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TRANSPORT AND TRANSFORMATION OF POLLUTANT IN THE LAKE MICHIGAN AREA

by

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DISCLAIMER

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ABSTRACT

The transport and the transformation of pollutants emitted from the Milwaukee and the Chicago areas were studied during August 1976. The study is part of the MAP3S program sponsored by ERDA-DBER. The experiments were conducted in approximately Lagrangian frames of reference utilizing two instrumented aircraft and surface support units. It was found that:

1. A build up of ozone downwind of the areas occurred.
2. Sulfate concentrations are higher in the urban plume than those upwind, and progressively increase with distance from the source.
3. Significant concentrations of sulfate, probably associated with long range transport of sulfur, are often detectable above the mixing layer.
4. Vertical profiles of pollutants over the land and the lake show a definite effect of changing atmospheric stability when the pollutants are advected over the lake and vise versa.

The objectives of the PNL-Areosol and Trace Gas Transformation Program are to measure and develop quantitative expressions to characterize pollutant transformation in plumes from urban areas and power plant complexes. The geographical setting of interest is the energy intense northeastern United States, which is the focus of the MAP3S program (Multi-State Atmospheric Power Production Pollution Study). Of particular interest is

SO_2-SO_4 conversion. Field experiments conducted under this program are supported by diagnostic modeling and data interpretation with the ultimate goal of providing parameterized input for use by the MAP3S modeling community.

This paper focuses on pollutant transformations in urban plumes. Other aspects of this experiment are discussed in a campanion paper (1).

EXPERIMENTAL DESCRIPTION

The experiments described in this report were conducted during August 1976, downwind of the Chicago-Milwaukee Megalopolis. During the summer months the urban plume often is transported within air masses that become stabilized when advected over Lake Michigan. This feature as well as isolation from significant downwind sources creates a situation where the competing effects of dry deposition and diffusion may be easily factored into the data interpretation process. The city of Milwaukee was utilized as the principal source in the study. Data were collected from two aircraft and mobile surface sampling units. An instrumented DC-3 aircraft conducted plume profile measurements at different downwind distances, which were determined by wind speed and direction data recorded by onboard instrumentation. A second, light twin engine aircraft flew a simultaneous mission collecting high volume aerosol samples and SO_2 data upwind and outside the plume. Surface sampling was coordinated with aircraft activities within the urban plume utilizing lundgren impactors, high volume samplers, SO_2 bubblers and CCl_3F collection bottles.

The parameters measured in real-time onboard the DC-3 aircraft were as follows: temperature, dew point temperature, wind speed, wind direction, standard aircraft parameters (altitude, air speed, etc.) O_3, SO_2, NO, NO_2, light scattering, particle concentration, and aircraft position (longitude, latitude). In addition, the plume was further characterized using several integrated sampling techniques. Evacuated bottles opened during the course of the flight were used to obtain samples for CCl_3F analysis. Air samples were also captured in Tedlar bags and sent to the Environmental Protection Agency for hydrocarbon analysis. Three different high-volume samplers were used to characterize the aerosol component of the plume. The first one employed an IPC filter which was later analyzed via X-ray fluorescence and neutron activation techniques for trace metals. The second high volume sampler, supplied by Brookhaven National Laboratory, provided a measure of the principle atmospheric sulfur species. It consisted of a H_3PO_4 treated quartz filter in combination with base-impregnated back-up filters for SO_2 capture. Analyses of the collected samples were conducted at BNL. The third sampler employed a 47mm Fluoropore filter. The exposed filters were analyzed by infrared spectroscopy at Argonne National Laboratory or electron spectroscopy at Lawrence Berkeley Laboratory.

Results from the flights made during the August 19-30 test period are summarized in figure 1. The location of each plume cross section is identified for each of the 7 flights in this series. Each line represents a series of plume traverses at different altitudes.

