



## Project Summary

# Ambient Hydrocarbon and Ozone Concentrations Near a Refinery

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Atmospheric emissions from the Marathon Oil Company refinery at Robinson, Illinois were investigated during June and July 1977. Surface and aerial measurements were used in an integrated, three-dimensional monitoring network. The study focused on three major areas: (1) characterization of gaseous components within the refinery effluent, especially non-methane hydrocarbons (NMHCs) and nitrogen oxides ( $\text{NO}_x$ ); (2) sunlight bag-irradiation experiments to examine ozone-forming potential of refinery emissions; and (3) aerial measurements of changes in plume chemistry during the first six to eight hours of transport. Concentrations of ozone, nitrogen oxides, sulfur dioxide, methane, carbon dioxide, individual nonmethane hydrocarbons, and halocarbons were recorded on a routine basis. In addition, meteorological parameters such as wind speed, wind direction, solar radiation, and mixing height were also measured. Results indicate that levels of hydrocarbons and nitrogen oxides were elevated downwind of the refinery. In the effluent, concentrations of hydrocarbons and of nitrogen oxides exceeded background values by as much as 300-fold and 10-fold, respectively. Irradiations of captured refinery emissions suggest that ozone can be produced photochemically in amounts that vary according to NMHC/ $\text{NO}_x$  ratios and initial NMHC concentrations. Continuous measurements made from an aircraft documented instances of ozone buildup in the refinery plume as it drifted downwind.

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*Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Pollution caused by photochemical oxidant production is becoming an increasingly widespread problem in the United States, despite regulatory actions to limit emissions of precursors to oxidants. Once thought to be exclusively an urban phenomenon, ozone ( $\text{O}_3$ ) levels in many suburban and rural areas routinely violate the current 120-ppb National Ambient Air Standard. Recognition of the importance of long-range multi-day transport of airborne pollutants has directed attention to the regional nature of ozone/oxidant pollution episodes and underscored the need for effective control strategies. Requirements for retrofit emissions control measures on major stationary sources are an integral part of contemporary regulatory policy. Before the efficacy of these control measures can be evaluated, the relative contribution of specific point-source categories to observed downwind  $\text{O}_3$  buildup must be known.

Petroleum refineries are major sources of several primary pollutants, including hydrocarbons, nitrogen oxides ( $\text{NO}_x$ ), carbon monoxide (CO), and particulate matter. Concerns about refinery emissions have focused primarily on nonmethane hydrocarbon (NMHC) releases, and control measures, such as floating roof storage tanks, have been instituted at most sites. Because airborne emissions from refining operations contain significant quantities of hydrocarbons and nitrogen oxides, it is reasonable to assume that ozone is formed within the plume during appropriate meteorological conditions.



This report summarizes the results of an ambient air monitoring study conducted during June and July 1977 near the Marathon Oil Company refinery at Robinson, IL. The refinery which processes approximately 200,000 barrels of crude oil per day is located in a rural region away from other major pollution sources. Aerial and ground-level measurements were designed to examine chemical transformation within the plume during the first six to eight hours of transport. Results of continuous monitoring at the field laboratory, captive air irradiation studies of refinery emissions, and aerial measurements in the plume during transport are presented. Discussion focuses on the evaluation of local O<sub>3</sub> concentrations due to photochemical production of ozone in the refinery emissions.

### **Procedure**

Both surface and aerial monitoring stations were used to investigate the refinery emissions. The focal point for ground-level operations was a 7-m instrumented trailer located approximately 5 km east of the refinery. Pollutant parameters measured at the field laboratory included concentrations of O<sub>3</sub>, NO<sub>x</sub>, methane (CH<sub>4</sub>), CO, total hydrocarbons, individual C<sub>2</sub> - C<sub>10</sub> NMHC and halocarbons; wind speed and direction; turbulence; dew point; solar radiation; and temperature. In addition, vertical temperature discontinuity was recorded continuously using a monostatic acoustical sounder. Natural sunlight irradiation experiments were also conducted at this site using 500-1 Teflon bags filled with either refinery emissions or background air.

A twin-engine Rockwell Aero Commander served as an airborne monitoring platform. Instruments on board the aircraft allowed for continuous measurements of O<sub>3</sub>, NO<sub>x</sub>, sulfur dioxide (SO<sub>2</sub>), and condensation nuclei (CN) visual range, and flight parameters. Six-liter grab samples were collected in stainless steel canisters or Teflon bags and returned to the field laboratory for gas-chromatographic analysis.

