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# THE FATE OF NITROGEN OXIDES IN THE ATMOSPHERE

Chester W. Spicer

Battelle Columbus Laboratories

Prepared for:

Environmental Protection Agency

13 September 1974

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Final Report

# THE FATE OF NITROGEN OXIDES IN THE ATMOSPHERE

Battelle
Columbus Laboratories

A report of research conducted for the
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REPORT

on

# THE FATE OF NITROGEN OXIDES IN THE ATMOSPHERE

to

COORDINATING RESEARCH COUNCIL, INC.
(CAPA-9-71)

and

U.S. ENVIRONMENTAL PROTECTION AGENCY
(Contract No. 68-02-0799)

September 13, 1974

Prepared by: Chester W. Spicer

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Dr. John Pierrard

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on

# THE FATE OF NITROGEN OXIDES IN THE ATMOSPHERE

to

COORDINATING RESEARCH COUNCIL, INC.
(CAPA-9-71)

and

U.S. ENVIRONMENTAL PROTECTION AGENCY
(Contract No. 68-02-0779)

from

BATTELLE
Columbus Laboratories

September 13, 1974

## INTRODUCTION

The objective of this program is to determine the distribution and ultimate fate of nitrogen oxides in the atmosphere. A secondary goal of the project is to uncover relationships among the nitrogen compounds and other atmospheric parameters in order to define the conditions under which nitrogen oxides are removed and nitrogen reaction products accumulate in the atmosphere. Nitrogen oxides long have created problems in understanding smog chemistry due to the multifarious nature of their reactions. Nitrogen oxides are involved in virtually every aspect of photochemical smog formation, and although much has been learned about the mobile and stationary sources of nitrogen oxides, the fate or ultimate disposition of these species in polluted atmospheres has remained a mystery. Because of the possibility that undetermined nitrogen-containing reaction products may be biologically hazardous and because of the need for smog modelers and persons responsible for control strategies to understand the mechanism of photochemical smog formation, this study was undertaken.

## SCOPE AND SUMMARY OF PROGRAM

The current program consisted of three distinct phases involving analytical methods development, field studies, and analysis and interpretation of the field study results.

The analytical development phase of the program involved developing or refining state-of-the-art techniques for the determination of ambient levels of PAN, $NH_3$, $HNO_3$, and $NH_4^+$.

The field sampling phase of the program consisted of 5 weeks of air monitoring and particulate collections in St. Louis, Missouri, and 5 weeks in West Covina, California. In addition to the chemical measurements mentioned above, NO, $NO_2$, $O_3$, $NO_2^-$, $NO_3^-$, and C,H,N were determined. Meteorological variables including wind speed, wind direction, temperature, relative humidity, and solar intensity were also monitored continuously. In St. Louis, several rainfall samples were collected and analyzed for trace nitrogen compounds. Vertical $NO_x$ sampling using a fixed-wing aircraft was conducted during several days in St. Louis. Composite

dust samples were collected in both cities and analyzed for nitrogen constituents. Silver-membrane filter samples were also taken in West Covina for analysis by electron spectroscopy chemical analysis (ESCA).

The analysis and interpretation phase of the program involved statistical analysis of the data from both cities with the purpose of deriving relationships among chemical and meteorological parameters in order to help us improve our understanding of the fate of nitrogen oxides.

Although the analysis and interpretation of our results will continue into another year, there are a number of observations and tentative conclusions which stand out at this time. Several of these are summarized below.

During the early phases of this program, two techniques for monitoring nitric acid were developed. The first of these is a continuous procedure which utilizes a modified, acid-detecting coulometric instrument. The second technique is an integrating method wherein nitric acid in the air is separated from nonvolatile particulate nitrate and collected in solution. The solution is subsequently analyzed for nitrate. These two methods have been employed successfully in smog chamber research and in the field studies described in this report. Based on these two techniques, nitric acid was observed in the atmospheres of both St. Louis and West Covina. The nitric acid concentration was found to vary from less than 1 ppb to greater than 30 ppb on an hourly average basis.

In order to derive a "balance" between nitrogen oxide reactant and $NO_x$ reaction products, it was necessary to determine the fraction of $NO_x$ which was converted to products or removed from the atmosphere at any given time. This "$NO_x$ Loss" was derived using the equation

$$NO_x \text{ Loss} = \frac{(CO)_{measured}}{(CO/NO_x)_{emission\ inventory}} - (NO_x)_{measured}$$

where $(CO/NO_x)_{emission\ inventory}$ is the ratio based on emissions inventory estimates and $(CO)_{measured}$ and $(NO_x)_{measured}$ are the actual concentrations of CO and $NO_x$ at any point in time. The first term on the right hand side of the equation can be thought of as a predicted $NO_x$ concentration based on the estimated emissions ratio of CO and $NO_x$ and the measured CO concentration at any given time. The assumption is made here that over short time periods (several hours) CO is inert and can be used as a tracer for $NO_x$ concentration. Substracting the actual measured $NO_x$ concentration from the predicted concentration yields the term "$NO_x$ Loss".

Based on our "$NO_x$ Loss" calculations it appears that the mechanisms by which the nitrogen oxides are removed from the atmosphere involve relatively slow processes.

In West Covina, the greatest loss of nitrogen oxides was observed during midafternoon on high photochemical smog days. This portion of the "$NO_x$ Loss" profile was highly correlated with ozone concentration. If certain assumptions are accepted, the afternoon or photochemical loss of nitrogen oxides appears to be largely accounted for by the sum of the PAN and nitric acid concentrations.

There was some evidence that nitric acid is removed from the air by alkaline-surface glass-fiber filters, but not by high-purity quartz-fiber filters. If true, this would mean that much particulate nitrate data collected over the years may have been strongly influenced by gaseous nitric acid.

There was also some indication that ozone is transported into the St. Louis region during early morning hours. While the source of this ozone is not yet clear, there is some evidence that PAN and possibly nitric acid are associated with the nighttime ozone.

The program is continuing, and the second year effort will be devoted in part to further validation and documentation of our nitric acid measurements and in part to further analysis and interpretation of our first-year field results. Special emphasis in the second year will be placed on expanding our data base to include data collected at the same time by other research groups in the St. Louis and Los Angeles area. Inclusion of these data in our analyses will increase both the scope of the investigation and the accuracy of the results.

# TECHNICAL BACKGROUND

This section contains a discussion of previous laboratory and atmospheric studies relating to the distribution and fate of nitrogen oxides in the atmosphere.

## TECHNICAL BACKGROUND

To give some insight into previous investigations of the chemistry of the nitrogen oxides in laboratory studies and in the atmosphere, a review of pertinent research is in order. We believe much can be learned from laboratory simulations of photochemical smog reactions and will therefore start by reviewing attempts to determine nitrogen balances in smog chamber studies.

### Nitrogen Distribution in Smog Chamber Studies

The question of the fate of atmospheric nitrogen oxides probably first arose from the lack of an adequate nitrogen balance in laboratory studies of photochemical smog-type reactions. Early investigators attributed the loss of nitrogen during irradiation experiments to adsorption of nitrogen oxides on the reaction vessel walls or to the formation of complex polymers of carbon and nitrogen.

