

December 22, 2009

Mr. Steven M. Feisal  
Regulatory Attorney  
Chesapeake Energy Corporation  
P.O. Box 18496  
Oklahoma City, OK 73154-0496

**Re: Summary of Rice University *Analysis of AutoGC and VOC Canister data in the DFW area Report***

Dear Mr. Feisal:

As requested by Chesapeake Energy Corporation ("Chesapeake"), ENVIRON has reviewed the *Analysis of AutoGC and VOC Canister data in the DFW area report* authored by Dr. Birnur Guven, Rice University, and dated August 26, 2009 (the "Rice Report") and prepared the following summary.

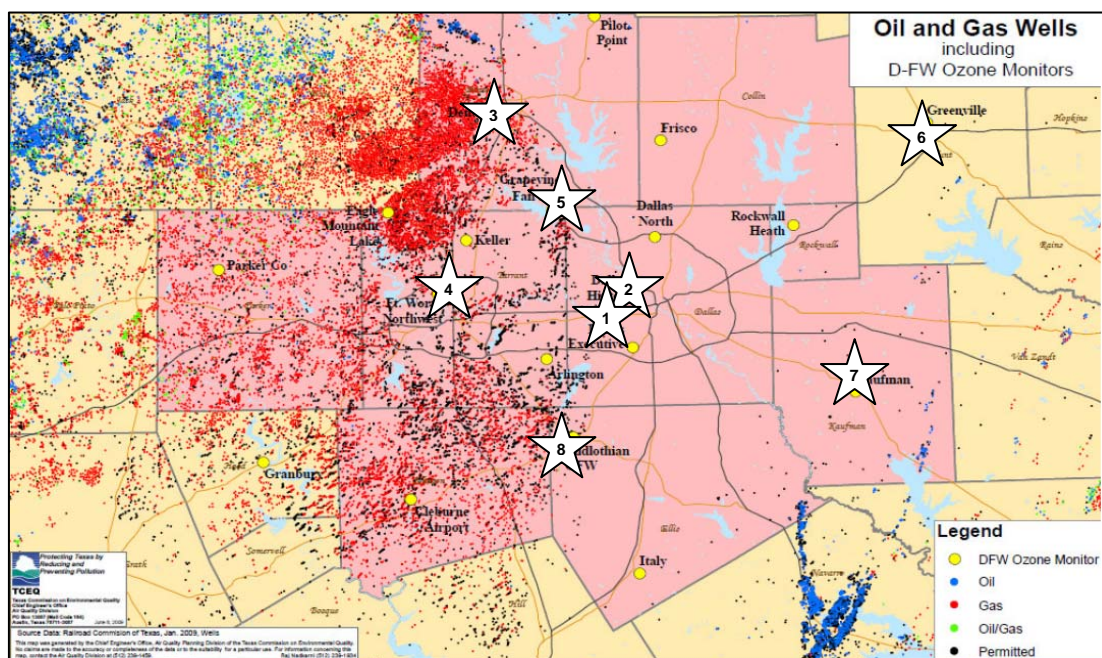
### **Scope of Rice Report Study**

Dr. Birnur Guven, Rice University, performed an evaluation of existing ambient monitoring data for the purpose of determining the impacts of Volatile Organic Compound ("VOC") emissions from oil and gas exploration and production activities in the Barnett Shale on air quality in the Dallas-Fort Worth ("DFW") region. Prepared for Dr. Ramon Alvarez, Environmental Defense Fund, the analysis was conducted primarily using Texas Commission on Environmental Quality ("TCEQ") VOC canister sampling data from nine monitoring sites:

1. Boys Club
2. Dallas Hinton
3. Denton Airport South
4. Fort Worth Northwest
5. Grapevine Fairway
6. Greenville
7. Kaufman
8. Midlothian OFW / Midlothian Tower

Automated Gas Chromatograph (AutoGC) data collected at two of the sites – Dallas Hinton and Fort Worth Northwest – was obtained from EPA and also included in the analysis. The locations of these nine monitoring sites are shown as white stars in Figure 1. The numbers on the stars correlate with the above list of monitoring sites. Note that the two Midlothian sites are marked with the same star – Number 8. The red, blue, green and black dots on the map represent oil and natural gas production wells in the DFW area. The closest monitoring site to DISH, Texas, is Denton Airport South.

The work included spatial and temporal analysis of AutoGC and canister data, examination of any correlations between wind direction and pollutant species concentrations, and conduct of a preliminary source apportionment of AutoGC data from Dallas Hinton and Fort Worth Northwest sites.