EXPERIMENTAL RESULTS

Typically, during this time of year, the air and surrounding land masses are warmer than the lake surface. Under such circumstances air advected over the lake experiences a distinct change toward increasing stability. This effect can be seen from the ozone data shown for August 27 and 28 (Figure 2). Each point in the figure is an average of the concentration measured at one altitude. At the first downwind distance from Milwaukee,

Table 1 - Summary of Data Collected on August 27 and 28

	August 27	August 28
Average SO_4 ($\mu g/m^3$)	19.5	1.57
Average NH_4 ($\mu g/m^3$)	3.34	0.42
Average Pb (ng/m^3)	225.	60.
Average Ca (ng/m^3)	1700.	1820.
Average Mn (ng/m^3)	34.	96.
Average Fe (ng/m^3)	1300.	4130.
Average Zn (ng/m^3)	77.	24.
Ozone (ppb) max.	108.	49.
Average Temperature ^oC	28.	25.
Average R.H. %	58.	56.
k, % $hour^{-1}$	6.8	0
Initial SO_2, $\mu g/m^3$	50.	64.
Light scattering	inc. with dist.	constant
Average acetaldehyde (ppb C)	52.	7.

the concentrations are nearly constant with altitude. Presumably, the air mass has not had enough time to adjust to the new surface temperature. However, the successive profiles show some vertical structure. The fifth profile, which was obtained a few miles inland on the opposite side of the lake, indicates a well mixed atmosphere. In contrast to these over-water flights, the profile measurements over land display a rather uniform distribution of ozone throughout the mixing layer. All flights, however, indicate that ozone is being generated within the city plume and that the concentration is increasing with distance from the city. This is a feature which has been reported previously for other metropolitan areas (2) (3) (4).

The data generated during this test series are of particular significance in terms of the insight provided to the course of atmospheric oxidation of SO_2. Chamber and modeling studies have provided an indication of the features of potentially significant atmospheric reactions. Examination of our urban plume data in the light of these results suggests that homogeneous free radical oxidation of SO_2 may be the dominant oxidation path during the events studied. This suggestion is supported both by the occurrence and the formation rates of sulfate observed during these experiments. The occurrence of sulfate, for example, was observed to correlate more strongly with ozone (correlation coefficient of 0.56) than with trace metals, which typically exhibited correlation coefficients of much less than 0.4. Similar relationships were noted for the production rates of sulfate in the plumes, which were estimated from the data using the method of Alkezweeny and Powell (5). The August 27 and 28 data (see table 1), for example, were obtained under similar meteorological circumstances and SO_2 loadings, but exhibited marked variations in sulfate production rate. August 27 was characterized by large increases of aerosol in the light scattering range with distance downwind, and the relatively large sulfate production rate of 6.8% per hour. August 28, in contrast, exhibited essentially no sulfate production with no detectable increase in light scattering downwind. In these cases, ozone concentration again showed a rather strong correlation with sulfate production rate, while the concentrations of potential heterogeneous catalyst (eg. iron, manganese) did not.

The concurrent formation of sulfate and ozone noted in these experiments suggests that a rather strong linkage exists in the reaction change leading to these products. This is certainly in concordance with current concepts of oxidation via free radical chains involving species such as HO_2 and RO_2, which are generated in systems containing NO_x and hydrocarbons and can react to form both sulfate and ozone as oxidation products. Limited additional support for the free radical mechanism is given by hydrocarbon measurements obtained on these days. Concentration of the radical precursor acetaldehyde on August 27 for example, was 52 ppb while on August 28 it was reduced to 7 ppb.

Current laboratory and theoretical evidence suggests that the peroxy radicals perdominate in the oxidation process. The recent experimental modeling study of Walter et al. (7) involving the trans-2-butene - SO_2 - ozone system, for example, indicates that the radicals HO_2 and RO_2 can account for most of the observed oxidation.

Another interesting result of the Lake Michigan experiment is the detection of sulfate layers above the mixing layer (Table 2). These layers were seen only when the wind was from the east or the northeast direction. For example on 8/23, a 7.4μg/m^3 sulfate concentration was found at 10,000 feet MSL. This value is higher than the 6.27μg/m^3 measured inside the Milwaukee plume. It is possible that SO_2 or sulfate was lifted to high altitudes from the northeast and then transported to this area.

