Photochemical Ozone Formation in Urban and Point-Source Plumes

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Results of aerial measurements in plumes from large urban areas, petroleum refineries, automotive-painting operations, fossil-fuel power plants, and controlled burning of forest slash are presented. Field monitoring studies occurred during summer months between 1974 and 1980 and emphasized collection of data on in-plume ozone buildup and associated precursor concentrations. Photochemical ozone formation in excess of ambient background levels was documented in all plumes studied, with the exception of power-plant emissions. Examination of NMHC/NO\textsubscript{2} ratios indicates ozone production, or depletion in the case of power-plant effluents, was consistent with the traditional HC-NO\textsubscript{2}-UV light model. Urban non-methane hydrocarbon composition was similar for the cities monitored, but marked variation was observed between plumes from other sources.

Introduction

During 1974–1980, surface and aerial measurements of ozone, non-methane hydrocarbons (NMHC), and nitrogen oxides were recorded downwind of a number of urban and point sources. The ambient monitoring program was specifically aimed at investigating the relationship between ozone and ozone precursors in plumes from large metropolitan areas, petroleum refineries, automotive-painting facilities, fossil-fuel power plants, and controlled burning of forest slash. Results are presented emphasizing the relative magnitude of photochemical ozone formation over time periods of 6–8 h and associated in-plume concentrations of hydrocarbon and nitrogen oxides precursors.

Experimental Section

Ground-level measurements were centered around a 25-ft instrumented trailer which served as a field laboratory. Typically, the trailer was located near the emissions source being investigated. Continuous monitoring of O\textsubscript{3}, NO, NO\textsubscript{2}, NO\textsubscript{x}, CH\textsubscript{x}, CO, total hydrocarbon, selected halocarbons, and a variety of meteorological parameters was accomplished at this site. Non-methane hydrocarbon samples were collected at the surface and by an instrumented aircraft in Teflon bags or stainless steel canisters and then returned to the field laboratory. Individual hydrocarbon identification was accomplished by using two Perkin-Elmer gas chromatographs. From 1974 to 1975 only C\textsubscript{2}-C\textsubscript{6} NMHC were measured, but after 1975 C\textsubscript{2}-C\textsubscript{10} hydrocarbon compounds were analyzed for all samples. Instruments carried by the aircraft allowed for continuous measurement of O\textsubscript{3}, NO, NO\textsubscript{2}, NO\textsubscript{x}, visual range, condensation nuclei, temperature, and relevant flight parameters (e.g., airspeed, altitude). Beginning in 1977, a pulsed fluorescent SO\textsubscript{2} analyzer provided continuous data on ambient SO\textsubscript{2} levels. Hydrocarbon grab samples were also collected and returned to the field laboratory for analysis. A Metodat acquisition system was employed in both the trailer and the aircraft, allowing for storage of continuous data on nine-track magnetic tape. A more complete description of study designs, instrument manufacturers, measurement techniques, and calibration procedures is available elsewhere (1–6).

Results

Pollutant measurements in selected urban and point-source plumes during the first 6–8 h of transport were conducted by using an instrumented aircraft. Field studies occurred during summer months (1974–1980) and focused on documenting in-plume photochemical transformations. Research efforts emphasized collection of data on ozone enhancement (or depletion), concentration and composition of non-methane hydrocarbons, and levels of nitrogen oxides. Sources investigated included large urban areas (Chicago, IL; Milwaukee, WI; Houston, TX), petroleum refineries (Benicia, CA; Lawrenceville and Robinson, IL), an automotive-painting facility (Janesville, WI), fossil-fuel power plants (western shore of Lake Michigan), and controlled burning of forest slash (rural areas in Washington State).

Large Urban Centers. Airborne emissions downwind of Chicago, Milwaukee, and Houston were monitored in order to provide a comparison of ozone and ozone precursor levels. Chicago and Milwaukee are located in the Great Lakes region and have not been as well studied as some other urban centers. Houston is situated along the Gulf Coast and has been the subject of several air pollution studies.

Measurements in the Chicago and Milwaukee plumes were obtained in conjunction with field studies in 1976 (7) and 1977 (4). Migratory high-pressure systems dominate summertime and fall meteorology in this region, and the relationship between anticyclones and air quality in the Midwest has been well documented (8). Mesoscale lake breezes have been shown to have a significant impact on pollutant concentrations in areas immediately adjacent to Lake Michigan, especially downwind of Chicago and Milwaukee (9–11).

