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Project Summary

Nonmethane Organic Carbon Concentrations in Air Masses Advected Into Urban Areas in the United States

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The purpose of this study was to measure non-methane organic carbon (NMOC) levels aloft in the upwind vicinity of several U.S. cities. An instrumented aircraft was employed to collect samples during the months of July and August in 1985 and 1986. NMOC, ozone and oxides of nitrogen concentrations were measured during the 0400 to 0900 period in background air masses advected into Dallas-Ft. Worth, Tulsa, Atlanta, and Birmingham in 1985 and Philadelphia and New York City in 1986. Measurements were concentrated in the layer above the morning surface inversion but below the normal afternoon mixing height. This is the air mass that would eventually mix with the surface layer within the urban area after the break-up of the morning inversion. Special emphasis was placed on NMOC speciation. Individual hydrocarbons were identified by gas chromatography (GC) and derivatized carbonyl compounds were measured by high performance liquid chromatography (HPLC). Details concerning the experimental design and quality assurance aspects of the program are provided within the report.

A tabulation of airborne data collected during the two year study period is provided. A data summary is presented for each day which includes a flight map, table of ozone and NO_x concentrations, a listing of NMOC information, and data recorded during aircraft ascents and/or descents. A brief comparison of the NMOC results obtained for the various cities investigated is also provided.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle 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

Characterization of NMOC levels in transported air masses is currently of interest in terms of oxidant production and the formation of acidic species in the atmosphere. Organic species in the layer above a morning surface inversion and below the afternoon mixing level are of interest because oxidant precursors in this layer mix with urban plumes following breakup of the surface inversion. Most photochemical models that are designed for regulatory purposes incorporate oxidant precursors from aloft. Recent modeling studies have indicated that control requirements are quite sensitive to the concentration and composition of organics entrained from aloft. Therefore, it is important that NMOC concentrations in this layer be defined.

NMOC concentrations aloft have been determined in several oxidant field study

programs, however, the emphasis in these previous studies was centered around urban plumes. Prior to the field work described herein, there had not been a study with the primary objective being to define NMOC levels transported into urban areas from aloft. Organic species were measured in air masses advected into Dallas, Tulsa, Atlanta, and Birmingham during the summer of 1985; Philadelphia and New York City during the summer of 1986. In this report we will summarize the types and concentrations of organic species measured aloft. Relationships between the organics and other pollutant and meteorological parameters will be described as well. The areas investigated in 1985 were isolated urban areas whereas those investigated in 1985 were part of a complex urban area where major upwind sources may exist under certain meteorological conditions.

Experimental Procedures

The aircraft flew arcs upwind of the urban areas during the early morning hours. On most days, there were three arcs flown at two different altitudes above the morning surface inversion but below the normal afternoon mixing height. Figure 1 provides a schematic illustration of the flight pattern. Sample collection involved transferring air from a ram-air manifold inside the aircraft to the collection medium. For hydrocarbons, this entailed filling a metal canister to a positive pressure with a metal bellows pump. Carbonyl compounds were trapped by passing air through adsorbent cartridges impregnated with dinitrophenyl hydrazine. The hydrazones that formed were analyzed by HPLC. An attempt was made to measure PAN levels aloft by collecting air samples in Tedlar bags and measuring the PAN content by EC-GC immediately after the aircraft landed. Analytical difficulties along with the absence of a reliable field calibration standard compromised the quality of the PAN data and consequently it is not included in this report.

Ozone, NO_x, temperature and relative humidity were measured continually in the aircraft. These parameters were employed to define the morning mixing level as well as to provide additional information for modeling the urban photochemistry.

A complete description of the air quality instrumentation used, calibration methods data processing and validation procedures are included in Appendix G of the report.

Winds reported at 3000 feet were obtained from the local flight service station. This information was used to plan the location of upwind flight paths each morning.

Results and Discussion

Table 1 provides a summary of the average non-methane hydrocarbon (NMHC) and aldehyde concentrations measured aloft over the six cities. Mean hydrocarbon concentrations varied between 14 and 39 ppbC with the highest average concentrations recorded upwind of Tulsa. The low mean value determined in Birmingham may not be truly representative of that particular urban area. The morning flights were plagued with bad flying weather while in Birmingham and consequently fewer samples were collected. The mean NMHC concentration for all cities combined was 22 ppbC with a coefficient of variance of approximately 40%. Paraffinic species were by far the major class of hydrocarbons measured aloft. These compounds comprised approximately 78% of the identified hydrocarbons while the mean aromatic contribution was about 17% and the olefins averaged 3%.