In his study of trans-2-butene photooxidation, Tuesday[1] reported that all of the initial nitrogen in his system was recoverable as peroxyacetyl nitrate (PAN), methyl nitrate, and residual nitrogen dioxide. However, Gay and Bufalini[2] have pointed out that the application of Stephens'[3] more recent infrared absorption coefficient to Tuesday's data reveals an actual nitrogen balance of only 78 percent at the end of his experiment. Altshuller and Cohen[4] reported only a 13 percent recovery of nitrogen as nitrogen dioxide and methyl nitrate at the conclusion of ethylene photooxidation. In the photooxidation of the propylene-nitrogen oxide system, Altshuller, et al.[5], reported good nitrogen balances up to the time when nitrogen dioxide reached a maximum. After that time, the nitrogen balance depended on the initial nitrogen oxide concentration. When the initial $NO_x$ was less than 0.2 ppm, all of the nitrogen could be accounted for as PAN. Between 0.2 and 0.5 ppm initial $NO_x$, 50 to 90 percent of the nitrogen oxide which reacted was attributable to PAN. At initial $NO_x$ levels between 0.5 and 1.5 ppm, only 35 to 75 percent of the nitrogen oxide consumed could be recovered as PAN. Methyl nitrate was also detected but it accounted for only a minute fraction of the missing nitrogen. No other organic nitrogen compounds could be found in their system. Altshuller, et al.[6] irradiated both toluene-$NO_x$ and m-xylene-$NO_x$ systems. Peroxyacetyl nitrate accounted for only 10 to 20 percent of the reacted nitrogen in the former case and 10 to 75 percent in the latter. However, as found previously, the percentage of recovered nitrogen increased rapidly as the initial nitrogen oxide concentration was decreased below 1.2 ppm.

Several other organic nitrogen compounds have been investigated in laboratory photooxidations in the hope that they would improve the poor nitrogen balances. Chief among these are the alkyl nitrates and various nitroolefins. Methyl and higher molecular weight alkyl nitrates have been identified by several researchers[1,7-10] in laboratory photooxidations of olefins and aromatic hydrocarbons with $NO_x$. Several alkyl nitrates have also been identified as products in irradiated automobile exhaust.[11,12] The yields of alkyl nitrates are much lower than PAN yields, however, and can account for only a small percentage of the missing nitrogen. The possible presence of nitroolefins has been tested in irradiated propylene-$NO_2$ mixtures, in irradiated auto exhaust, and in the atmosphere.[13] The conclusion was reached that these compounds could not be present in concentrations greater than one or two parts per billion.

Our understanding of the fate of nitrogen oxides was increased by the study of Gay and Bufalini[2], wherein nitrate (presumably derived from nitric acid formed on the reaction vessel walls by hydrolysis of nitrogen pentoxide) was identified as one of the principal nitrogen-containing products. By determining nitrate and nitrite in the liquid used to scrub their reaction-chamber walls, they obtained nitrogen balances of 97 percent for 2-methyl-2-butene photooxidation, 90 percent for m-xylene, 72-80 percent for isopropylbenzene, 92-100 percent for 1,3 butadiene, and 100 percent for both propylene and 1-butene. In addition to the excellent nitrogen balances they achieved, Gay and Bufalini also demonstrated that neither molecular nitrogen nor nitrous oxide is a likely product of photochemical smog reactions.

In the recent study by Spicer and Miller[14] of nitrogen balances in smog chamber systems, both PAN and $HNO_3$ were monitored continuously for the first time. Excellent nitrogen balances were reported throughout smog chamber irradiations in single hydrocarbon/$NO_x$ and synthetic auto exhaust/$NO_x$ systems. The primary nitrogen-containing reaction products were reported to be PAN and $HNO_3$, with the ratio of PAN/$HNO_3$ dependent on the amount and nature of the surface available for heterogenous reaction and the overall reactivity of the hydrocarbon system.

## Nitrogen Distribution in the Atmosphere

While much effort has gone into identification and analysis of nitrogen-containing compounds in the atmosphere, there has never been a concerted effort to determine all the various nitrogen-containing species at one place and at one time. The greatest level of effort in the measurement of atmospheric nitrogen compounds has been accorded to nitric oxide and nitrogen dioxide. Almost all of the oxides of nitrogen emitted from both mobile and point sources is released as NO. The means by which the NO is converted to $NO_2$ has been a subject of controversy. However, the result of the conversion process is approximately equal concentrations of NO and $NO_2$, on a yearly average basis, at most monitoring locations. Naturally, figures for yearly averages and maximum daily averages vary from one location to another. Using Los Angeles $NO_x$ levels as examples, the yearly averages have been reported[15] as 0.08 ppm and 0.06 ppm for NO and $NO_2$, respectively. Kopczynski, et al.[16], found morning $NO_x$ levels in downtown Los Angeles averaging 0.41 ppm in the fall of 1968. The morning concentrations were found to vary from 0.09 to 1.06 ppm $NO_x$ during the period of the study.

Most of the investigations which have determined atmospheric PAN and PPN levels have been carried out in the general Los Angeles area. Examples of such studies are those of Darley, et al.[17], Stephens and Price[13], and Kopczynski, et al.[16]. Darley and co-workers found 50 ppb PAN and 6 ppb PPN during a day of heavy air pollution in Riverside, California. Samples taken during April and May of 1968 by Stephens and Price showed between 5 and 40 ppb PAN in Riverside. Kopczynski, et al., studying reactions in Teflon bags in downtown Los Angeles, reported between 8 and 97 ppb PAN formed in naturally irradiated Los Angeles morning air.

A search for some atmospheric nitroolefins was carried out by Stephens and Price[13] in the metropolitan Los Angeles area in the spring of 1964. None of the samples collected showed any trace of nitroolefins.

There is good reason to suspect alkyl nitrates as products of smog reactions. These compounds are known decomposition products of PAN and they have been identified in many laboratory smog chamber studies. However, Stephens and Darley[18] found no evidence of alkyl nitrates in atmospheric samples. They would have detected as little as 0.5 ppb.

Ammonia concentrations in nonurban atmospheres rarely exceed 0.015 ppm.[19] For example, Hodgeson, et al.[20], report ammonia concentrations ranging between 0.002 and 0.010 ppm in the Research Triangle Park area. Urban $NH_3$ concentrations reported by the National Air Surveillance Network (NASN)[19] have been considerably higher than the nonurban concentrations. Ammonia concentrations between 0.10 and 0.22 ppm were found by Morgan and co-workers[21] in several urban and nonurban locations. However, the method of chemical analysis for $NH_3$ used by NASN is subject to some uncertainty and has been discontinued as a routine measurement.

A recent study of ammonia concentrations at Harwell in Great Britain[22,23] found the average ammonia concentration to be 1-3 ppb. The ammonia profile at Harwell is almost constant with the highest ammonia levels reaching only 7 ppb. Lodge, et al.[24], have reported on ammonia concentrations in the St. Louis, Missouri, area. They generally found ammonia present at 0-10 ppb and could find no firm evidence that ammonia was associated with the urban plume of St. Louis. Their results indicate that, within experimental error, the concentration of $NH_3$ within the urban plume is probably the same as that outside the plume.

All reported attempts to identify nitric acid in the gas phase in urban atmospheres have met with failure. Scott, et al.[25], tested for $HNO_3$ by an infrared technique which should have detected as little as 0.1 ppm. Recent long-path Fourier transform infrared measurements made by Hanst and co-workers[26] have also failed to uncover nitric acid. The possibility remains, however, that $HNO_3$ is present in urban air but at levels below the detection limits of current instruments; or it may be present but has gone undetected either due to its reaction with other atmospheric constituents or its adsorption on the walls of the infrared sampling system.

Nitric acid has been identified in the lower stratosphere by Murcray, et al.[27], using infrared absorption techniques during balloon flights. The nitric acid appears to be concentrated in a layer between 22 and 30 km altitude and is apparently associated with the ozone layer. Rhine, et al.[28], have attempted to quantitate the stratospheric nitric acid reported by Murcray, et al.[27], and report approximately 3 ppb $HNO_3$ associated with the ozone layer. They suggest that the reaction of HO with $NO_2$ may be the most important producer of nitric acid in the ozone layer. However, the smog chamber evidence from the study of Spicer and Miller[14] implicates the heterogenous reaction of $N_2O_5$ with $H_2O$ as the primary source of nitric acid in photochemical smog, with only a minor contribution from the HO + $NO_2$ reaction. Reaction conditions in the lower stratosphere are quite different from those occurring in urban atmospheres, however, so the mechanism of nitric acid formation may be quite different at the two altitudes. Crutzen[29] has calculated production rates and concentrations of ozone, nitric acid, and several other species in the stratosphere, and reports that the nitric acid values found by Mulcray, et al.[27], in the ozone layer are much higher than the levels which are predicted using current rate constants.