The Chicago plume was observed on several occasions to be transported downwind as a discernible entity for more than 100 miles. During periods of synoptic airflow from the southeast, emissions from the Chicago-Gary urban complex were shown to have a significant effect on local pollutant levels in southern Wisconsin (12). Peak in-plume ozone enhancement under these conditions was on the order of 80 ppb above background levels, while NMHC and NO\textsubscript{x} concentrations 60 miles from Chicago were approximately 75 ppbC and 15 ppb, respectively. In samples collected just downwind of the city, hydrocarbon values typically were greater than 500 ppbC and NO\textsubscript{x} levels were near 100 ppb.

Highest ozone concentrations were commonly recorded along the Lake Michigan shoreline to the north of Chicago during lake breeze fumigation. In the most frequent observed scenario, primary emissions from the Chicago-Gary area drifted to the northeast over Lake Michigan during the morning hours. Secondary pollutants were formed in the polluted air mass over the lake and then advected onshore by the afternoon lake breeze winds.
Peak afternoon ozone values in the shoreline region of fumigation typically exceeded 200 ppb at ground level (100 ppb above background), and concentrations as high as 300 ppb were recorded by the instrumented aircraft. Associated hydrocarbon and NO\textsubscript{x} levels were about 300–500 ppbC and 25–100 ppb, respectively.

Milwaukee is a smaller, less industrialized city than Chicago, located approximately 50 miles north along the shore of Lake Michigan. As in the case of the Chicago plume, emissions from Milwaukee were shown to produce elevated levels of photochemical ozone as they drifted over the lake. On several occasions, fumigation of the shoreline by the Milwaukee plume resulted in peak ozone concentrations in excess of 200 ppb near Sheboygan, 50 miles north of the city. Precursor concentrations measured in the effluent from Milwaukee were routinely less than for Chicago, with NMHC levels between 200 and 300 ppbC and NO\textsubscript{x} less than 50 ppb. It is important to note that although excess ozone concentrations in the Milwaukee and Chicago plumes were similar (100–150 ppb), the Chicago plume was normally larger.

Observations of pollutant levels in the Houston plume were obtained during an intensive monitoring study in 1978 (6). During the period of investigation in Aug and Sept, relatively low pollution concentrations were advected into the Houston area; however, afternoon ozone buildup downwind of the city was consistently recorded. Ozone concentrations in the urban plume typically exceeded ambient background levels by 100–250 ppb, with elevated values persisting for more than 100 miles downwind.

Peak photochemical ozone formation was associated with NMHC concentrations of 700–800 ppbC and NO\textsubscript{x} levels of approximately 50 ppb. Highest ozone concentrations were noted when easterly winds caused industrial discharges from the ship-channel region to mix rapidly with Houston urban emissions. Attempts to quantify relative contributions of NMHC and NO\textsubscript{x} precursors from Houston, the ship channel, and nearby industrial locations, such as Baytown and Texas City, have not been successful to date. Yet all these sources undoubtedly contribute to emissions which are labeled as the "Houston plume" (13). Data from the urban plumes discussed above are summarized in Table I.