Formaldehyde and acetaldehyde levels in Atlanta and Birmingham were generally below the detection limit of the analytical procedure. In Dallas, Tulsa, Philadelphia and New York City the two carbonyls accounted for about 10% of NMOC that was identified. A positive correlation between NMHC and aldehyde concentrations was generally observed. For example, NMHC levels upwind of Dallas on the morning of July 6, 1985 averaged 30 ppbC with a corresponding mean aldehyde concentration of about 2 ppb On July 14, Dallas NMHC levels were down to about 4 ppbC and the aldehyde concentrations ranged from below the detection limit (~0.1 ppb) up to 0.7 ppb (see Table 2).

The data base makes it possible to examine the variability in NMHC concentrations aloft during the morning hours since sampling arcs were flown at different distances and altitudes upwind of the urban area. Generally, one or more samples were collected along each of three upwind arcs. Figure 2 graphically illustrates the daily variations in NMHC levels observed in each of the six areas. The horizontal lines in Figure 2 represent measured NMHC levels in individual samples. The vertical lines connect maximum and minimum levels each day. On most days, the high NMHC measurement exceeds the low value b at least a factor of two and on severa occasions by as much as a factor of ter As can be seen in Figure 2, on day when the NMHC concentration range wa large, one sample exhibited a muc higher hydrocarbon level than others The reason for this anomalous behavic is not immediately obvious. The hig readings showed no consisten correlation with altitude or distance fror the city.

NMHC compositions were generall consistent from city to city; howeve influences from selected source type were periodically observed. For exampl in Tulsa occasional elevated levels of th C_2 to C_4 paraffinic hydrocarbons wer observed, possibly from the refinerie located upwind of the city. In Atlant relatively large concentrations of toluen were occasionally observed. The upwin source for this compound was nc identified.

Also of interest is the correlation c NMOC aloft with other pollutants Generally speaking, there appeared to b a direct relationship between NMO concentrations with ozone and NC levels. For example, Table summarizes NMOC, O_3 and NO_x dat collected upwind of Dallas on th mornings of July 6 and 14, 1985. It evident that elevated NMOC levels o July 6 are associated with ozone an NO_x concentrations which ar considerably higher than those recorde on July 14.

Philadelphia and New York City wer chosen for a preliminary examination possible correlations between weathe patterns and oxidant precursor levels the air advected from aloft. Becaus they are geographically close, it expected that they would receive a masses from the same source area under westerly and northwesterly flo conditions

Two sets of days with similar mornin wind speed and direction are compare in Table 3. In the first group, whic includes two days with westerly winc exceeding 20 kts, oxidant precurso levels are nearly identical. The maximu ozone levels recorded at surface statior in each of the urban areas on July 14 ar August 8 were very comparable, as we A similar pattern exists for the two da listed with westerly winds less than kts. Precursor levels are ver comparable as are the surface ozor concentrations which in this case a elevated when compared to the hig wind conditions of the first group. Th fact that higher surface ozone levels a

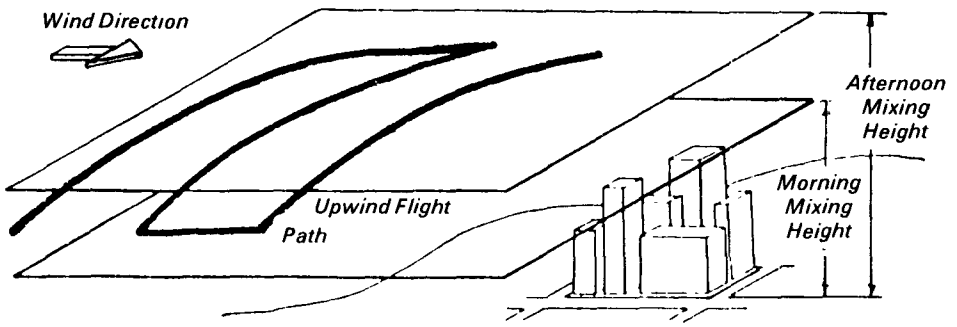


Figure 1. *Schematic diagram of aircraft flight pattern.*

Table 1. *Mean NMHC Concentrations Measured Aloft*

City	Sampling Dates	Identified NMHC (ppbC)	Formaldehyde (ppb)	Acetaldehyde (ppb)
Dallas	July 5-14, 1985	23	1.7	0.2
Tulsa	July 16-24, 1985	34	3.5	0.9
Atlanta	Aug. 13-23, 1985	25	<0.7	<0.3
Birmingham	Aug. 26-29, 1985	14	<0.7	<0.3
Philadelphia	July 8-Aug. 14, 1986	16	1.8	0.7
New York City	July 8-Aug. 14, 1986	19	1.9	0.7

recorded under more stagnant meteorological conditions agrees with expectations.