Based on an 8-year study[30] of the mean concentration of selected particulate contaminants in the atmosphere of the United States, it appears that nitrate on the average contributes somewhat less than 2 percent of the total suspended particulate weight. The figures vary depending on location. Several representative urban areas were Atlanta at 2.0 $\mu g/m^3$, Chicago at 2.5 $\mu g/m^3$, Boston at 2.3 $\mu g/m^3$, and Pittsburgh showing 3.0 $\mu g/m^3$.

Air samples from Cincinnati, Chicago, Philadelphia, and Fairfax, Ohio, were collected and analyzed for phosphate, nitrate, chloride, and ammonium by Lee and Patterson.[31] These investigators obtained size distributions on the nitrate aerosol which showed that nitrate is primarily associated with submicron particles. They concluded that suspended nitrate originates from a gaseous source rather than a wind-erosion source. Reaction of $HNO_3$ with their filter materials was not discussed. Average nitrate concentrations reported by Lee and Patterson were 2.96 $\mu g/m^3$ in Cincinnati and 2.83 $\mu g/m^3$ in Fairfax, Ohio.

Recent work by Miller, et al.[32], in Columbus, Ohio, and the New York City area differs from the Lee and Patterson results in that up to 50 percent of the nitrate was found in particles greater than 2 $\mu m$ in diameter. Gordon and Bryan[33] have reported the presence of $NH_4NO_3$ in the Los Angeles aerosol based on infrared spectra of high-volume filter extracts and a molar ratio of $NO_3^-/NH_4^+$ very close to one over the past several years. However, reactions and interactions of $NH_3$ and $HNO_3$ with glass fiber filters employed in their study were not considered.*

The size distribution and concentration of ammonium aerosols has been investigated by Lee and Patterson[31] in Chicago, Philadelphia, and Fairfax, Ohio. Ammonium concentrations were found to be 4.00 $\mu g/m^3$, 9.45 $\mu g/m^3$, and 5.74 $\mu g/m^3$, respectively. They found that ammonium particulate is predominantly submicron in size. A similar size distribution was also reported by Miller, et al.[32]. The size distributions suggest that ammonium originates from gaseous materials rather than from wind erosion. Evidence was also obtained that at least some of the ammonium present in the atmosphere is in the form of $(NH_4)_2SO_4$. Junge[34] has reported a high correlation between ammonium and sulfate in ratios close to that for $(NH_4)_2SO_4$, and Dubois and co-workers[35] in a recent presentation have also shown correlation between atmospheric ammonium and sulfate using $NH_4^+$ specific ion electrodes.

A somewhat different view of nitrogen species in aerosol samples has been reported by Novakov, et al.[36], who employed electron spectroscopy chemical analysis (ESCA) to determine the oxidation states of elements found in Pasadena aerosol samples. They report nitrate to be associated primarily with larger (2-5 $\mu m$) particles. However, they find most of the nitrogen in the aerosol in the 0.6-2.0 $\mu m$ size range, this nitrogen reportedly consisting of pyridino, amino, and to a lesser extent ammonium compounds. The ESCA technique was also employed for several samples collected for this program.

*We believe such reactions may be important on typically alkaline glass filters and will discuss such interactions later in the report.

## Atmospheric Nitrogen Balance

### Global Considerations

A study of the global nitrogen cycle, reported by Robinson and Robbins[37], estimates the background concentrations of the major trace atmospheric constituents as shown in Table 1.

**TABLE 1. BACKGROUND LEVELS OF ATMOSPHERIC NITROGEN COMPOUNDS**

| Compound | Ambient Concentration |
|---|---|
| $N_2O$ | 0.25 ppm |
| NO | 2 ppb over land |
| $NO_2$ | 4 ppb over land |
| $NH_3$ | 6 ppb |
| $NO_3^-$ | 0.2 $\mu g/m^3$ |
| $NH_4^+$ | 1.0 $\mu g/m^3$ |

Nitrous oxide accounts for most of the mass of trace nitrogen compounds. Its cycle is independent of the other nitrogen compounds in the troposphere, consisting largely of a balanced system of biological production and biological removal from the atmosphere. Another minor sink exists above 30 km, where $N_2O$ can participate in photochemical reactions. However, in the troposphere $N_2O$ appears to play no part in photochemical smog reactions. Gay and Bufalini[2] have also established that $N_2O$ is not a product of smog reactions.

Ammonia and ammonium aerosols are reportedly produced primarily in soil with an estimated atmospheric residence time for $NH_3$ of less than one week. The major scavenging processes on a global basis are gaseous deposition and aerosol formation. Ammonium aerosols are subsequently removed from the atmosphere by precipitation and dry deposition. An earlier report by Robinson and Robbins[38] that $NH_3$ is oxidized in the atmosphere to oxides of nitrogen is discredited in their most recent work.

The NO and $NO_2$ cycle involves both natural and anthropogenic sources at an emissions ratio of approximately ten to one. On a global basis the NO is scavenged largely by oxidation to $NO_2$, with the $NO_2$ removed by gaseous deposition and aerosol formation. Nitrate aerosol is removed by precipitation and dry deposition.

The sources and sinks for atmospheric nitrogen compounds reported by Robinson and Robbins are of utmost importance when considering global nitrogen balance. However, the sources and removal paths for the same nitrogen species are quite different in urban polluted atmospheres. While the global sinks for the minor nitrogen compounds are sufficient to prevent long-term buildup of their concentrations, still the natural scavenging processes are not rapid enough to affect nitrogen compound concentrations over short time intervals (hours) in urban atmospheres. Therefore, short-term losses of nitrogen compounds in polluted atmospheres must depend on other atmospheric processes.

Levy[39] has formulated a steady-state model of the chemistry in the lower troposphere and used it to calculate the hourly concentrations of a number of species including $NO_3^-$, $N_2O_5$, $HNO_3$, and $HNO_2$. It must be emphasized that this model was developed for the troposphere in general and is not meant to

simulate the rather unique chemistry of urban polluted atmospheres. The model predicts the major nitrogen products of daytime reactions to be $HNO_3$ and $HNO_2$, with $HNO_3$ predominating. Levy suggests that nitric acid never approaches its full potential concentration (~100 ppb) due to the formation of nitrate aerosols and their subsequent scavenging by precipitation. However, the nitrate rain-out rate which follows from the model is almost two orders of magnitude higher than the measured rate reported by Erickson.[40] Levy concludes that ". . . the question of nitrogen balance in the troposphere and the role of $HNO_3$ are far from settled".

Junge[41] has examined the distribution of ammonium and nitrate in rainwater over the United States and reports ammonium levels of 0.1-0.2 mg/liter in the St. Louis area during the summer and about 1.0 mg/liter in the Los Angeles vicinity during early summer. Rainwater nitrate levels were approximately 0.3-0.4 mg/liter for St. Louis and 0.5 mg/liter for Los Angeles during early summer. These results are for the years 1956-1957. The distribution pattern for nitrate in rain samples seems to eliminate the photochemical production of $NO_2$ in the stratosphere as a source of tropospheric nitrate. There was also no correlation of $NO_3^-$ in rainwater with thunderstorm activity, thus ruling out the argument that a large fraction of the nitrate is formed by lightning. The conclusion reached by Junge was that the major fractions of both $NH_4^+$ and $NO_3^-$ in rainwater have as their source the earth's soil. Alkaline soils especially appear to generate large quantities of ammonia. The formation of small amounts of NO and $NO_2$ in soil was also postulated.