### Table I. Summary of O\textsubscript{3}, NO\textsubscript{x}, and NMHC Data from Urban and Point-Source Plumes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Chicago plume (11)</th>
<th>Milwaukee plume (11)</th>
<th>Houston plume (13)</th>
<th>Marathon oil refinery (5)</th>
<th>GM painting plant (16)</th>
<th>power plants (7)</th>
<th>forest-slash burn (19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔO\textsubscript{3}, ppb</td>
<td>100–200</td>
<td>100–150</td>
<td>100–250</td>
<td>15–30</td>
<td>5–15</td>
<td>depletion</td>
<td>40–50</td>
</tr>
<tr>
<td>NMHC/NO\textsubscript{x}</td>
<td>5–10</td>
<td>5–15</td>
<td>7–10</td>
<td>10–20</td>
<td>10–15</td>
<td>&lt;1</td>
<td>5–10</td>
</tr>
<tr>
<td>NO\textsubscript{2}, ppb</td>
<td>50–100</td>
<td>&lt;50</td>
<td>50–100</td>
<td>25</td>
<td>20–30</td>
<td>100–400</td>
<td>50–100</td>
</tr>
<tr>
<td>NMHC, ppbC</td>
<td>550</td>
<td>250</td>
<td>750</td>
<td>350</td>
<td>250</td>
<td>near 700</td>
<td></td>
</tr>
<tr>
<td>olefins, %</td>
<td>11</td>
<td>10</td>
<td>8</td>
<td>5</td>
<td>6</td>
<td>&lt;5</td>
<td>45</td>
</tr>
<tr>
<td>aromatics, %</td>
<td>22</td>
<td>25</td>
<td>11</td>
<td>10</td>
<td>35</td>
<td>5–15</td>
<td>25</td>
</tr>
<tr>
<td>paraffins, %</td>
<td>67</td>
<td>65</td>
<td>80</td>
<td>85</td>
<td>58</td>
<td>85</td>
<td>25</td>
</tr>
<tr>
<td>plume width, miles</td>
<td>20–30</td>
<td>10–15</td>
<td>10–20</td>
<td>3–5</td>
<td>3–5</td>
<td>3–5</td>
<td>1–4</td>
</tr>
<tr>
<td>time req'd for O\textsubscript{3} buildup, min</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>&lt;30</td>
<td>60–120</td>
<td>60–120</td>
<td>NA</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

* a Observed maximum ozone enhancement above background levels.  b Typical value recorded in region of peak ozone buildup.  c Less than 100 ppbC in most cases.  d Approximate time from precursor release to production of photochemical O\textsubscript{3} in excess of local ambient background concentrations.  e Not applicable.

In Sept 1975, a 2-week investigation was conducted to measure in-plume pollutant concentrations in the plume from the Exxon refinery at Benicia, CA (2, 14). Because of interferences from nearby industrial sources, Exxon emissions could be tracked for only about 8 miles (approximately 30 min irradiation time). In-plume ozone values were either less than or equal to background levels out to that distance. Non-methane hydrocarbon concentrations in the plume were in the range 500–1000 ppbC and NO\textsubscript{x} values varied from 50 to 150 ppb. Ozone buildup was consistently recorded in the delta region of the Sacramento river, approximately 30 miles downwind. However, it was not possible to define the contribution of Exxon emissions.

During July 1977, a field monitoring program near the Marathon refinery at Robinson, IL (3, 5), revealed ground-level NMHC and NO\textsubscript{x} concentrations on the order of 5000 ppbC and 25 ppb, respectively. Downwind of the plant, NMHC values were typically 1000–2000 ppbC at less than 2 miles, decreasing to 300–400 ppbC at 5 miles and 100–150 ppbC at 10 miles. In-plume NO\textsubscript{x} levels were commonly 10–25 ppb, with elevated NO\textsubscript{x} and NMHC recorded out to 20 miles from the refinery. Excess ozone formation was observed in conjunction with the Marathon plume during some afternoon flights. Peak ozone levels were typically between 15 and 30 ppb above background concentrations and were most frequently observed in the region 5–15 miles downwind of the plant. The data pertinent to ozone formation in petroleum-refinery plumes are given in Table I.

### Automotive-Painting Plant

Photochemical ozone generation near the General Motors Assembly Division plant at Janesville, WI, was examined in 1977 and 1978 (4, 15, 16). The majority of organic volatiles measured in the GM plume consisted of hydrocarbons in the C\textsubscript{5}–C\textsubscript{10} molecular weight range, with toluene, C\textsubscript{8} alkanes, ethylbenzene, and the three isomeric xylenes predominating. Ground-level measurements near the plant revealed NMHC concentrations of 3000 ppbC, while downwind levels were approximately 200–300 ppbC at 5–10 miles. Aerial measurements showed NO\textsubscript{x} values varying from 20 to 30 ppb within plume boundaries. Isolated instances of elevated ozone concentrations attributable to GM emissions were recorded in both 1977 and 1978. Excess ozone formation was consistently between 5 and 15 ppb above background. Information from the GM study is given in Table I.

### Fossil-Fuel Power Plants

Ozone production in power-plant plumes along the western shore of Lake
Michigan was examined in 1976 (7). Ozone concentrations in the definable portion of the plume were commonly depleted compared to background levels due to scavenging by nitric oxide. Non-methane hydrocarbon values within plume boundaries were on the same order as existing background concentrations. Elevated in-plume NOx levels were always observed. Although no instances of photochemical ozone production due solely to power-plant emissions were observed, other investigators have reported ozone buildup in power-plant effluents (17, 18). Measurements of O3, NOx, and NMHC concentrations in fossil-fuel power-plant plumes are given in Table I.