**Figure 1. Locations of Monitoring Sites**  
(Extracted from Rice Report)

## Rice Report Annual Pollutant Concentration Analysis

Figure 2 shows the annual trends of Total Nonmethane Organic Compounds (“TNMOC”) concentrations at six of the canister monitoring sites.<sup>1</sup> The units of concentration are parts per billion of carbon.<sup>2</sup> As shown, the Denton Airport South monitor has the highest TNMOC concentrations for the years 2002 through 2008, with a downward trend in concentrations since peaking in 2004.<sup>3</sup> With respect to certain individual compounds, the monitoring sites with the highest annual concentrations are as follows.

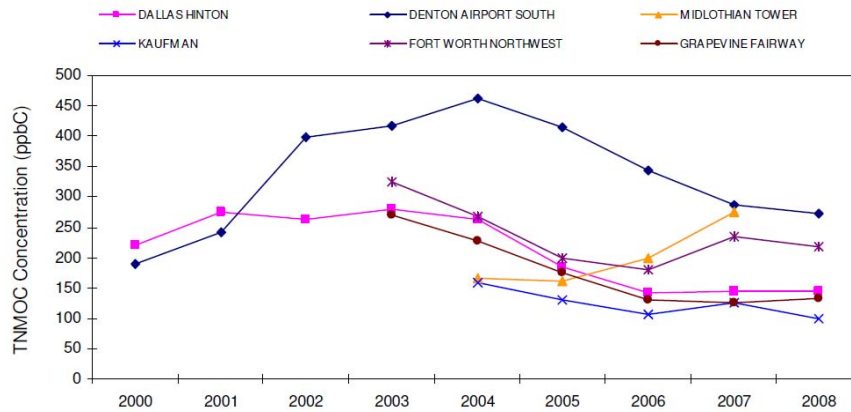
Ethane & Propane .....	Denton Airport South (2008)
Butanes & Pentanes .....	Denton Airport South (2008)
Ethylene .....	Boys Club (2007) / Fort Worth NW & Dallas Hinton (2008)
Propylene .....	Boys Club (2007) / Fort Worth NW & Dallas Hinton (2008)
Toluene .....	Dallas Hinton / Fort Worth NW (2008)
Benzene .....	Boys Club (2007) / Fort Worth NW (2008)
n-Hexane.....	Midlothian Tower (2007) / Denton Airport South (2008)
m-p Xylenes .....	Boys Club (2007) / Fort Worth NW & Dallas Hinton (2008)

No data is presented within the Rice Report for Boys Club and Midlothian Tower for 2008.

<sup>1</sup> Per TCEQ guidance, to be representative of long-term average concentrations, canister samples over a 24-hour period are to be collected a minimum of every six days over the course of a year, or about 60 samples per year.

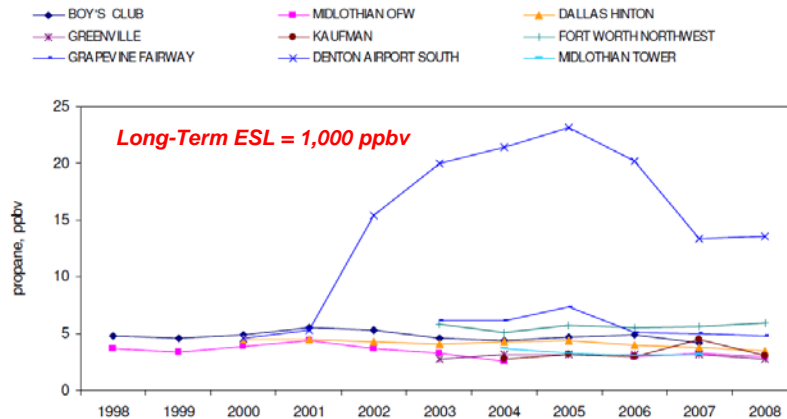
<sup>2</sup> To put a *part per billion* into an understandable context, think of a single, 6-member family among the approximately 6 billion people on earth. That family constitutes one part per billion of the human race.

<sup>3</sup> From 2005 through 2007, TNMOC concentrations at the Midlothian Tower monitor trended upward. If that trend continued into 2008, the Midlothian Tower monitor would have had the highest TNMOC concentration of the six sites.