Georgii[42] has also studied oxides of nitrogen and ammonia in the atmosphere, primarily by examining the concentrations of these species in precipitation. He reports nitrite present in rainwater at up to 10 percent of the nitrate concentration. He also suggests and gives evidence for the formation of $HNO_3$ and $HNO_2$ by simple absorption of gaseous $NO_2$ in rainwater.

The results of these investigations into the global nitrogen budget have a considerable bearing on the study of the fate of nitrogen oxides in urban atmospheres. However, the processes for forming and scavenging nitrogen compounds on a global scale are generally too slow to have a significant influence over the short-term balance of nitrogen species in an urban area. The following section discusses the investigations which have attempted to examine this short-term balance.

**Urban Environments**

Perhaps the first report of urban nitrogen balance resulted from the study of Gordon, et al.[43], in Los Angeles. In that investigation, hourly bag samples were collected in downtown Los Angeles (DOLA) and Azusa from 5:00 a.m. through 5:00 p.m. for 46 weekdays. The bag samples were subsequently analyzed for $C_2$-$C_5$ hydrocarbons. Hourly averages for oxidant, nitrogen oxides, and carbon monoxide were obtained from the DOLA and Azusa monitoring stations. From the integrated bag sample values for acetylene and the hourly average $NO_x$ concentrations from the monitoring stations, ratios of acetylene to $NO_x$ were computed for several hours during the day. The average ratios vary between about 0.30 and 1.00, considerably higher than the acetylene to nitrogen oxide ratio reported[44] for integrated bag samples collected during the California test driving cycle. This discrepancy could result from a nonrepresentative driving cycle[43], from a loss of atmospheric $NO_x$, or from a nonautomotive source of atmospheric acetylene. Since acetylene has been found to originate almost entirely from the automobile in urban atmospheres, we are left with the possibilities of a nonrepresentative driving cycle or a rapid atmospheric loss process for $NO_x$. For most of the hourly average ratios, the magnitude of the daily oxidant level appeared to have little influence on the difference between the driving cycle ratio and the atmospheric ratio. In other words, the discrepancy between the two ratios was similar on both high and low oxidant days. This is an important fact, since many processes which may be important in removing nitrogen oxides from the atmosphere involve reactions of ozone and would be expected to increase on high oxidant days. If this were the case, then a difference between the acetylene/$NO_x$ ratios would be expected for low and high oxidant days.

Another investigation which employed the ratio approach to study atmospheric nitrogen balance has been reported by Eschenroeder and Martinez.[45] In their analysis of Los Angeles atmospheric data from 1968 to 1969, these researchers employed both CO and $C_2H_2$ as tracers in order to study the nitrogen

balance. Both CO and $C_2H_2$ are derived almost exclusively from auto exhaust and both are relatively inert to photochemical smog reactions. Since reasonably reliable emissions data are available for CO and $NO_x$ and since the $C_2H_2/NO_x$ auto exhaust ratio has been determined in the California driving cycle, one has available the $CO/NO_x$ and $C_2H_2/NO_x$ ratios from the emissions sources. Two types of ratios are pertinent to our discussion. The "vehicular" ratio of $CO/NO_x$ and $C_2H_2/NO_x$ is the ratio of these pollutants present in auto exhaust. The "all sources" ratio is somewhat lower than the vehicular ratio, due to $NO_x$ emission from sources other than the automobile. This ratio includes the emissions input from all known sources of CO, $C_2H_2$, and $NO_x$. Once the emissions ratio for $CO/NO_x$ or $C_2H_2/NO_x$ is determined for a given region, the discrepancy between the theoretical or emissions inventory ratio and the measured ratio can be used as an indication of nitrogen oxide losses, assuming CO and $C_2H_2$ are inert over short time intervals.

In the report of Eschenroeder and Martinez, $C_2H_2/NO_x$ ratios were averaged over all the days in 1969 in Commerce, California, and the composite hourly averages plotted as a function of time. Similar plots were made of the $CO/NO_x$ ratios from Huntington Park, California, for a limited number of days in 1968 and for Commerce throughout 1969. The $CO/NO_x$ ratios were also separated into high oxidant ($\geq$0.2 ppm) and low oxidant ($<$0.2 ppm) days and plotted accordingly.

The 1968 $CO/NO_x$ ratios from Huntington Park differed considerably from the emissions ratios, with high oxidant days showing much higher ratios (presumably greater $NO_x$ losses) than the low oxidant days. At its maximum (approximately 7:00 a.m.) the $CO/NO_x$ curve for high oxidant days exceeded the "all sources" emissions ratio by a factor of four, indicating very large and rapid nitrogen oxide losses.

The ratios of both $CO/NO_x$ and $C_2H_2/NO_x$ for all days in 1969 at Commerce showed rather different trends than the limited 1968 data. The $C_2H_2/NO_x$ ratios varied between the vehicular and all sources ratios with a rise toward late morning. The $CO/NO_x$ ratios for low oxidant days showed the same behavior. On high oxidant days, the trend was similar, but the curve was generally higher (greater $NO_x$ losses) than on low oxidant days. The indication from the 1969 data is that losses of nitrogen oxides are rather small on low oxidant days, with slightly greater losses occurring on days of higher oxidant. In general, the maximum losses appeared between 10:00 a.m. and 12:00 a.m.

The difference in $NO_x$ losses between the 1968 and 1969 data may reflect the relatively small number of sampling days from 1968 as opposed to the full year's data for 1969. In this regard, one would expect the 1969 results to be the more reliable because of the much greater number and wider range of sample days.

It should be pointed out that two interpretations can be made of the greater $NO_x$ loss on high oxidant days. One view is that reactions of ozone lead to $NO_x$ loss, with the loss consequently higher on high oxidant days. Another interpretation holds that, on certain days, some undefined process removes $NO_x$ from the atmosphere leading to a higher hydrocarbon/$NO_x$ ratio and a more rapid formation of oxidant. From this point of view, the lower $NO_x$ *causes* the high oxidant day.

Another study which reported on the fate of nitrogen oxides in an urban area was carried out by Lodge, et al.[24], in St. Louis, Missouri. A number of pollutants were investigated in the program. Although the results of the study are very interesting, little was learned about the fate of nitrogen oxides because the experimental design did not take into account $NO_x$ input to the urban plume from localized $NO_x$ sources along the plume's path.

# EXPERIMENTAL METHODS

This section contains a discussion of the experimental methods employed during the field sampling phase of the program.

## EXPERIMENTAL METHODS

Battelle-Columbus' Mobile Air Quality Laboratory, pictured in Figure 1, was used in St. Louis, Mo., and West Covina, Calif., to monitor meteorological conditions, solar irradiation intensity, and gas-phase composition, while simultaneously collecting aerosol samples for subsequent chemical analysis. Data from all instruments were fed to a Digi-Tem data acquisition system where the analog input is converted to digital form, serialized by bit, and presented in ASC II code on paper tape. Each instrumental channel was interrogated every 10 minutes for 23 hours each day, from 11:30 p.m. to 10:30 p.m. The information on paper tape was read into Battelle's CDC-6400 computer, conditioned, and permanently stored on magnetic tape. A computer program was used to average all analyses (except wind direction) and plot all analyses as 23-hour profiles.

Instrumentation and experimental methods employed in the Mobile Laboratory are discussed in the following paragraphs.

### Meteorological Measurements

The Battelle Mobile Laboratory makes use of an automated MRI, Inc., Model 1071 weather station. The instruments listed in Table 2 provide a continuous readout of temperature, relative humidity, wind speed, and wind direction. The laboratory also employs an Eppley Laboratory, Inc., 180° pyrheliometer to determine global radiation (total sun and sky).