Figure 3 shows the average NMOC concentrations measured aloft during this study and compares them to the concentrations measured at a rural, surface site near State College, Pennsylvania and on the ground in Philadelphia. As is readily apparent, NMOC concentrations at the rural site are comparable to those found aloft and much less than those measured in Philadelphia. The NMHC levels recorded in the urban area are on the order of twenty times those observed in the background air while the aldehyde levels are three to four times that found aloft or at the rural site. Since the rural surface NMOC levels are comparable to those collected aloft, it appears that surface data could be utilized as boundary condition values for modeling urban oxidant production when aircraft data is not available.

Summary and Conclusions

The NMOC results reported for the six cities studied indicate that the air above urban areas for the most part represents an aged air mass that is depleted in the more reactive hydrocarbons. The average NMHC composition contains 78% paraffinic, 17% aromatic and 3% olefinic compounds. The organic carbonyl levels in 4 of the 6 urban areas contributed on the average of 10% to the total NMOC levels. The carbonyl levels at the other two sites were below detectable limits of the analytical procedure. On some flights the NMOC levels and compositions were quite consistent on each of the three sample arcs flown. At other times, however, NMOC levels and composition changed significantly. A positive correlation between NMHC and organic carbonyl levels was generally observed. The mean NMHC concentration for all cities was 22 ppbC with a coefficient of variance of 40%. Synoptic meteorological conditions are likely to have an impact on the NMOC concentration level observed in the background air. From the limited data available, it appears that the NMOC levels measured aloft agree reasonably well with those measured at remote ground level locations. More data are required to confirm this relationship.

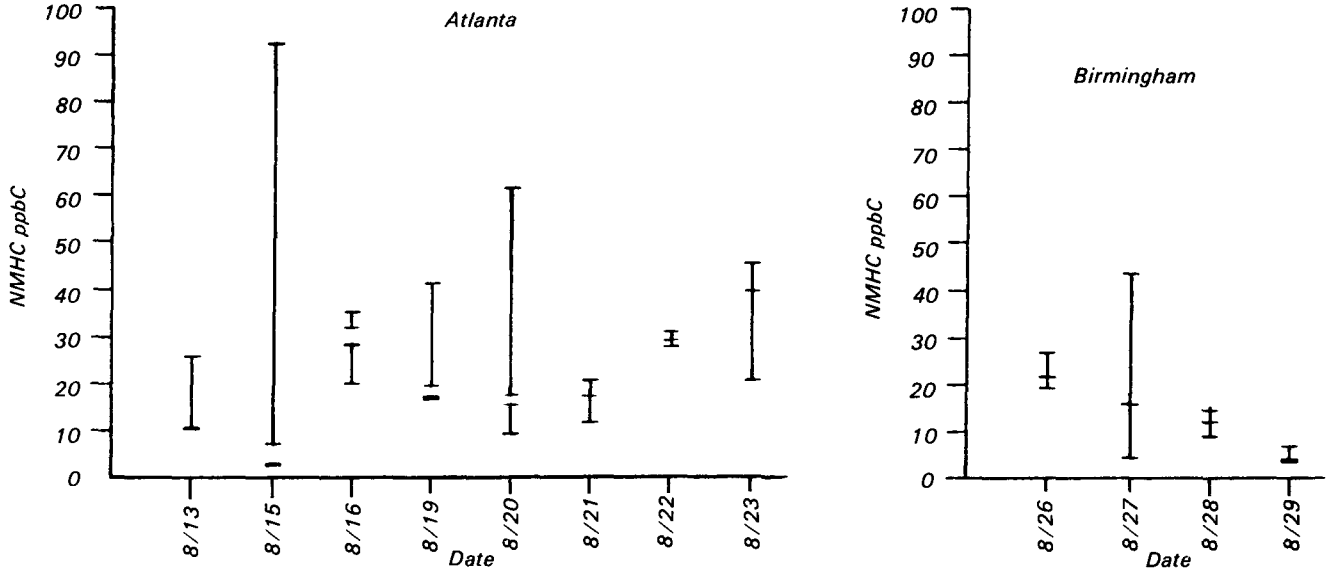


Figure 2. *Variability in daily NMHC concentrations observed in (a) Atlanta, (b) Birmingham, (c) Dallas, (d) Tulsa, (e) New York City, a (f) Philadelphia.*