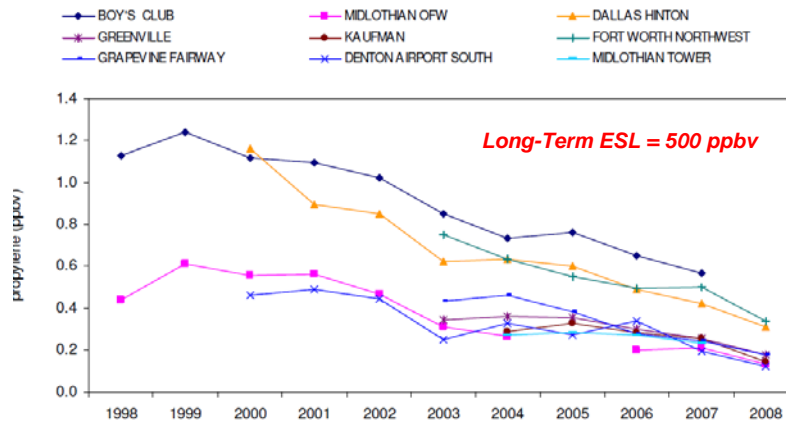


**Figure 2.** Annual Concentration Trends for TNMOC  
(Extracted from Rice Report)

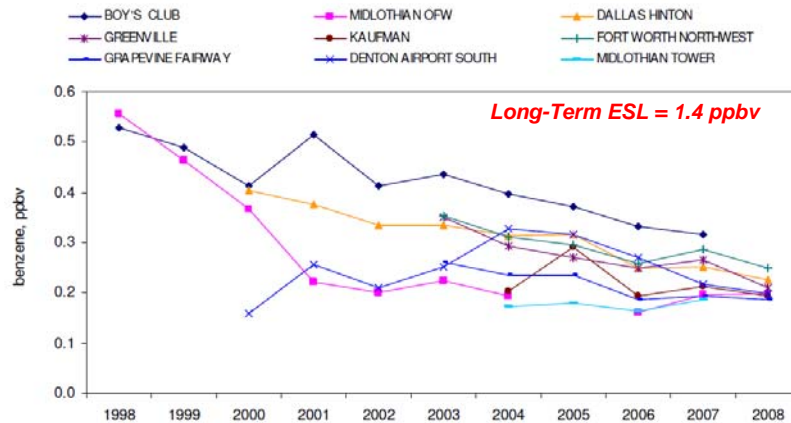
The trends for a representative light alkane (propane), a representative olefin (propylene) and a representative aromatic (benzene) are shown in Figures 3, 4 and 5, respectively, for all nine monitoring stations.



**Figure 3.** Annual Concentration Trends for Propane  
(Extracted from Rice Report)



**Figure 4.** Annual Concentration Trends for Propylene  
(Extracted from Rice Report)

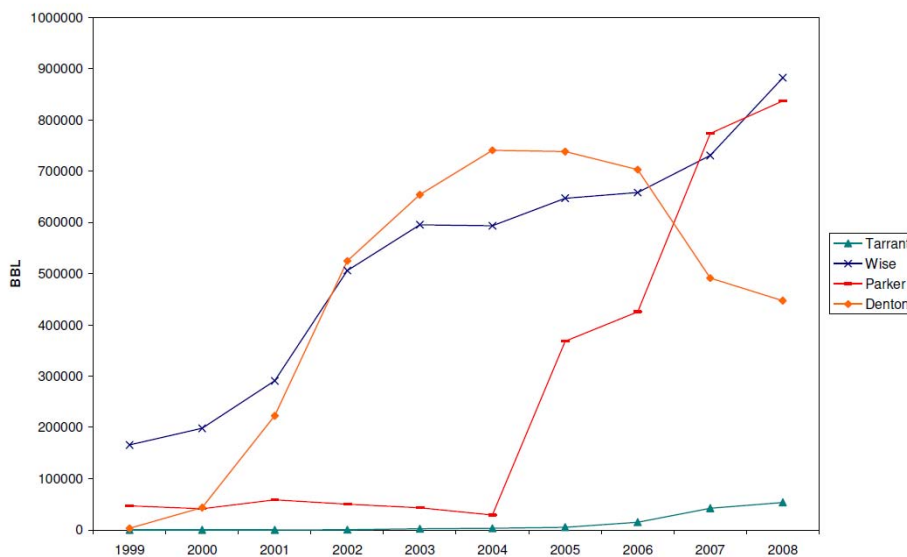


**Figure 5.** Annual Concentration Trends for Benzene  
(Extracted from Rice Report)

As stated on page 10 of the Rice Report:

*“Denton site has consistently the highest concentrations of ethane, propane, n-butane, isobutene, n-pentane, and isopentane, all signature compounds of oil/natural gas/condensate production. The temporal trends of all these compounds are similar; increasing until 2004-2005 and start decreasing through 2008. The trend of these compounds is quite similar to the change in annual condensate production in Denton County as reported by the State of Texas.”*

Condensate production by year and by county is shown in Figure 6.