## **Results**

### **Ground-Level Measurements**

Continuous ground-level monitoring was conducted at the field laboratory 5 km east of the refinery complex. Measurements at this site during periods of fumigation provided an indication of pollutant concentrations associated with the refinery effluent. Nonmethane hydrocarbons and NO<sub>x</sub> were the best indicators of refinery emissions at the surface, and CO and CH<sub>4</sub> also exhibited

higher values during fumigations. Nitrogen oxides and NMHC concentrations typically jumped from background levels of < 10 ppb and < 0.1 ppmC, respectively, to approximately 20 ppb and 5 ppmC as emissions passed over the trailer. In-plume CO concentrations commonly increased about 0.2 ppm and CH<sub>4</sub> values exceeded background levels by 0.4 ppm.

Because NMHC are a major component of refinery emissions, considerable effort was devoted to determining hydrocarbon concentrations and composition in the plume. Hydrocarbon concentrations in morning samples 0600-0800 CDT collected at the fence line commonly exceeded 1000 µg/m<sup>3</sup> (1,500 ppbC), with values varying from 200 - 18,000 µg/m<sup>3</sup> (300 - 27,000 ppbC). Observed in-plume hydrocarbon values at the surface were found to be negatively correlated with early morning mixing height as determined by the acoustical-sounder records. The proportion of olefins, aromatics, and paraffins measured in refinery emissions remained relatively constant throughout the monitoring program. Olefins routinely comprised 1 - 5% of each plume sample, aromatics 5 - 15%, and paraffins 80 - 95%.

More detailed gas-chromatographic analysis was performed to investigate identities of C<sub>2</sub> - C<sub>10</sub> NMHCs present in background and plume samples. Ground level samples from outside the plume were composed primarily of the paraffinic species ethane, propane, i-butane, n-butane, i-pentane, and n-pentane. Refinery emissions were also composed principally of paraffins, with ethane, propane, i-butane, n-butane, i-pentane, and n-pentane frequently accounting for more than 50% of the total. Other compounds present at relatively high concentrations within the plume included 2-methylpentane, 3-methylpentane, n-hexane, methylcyclopentane, 2,4-dimethylpentane, benzene, 2,3-dimethylpentane, 3-methylhexane, 2,2,3-trimethylpentane, n-heptane, methylcyclohexane, toluene, and the isomeric xylenes.

### **Captive-Air Irradiations**

Natural sunlight irradiations of 500-1 Teflon bags filled with petroleum refinery emissions or background air were used to assess ozone-forming potential. Three bags (2 refinery and 1 background) were collected between 0600-0800 CDT and initial NMHC, O<sub>3</sub>, and NO<sub>x</sub> concentration measurements were performed at the field laboratory before exposing the chambers to sunlight. Additional nitric oxide (NO) was added to selected refinery samples in order to examine the effects of varying NMHC/NO<sub>x</sub> ratios. Changes in O<sub>3</sub>, NO,

and nitrogen dioxide (NO<sub>2</sub>) were monitored periodically throughout each run. Ozone production in plume and non-plume samples was compared to provide an indication of ozone-forming potential associated with refinery emissions.

Maximum amounts of O<sub>3</sub> produced in background samples were less than 80 ppb in all cases, while refinery samples to which no NO had been added had O<sub>3</sub> concentrations as high as 220 ppb. Plume samples to which additional NO had been added showed maximum O<sub>3</sub> generation on the order of 500 ppb. Irradiation experiments revealed that NMHC/NO<sub>x</sub> ratios and absolute amounts of NMHC were important factors in determining O<sub>3</sub> concentrations. Optimum conditions for photochemical ozone production occurred at NMHC/NO<sub>x</sub> ratios between 10 and 20, and the amount of O<sub>3</sub> generated was proportional to initial NMHC levels.

### **Aerial Measurements**

The instrumented aircraft made several flights downwind of the refinery to investigate in-plume pollutant levels. Elevated hydrocarbon concentrations were documented in the plume, with peak values in the range of 200-300 µg/m<sup>3</sup> (300 - 400 ppbC) at 8 km, decreasing to 75 - 100 µg/m<sup>3</sup> (100 - 150 ppbC) at 15 km. Levels of NO<sub>x</sub> (+5 to +15 ppb), SO<sub>2</sub> (+25 to +30 ppb), and condensation nuclei were also higher in the plume than outside the plume. On two occasions, July 8 and July 21, 1977, O<sub>3</sub> in the plume exceeded background concentrations. Peak in-plume O<sub>3</sub> enhancement was approximately 30 ppb on July 8 and 15 ppb on July 21. Background O<sub>3</sub> levels for the two days were 85 ppb and 70 ppb respectively. Both instances of ozone buildup occurred when prevailing southerly winds carried emissions to the north of the plant.

Data from two flights on July 21, 1977 are typical of pollutant levels measured in the plume at various distances downwind. The initial flight was conducted between 0630 - 0745 CDT before sufficient solar radiation was available for maximum photochemical activity. During this period, prevailing winds carried Marathon emissions to the northeast of the refinery. After a vertical spiral to 4300 m over the plant, the aircraft made several passes through the area of plume drift and then flew to 19 km from the refinery.