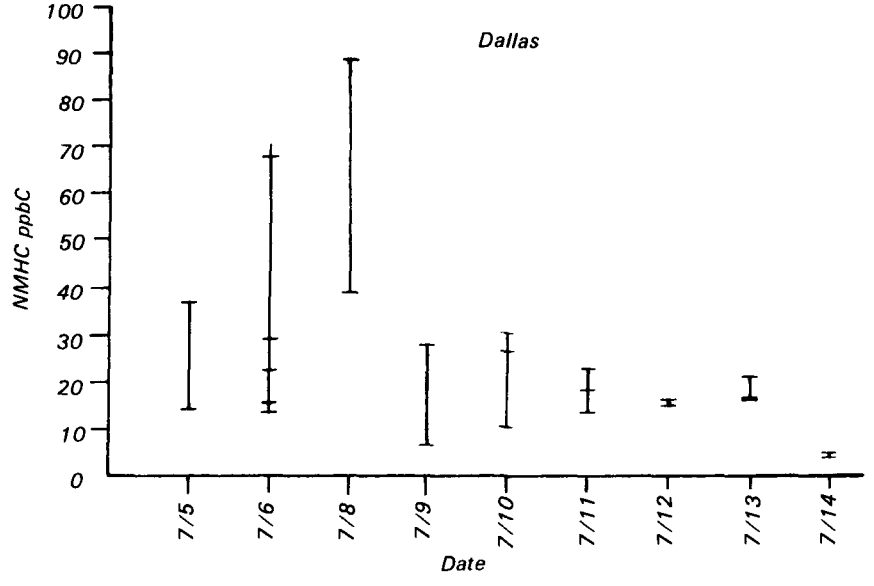
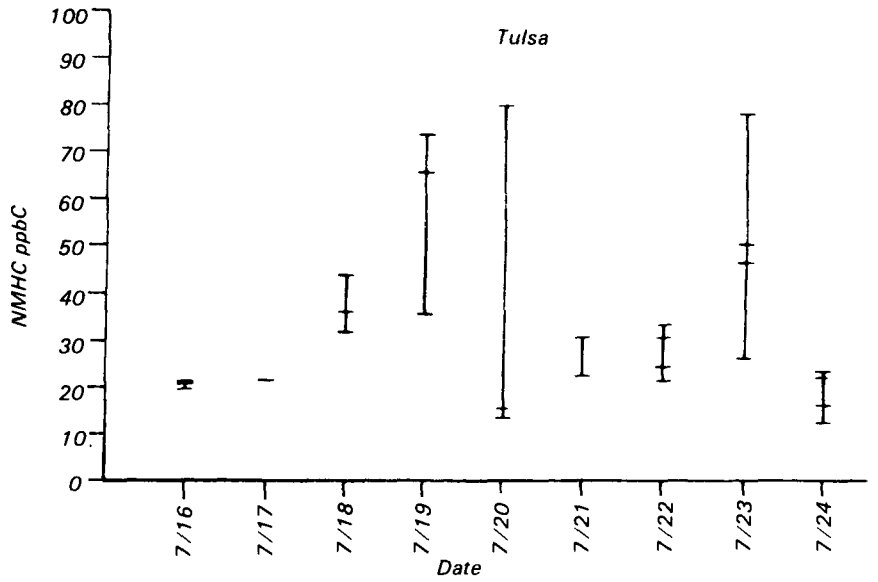