**Figure 6.** Annual Barnett Shale Condensate Production by County  
(Extracted from Rice Report)

For comparative purposes, included as Attachment A is a summary prepared by the Houston Regional Monitoring Corporation (“HRM”) showing 2008 annual average benzene concentrations for monitoring sites across Texas and across the nation. The Fort Worth Northwest and Dallas Hinton sites are included on the chart. The annual average benzene concentrations at these two sites are generally comparable with measurements taken at other monitoring sites located within or near major metropolitan areas that don’t have a high concentration of petrochemical industry facilities.

VOCs are regulated for two primary reasons: 1) their potential contribution to formation of ground-level ozone, and 2) their potential human health effects. Table 1 presents TCEQ long-term health effects screening levels (“ESLs”) and Maximum Incremental Reactivity (“MIR”) for certain compounds addressed within the Rice Report.<sup>4</sup> In general, the lower the ESL the greater the concern about human health effects and the higher the MIR the greater the photochemical reactivity and the potential for contribution to ground-level ozone formation. Benzene, hexane, toluene and xylenes are also listed Hazardous Air Pollutants (“HAPs”) under the Federal Clean Air Act.

**Table 1. ESLs and MIRs**

<b>Compound</b>	<b>TCEQ Long-Term ESL<sup>a</sup> (ppb)</b>	<b>MIR (g Ozone/g Carbon)</b>
Ethane	1,000	0.25
Propane	1,000	0.48
n-Butane	800	1.02
Isobutane	204	1.21
n-Pentane	120	1.04
Isopentane	120	1.38
Ethylene	30	7.4
Propylene	500	9.4
Acetylene	2,500	0.5
Toluene	330	2.7
Benzene	1.4	0.42
n-Hexane	57	0.98
m-p Xylenes	42	7.4

<sup>a</sup> From October 2009 list of ESLs.

Of these compounds, using the ESL as a guide, benzene is of greatest concern with respect to long-term health effects. Using the MIR as a guide, the compounds with the greatest potential for contributing to ground-level ozone formation are ethylene, propylene and xylenes. The light alkanes (ethane through isopentane in Table 1) are generally of lesser concern with respect to both human health effects and photochemical reactivity. Ethane has such low photochemical reactivity that it is excluded from the federal definition of VOC in 40 CFR 51.100.

For all 64 of the chemicals considered in the Rice Report and for all of the years considered (2000 through 2008), measured concentrations at all monitoring sites were below the TCEQ long-term ESLs. As the TCEQ states on their website (<http://www.tceq.state.tx.us/implementation/tox/esl/ESLMain.html>):

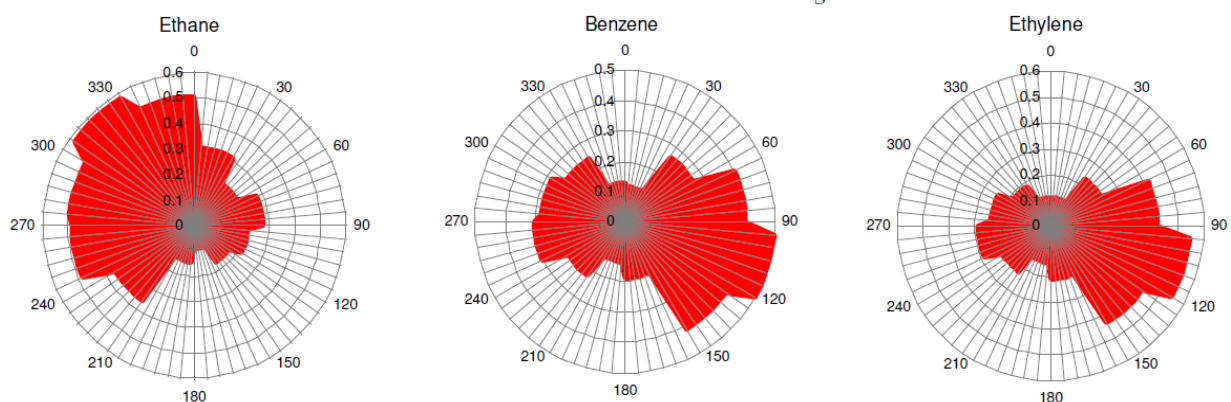
<sup>4</sup> The MIR values, posted to EPA’s Photochemical Assessment Monitoring Stations website ([http://www.epa.gov/oar/oaqps/pams/analysis/ozone/ozone.html#reactivity\\_of\\_identified\\_hydrocarbons](http://www.epa.gov/oar/oaqps/pams/analysis/ozone/ozone.html#reactivity_of_identified_hydrocarbons)), are from Carter: Carter W.P.L. (1994) Development of ozone reactivity scales for volatile organic compounds. J. Air & Waste Manag. Assoc. 44, 881-899.