Temperature variations with altitude, recorded during the spiral at 0640 CDT, showed a distinct temperature inversion at approximately 350 m. Above the inversion, O<sub>3</sub> values were relatively constant at 70 ppb, while beneath this level concentra-

tions decreased to less than 30 ppb near the surface. The July 21 acoustical sounder tracing revealed the presence of a low-level radiation inversion at about 50 m from 0300-0600 CDT, with a gradual weakening and lifting between 0600 - 0930 CDT. Sounder records indicate a breakup of the inversion by 0930 CDT and well-mixed conditions prevailing up to at least 500 m.

Downwind of the refinery, the aircraft made a number of passes through the Marathon plume. In-plume SO<sub>2</sub> values were about 100 ppb higher than background levels at 8 km and 35 ppb higher at 16 km. Condensation nuclei levels on both passes showed a ten-fold increase over background levels. Ozone concentrations, on the other hand, exhibited marked depletion due to scavenging by NO in the plume. In-plume ozone values were depleted below background levels by approximately 35 ppb at 8 km and 10 ppb at 16 km.

Hydrocarbon grab samples collected by the aircraft revealed elevated C<sub>2</sub> - C<sub>10</sub> NMHC concentrations in the plume. The NMHC concentration in background sample taken outside the plume was less than 20 µg/m<sup>3</sup> (30 ppbC). The NMHC level exceeded 1000 µg/m<sup>3</sup> (1500 ppbC) in a plume sample collected 0 - 3.5 km downwind, while at 8 - 11 km the concentration was greater than 200 µg/m<sup>3</sup> (300 ppbC).

In order to investigate the possibility that O<sub>3</sub> is produced within the effluent, a second flight was conducted on July 21 from 1005 - 1200 CDT. Data collected during this flight demonstrate that O<sub>3</sub> buildup does occur in the refinery's discharges. Emissions were observed to the northeast of the plant, and plume boundaries were well defined out to 26 km downwind. Temperature data indicate that the inversion observed on the earlier flight had completely dissipated by 1015 CDT, thus confirming the acoustical-sounder tracings. Ozone concentrations were relatively constant up to 1200m, suggesting that the mixing layer extended to at least that altitude. Measurements at 19 km from the plant tend to corroborate this observation since emissions were detected at 1000 m.

Cross-plume passes at 8, 13, 19, and 26 km downwind of the refinery revealed that SO<sub>2</sub>, CN, and O<sub>3</sub> concentrations were higher inside the plume boundaries than outside. The buildup of O<sub>3</sub> within the plume amounted to 7 ppb at 8 km, 8 ppb at 13 km, 15 ppb at 19 km and 8 ppb at 26 km. Plume traverses at several altitudes 19 km from the refinery suggested that

refinery emissions were stratified, with maximum O<sub>3</sub> enhancement and plume width occurring near the surface. Greatest ozone concentrations inside plume boundaries on this flight were measured at 250 m, 19 km from the plant.

## Conclusions and Recommendations

Photochemical O<sub>3</sub> formation from refinery emissions is clearly a complex phenomenon, depending on many meteorological variables and emission characteristics. The fact that in-plume O<sub>3</sub> buildup was recorded in the effluent on two out of six flights shows that O<sub>3</sub> can be generated solely from petroleum refinery discharges. Meteorological and plume composition data do not account for the absence of O<sub>3</sub> enhancement on two-thirds of the sampling days. Further investigations of the reasons for sporadic O<sub>3</sub> formation may provide

valuable information about photochemical activity in ambient atmospheres.

Data reported here concentrated on O<sub>3</sub> production during the first six to eight hours of transport. It may be that maximum O<sub>3</sub> levels occur much later, because 80 - 90% of NMHC emissions from refineries are in a relatively slow-reacting classification, the paraffinic compounds. Although the contribution of low molecular weight hydrocarbons to long-range multi-day transport of ozone is not well understood, the potential impact of these emissions on regional pollution levels should not be ignored.

Future captive air studies should involve the use of NO<sub>2</sub> instead of NO. Too much time is required to oxidize the NO to NO<sub>2</sub> by the NO addition. Also, the initial O<sub>3</sub> is titrated with the NO addition. Thus, the NO spiked air samples do not have sufficient daylight to both oxidize NO and generate maximum O<sub>3</sub>.

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*The complete report, entitled "Ambient Hydrocarbon and Ozone Concentrations Near a Refinery," (Order No. PB 83-195 958; Cost: \$23.50, subject to change) will be available only from:*

*National Technical Information Service*

*5285 Port Royal Road*

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