**Controlled Burning of Forest Slash.** Measurements in slash-burn plumes from predominantly rural regions of Washington State revealed consistent ozone buildup of 40–50 ppb (19). Ozone production appeared to occur very rapidly in the plume, with excess O3 frequently recorded directly over the forest burn. Hydrocarbon analysis showed that many photochemically reactive olefins were present in airborne emissions and favorable NMHC/NOx and NOx/NO2 ratios were often observed. Nitrogen oxides concentrations between 50 and 100 ppb were commonly associated with the plume, while NMHC values as high as 600–700 ppb were recorded. The olefinic compounds propene, 1-butene, 2-methylpropene, cis-2-butene, and trans-2-butene typically constituted about 20% of the total NMHC. Data from forest-slash burning are summarized in Table I.

**Discussion**

Factors such as UV radiation, temperature, irradiation time, absolute NMHC concentrations, NOx/NO ratio, and especially the NMHC/NOx ratio have been shown to be important determinants of photochemical ozone generation. Due to the difficulties of aerial monitoring in narrow plumes, determining the effects of these variables on ozone buildup in real atmospheres is not straightforward. The situation is further complicated by the fact that precursor concentrations vary both spatially and temporally due to changing meteorological parameters and fluctuating emission rates. The data in Table I show maximum ozone enhancement recorded within various plumes and concentrations of NMHC and NOx measured in conjunction with these peak values. In all instances where ozone buildup due to urban or point-source emissions was documented, NMHC/NOx ratios were in the region between 5 and 20. This is the range (typically between 5 and 15) where maximum ozone production is expected to occur (20). Results are surprisingly consistent given the complex nature of photochemical processes and limitations of available monitoring devices. The fact that no in-plume ozone enhancement was attributable to fossil-fuel power-plant emissions was probably due to low NMHC/NOx ratios and O3 scavenging by nitric oxide.

The composition of NMHC in urban plumes was relatively consistent, particularly for Chicago and Milwaukee. The lower proportion of aromatics and higher percentage of paraffins recorded in the Houston plume are not unexpected since petrochemical industrial emissions account for a significant fraction of that city’s emission inventory. As shown in Table I, NMHC levels in the Houston effluent are similar in makeup to those recorded downwind of the Marathon petroleum refinery. In contrast to the similarities in NMHC composition between urban areas, the hydrocarbon mix in plumes from oil refineries, painting plants, and slash burns shows marked variation. Petroleum-refinery emissions are composed principally of paraffinic compounds with few olefins. Painting discharges contain few olefins, but over a third of the total is aromatics. Forest-burn emissions are almost half olefins, with the remaining fraction divided evenly between aromatics and paraffins.

Because of differences in hydrocarbon reactivities, the variations observed in hydrocarbon composition are potentially important in influencing maximum ozone production. Olefins have been shown to be the most reactive class of hydrocarbon compounds and will be the fastest promoters of ozone buildup. Aromatics are the next most reactive category followed by paraffins. While the paraffinic species are the slowest reacting group, they can contribute to ozone formation over longer time periods and may be important photochemical ozone precursors in cases of long-range midday transport. The rapid generation of ozone recorded in slash-burn plumes is partially a result of the high olefinic content in burn emissions. Conversely, ozone buildup in petroleum-refinery plumes was only noted after 1–2 h of transport. Since the vast majority of refinery emissions are slow-reacting paraffins, more irradiation time was required before in-plume ozone concentrations exceeded background levels.

Photochemical ozone formation in urban plumes is a somewhat different situation than that for point sources. In petroleum refineries, for instance, hydrocarbon emissions occur primarily at ground level due to evaporation and have little thermal buoyancy. Nitrogen oxides emissions result from processing operations and commonly are vented to the atmosphere from a stack. Only after these primary pollutants have mixed together downwind of the plant will NMHC/NOx ratios favor ozone formation. Similarly, nitrogen oxides and other pollutants are released from fossil-fuel power plants through tall stacks and are not expected to exhibit excess ozone formation unless entrainment of background NMHC is sufficient to cause favorable NMHC/NOx ratios.