*“Effects Screening Levels are used to evaluate the potential for effects to occur as a result of exposure to concentrations of constituents in the air. ESLs are based on data concerning health effects, the potential for odors to be a nuisance, effects on vegetation, and corrosive effects. They are not ambient air standards. If predicted or measured airborne levels of a constituent do not exceed the screening level, adverse health or welfare effects are not expected. If ambient levels of constituents in air exceed the screening levels, it does not necessarily indicate a problem but rather triggers a review in more depth.”*

Therefore, according to TCEQ guidance, none of the monitored concentrations of any VOC at any monitoring station in the DFW region during any year since 2000 are high enough to cause concern about adverse health or welfare effects.

## Rice Report Wind Directional Analysis

Hourly average AutoGC concentration data collected at the Fort Worth Northwest and Dallas Hinton sites was analyzed along with hourly wind direction data to determine the direction of potential emission sources. Figure 7 presents an analysis of 2007 (full-year) data for the Fort Worth Northwest monitor for ethane, benzene and ethylene. As described on Page 24 of the Rice Report, the highest 25% of measured VOC concentrations were assigned to the associated wind direction (in 30 degree bins). The plots show the fraction of hourly samples coming from a given direction that have a “high” (in the highest 25%) concentration and point to the direction from which the wind was blowing. For example, for ethane, 60% (0.6 fraction) of the hours when the wind was blowing from 300 to 330 degrees had concentrations in the highest 25% of all measured concentrations. These plots indicate a potential direction of contributing sources.

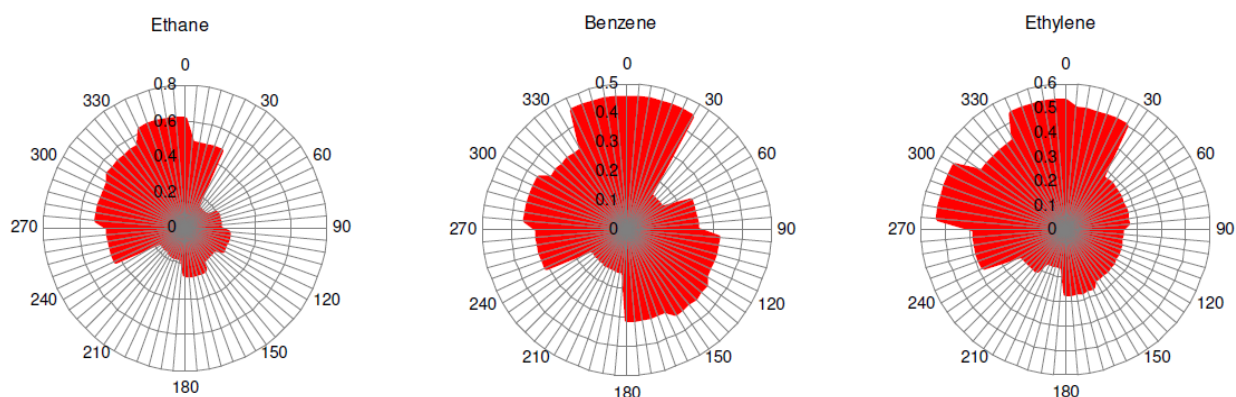


**Figure 7.** Wind Directional Analysis for Fort Worth Northwest AutoGC Data for 2007  
(Extracted from Rice Report)

As stated on Page 24 of the Rice Report:

*“In general, at the Fort Worth monitor for ethane, propane, n-butane, isobutene, and n-pentane, the likely sources are located to the north-northwest . . . The plots for light alkenes . . . and benzene point to both northwest and southeast of the site. In addition to the influence from the FW urban center, the interstate highways to the north and east are also likely bring emissions of these compounds to the FW NW site.”*

Figure 8 presents an analysis of 2007 summer (June through August) data for the Dallas Hinton monitor.



**Figure 8.** Wind Directional Analysis for Dallas Hinton AutoGC Data for Summer 2007  
(Extracted from Rice Report)

As stated on Page 24 of the Rice Report:

*“At Dallas Hinton site, until 2006, high ethane concentrations are associated with winds blowing from north-northwest and to a smaller extent from the southeast (Dallas urban area). The main source of main source of ethane in urban areas is typically liquefied petroleum gas or natural gas leakage . . . In 2006 and 2007 only the northwest direction was dominant, potentially pointing to well development in that direction. Benzene and ethylene wind direction plots point to several directions, most dominant ones being north-northwest and south-southeast, likely indicating both mobile source effect and some industrial effect from those directions.”*

