

Final Report

Texas Environmental Research Consortium Project H-13

Variable Industrial VOC Emissions and their impact on  
ozone formation  
in the Houston Galveston Area

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## I. Executive Summary

The Houston-Galveston area (HGA) is designated as a severe ozone non-attainment region, and the State of Texas is charged with developing a State Implementation Plan (SIP) for reducing emissions that lead to ozone formation. A first step in developing the SIP is to characterize and quantify the emissions that lead to high ozone concentrations. In the HGA, developing inventories of emissions that lead to high ozone concentrations is more complicated than in many other urban areas because of the extensive industrial operations in the region.

Emissions from industrial facilities (point sources) are generally assumed, for SIP development purposes, to be continuous and at a nearly constant level. Emissions from Electricity Generating Units (EGUs) are the exception, and the State of Texas, and most other regions of the United States, use continuously collected data on emissions to characterize the role of EGUs in ozone formation. For petroleum refineries, chemical manufacturing facilities, and other industrial operations (non-EGUs), however, SIP analyses generally assume emissions are constant and continuous. This assumption is made because many non-EGUs operate 24 hours per day, 7 days per week, and their material throughput is nearly constant.

Recent evidence, from a variety of sources, demonstrates that while some types of emissions of volatile organic compounds from non-EGU point sources are constant, others are not. The evidence includes emission event reports, air pollutant measurements made by aircraft, air pollutant measurements made by ground monitors, and industrial process measurements. Daily emissions from a single facility can vary from annual average emissions by a factor of 10-1000. Variations of this magnitude at any single facility typically occur only a few times per year, but because there are so many facilities in the HGA, on many days, there is likely to be a facility experiencing significant emission variability.

Air quality measurements taken in recent field studies have also found evidence of localized regions with elevated concentrations of highly reactive volatile organic compounds (HRVOC). These regions with elevated HRVOC concentrations are frequently associated with very rapid ozone formation, leading to exceedances of the ozone air quality standard.

This report documents the evidence for HRVOC emission variability from non-EGU point sources, characterizes the nature of the variability and assesses the impact of variability on ozone formation processes in the HGA. The analyses presented in the report are summarized in a series of Findings.

**Finding 1: Variability in HRVOC emissions from point sources is significant and is due to both variability in continuous emissions and discrete emission events<sup>1</sup>.** *Roughly 3 times per month in 2003, reported emission events caused single facilities to have HRVOC emissions that were greater than 10,000 lb/hr (the total annual average emissions of HRVOCs, from all industrial point sources in the Houston-Galveston region is approximately 5,000 - 10,000 lb/hr). Roughly 3 times per week in 2003, reported emission events caused single facilities to have HRVOC emissions that were greater than 1,000 lb/hr. Roughly once a day in 2003, reported emission events caused single facilities to have HRVOC emissions that were greater than 100 lb/hr. Variability in continuous emissions is more difficult to quantify than emission variability due to reported emission events, but preliminary modeling indicates that variations in continuous (as opposed to discrete) emissions could cause emissions of total VOCs, averaged over areas larger than 100 km<sup>2</sup>, to vary by 5-10%.*

*2-3 times per month HRVOC emissions variability > 10,000 lb/hr*

*2-3 times per week HRVOC emissions variability > 1,000 lb/hr*

*daily HRVOC emissions variability > 100 lb/hr*

The impact of emission variability on ozone formation can take multiple forms. If the emission variability is large enough, and the meteorological conditions are sufficiently ozone conducive, the variability in emissions may be sufficient to cause an exceedance of the National Ambient Air Quality Standard (NAAQS) for ozone (concentrations averaged over 1-hour) that would not have occurred in the absence of the emission event. Documentation, from the Texas Commission on Environmental Quality (TCEQ), is provided in the report for a 6700 pound release of ethylene that caused ozone NAAQS exceedances at multiple monitors.

As noted in Finding 1, however, very large variations in emissions are less common than smaller variations in emissions. While very large variations in emissions might lead to ozone NAAQS exceedances directly, more frequent, smaller variations in emissions have the potential to marginally increase the magnitude of ozone concentrations. If the HRVOC emission variability occurs at critical times and locations, it can marginally increase the peak ozone concentration that might be expected in the Houston-Galveston area. Air quality modeling analyses were performed to assess the changes in peak, region-wide ozone concentrations that might be expected from HRVOC emission variability in the range of 100-5000 lb/hr.

**Finding 2: HRVOC emission variability in the range of 100-1000 lb/hr, which has been reported daily in the Houston-Galveston area, can increase peak, region-wide ozone concentrations, if the emission variability occurs in regions upwind of the location of the peak, region-wide ozone concentration.** *The magnitude of the increase in ozone concentration depends on the location of the emission variability, the time of day when the emission variability occurs and the magnitude of the non-variable ozone precursor emissions. At the most sensitive locations, at the most sensitive times of day, releases over approximately a two to three hour period can lead to increases of 2-3 ppb in peak ozone concentration per 1000 lb of additional HRVOC emissions. This sensitivity may increase as non-variable HRVOC emissions decrease and NO<sub>x</sub> emissions increase.*

Finding 1 suggests that HRVOC emission variability in the range of 100 to 1000 pounds per hour can be expected daily, at some time and some location in the Houston-Galveston area. Finding 2 suggests that if the emission variability occurs at a sensitive time and a sensitive location, that peak ozone concentration could be increased by 2-3 ppb for every 1000 lb of HRVOC emissions released. In order to link these two findings, it was necessary to assess how frequently emission variability might occur at sensitive times and sensitive locations.

The bases for the frequency analysis were a TCEQ database on event emissions, described in the report, and meteorological assessment of the frequency of ozone-conducive conditions. The frequency analysis suggests that, if the emission variability is not large enough to directly cause an ozone exceedance, then the probability that additional emissions will occur at the right time and at the right location to marginally enhance ozone peak concentration is small. The exact probability has significant uncertainty, but is most likely of order 1 in 20 to 1 in 200. Stated differently, only 1 in 20 to 1 in 200 randomly selected instances of emission variability is likely to be at the right time and in the right location to influence peak ozone concentration. However, because the regulatory goal is not to exceed the national ambient air quality standard for ozone more than once per year, even if the probability of an event being in the right place at the right time is 1 in 100, the frequency analysis documented in this report shows that emission variability of roughly 1000 lb/hr should be expected upwind of peak, region wide ozone concentrations.

This would suggest that, if no actions were taken to reduce emission variability, it would be necessary to plan for an event of 1000 pounds in an attainment demonstration, at a location that would influence peak ozone concentrations. If actions are taken to reduce emission variability, however, the magnitude of the emission variability that should be expected upwind of peak, region wide ozone concentrations, could be decreased.

**Finding 3: Based on current data, emission variability of roughly 1000 lb/hr should be expected in the regions upwind of peak, region wide ozone concentration at least once per year in the Houston-Galveston area.** *This finding is based on estimates of the frequency of ozone conducive conditions and the frequency and magnitude of HRVOC emission events reported through a TCEQ database. This expected value could potentially be decreased by imposing short term limits on HRVOC emission variability.*

<sup>1</sup>Reportable emission events are defined by Texas Administrative Code (TAC) Title 30 Chapter 101. Section 101.1, paragraph (83) defines a reportable emissions event as “Any emissions event which, in any 24-hour period, results in an unauthorized emission equal to or in excess of the reportable quantity...”. The reportable quantity for HRVOCs is 100 lb. Emission variability, either discrete, or routine, may not in all cases result in a reportable emission event.