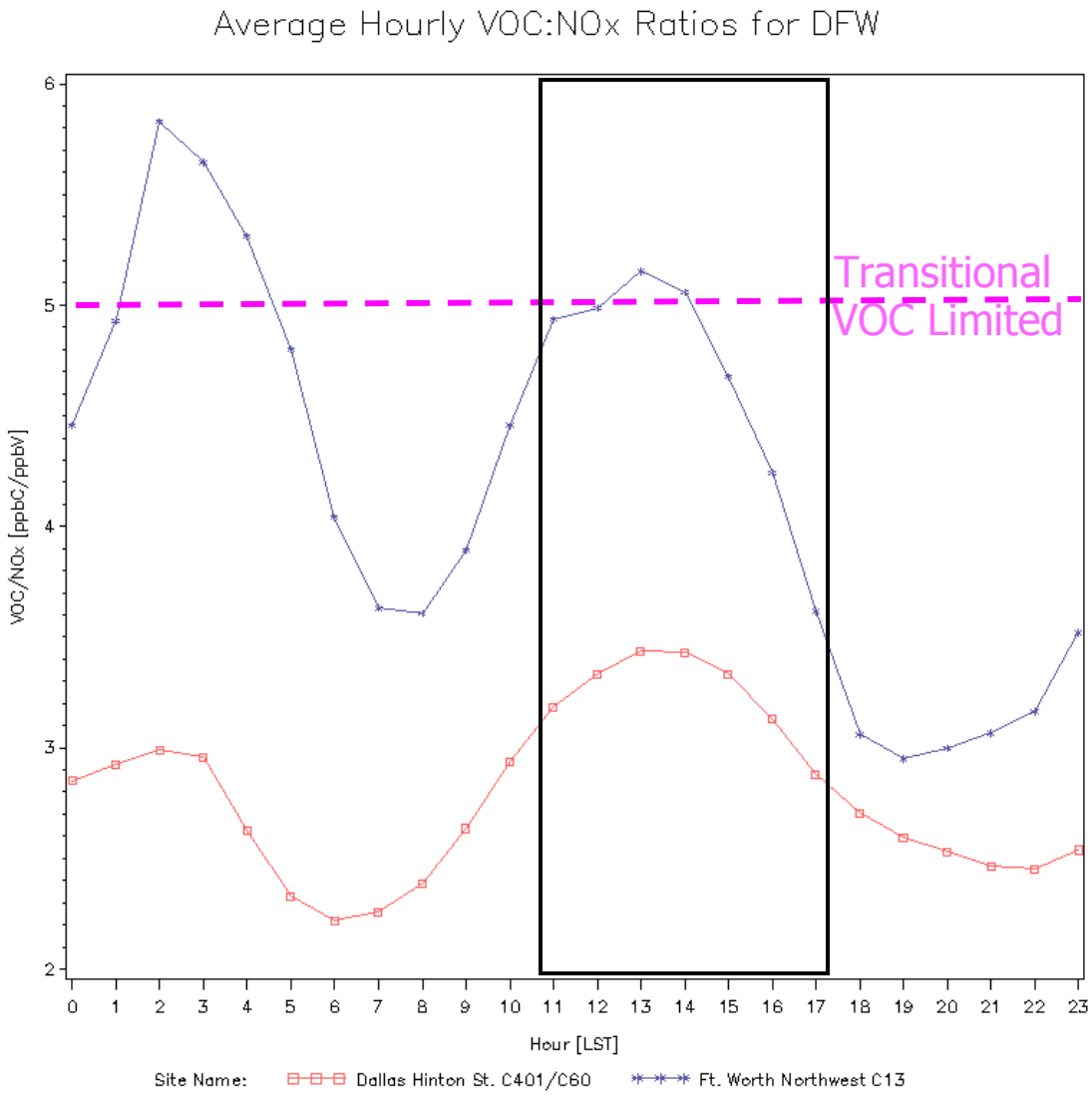
Hinton AGC 1999-2004 Ratios



Northwest AGC 2003-2004 Ratios

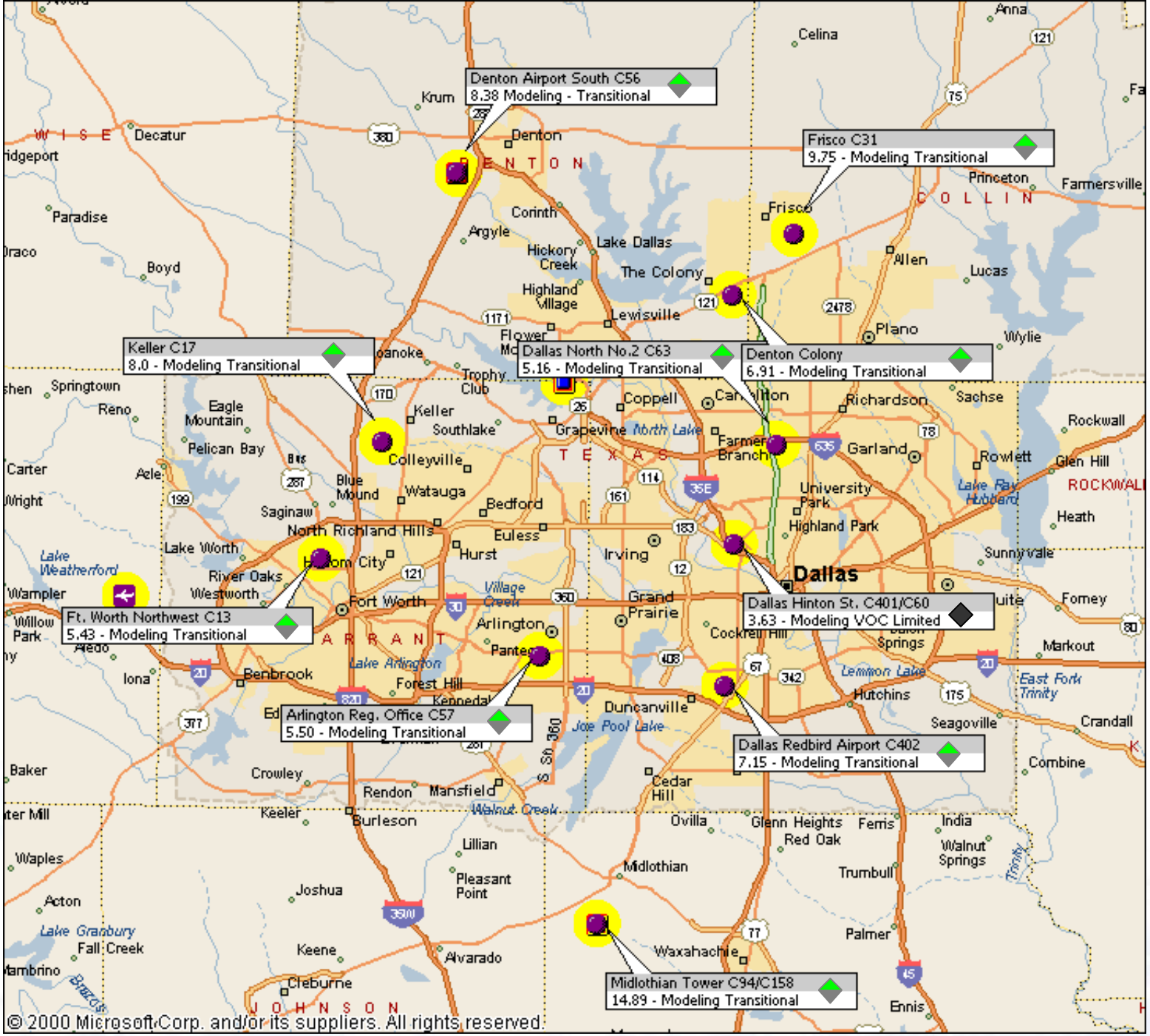


Auto GC Diurnal Pattern

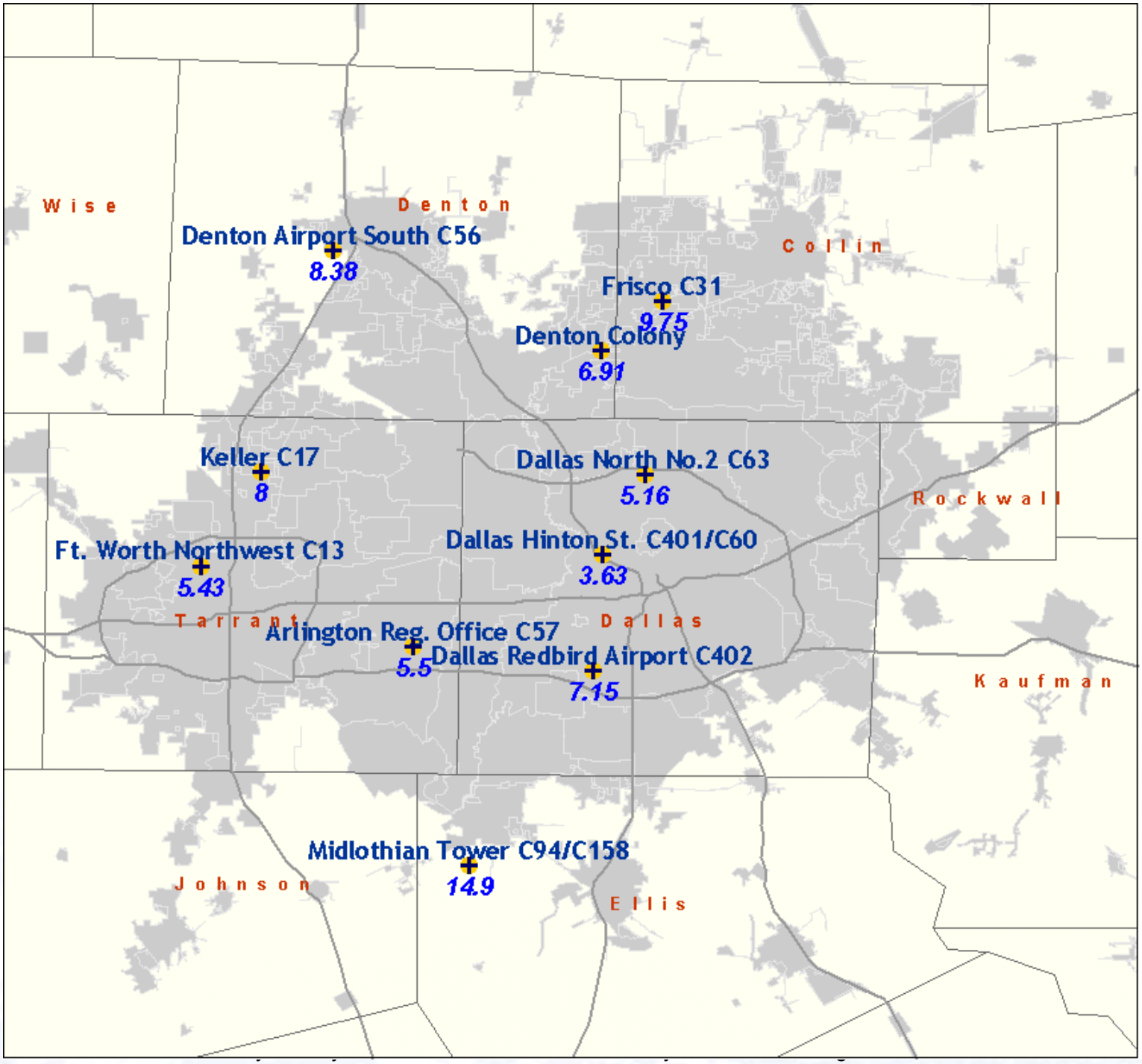


CAMx VOC:NOx Ratios

- NOx Limited
- Transitional
- VOC Limited

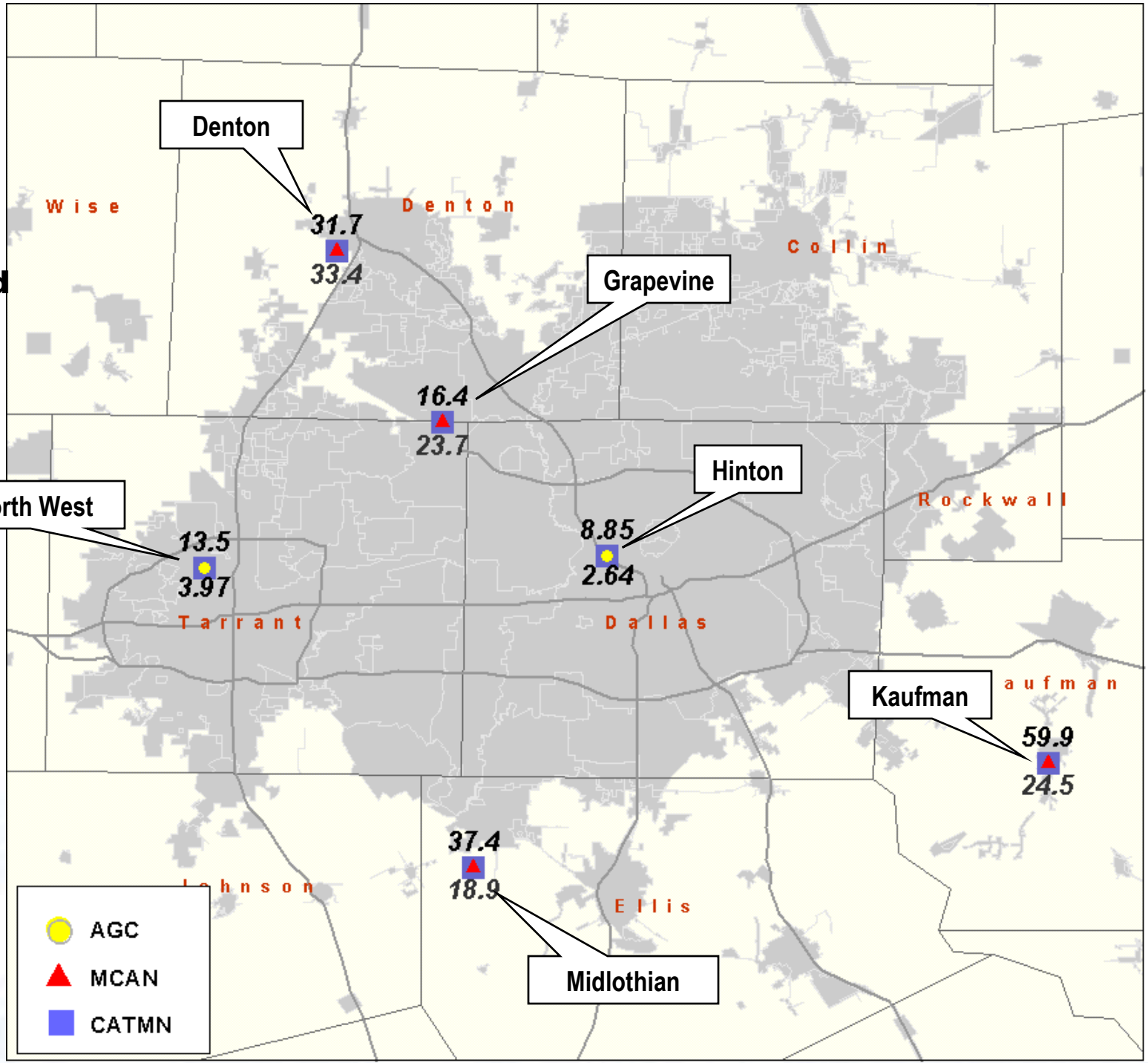


CAMx VOC:NOx Ratios



ACG, MCAN and CATMN VOC:NOx Ratios

ACG, MCAN and CATMN VOC:NOx Ratios