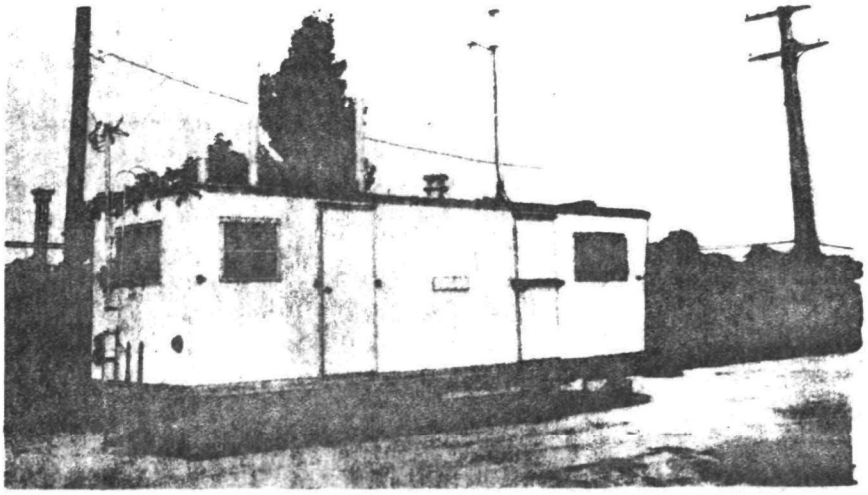
Laboratory and newspaper records were kept of general weather conditions such as cloud cover and intervals during which rain occurred.

TABLE 2. METEOROLOGICAL MEASUREMENTS

| Analysis | Instrument |
|---|---|
| Wind Speed and Direction | MRI, Model 1074-2 sensor |
| Temperature | MRI, Model 802 sensor |
| Relative Humidity | MRI, Model 907 sensor |
| Global Radiation Intensity | Eppley Lab, 180° pyrheliometer |

### Air Quality Measurements

The instruments used for air quality monitoring are listed in Table 3. Air samples are pulled into the Mobile Laboratory through an aluminum stack used for high-volume aerosol sampling. The top of the stack is about 15 feet above the trailer roof or roughly 25 feet above the ground. Flow rate through the stack is at least 30 cubic feet per minute, so that the residence time is no more than about 6 seconds in the stack. From the stack the samples are transported through short lengths of 1/4-inch Teflon tubing to the appropriate instrument. A brief description of the instrumental methods employed in this study follows.



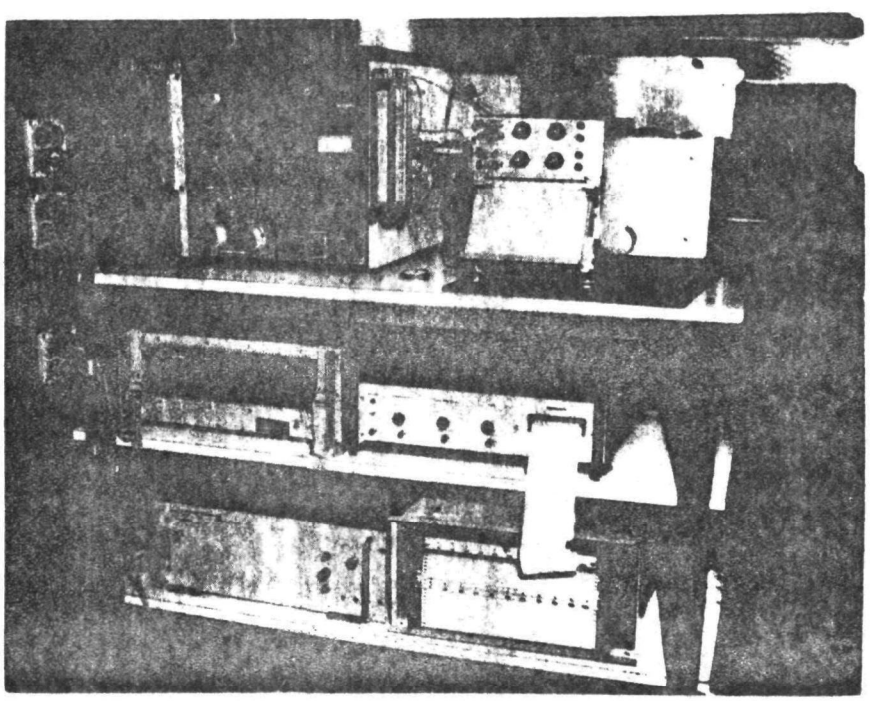


**FIGURE 1. BATTELLE-COLUMBUS' MOBILE AIR QUALITY LABORATORY**

TABLE 3. AIR MONITORING INSTRUMENTATION

| Analysis | Instrument |
|---|---|
| $O_3$ | REM, Model 612 chemiluminescence monitor |
| NO, $NO_x$, $NO_2$ (by difference) | Bendix, Model 8101-B chemiluminescence analyzer, carbon catalytic converter |
| $NH_3$ | Bendix, Model 8101-B chemiluminescence analyzer, dual stainless steel and carbon catalytic converters |
| Peroxyacetyl Nitrate (PAN) | Varian Series 1200 gas chromatograph with electron-capture detection |
| $HNO_3$-continuous | Modified acid-detecting Mast coulometric analyzer |
| $HNO_3$-integrated | Modified chromatropic acid procedure |

**Ozone**

Ozone determination is based on the detection of the chemiluminescence from the reaction of $O_3$ with excess ethylene. Peak intensity from this reaction is in the 4000-4500 A region. The technique is thought to be free from major interferences. The sensitivity of the instrument used for this study is about 0.001 ppm. The instrument was zeroed daily and was calibrated at the beginning and end of the field study using a calibrated McMillan Electronics Corporation ozone generator. A heated Hopcalite catalyst bed was used to destroy the ethylene effluent from this instrument.

**$NO$-$NO_2$-$NO_x$**

The instrument used for nitrogen oxide determination employs the reaction of nitric oxide with excess ozone for the generation of infrared (1.2 $\mu$ peak) chemiluminescence. The infrared radiation passes through a filter and is detected by a sensitive photomultiplier tube. Noise from the photomultiplier tube is reduced by cooling the tube to subambient temperatures. The instrument used here has a sensitivity of 0.005-0.010 ppm and is linear over a range of 0.005-5.00 ppm. Activated carbon is used to remove ozone from the instrument's exhaust gas.

The chemiluminescent technique works quite well for nitric oxide, with no interferences having been documented. The determination of nitrogen dioxide by chemiluminescence requires initially a reduction of $NO_2$ to NO with subsequent NO determination as described above. A carbon catalyst operated at 260 C has been employed during this study to reduce $NO_2$ to NO. The efficiency of this converter is excellent – i.e., greater than 99 percent as measured before and after the field program.

Basic nitrogen compounds such as $NH_3$ and amines are known to interfere if high-temperature catalytic converters are used, but the use of low-temperature carbon converters eliminates this interference. However, we found in the initial stages of this program that several more highly oxidized nitrogen-containing molecules are reduced to and detected as nitric oxide, even by the relatively low-temperature carbon converter. Any specie which is reduced to NO by the converter will give a positive $NO_2$ response. The interference caused by nitric acid, while showing considerable variation, was often close to quantitative. There

was some indication that the response was initially quantitative but slowly decreased as if the catalyst were subject to fatigue or poisoning. Nearly 100 percent response was found for ethyl nitrate at low concentrations. Peroxyacetyl nitrate was also found to interfere, although we have not yet determined the response factor. The possible effects of these interferences on the current program will be discussed later in this report.

The nitrogen oxide chemiluminescent instrument was zeroed and spanned each day. The concentration of the nitric oxide (in nitrogen) calibration gas was determined at the beginning and end of the field program by an ozone titration technique.