Urban emissions, on the other hand, occur over a wide area with NMHC and NOx often emitted near ground level and in close proximity (e.g., automotive emissions). These pollutants mix with discharges from industrial sources and together make up the urban plume. Maximum ozone concentrations associated with urban emissions are observed typically 1–2 h downstream. However, the bulk of in-plume ozone was consistently recorded over or directly downstream of urban centers. The rapid production of ozone was probably due to the high olefinic content of automotive emissions, the close proximity of NMHC and NOx sources at or near ground level, and the disperse nature of these sources, which allowed for rapid mixing across a wide area.

**Conclusions**

Observations in urban and point-source plumes under a variety of meteorological conditions indicate that photochemical ozone formation is qualitatively consistent in all cases with the traditional HC–NOx–UV light model. In-plume ozone buildup occurred when NMHC/NOx ratios were in the range 5–20, and longer irradiation periods were required for emissions containing mainly slower reacting hydrocarbons. Although non-methane hydrocarbon composition was found to vary between plumes from petroleum refineries, painting operations, power plants, and forest burning, urban NMHC emissions were similar for the cities studied.

**Registry No.** O3, 10028-15-6; NOx, 11104-93-1.

**Literature Cited**

Partition Equilibria of Nonionic Organic Compounds between Soil Organic Matter and Water†

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Equilibrium isotherms for the simultaneous uptake of binary nonionic organic compounds from water on soil indicated no competitive effect between the two solutes. This observation supports the hypothesis that partition to the soil organic phase is the primary process for sorption of nonionic organic compounds from water on soil. The partition process between soil organic matter and water was analyzed by using the conventional solution concept for solutes in water and the Flory–Huggins treatment for solutes in the polymeric humic phase. Sorption determined for 12 aromatic compounds on a Woodburn soil shows that the extent of solute insolubility in water (S) is the primary factor affecting the soil organic matter–water partition coefficient (Ksw) and that the effect of solute incompatibility with soil organic matter is significant but secondary. This explains the commonly observed correlations of log Ksw vs. log S and log Ksw vs. log Kow (octanol–water).

Introduction

Earlier publications (1, 2) provided evidence that sorption of nonionic organic compounds from water on soil consists primarily of partition into the soil organic phase; adsorption by the soil mineral fraction is relatively unimportant in wet soils presumably because of the strong dipole interaction between soil minerals and water, which excludes neutral organic solutes from this portion of the soil. We here report further support for the partition hypothesis in soil–water systems and present a novel analysis of partition equilibria between soil organic phase and water, taking into account the solute solubility in polymeric humic substances.

Partitioning of organic solutes between the soil organic phase and water may be treated in a manner similar to that between an organic solvent phase and water (3, 4). To analyze the relative effects on partition coefficient of solute solubility in water, compatibility with soil organic phase, and alteration of water solubility by soil organic components dissolved in water, a reference “ideal line” (3) relating sorption coefficient with water solubility is needed. We assume that the effect of soil–water mutual saturation on the solute’s water solubility is insignificant with topsoil since the fraction of water-soluble organic components (which may have a potential effect on solute solubility) is usually negligible. We consider the major components of soil humus to be amorphous polymeric (macromolecular) substances and therefore adapt the Flory–Huggins theory (5, 6) to account for the solute activity in an amorphous polymer. The partition process with soil organic matter is conceived to be analogous to that involved with synthetic resins used in ion-exclusion, salting-out, and solubilization chromatography for separating nonionic species (7–10).

The relation between partition coefficient and water solubility for slightly water-soluble organic solutes in an organic solvent–water mixture, in which the solvent has small solubility in water, is given by (3)

$$\log K = -\log S - \log V_0^* - \log \gamma_o^* + \log \left( \gamma_w^*/\gamma_w \right)$$  (1)

where $K$ is the solute partition coefficient, $S$ is the molar water solubility of the liquid or supercooled liquid solute, $V_0^*$ is the molar volume of water-saturated organic phase, $\gamma_o^*$ is the solute activity coefficient (Raoult's law convention) in water-saturated solvent phase, $\gamma_w^*$ is the solute activity coefficient in solvent-saturated water, and $\gamma_w$ is

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†Oregon State Agricultural Experiment Station Technical Paper No. 6480.