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Table 2 - Sulfate and Trace Metals Upwind of Milwaukee

Date	Alti. in feet	Sulfate $\mu g/m^3$	Ca ng/m^3	Mn ng/m^3	Fe ng/m^3	Pb ng/m^3
8/23	1,500	1.6	239	6.3	159	7.1
	10,000	7.4	28	ND	17	4.4
8/24	1,500	5.4	3140	25.6	614	46.
	6,000	9.0	88	3.4	73	24.
	8,000	ND	ND	ND	ND	ND
8/29*	1,000 to 6,000	0.3	79	1.7	54.9	3.6
8/30	5,000	0.9	535	17.3	539	ND

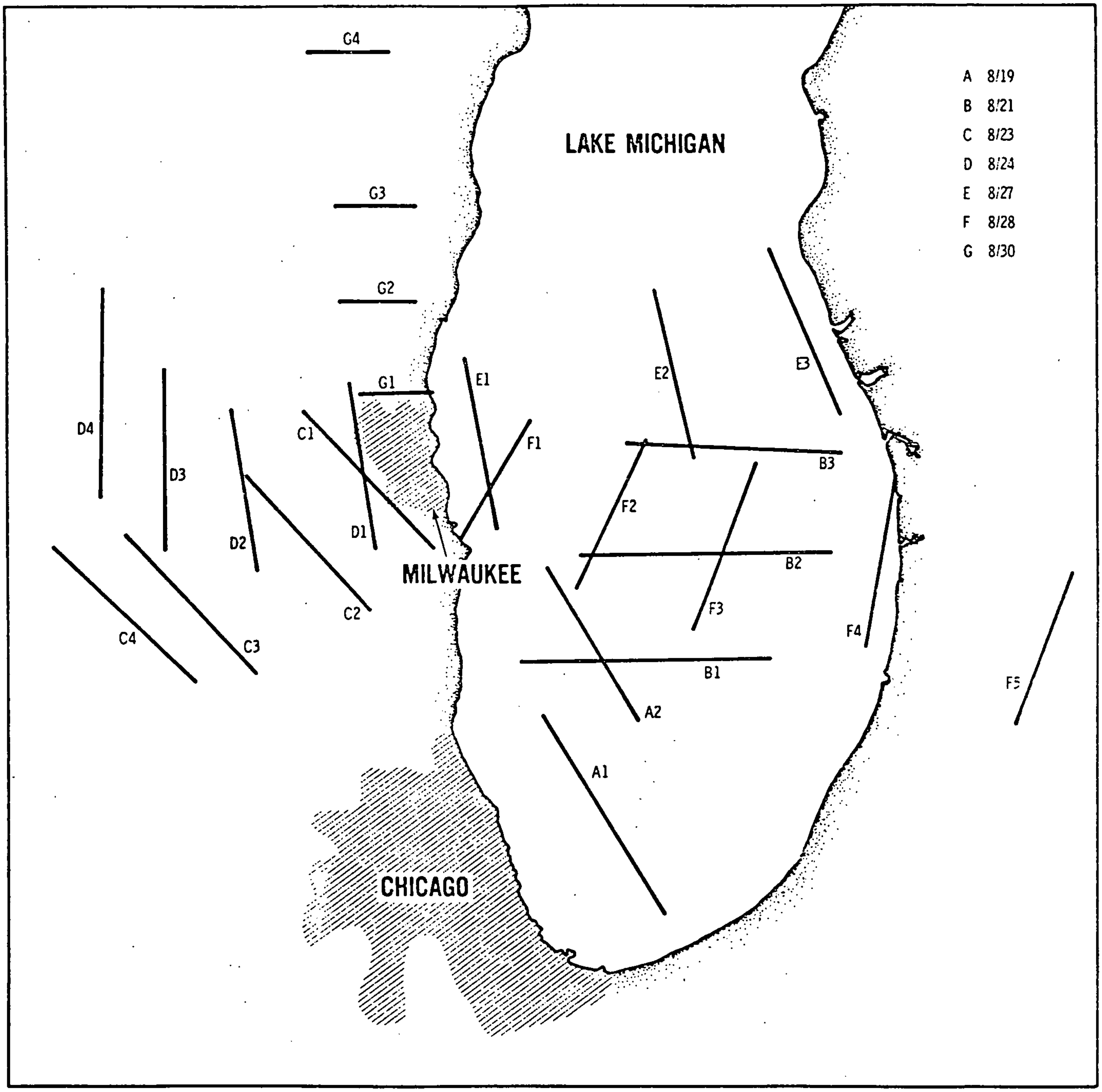
ND = Not Detected