**Ammonia**

The continuous determination of gaseous ammonia was accomplished through the use of a dual catalyst chemiluminescent technique which has been described by Hodgeson and co-workers.[46-48] The procedure capitalizes on the fact that basic nitrogen compounds such as ammonia are oxidized to NO by high-temperature (>650 C) catalytic converters but not by low-temperature catalysts. Higher oxides of nitrogen are reduced to NO by either high- or low-temperature converters. Passing the sample air stream through the high-temperature converter yields total $NO_x + NH_3$, while passing the sample gas through the lower temperature converter yields only total $NO_x$. The difference between the two outputs is the ammonia gas concentration.

The instrument used for this study was a Bendix Model 8101-B $NO\text{-}NO_2\text{-}NO_x$ chemiluminescent analyzer which was modified by the addition of a Thermo Electron, Inc., high-temperature stainless steel converter operated at 700 C. The air stream was alternately passed through the high-temperature and low-temperature converters with the difference in output equaling the ammonia concentration. Because of the strong tendency toward ammonia adsorption, the instrument was further modified by moving the flow-restricting capillary, which is normally positioned just prior to the detector cell, to the inlet of the instrument. This modification permitted the entire instrument to operate under a partial vacuum of 460 torr rather than at atmospheric pressure and therefore helped reduce $NH_3$ adsorption. Teflon tubing was used throughout the system where possible to further minimize adsorption effects. Even after these modifications, however, the instrument's $NH_3$ signal, while ultimately quantitative, exhibited a 10 to 20-minute delay in responding to a step change in ammonia concentration. Thus, short-term fluctuations in ammonia concentration in the atmosphere are not discerned by this instrument.

The instrument used for $NH_3$ determination was zeroed daily and spanned at least every 2 weeks by successively diluting gas from a known high-concentration cylinder of $NH_3$ in nitrogen. The concentration of $NH_3$ in the cylinder was confirmed by an extended range chemiluminescent instrument equipped with a high-temperature stainless steel converter.

**Peroxyacetyl Nitrate (PAN)**

Determination of PAN was carried out with a Varian Series 1200 gas chromatograph fitted with a tritium-source electron-capture detector. A 19-inch column of 1/8-inch Teflon packed with 10 percent Carbowax 400 on Anakrome ABS was operated at 30 C with oxygen-free nitrogen at 30 cc/minute as the carrier gas. The gas chromatograph was calibrated with authentic samples of PAN which had been analyzed prior to dilution using the infrared absorption coefficients reported by Stephens.[3] Known concentrations of ethyl nitrate were included with the dilute PAN samples so the ratio of sensitivities of PAN to $C_2H_5ONO_2$ could be determined. This ratio was very similar to that reported by Dimitriades.[49] The lower limit of detection for PAN was approximately 0.001 ppm.

During the field program the instrument was occasionally checked for sensitivity by preparing and analyzing low concentrations of ethyl nitrate in Teflon bags. PAN sensitivity can then be determined using the ratio of $PAN/C_2H_5ONO_2$ sensitivities determined earlier. A daily check of detector standing current was used to correct short-term sensitivity fluctuations.

Another check of the accuracy of the gas chromatograph technique was made during the St. Louis phase of the field study. Comparisons were run between an EPA-operated gas chromatograph and the Battelle instrument using PAN samples diluted down from a high-concentration cylinder of PAN provided by EPA. The EPA and Battelle instruments agreed within 10 percent on the PAN concentration in the cylinder.

Occasionally, during the field program a 3-foot chromatographic column of the same composition as described earlier was operated at 0 C in an attempt to detect methyl and ethyl nitrate. There was some indication that both nitrates were present; however, the concentrations never exceeded about 0.001 ppm. Exact determination of these alkyl nitrates was complicated by peaks, perhaps Freons, which eluted from the chromatograph with retention times very similar to the nitrates.

**Nitric Acid**

Two techniques, one continuous and one integrated, have been developed at Battelle-Columbus for nitric acid analysis. The continuous technique employs coulometry for detection, in effect detecting nitric acid by its acid properties. The integrated method involves a colorimetric procedure which makes use of the nitrate moiety for quantitative detection.

**Continuous Monitoring.** The technique used for continuously monitoring nitric acid has been described in detail by Miller and Spicer[50] and will be discussed only briefly here. The instrument used was a Mast microcoulomb meter (Model 724-21) which was adapted for sensing acids rather than oxidants. Details concerning the configuration and theory of operation of the Mast meter in monitoring oxidants have been reported by Mast and Saunders.[51] Adaptation of the meter to permit detection of acid gases was reported by Miller, et al.[52] Since many atmospheric gases, among them $O_3$, $NO_2$, and $SO_2$, are detected by the acid-sensing coulometric cell, sample pretreatment is necessary to provide specificity for nitric acid. The apparatus for sample conditioning consists of a gas-titration cell with an ethylene source to remove interference due to ozone. The sample stream, after ozone titration, is passed alternately (1) directly into the detection cell and (2) through a trap containing loosely packed nylon fiber (Atlas Electronic Devices Company) enroute to the detector. The manner of packing the nylon trap is critical. It must be sufficiently loaded to remove all the $HNO_3$ yet not so heavily that it starts to adsorb $SO_2$ or $NO_2$. The reading obtained from direct operation is an indication of total acid content; the reading after passing the sample through the nylon trap indicates essentially all acid gases except nitric. The nitric acid concentration is thus obtained by difference. A timer is set to take the instrument through a complete sample/zero cycle every 15 minutes, thus generating a series of square waves on a recorder, with the difference between each peak and valley being attributed to nitric acid. In practice the data are reduced manually by drawing a continuous curve through the level portion of all the "sample" intervals and a second curve through the level portion of all the "zero" intervals. The average difference between the two curves is the average nitric acid concentration. Large changes in $SO_2$ or $NO_2$ concentrations manifest themselves as changes in both the sample and zero curves and have generally been noted to have a time constant which is much longer than one instrument cycle. If the $SO_2$ or $NO_2$ level were to increase or decrease markedly and then return to the original value in the course of 2-3 minutes, that is, completely within the sample mode or zero mode of the instrument, then a positive or negative interference could result, depending on the direction of the change and the instrument mode. Such sudden changes would be very obvious but have not been observed in our sampling programs. They might be expected to occur much more frequently in the vicinity of major $SO_2$ or $NO_2$ sources.

The theoretical response of the detector cell to a strong acid can be determined from Faraday's Law and the parameters of the Mast titration cell to be 10 $\mu$ ampere/ppm acid. The instrument was calibrated by preparing and purifying nitric acid on a high-vacuum line and isolating known (pvt) volumes of acid in transfer flasks. Acid was subsequently injected into 50-cu-ft Teflon bags. Within an estimated accuracy of 5 percent, the instrument's response to nitric acid was quantitative; i.e., 10 $\mu$a/ppm $HNO_3$ (using a conventional 500-ohm resistor in series with the meter, the equivalent response in millivolts dc is 5/ppm $HNO_3$). Additional verification of the calibration was obtained from time-integrated analyses of nitric acid using a colorimetric method described in the next section. The sensitivity of the instrument at a signal-to-noise ratio of 2/1 is about 2 ppb.

While calibrating, several important observations were made which are worth noting here: (1) at low to moderate humidities nitric acid persists in the gas phase. When pure $HNO_3$ at the ppm level was injected into bags at somewhat higher humidities, the acid seemed to cluster as aerosols with water, as indicated by a condensation nuclei counter (Environment One). Simultaneous measurements of the condensation nuclei concentrations and nitric acid concentrations indicated further that such clusters may be labile; (2) the acid will significantly absorb then desorb from Teflon sampling tubing; and (3) chemiluminescence instruments commonly used for determining $NO_2$ as NO by catalytic reduction also respond to nitric acid.

