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Project Summary

Studies of NO_X Reactions and O_3 Transport in Southern California, Fall 1976

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This report describes a four-week study of oxides-of-nitrogen chemistry and ozone transport in and around the southcoast air basin of California. The data base was obtained using three ground-level monitoring stations and a twin-engine instrumented aircraft. The ground stations were located approximately 20, 35, and 50 mi from central Los Angeles in the prevailing downwind direction. Measurements were made at each of these sites from 0900-1700 PST for ozone, nitric oxide, oxides of nitrogen, nitric acid, peroxyacetylnitrate, sulfur dioxide, freon-11, nonmethane hydrocarbon, carbon monoxide, methane, ethylene, ethane, nitrate, sulfate, ammonium, and total nitrogen. The aircraft made up to three flights per study day measuring ozone, nitric oxide, oxides of nitrogen, peroxyacetylnitrate, nonmethane hydrocarbon, methane, carbon monoxide, ethylene, ethane, freon-11, and temperature. In all, 42 monitoring flights were conducted over the 22-day study.

The original report summarizes the results of the study in tables and detailed appendices. Battelle-Columbus experimenters selected a subset of 11 photochemically active days for which they examined average pollutant profiles and air quality trends. The report discusses the ground-station data in terms of aerosol nitrogen balance, size distribution of aerosol constituents, distribution of oxidized nitrogen, nitrogen/sulfur relationships and nitrogen mass balance. The experimenters chose specific study days for detailed analysis as case studies, and examined aircraft and ground data for these days for evidence of ozone transport, oxidized nitrogen distribution, nitrogen balance, and oxides-of-nitrogen transformation rate.

This Project Summary was developed by EPA's Environmental 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

The project report presents the results of a field investigation of atmospheric transformations of oxides of nitrogen (NO_x) and transport of ozone (O_3) conducted by Battelle-Columbus Laboratories under the sponsorship of the U.S. Environmental Protection Agency (EPA). The program focused on reactions and transport in the urban plume of Los Angeles.

The ambient air reactions of NO_x are not well characterized. Previous characterization efforts have focused on developing analytical methods suitable for studying such reactions, identifying the major NO_x reaction products, and quantifying the nitrogen mass balance. Earlier studies in Los Angeles confirmed smog-chamber observations that peroxyacetylnitrate (PAN) and nitric acid (HNO_3) are the major initial products of photochemical reactions of NO_x in polluted air. Over a five-week period in Los Angeles, PAN accounted for 68% of reacted NO_x, HNO_3 accounted for 10% and particulate nitrate (NO_3^-) for about 3%. Approximately 12% of the reacted NO_x could not be accounted for as

one of these products. The nitrogen distribution ratio, F_N*, averaged about 7% at night and 21% during the day at a site downwind of Los Angeles. The earlier study provided the first measurements of ambient HNO_3 and the first indication that HNO_3 could be present at much higher concentrations than particulate NO_3^-. Little information on the rate of NO_x transformation to products was obtained, although an average pseudo-first-order rate constant of 0.10 ± 0.05 hr^{-1} was consistent with most of the experimental data. The investigation of NO_x reactions summarized here was designed to extend and validate the earlier results and provide more information on NO_x conversion rates. The program involved detailed ground-level and aircraft-monitoring studies as well as the analysis and interpretation of the resulting data.

Objectives

The overall objectives of the program were (1) to determine the distribution of atmospheric nitrogen compounds and the relationships among these compounds and other atmospheric parameters and (2) to determine the propensity of air masses to generate and transport O_3 over long distances. Specific objectives of the project were:

- To determine the spatial and temporal distribution of oxidized nitrogen species in the Los Angeles basin,
- To determine the extent to which measured NO_x products can account for NO_x removal from the air (i.e., nitrogen mass balance),
- To investigate differences in the transformation processes for NO_x relative to oxides of sulfur (SO_x),
- To estimate the rate of NO_x transformation under photochemically reactive conditions, and
- To investigate the transport of O_3 and precursors from urban areas.

Methodology

Field experiments were conducted from October to November, 1976, in southern California, and included both ground-level and airborne monitoring. The experimenters utilized three ground stations and an instrumented twin-engine aircraft for monitoring. The ground stations were located approximately 20, 35, and 50 mi from central Los Angeles in the prevailing downwind direction, and are shown in Figure 1 as sites A (Temple City), B (Upland), and C (Rubidoux). Measurements were made at each of these sites between 0900 and 1700 PST for O_3, nitric oxide (NO), NO_x, HNO_3, PAN, sulfur dioxide (SO_2), freon-11 (F-11), nonmethane hydrocarbon (NMHC), carbon monoxide (CO), methane (CH_4), ethylene (C_2H_2), ethane (C_2H_4), NO_3^-, sulfate ($SO_4^=$), ammonium (NH_4^+), and total nitrogen. The aircraft made up to three flights per day measuring O_3, NO, NO_x, PAN, NMHC, CH_4, C_2H_2, C_2H_4, CO, F-11, and temperature. In all, 42 monitoring flights were conducted over 22 days. The data from the field experiments are contained in appendices to the report. Much of the data also appears summarized within the text of the report itself.

Results and Conclusions

The results of the experimental phase of the program and the details of the experimental methods are summarized in the final project report. Detailed data are included in two appendices. Appendix A lists the daily air quality measurements for each of the three ground stations. Appendix B contains flight plans for each aircraft monitoring mission, together with maps of O_3, NO, and NO_x concentrations, integrated sample collection positions, and vertical profile sites. Appendix B also includes the vertical temperature and O_3 profiles.