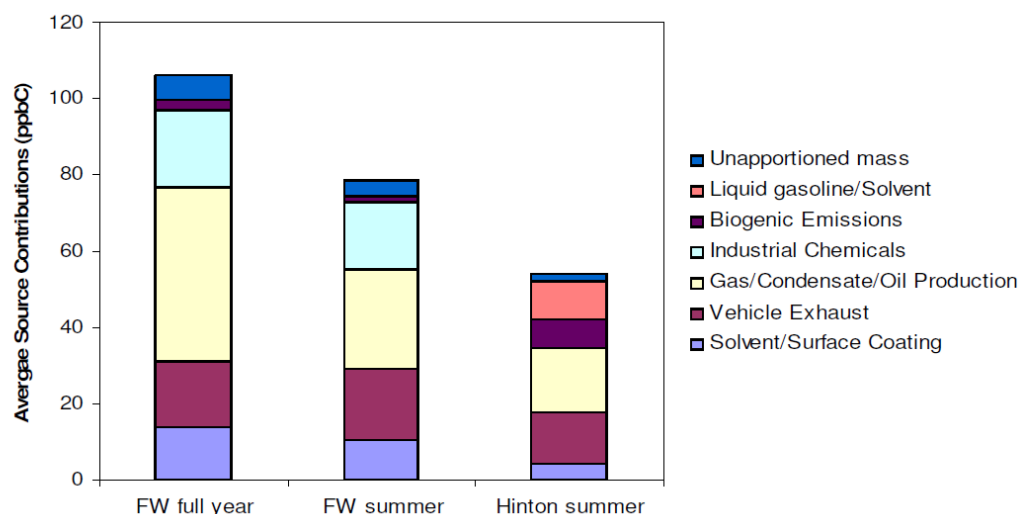
## Source Apportionment Analysis

As discussed on Page 48 of the Rice Report, the Positive Matrix Factorization (“PMF”) model is used to apportion emissions by source type using AutoGC data collected at the Fort Worth Northwest and Dallas Hinton monitors. The source type profiles and associated dominant species used in the PMF model are presented in Table 2.

**Table 2.** PMF Model Source Profiles

Potential Source Type	Dominant Species
Industrial Chemicals	Butenes, acetylene, propylene
Motor Vehicles	Ethylene, acetylene, benzene, propylene, ethylbenzene, toluene, xylenes
Biogenic	Isoprene
Natural Gas/Oil/Condensate Production	Ethane, propane, n-butane, isobutane
Solvents & Surface Coating	Various other VOCs

Figure 9 shows the average source contribution, in parts per billion carbon, by source type, as determined using the PMF model.



**Figure 9. Average Source Contribution Estimated Using PMF Model**  
(Extracted from Rice Report)

As shown in Figure 9, for the 2007 summer samples, the average contributions to total mass from natural gas/oil/condensate production were estimated as approximately 35% for the Fort Worth Northwest monitoring site and 32% for the Dallas Hinton site. For full-year 2007, national gas/oil/condensate production was estimated to contribute approximately 46% of the TNMOC mass measured at the Fort Worth Northwest monitor. For select individual species, approximate percentage contributions from natural gas/oil/condensate production were estimated as presented in Table 3. Also presented in Table 3 are the presumed primary sources of emissions based on the PMF model analysis.

Compound	Contribution from Natural Gas/ Oil/Condensate (Mass %)		Primary Source(s) <sup>a</sup>
	Fort Worth NW	Dallas Hinton	
Ethane	65	60	Oil & Gas
Propane	65	65	Oil & Gas
n-Butane	60	65	Oil & Gas
Isobutane	60	65	Oil & Gas
n-Pentane	40	45	Oil & Gas, Industrial
Isopentane	20	30	Vehicles, Industrial, Oil & Gas
Ethylene	5	10	Vehicles
Propylene	<5	10	Vehicles, Industrial
Acetylene	5	10	Vehicles, Industrial
Isoprene	0	0	Biogenic
Toluene	5	10	Vehicles
Benzene	10	25	Vehicles, Industrial
n-Hexane	30	30	Vehicles, Oil & Gas
m-p Xylenes	<5	5	Vehicles

<sup>a</sup> "Vehicles" includes exhaust and evaporative fuel losses.

