United States
Environmental Protection
Agency

Environmental Sciences Research
Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/S3-83-028 Sept. 1983

EPA

Project Summary

Nitrogen Oxides Reactions Within Urban Plumes Transported Over the Ocean

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The rate of removal or conversion of nitrogen oxides was determined from airborne measurements in the urban plume of Boston. The mean pseudo-first-order rate constant for removal was 0.18 per hour, with a range of 0.14 to 0.24 per hour under daylight conditions for four study days. The removal process is dominated by chemical conversion to nitric acid and organic nitrates. The removal rate suggests an atmospheric lifetime for nitrogen oxides of about five to six hours in urban air.

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

Since the early 1970's interest in the atmospheric reactions of sulfur and nitrogen pollutants has continually increased. To date, sulfur compounds have been studied more thoroughly, especially in terms of the rate of ambient-air transformations; knowledge of the ambient-air reactions of nitrogen oxides (NO_x; defined as $NO + NO_2$) has lagged.

The aspect of atmospheric NO_x chemistry that is least understood is the rate at which NO_x are transformed to products. Few atmospheric studies have addressed this problem because of the technical difficulties involved. Breeding and coworkers (1) investigated the transformations of several pollutants around St. Louis. Their results suggest a 2- to 4-h half-life for NO in the St. Louis plume, but their NO_2 data are inconclusive. Thus, little was learned about the important conversion of NO_x to products.

Spicer et al. (2) investigated the fate of NO_x in the St. Louis and Los Angeles urban areas in 1973 to identify the major NO_x reaction products and, to the extent possible, to define the nitrogen mass balance. The experiment was not designed to obtain data on conversion rates, but if certain assumptions are accepted, a transformation rate of 0.10 ± 0.05 h^{-1} is consistent with the Los Angeles data. (The quoted value is in the form of a rate constant. Since it is calculated from an average percent conversion divided by a time interval, it should not be taken as a true rate constant and does not imply first-order kinetics.)

Calvert (3) used (LARP) data to estimate the rate of NO_x removal from Los Angeles air. He calculated a $(3.0 \pm 2.4) \times 10^{-4}$ ppm min^{-1} rate of conversion to products that were not detected by the LARP chemiluminescence monitors. This rate is somewhat higher than our measurements suggest for conversion to all products under moderate Los Angeles smog conditions.

In experiments downwind of Los Angeles in 1976, we observed lower-limit NO_x conversion rates of 0.02 to 0.16 h^{-1} in ground-level and aircraft sampling. Typical rates were 0.05 to 0.10 h^{-1}. Transformation to peroxyacetyl nitrate (PAN) ranged from < 0.01 to 0.08 h^{-1}.

The Los Angeles conversion rates are generally higher than those observed in Phoenix, Arizona, in 1977. Phoenix was selected for study because it is an isolated

source; thus, the NO_x reactions could be followed downwind of the city, over the desert, where complications due to fresh NO_x and tracer emissions were minimal. The Phoenix study was the first experiment designed principally to determine NO_x conversion rates. Based on the NO_x and tracer concentration levels and instrument sensitivities, NO_x conversion rates of 0.05 h^{-1} should have been detectable around Phoenix. This conversion rate was rarely exceeded, a puzzling result, since it is inconsistent with the earlier field results in Los Angeles and the expectations derived from modeling and smog-chamber studies.

While much has been learned of the distribution, balance, and fate of oxidized nitrogen in urban atmospheres, this brief review clearly indicates that much uncertainty remains regarding the rates of NO_x transformations in ambient air. The few measurements available of this conversion rate cover a broad range and seem to be city-specific. To better understand and model atmospheric NO_x reactions and to assess their impact on health, visibility, and precipitation chemistry, much more exact NO_x conversion rates must be known, and the factors that affect these rates must be identified.

We were able to accurately estimate NO_x lifetime in polluted urban air. The results of the experimental phase of the program and the details of the experimental methods are presented in this project report.

The aim of the Boston urban plume study from July 27 to August 30, 1978 was a better understanding of NO_x reactions and especially the NO_x reaction rate in polluted urban air.

Aircraft field measurements were obtained in the Boston plume as it was transported eastward over the ocean. A mobile laboratory located at the Beverly, Massachusetts airport provided ground support for the flight program and obtained ground-level data on air quality and meteorological conditions.

Project Description

To better define the rates of NO_x transformations within urban plumes in the least ambiguous way, it was desirable that the urban source be isolated so that downwind emissions into the urban plume are minimal. The city must also be a strong source of NO_x, and the downwind terrain should be relatively smooth. Based on these considerations, Boston was selected for this study. The predominant summer winds from the west and southwest take the city's polluted air eastward over the ocean, where smooth terrain and minimal fresh emissions are the rule. As a northeastern coastal city, Boston also contrasts sharply with the hot, dry Phoenix site studied earlier.

