

BNL-

QUANTIFICATION OF FUGITIVE REACTIVE ALKENE EMISSIONS FROM
PETROCHEMICAL PLANTS WITH PERFLUOROCARBON TRACERS

Gunnar I. Senum and Russell N. Dietz
Environmental Science Department
Atmospheric Science Division
Brookhaven National Laboratory
Upton NY 11973-5000

Final Report to
Houston Advanced Research Center (HARC)

June 2004

Research by BNL investigators was performed under the auspices of the U.S. Department of Energy under Contract No. DE-AC02-98CH10886.

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Introduction

Recent studies demonstrate the impact of fugitive emissions of reactive alkenes on the atmospheric chemistry of the Houston Texas metropolitan area (1). Petrochemical plants located in and around the Houston area emit atmospheric alkenes, such as ethene, propene and 1,3- butadiene. The magnitude of emissions is a major uncertainty in assessing their effects. Even though the petrochemical industry reports that fugitive emissions of alkenes have been reduced to less than 0.1% of daily production, recent measurement data, obtained during the TexAQS 2000 experiment indicates that emissions are perhaps a factor of ten larger than estimated values. Industry figures for fugitive emissions are based on adding up estimated emission factors for every component in the plant to give a total estimated emission from the entire facility. The dramatic difference between estimated and measured rates indicates either that calculating emission fluxes by summing estimates for individual components is seriously flawed, possibly due to individual components leaking well beyond their estimated tolerances, that not all sources of emissions for a facility are being considered in emissions estimates, or that there are known sources of emissions that are not being reported. This experiment was designed to confirm estimates of reactive alkene emissions derived from analysis of the TexAQS 2000 data by releasing perfluorocarbon tracers (PFTs) at a known flux from a petrochemical plant and sampling both the perfluorocarbon tracer and reactive alkenes downwind using the Piper-Aztec research aircraft operated by Baylor University.

PFTs have been extensively used to determine leaks in pipelines, air infiltration in buildings, and to characterize the transport and dispersion of air parcels in the atmosphere. Over 20 years of development by the Tracer Technology Center (TTC) has produced a range of analysis instruments, field samplers and PFT release equipment that have been successfully deployed in a large variety of experiments. PFTs are inert, nontoxic, noncombustible and nonreactive. Up to seven unique PFTs can be simultaneously released, sampled and analyzed and the technology is well suited for determining emission fluxes from large petrochemical facilities.

The PFT experiment described here was designed to quantitate alkene emissions from a single petrochemical facility, but such experiments could be applied to other industrial sources or groups of sources in the Houston area.

Conclusions

1. The use of PFTs for the determination of fugitive emission fluxes has been successfully demonstrated in this field study. The two PFTs used in this study were well correlated in the canister samples when the two PFTS were in the same emission plume.
2. During certain meteorological conditions, two plumes were emanating from the Sweeny plant, one from the relatively hot core of the plant and other from the

relatively cooler water chiller. The aircraft samples were more often from the cooler water chiller plume.

3. The ethene emission flux has been measured as 106 ± 29 kg/hr, based on the ethene and PFT concentrations in the downwind aircraft canister samples and known PFT emission flux released inside the Sweeny plant. This is the average of three sampling dates, 11/25, 12/7, and 12/14/2003. This is 6 times higher than the 2000 TRNCC estimate.
4. The propene emission flux has similarly been measured as 82 ± 1 kg/hr on 11/25, 277 ± 55 kg/hr on 12/7 and 51 kg/hr on 12/14/2003. The varying results from different sampling dates is either a genuine variation in the plant propene emission rate or due to a large variability in the propene concentration in the hydrocarbon analyses. The high correlation between the PMCP and the RAD measurement of reactive alkenes, implies there are variabilities in the hydrocarbon analyses. The propene flux measurements are respectively 4.8, 16.2 or 3 times larger than the 2000 TRNCC estimate.
5. The NO_y emission flux has been estimated as 230 ± 40 kg/hr based on the PMCP concentration in the aircraft sampled canister and a 25 second average of the NO_y realtime concentration. It can be compared to the 2000 TRNCC estimate of 554 kg/hr.