Considerable effort has been devoted to investigating potential interfering species which might be encountered under the conditions for which the monitor was designed to operate. No detectable interference has been observed for $SO_2$ (0.5 ppm), $NO_2$ (1 ppm), PAN (0.2 ppm), $H_2SO_4$ (0.2 ppm), and $CH_2O$ (0.5 ppm). Minor interference has been observed for $HCO_2H$. Interference testing is still continuing at Battelle-Columbus, particularly for $N_2O_5$ and organic acids. At this time, however, we believe strongly in the specificity of the technique under conditions likely to be encountered in atmospheric and laboratory situations. This confidence has been gained through examining nitric acid data from numerous smog-chamber experiments conducted under a variety of common and exaggerated atmospheric conditions.

**Integrated Analysis.** Because of the possibility, discussed earlier in this report, that up to 100 ppb of nitric acid might be found in the troposphere (and presumably even higher concentrations in urban polluted atmospheres), it was thought that a second check on the nitric acid concentration could be carried out by colorimetry. The procedure described below can be used to measure moderate to high levels of nitric acid (>20 ppb) with reasonable accuracy. At low levels of $HNO_3$, less than 10-20 ppb daily average, interference by $NO_2$ becomes a major problem, affecting the accuracy of the method. At these lower $HNO_3$ levels it is best to consider the procedure only as an upper limit method.

The vapor pressure of pure nitric acid at 20 C is close to 47 torr[53,54], so that several tons of thousands of parts per million of pure nitric acid could be present in ambient air without reaching saturation. The vapor pressure drops quite drastically when nitric acid is combined with water, however, so the possibility of nitric acid-water mixtures forming as aerosols or adsorbed on the surface of existing aerosols should be considered. The integrated method developed for nitric acid analysis makes use of the highly volatile nature of nitric acid to separate the acid, whether in the gas or aerosol phase, from the nitrate particulates present in the atmosphere. Since separation depends on passing $HNO_3$ through a filter, it became necessary to demonstrate that nitric acid is indeed volatile enough to pass through a filter under simulated atmospheric conditions. Separation is accomplished by passing the sample air stream through a Teflon mat filter element (Millipore). Extensive testing prior to use of this method in the field has shown that nitric acid passes through such filters quantitatively under all conditions of relative humidity and aerosol loading studied. Even at 90 percent relative humidity and a particulate count of $10^7$ (latex beads and NiO; nuclei count just after addition to the chamber) the nitric acid passed quantitatively through the Teflon filter. Several interesting observations were made during these tests of nitric acid filtration:

(1) Teflon or stainless steel filter holders are a necessity; nylon or other plastic filter holders remove nitric acid from the sample stream. This is consistent with our earlier work, since nylon fiber was found to efficiently remove nitric acid when used in conjunction with the coulometric technique described earlier.

(2) Excellent agreement was observed between the coulometric and colorimetric procedures for synthetic mixtures of nitric acid in air. Both in turn agreed with the theoretical concentration of nitric acid added to the system.

(3) Both Teflon fiber filters and high-purity quartz filters passed nitric acid quantitatively. Polycarbonate membrane filters and glass fiber filters partially remove nitric acid from the air stream.

Operationally, the procedure employed for integrated nitric acid analysis consisted of drawing the ambient air sample through a Teflon mat filter in a Teflon filter holder, then through a fritted bubbler in 30 cc of 0.03 N NaOH, and finally through a moisture trap and pump. A jeweled orifice at the pump exit was used to accurately maintain the desired flow. During the field study, sampling was carried out at approximately 1 liter per minute for 23 hours a day, from 11:30 p.m. to 10:30 p.m., to cover the same time interval as the other gas-phase and aerosol analyses.

Nitrate in the NaOH solution was subsequently determined by a modification of the chromotropic acid method.[55,56] Of the many colorimetric methods available for nitrate determination, the chromatropic acid technique was chosen because of its sensitivity, its fairly wide acceptance among analysts, and its ready adaptability to field use.

The basic analytical procedure is that given by West and Ramachandran[56]. However, several modifications were incorporated to make the method suitable for air analysis and to simplify it for field use. These changes include

(1) Addition of five drops of sodium sulfite-urea solution to each 2.5 ml sample to eliminate interferences from nitrite and other oxidizing agents

(2) Elimination of an acidic antimony solution recommended[56] to remove chloride interference in water samples

(3) Nitrate interference is expected from the absorption of $NO_2$ in the basic solution according to the reaction

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \quad .$$

The fraction of $NO_2$ yielding $NO_3^-$ in solution has been reported[57] to be 28 percent. However, several laboratory experiments with our apparatus yielded a nitrate value of 20 percent. This value was used, along with our chemiluminescent data for $NO_2$ concentrations, to correct the integrated $HNO_3$ results. As stated earlier, at high average levels of nitric acid (>20 ppb) this correction for $NO_2$ interference will be small at typical ambient $NO_2$ concentrations. However, at low levels of nitric acid (less than 10-20 ppb on a daily average basis) the $NO_2$ interference becomes a major fraction of the nitrate signal, thus affecting the accuracy of the measurement. Under these conditions the integrated procedure is useful as an upper limit estimate of the nitric acid concentration.

High concentrations of formaldehyde were found to give a positive nitrate interference, even though the analytical wavelength for nitrate determination ($\lambda$ = 410 m$\mu$) is at a minimum in the absorbance curve for the formaldehyde-chromatropic acid complex ($\lambda$ max = 580 m$\mu$). Attempts to eliminate this interference by complexing or reducing the formaldehyde using sodium bisulfite, 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH), and phenylhydrazine were unsuccessful. In theory, a correction factor can be derived from the ratio of absorbances of the chromatropic acid complex at 410 and 580 m$\mu$, combined with the sample absorbance at $\lambda$ = 580 m$\mu$, as long as the nitrate complex does not interfere at 580 m$\mu$. While nitrate interference at 580 m$\mu$ was not a problem, the ratio $\frac{Abs_{\lambda = 410\ m\mu}}{Abs_{\lambda = 580\ m\mu}}$ for the formaldehyde complex was neither constant nor linear in formaldehyde concentration. Indeed, the absorbance of the formaldehyde complex at $\lambda$ = 410 m$\mu$ reached a limiting value beyond which it remained constant regardless of formaldehyde concentration. The reasons for this are unclear; however, it renders any formaldehyde correction based on the absorbance ratio ambiguous.

One technique which has been successfully used to minimize formaldehyde interference makes use of the absorbance limit reached by the formaldehyde complex. By adding an excess of formaldehyde to both sample solution and blank, the formaldehyde interference essentially is cancelled. Any difference in absorbance between sample and blank should be related only to the $NO_3^-$ concentration. As will be discussed shortly, this technique was unnecessary in our atmospheric work because of the relatively little formaldehyde present. However, it has been successfully employed in our smog chamber work to eliminate the interference due to high concentrations of formaldehyde (0.2-0.6 ppm).

The technique of adding excess formaldehyde to the sample solutions was unnecessary in our atmospheric work due to the low average formaldehyde levels in the atmosphere. Average formaldehyde levels of 0.04 ppm have been reported by Altshuller and McPherson[58] for 7 a.m. to 4 p.m. during the smog season in Los Angeles. During the highest oxidant levels in Los Angeles in 1973, Hanst, et al.[26], found no formaldehyde but up to 0.04-0.06 ppm formic acid, which will also likely interfere with the nitrate analysis. These concentrations are for peak daylight periods. The levels of formaldehyde have been shown to approach 0.02 ppm at night in Los Angeles. Therefore, a reasonable daily average formaldehyde or formic acid concentration might be 0.03-0.04 ppm. Based on the work done in this laboratory on the absorbance of the formaldehyde chromophore at 410 mμ, these average levels of formaldehyde would yield a 0.001-0.002 ppm interference with respect to nitric acid.

Although we correct for the positive interference due to $NO_2$ and believe the formaldehyde interference is minimal, still it is wise to consider the nitric acid results from the integrated procedure as upper limits, especially when the concentration of $HNO_3$ is low.