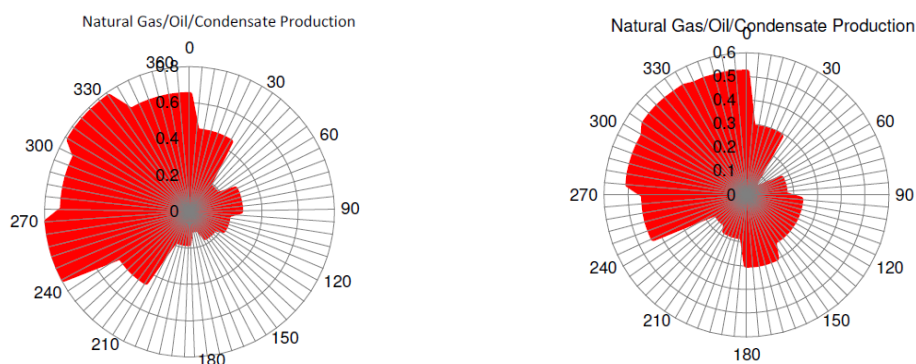
As presented in the Rice Report, the species with the highest ambient concentrations and mass contributions to measured TNMOC from natural gas/oil/condensate production activities are, in order from highest to lowest: ethane, propane, n-butane and isobutane. The dominant contribution of ethane to TNMOC mass is supported by information provided to ENVIRON by Chesapeake showing that the “wet” gas produced in the northwestern and western counties of the Barnett Shale typically has an ethane content over 10%.

As stated on Page 50 of the Rice Report:

*“Ethane and propane are photochemically stable compounds and tend to accumulate in the atmosphere as reactive species are depleted in photochemical reactions. Therefore, they can be major contributors to VOC mass.”*

As noted previously, while a component of TNMOC, ethane is not a VOC.

The associated wind directional analysis for the summer 2007 data is presented in Figure 10.



**Figure 10.** Wind Directional Analysis for Natural Gas/Oil/Condensate Production TNMOC  
(Extracted from Rice Report)

As shown, emissions from natural gas/oil/condensate production sources are primarily from the north, northwest and west at both monitoring sites with a smaller south and southeast contribution at the Dallas Hinton site.

In comparing the two sites, the Rice Report states on Page 73 that:

*“Although, source apportionment of Fort Worth and Hinton data seem to lead to similar results in source attribution of light alkanes, a portion of the gas/oil source contribution is likely to be attributed to evaporative gasoline emissions as also evidenced by the results of the preliminary data analysis. This portion is probably lower in the FW samples because of its proximity to the oil/gas activity, and higher in the Hinton samples because of its more urban character.”*

## Rice Report Recommendations

The author of the Rice Report makes the following recommendations:

- Conduct VOC sampling at sites in Parker, Wise, Hood and Johnson Counties to improve understanding of the impacts of Barnett Shale emissions in rural areas.
- Install additional AutoGCs in the DFW area to improve understanding of spatial and temporal variability of VOC concentrations and source directions.
- Conduct a more detailed source apportionment study using full-year AutoGC data for multiple years and with more robust evaluation of the data set with respect to quality of data.
- Verify the results of the source directional analysis with emissions inventory data and actual source locations.

## ENVIRON Conclusions

Based upon our review of the information contained within the Rice Report, ENVIRON draws the following conclusions:

1. Natural gas, oil and condensate production activities in the Barnett Shale and elsewhere in the DFW region appear to be contributing to regional ambient concentrations of TNMOC.
2. Natural gas, oil and condensate production activities appear to be the largest contributing source of light alkanes – those with fewer than 5 carbon atoms. This includes ethane, propane, butanes, and pentanes. Generally, these compounds are of lesser concern with respect to both health effects and potential contribution to ground-level ozone formation. The species with the greatest mass contribution to TNMOC emissions from natural gas/oil/condensate production activities, ethane, is not a VOC.
3. Motor vehicles, both exhaust and evaporative emissions of fuels, appear to be the largest contributing source of ambient aromatic hydrocarbon concentrations in the DFW region. Aromatic hydrocarbons include benzene, ethylbenzene, toluene and xylenes – all key components in gasoline. In general, these compounds are of greater concern with respect to human health effects. Benzene, ethylbenzene, toluene and xylenes are listed HAPs.
4. Motor vehicle exhaust appears to be the largest contributing source of ethylene, propylene and butenes in the DFW region. These olefins have high photochemical reactivity and are considered key contributors to ground-level ozone formation. One of the butenes, 1,3-butadiene, is also a listed HAP.
5. Annual ambient concentrations of all pollutants at all monitors for all time periods evaluated in the Rice Report are below TCEQ long-term ESLs. Per TCEQ guidance, adverse health or welfare effects are not expected due to exposures at the monitored concentrations.
6. Ambient annual concentrations of benzene monitored in the DFW area compare favorably with other major metropolitan areas that do not have a high concentration of petrochemical industry facilities.