The field experiment was conducted from July 27 to August 30, 1978. A twin-engine research aircraft was used for continuous monitoring and sample collection in the Boston urban plume. A mobile laboratory served as ground support for the aircraft program and continuously monitored ground-level air quality and meteorological conditions. The mobile lab and aircraft were based at Beverly Airport, in Beverly, MA, approximately 25 km northeast of Boston. Hourly meteorological data from several eastern Massachusetts stations were obtained by telephone several times each day and were used to construct working trajectories for Boston's polluted morning air mass. The morning air mass was followed throughout the day by three or more monitoring flights along these trajectories. Data were collected during multiple traverses of the urban plume on each flight to bracket the morning air parcel. Thus, data on pollutant concentrations within the air parcel were obtained from early morning through late afternoon. Transport out to ~150 km from the source was investigated. Background pollutant concentrations were also obtained. The variables measured during aircraft operations included NO_x, ozone (O_3), nitric acid ($HONO_2$), PAN, carbon monoxide (CO), nonmethane hydrocarbons (NMHC), fluorotrichloromethane (F-11), to C_1 to C_5 hydrocarbons, condensation nuclei, nitrate (NO_3^-), sulfate ($SO_4^=$), temperature and dew point. The ground station measured these and a number of other variables.

Results and Conclusions

Important findings of the study can be summarized as follows.

- The weather during the Boston plume study was generally rainy and overcast, interspersed with a few sunny clear days. Pollutant levels at the ground station in Beverly were usually low. On a few days, southwesterly winds transported Boston's polluted air to Beverly. One very clear case of pollutant transport occurred on August 16, when O_3, PAN, and light-scattering aerosol reached very high levels just before dawn.
- Table 1 gives the 24-h distribution of oxidized nitrogen for a subset of 14 days during which all the pertinent species were measured. The usual oxidized-nitrogen burden at Beverly Airport was low because of its location (the emissions density to the west, north, and east was quite low). On average, about 14% of the oxidized nitrogen was present in the form of reaction products. The ratio of the average PAN and $HONO_2$ concentrations was 1.8.
- The concentration of nitrate in the aerosol phase was extremely low at Beverly Airport, with gaseous nitrates accounting for 98% of the total atmospheric nitrate. For comparison, gaseous nitrate as a proportion of total nitrate for several geographical locations is given in Table 2. For many of the locations, gaseous nitrate dominated the total nitrate burden, as observed at Beverly.
- Based on four days of flights for which detailed analysis is presented, the removal of NO_x from the transported Boston plume followed first-order kinetics reasonably well. The pseudo-first-order rate constant for NO_x removal ranged from 0.14 h^{-1} to 0.24 h^{-1} with a mean of 0.18 hr^{-1}. Maximum O_3 concentrations in the plume on these four days ranged from 0.095 to 0.160 ppm.
- On the days when all the necessary data were available, the nitrogen balance in the plume was accounted for with PAN and $HONO_2$ accounting for nearly all the reacted NO_x. For example, during three transects of the urban plume on August 30, 1978, the nitrogen mass balance averaged 88%.

The pseudo-first-order rate constants obtained in these experiments provide a basis for estimating the lifetime of NO_x (as $NO + NO_2$) in transported urban air under photochemically active conditions. The lifetime, τ, can be defined as the time required for chemical and physical removal

Table 1. 24-Hour Distribution of Oxidized Nitrogen

	Concentration (ppm)	*Fraction of Total Oxidized Nitrogen (%)*
NO_x ($NO + NO_2$)	*0.018*	*86*
PAN	*0.0018*	*9*
$HONO_2$	*0.0010*	*5*
NO_3^-	*0.00004*	*1*

Table 2 *Gaseous Nitrate Measured at Several Locations*

Location	Gaseous Nitrate Total Nitrate
St. Louis, MO (1973)	*95*
West Covina, CA (1973)	*98*
Phoenix, AZ (1977)	*50*
Temple City, CA (1976)	*75*
Upland, CA (1976)	*.96*
Rubidoux, CA (1976)	*.45*
Beverly, MA (1978)	*.98*

processes to reduce the NO_x concentration to 1/e of its initial value (i.e. when $\frac{(NO_x)o}{(NO_x)t} = e$).
Substituting into the integrated form of the rate equation,

$$1n\frac{(NO_x)_o}{(NO_x)_t} = kt$$

$$1n\ e = k\tau$$

$$\tau = 1/k$$

For the four available experiments, τ ranges from 7.1 to 4.2 hr. The average of the four rate constants yields a lifetime of 5.5 h. The NO_x half-life defined as

$$t_{1/2} = \frac{0.69}{k}$$

averages 4.1 h.

To the best of our knowledge, this is the first determination of NO_x lifetime in polluted urban air. The reported values are applicable only to daylight hours under sunny, photochemically active conditions. Further research will be required before these conclusions can be extended to other areas with different meteorological conditions or emissions factors.

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The complete report, entitled "Nitrogen Oxides Reactions Within Urban Plumes Transported Over the Ocean," (Order No. PB 83-196 378; Cost: $17.50, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
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