Averaged VOC Limitation Results for Observed Data

Site Name	MCAN	CATMN	AGC
Frisco C31			
Dallas Hinton St. C401/C60		Transitional	VOC
Dallas North No.2 C63			
Dallas Redbird Airport C402			
Denton Airport South C56	NOx	NOx	
Denton Colony			
Midlothian Tower C94/C158	NOx	NOx	
Arlington Reg. Office C57			
Ft. Worth Northwest C13		Transitional	VOC
Keller C17			
Kaufman C71	Transitional	NOx	
Grapevine Fairway C70	Transitional	NOx	

VOC Limitation Results for CAMx Modeled Data, Averaged over the Modeling Period

Site Name	MODELING
Frisco C31	Transitional
Dallas Hinton St. C401/C60	VOC
Dallas North No.2 C63	Transitional
Dallas Redbird Airport C402	Transitional
Denton Airport South C56	Transitional
Denton Colony	Transitional
Midlothian Tower C94/C158	Transitional
Arlington Reg. Office C57	Transitional
Ft. Worth Northwest C13	Transitional
Keller C17	Transitional
Kaufman C71	
Grapevine Fairway C70	

Summary

- Sites within the city-core suggest VOC limited conditions and transitional.
- Sites outside of the city, mostly rural areas, suggest NOx limited conditions.
- CAMx modeled limitation ratios conditions roughly match observed.
- Observed VOC/NOx limitations show how ozone can be reduced immediately, but cannot show what will be needed to reach attainment.

Contributors

- Fernando Mercado
- Zhaohua Fang
- Kasey Savanich