Figure 2. *Continued.*



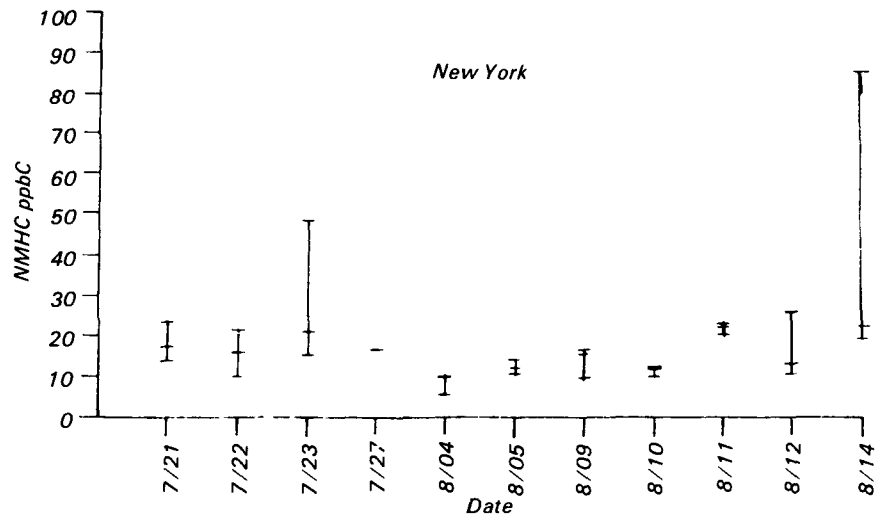


Figure 2. *Continued.*

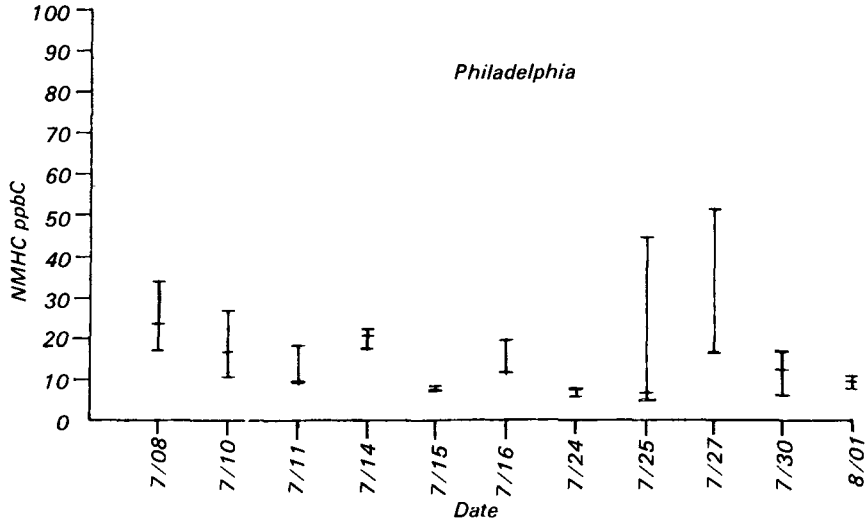


Figure 2. ***Continued.***

Table 2. *Summary of Airborne Data Collected Upwind of Dallas on July 6 and 14, 1985*

Date	Arc (mi)	Alt (ft)	NMHC ppbC	Formaldehyde (ppb)	Acetaldehyde (ppb)	O_3 (ppb)	NOx (ppb)
July 6	15	2000	22.4	1.5	0.5		
	20	3000	36.7	1 6	0 7	~50	~15
	25	2000	15.3	1.4	< 0 2		
July 14	25	2000	3.8	0.1	< 0.2		
	20	3000	-	0.3	< 0.2	~20	~5
	15	2000	4.7	0.7	0.7		

Table 3. *Oxidant Precursors and Wind Data*

Date	City	Wind Speed (kts)	Wind Direction (deg)	Ident. NMHC (ppbC)	Aldehyde (ppb)	NO_x (ppb)	Peak Surface O_3 (ppb)*
07/14	P	25	290	20 1	2.8	3	62
08/11	NY	22	270	21 8	2.7	4	64
07/16	P	8	290	15.5	5 0	3	114
07/22	NY	7	290	15.6	3.3	3	107

P = Philadelphia.

NY = New York.

*The O_3 data was taken from SAROAD sites 310720003F01 for 7/14, from 330280002F01 for 8/11, from 311760002F01 for 7/16, and from 313260001F01 for 7/22.

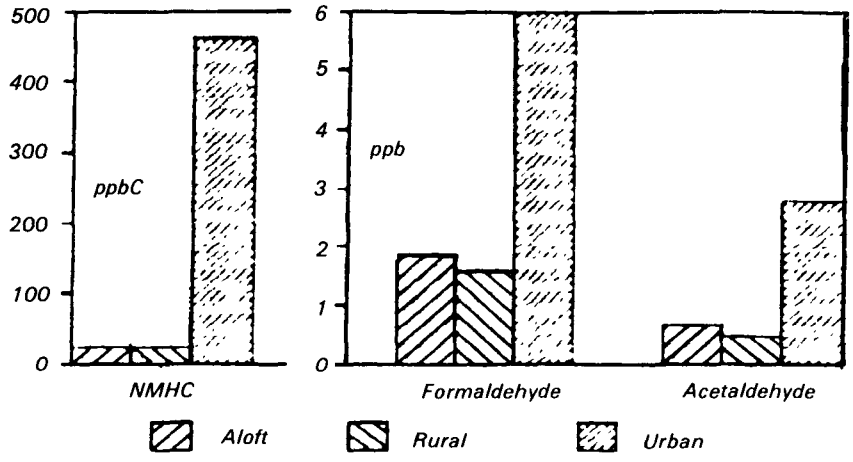


Figure 3. *Comparison of average NMOC concentrations measured at (1) a rural surface site in Pennsylvania, (2) urban Philadelphia, and (3) aloft in the vicinity of Atlanta, Birmingham, Dallas, Tulsa, New York City and Philadelphia.*