Upon review of this information, please let me know if you have any questions or if clarification is needed. I can be reached by telephone at +1 919.967.9135 or by email at [sramsey@environcorp.com](mailto:sramsey@environcorp.com).

Regards,



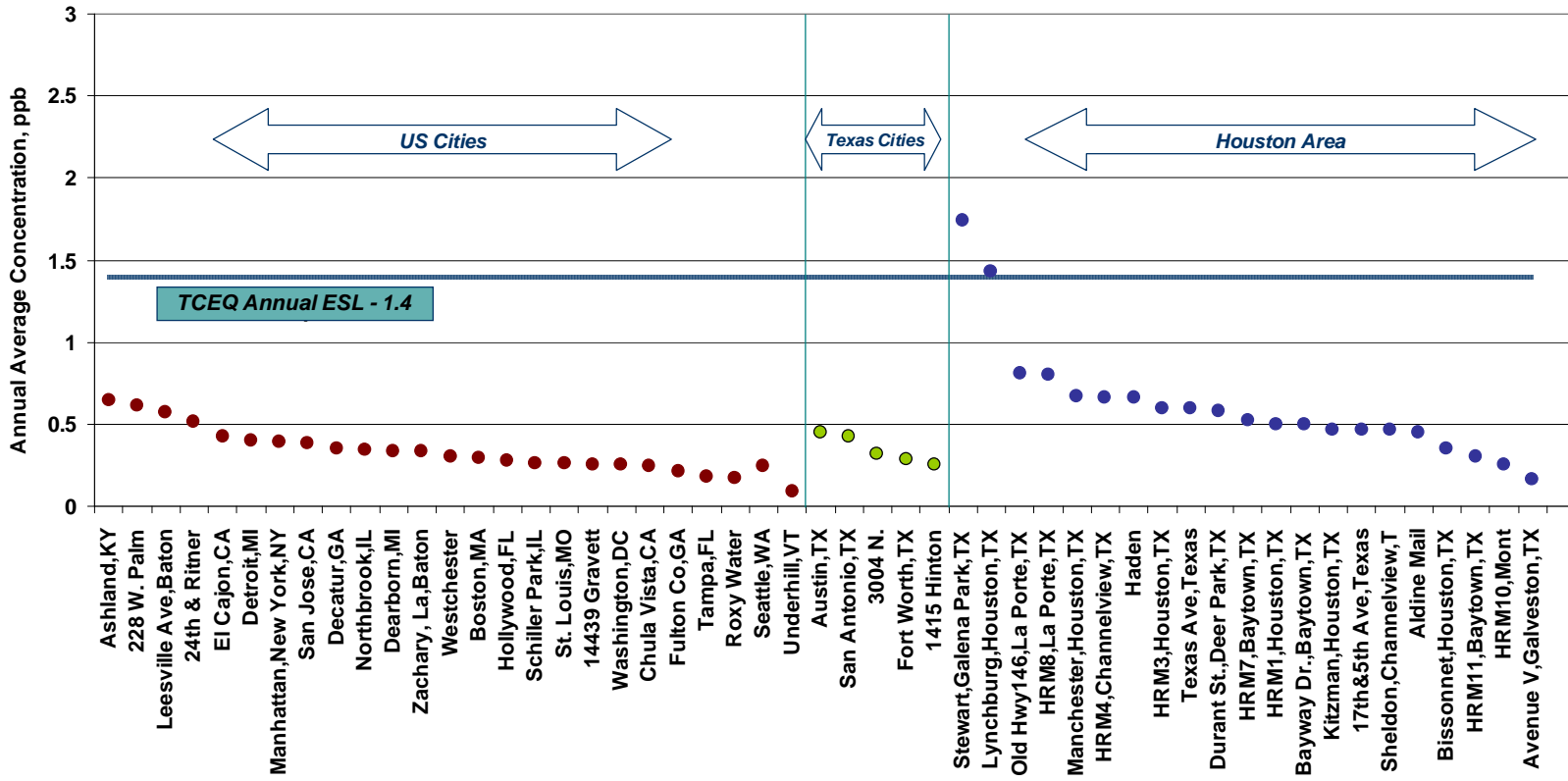
Steven H. Ramsey, P.E., BCEE  
Principal Consultant

Attachment

cc: Donnie Wallis, Chesapeake Energy Company  
Grover Campbell, Chesapeake Energy Company  
John Satterfield, Chesapeake Energy Company  
Robert Coffman, ENVIRON  
Shagun Bhat, ENVIRON

**Attachment A:**

**HRM 2008 Annual Average Benzene Concentration Graphic**



**Houston Area Benzene Compares Favorably To Other US Cities**  
*Lynchburg and Galena Park Monitors Showed Improvement in 2008*