The results of the ground-level and aircraft monitoring have been interpreted in terms of NO_x-reaction-product distribution, nitrogen balance, nitrogen/sulfur relationships, NO_x transformation rate, and O_3 transport. A few of the more importan study findings are summarized briefly below

During the Los Angeles study, the high est concentrations of primary pollutant generally occurred at the Temple City site which is closest to the Los Angeles urbar center. The highest concentrations of O and PAN were measured downwind at th intermediate site in Upland, whereas th concentration of particulate NO_3^- wa greatest at Rubidoux.

Table 1 gives the average daytime distri bution of oxidized nitrogen at the thre ground stations based on a subset of al photochemically active days. The per centage of the total measured nitroger contributed by each compound is show in parenthesis.

Particulate NO_3^- exhibited a strong east west gradient in the Los Angeles basin, i contrast to $SO_4^=$, which was relativel uniform. The average accountability o total aerosol nitrogen as NO_3^- and NH_4^- ranged from 70-85% for the three groun stations. On the average, 47% of the NO_3^- 90% of the $SO_4^=$, and 100% of the NH_4^- particles were ≤ 2.0 μm in size at th Upland site.

When both gas and aerosol species ar considered, the ratio of measured sulfu compounds to nitrogen compounds i quite close to the SO_x/NO_x emission inven tory ratio. The data confirm the earlie finding that most of the urban NO_3^- i present in the gas phase. Table 2 show the fraction of urban NO_3^- that exists i gaseous form for several cities.

Based on upwind tracer/NO_x ratios, th calculated nitrogen mass balances for th Upland and Rubidoux sites show tha ~90% of the nitrogen is accounted for.

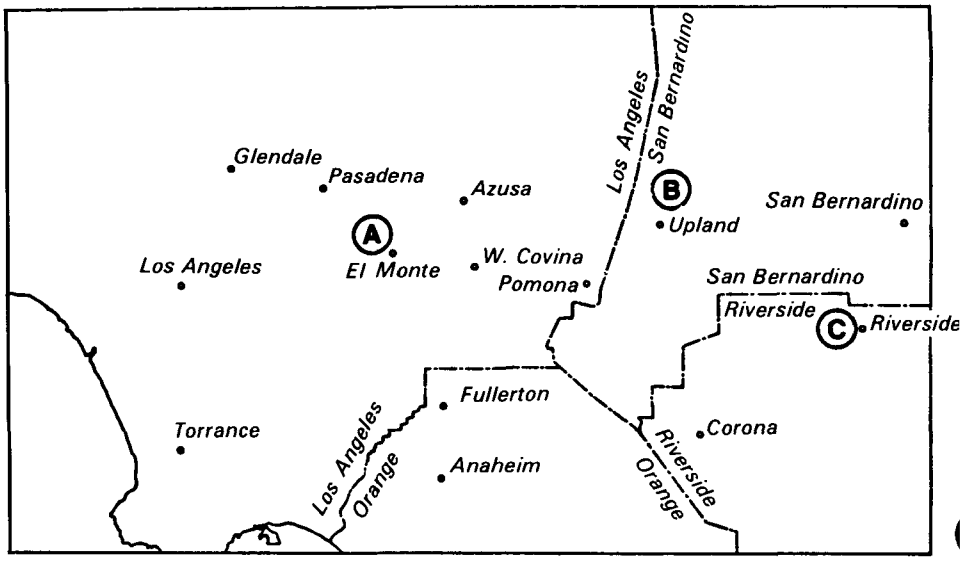

Figure 1. Locations of three ground monitoring stations in the Los Angeles basin.

$$*F_N = \frac{PAN + HNO_3}{NO + NO_2 + PAN + HNO_3}$$

Table 1. *Average Daytime Distribution of Oxidized Nitrogen at Three Ground Stations**

Pollutant	Sites		
	Temple City	Upland	Rubdioux
NO	21 ppb (19%)	5 ppb (10%)	≤5 ppb -
NO_2	87 ppb (78%)	33 ppb (66%)	41 ppb (78%)
PAN	3 ppb (3%)	11 ppb (22%)	5 ppb (10%)
$HONO_2$	≤6 ppb (-)	≤6 ppb (-)	≤6 ppb (-)
NO_3	0.8 ppb (1%)	0.6 ppb (1%)	6.1 ppb (12%)

*Based on 11 photochemically active days.

Table 2. *Fraction of Urban NO_3^- in Gaseous Form*

Site Location	Date	Gaseous NO_3^-/Total NO_3^- Ratio
St. Louis, Missouri	1973	0.95
West Covina, California	1973	0.98
Phoenix, Arizona	1977	0.50
Temple City, California	1976	0.75
Upland, California	1976	0.96
Rubidoux, California	1976	0.45
Beverly, Massachusetts	1978	>0.95

At both downwind sites (Upland and Rubidoux), NO_x conversion averaged 22%. Using average reaction times for air masses transported to these sites, a *lower limit* transformation rate of 0.02-0.03 h^{-1} is calculated. On individual study days the NO_x removal rate reached 0.16 h^{-1}, and the rate of transformation to PAN ranged from 0.01 to 0.08 h^{-1}.

This publication is a brief summary of the complete project report, which can be purchased from the National Technical Information Services.

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The complete report, entitled "Studies of NO_x Reactions and O_3 Transport in Southern California - Fall, 1976," (Order No. PB 83-200 360; Cost: $25.00, subject to change) will be available only from:
National Technical Information Service
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