*Over Lake Michigan, Wind from the North

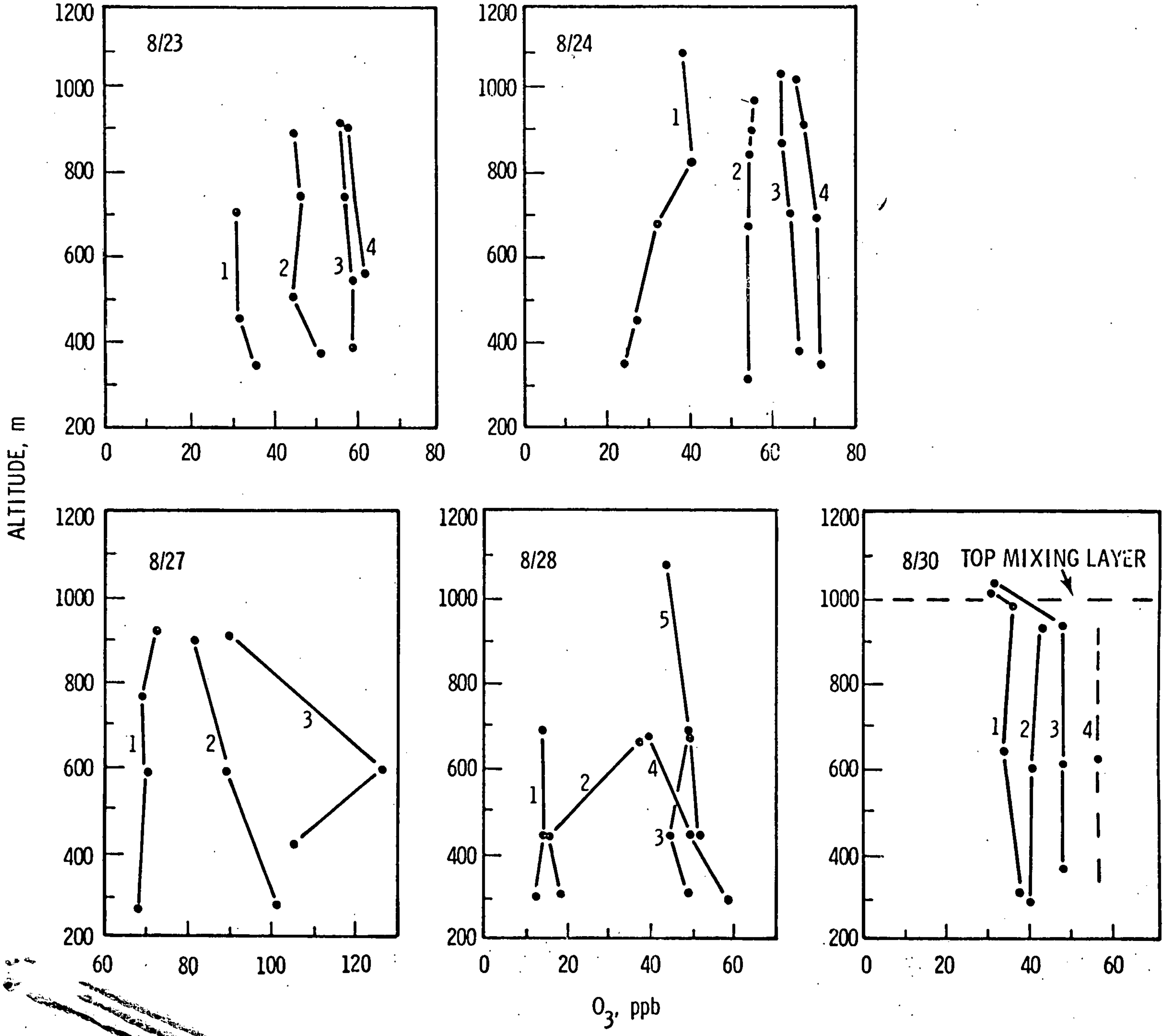
FIGURE CAPTION

Figure 1.- Summary of DC-3 sampling flights

Figure 2.- Verticle profiles of ozone at different downwind distances.



G4
G3
G2
G1
LAKE MICHIGAN
A 8/19
B 8/21
C 8/23
D 8/24
E 8/27
F 8/28
G 8/30
D4
D3
D2
D1
C1
C2
C3
C4
E1
E2
F1
F2
F3
F4
F5
B1
B2
B3
B3
A1
A2
MILWAUKEE
CHICAGO


8/23
8/24
8/27
8/28
8/30
TOP MIXING LAYER
ALTITUDE, m
O$_3$, ppb
1
2
3
4
5
200
400
600
800
1000
1200
0
20
40
60
80
100
120