## Aerosol Collections

Aerosol samples for nitrogen compound analyses were usually collected on a 23-hour-per-day basis, although some day/night collections were also made. Samples were collected from 25 feet above ground by two 6-inch-diameter aluminum stacks. High-volume blowers were used to maintain an average flow rate of 40 cfm. Pressure-drop measurements were made at the beginning and end of each day's sampling in order to correct for day-to-day fluctuations in flow rate. Initial calibration of the blowers was done with a calibrated venturi.

Aerosol samples were collected on 6-inch-diameter high-purity quartz mat filters (Pallflex Product Corporation) backed by a stainless steel fritted disk. Each filter was cut and preweighed in the laboratory at 40 percent relative humidity and then stored in an individual glassine envelope enclosed in a sealed polyethylene bag. After sampling, the filter was returned to its glassine envelope in its plastic bag, purged with and then sealed under argon. On return to the Columbus Laboratories the filters were equilibrated at 40 percent relative humidity and reweighed. The filters were then partitioned for analysis.

A third high-volume sampler incorporated a specially designed cyclone which served as a collector for particles $>2.5$ μm in diameter. The cyclone was operated for 23 hours per day for the entire sampling period in each city. The total particulate collected by the cyclone was analyzed as a representative average "dustfall" sample for each city.

Ten aerosol samples were collected in Los Angeles on 1-inch silver filters for analysis by ESCA (electron spectroscopy chemical analysis). The preweighed silver filters were held in a stainless steel filter holder and operated at a flow rate of either 10 liters/minute or 1 cfm. The filters were then stored in clean glass vials under argon prior to weighing and analysis.

## Aerosol Analysis

Filters from the field study were analyzed at Battelle's Columbus Laboratories for $NH_4^+$, $NO_2^-$, $NO_3^-$, and total carbon, hydrogen, and nitrogen. In addition, selected filters were analyzed for nitrogen compounds by several other laboratories to confirm and extend the determinations carried out at BCL. A brief description of the various methods follows:

- **Ammonium** was determined by dissolving soluble ammonium salts in water, adding NaOH, and measuring the resulting $NH_3$ with an ammonia gas sensing electrode.
- **Nitrite** was determined using an aliquot of the water extract of the filter and a diazotization-colorimetric method, ASTM 1254.

- Nitrate analysis made use of an aliquot of the water extract from the filter and and the brucine sulfate method, ASTM D992. Some samples were also analyzed by the chromotropic acid method described earlier.
- Total C, H, N were determined with a Perkin Elmer Model 240 Elemental Analyzer which employs pyrolysis and thermal conductivity detection for elemental analysis.

Several other research groups aided this study by undertaking collaborative analyses.

The following laboratories* performed the analyses indicated:

- California AIHL – ammonium determination by the indophenol blue method and nitrate by the 2,4 xylenol method
- Rockwell International – nitrate determination by a recently developed polarographic technique
- Lawrence Berkeley Laboratory, University of California – reduced and oxidized forms of nitrogen by electron spectroscopy chemical analysis (ESCA). Samples were cooled to liquid nitrogen temperature to avoid loss of volatiles under the vacuum conditions necessary for analysis.

### Rainfall Analysis

Rainfall samples were collected in two stainless steel rainfall jars mounted on the roof of the Mobile Laboratory. After a rain, the sample was sealed in a clean glass vial with a Teflon stoppered cap and returned to the Columbus Laboratories for $NH_4^+$, $NO_2^-$, and $NO_3^-$ analysis. A log was kept of the time during which rain occurred and the amount of rain which fell. Newspaper records were used for the latter determination.

### Dustfall Analysis

Particles larger than 2.5 $\mu$m were collected 23 hours per day by a special cyclone sampler connected to a high-volume blower. Air was delivered to the cyclone from 25 feet above ground through a 6-inch-diameter aluminum stack. At the end of sample collections in each city, the composite "dustfall" sample was returned to Battelle's Columbus Laboratories, weighed, and analyzed for $NH_4^+$, $NO_2^-$, $NO_3^-$, and total C, H, N. The results of these analyses are reported in percent by weight of the total dust sample.

### Vertical Measurements

Two days of vertical sampling for NO and $NO_x$ were carried out in St. Louis, Missouri. A twin-engined aircraft belonging to Battelle's Northwest Laboratories was stationed in St. Louis for another program and was made available for verticle nitrogen oxide measurements.** Nitrogen oxides measurements were made with a REM, Inc., NO-$NO_x$ instrument within the airplane. Temperature readings were taken simultaneously with the $NO_x$ data.

The aircraft was flown initially to the Mobile Laboratory site at St. Louis University. Data on temperature and nitrogen oxide concentration were then collected as the aircraft spiralled upward from 1000 feet to 5000 feet.

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## SAMPLING SITES

The two field sampling sites are described in this section of the report.

## SAMPLING SITES

### St. Louis, Missouri

The topography of the St. Louis region is gently rolling, with elevations from 480 feet above sea level in the downtown area to 550 feet at Lambert Field 12 miles to the northwest, with a slight ridge rising to about 600 feet in between. The Mississippi River marks the eastern boundary of the city and separates the downtown area from highly industrialized East St. Louis, Illinois. The elevation of the Mississippi River at this point is about 400 feet above sea level. The area is generally free from major land surface features which could strongly influence airflow characteristics over the area.

The Battelle Mobile Air Quality Laboratory was situated at St. Louis University approximately 2 miles due west from the St. Louis Arch. The laboratory was bounded by a small University faculty parking lot along the edge of a soccer field. The area immediately surrounding the University campus can best be characterized as nonindustrial urban. Our laboratory was located next to an EPA-CPL mobile laboratory which conducted detailed hydrocarbon analyses and CO determinations on integrated bag samples collected throughout St. Louis for several days simultaneously with our sampling program.

### West Covina, California

Sampling in the Los Angeles basin was carried out in West Covina, a suburban community located approximately 25 miles east of "downtown" Los Angeles. The city of West Covina is flanked by the San Gabriel mountains to the north and the Puente Hills to the south. The area is therefore centered in the corridor through which the prevailing easterly winds funnel the urban Los Angeles air mass.

The mobile laboratory was situated on West Covina school district property next to a seldom used athletic field approximately 1-1/2 miles south of the San Bernardino Freeway. The surrounding area can be described as suburban, consisting largely of single-family dwellings with no major industry.

# RESULTS

The results of the field sampling phase of the program are presented in this section of the report.

# RESULTS

Summaries of the field monitoring data collected in St. Louis, Missouri, and West Covina, California, will be presented in this section. To facilitate the presentation of the results, St. Louis and West Covina will be treated separately here and in the subsequent data analysis discussions.

## St. Louis, Missouri

A detailed summary of the air quality data for the 26 days of field monitoring in St. Louis in July and August, 1973, is given in Table 4. The gas-phase data are shown as both 23-hour averages and as maximum 1-hour averages. The weather during the field program can be generally categorized as hot and humid.

Figure 2 profiles the *average* diurnal air quality and meterology during the field program. The individual daily profiles are included as Appendix A in a separate volume of this report. Also included in Appendix A are the detailed hydrocarbon and CO data collected by the Environmental Protection Agency mobile laboratory situated next to our mobile laboratory in St. Louis. These data are provided as 2-hour averages from 6:00 a.m. to 7:00 p.m. for 5 simultaneous EPA-Battelle sampling days. All EPA hydrocarbon and carbon monoxide data were taken by gas chromatography. A summary of these EPA data is given in Table 5.

Three days of vertical $NO_x$ sampling were carried out in St. Louis using the Battelle-Northwest airplane and chemiluminescent NO-$NO_x$ analyzer. The results of these airborne studies are given in Table 6.

Table 7 presents the aerosol results from the St. Louis field program. Detailed inorganic nitrogen compositions are shown in the table along with total carbon, hydrogen and nitrogen, and total mass loading values. It must be emphasized that these aerosol samples were collected and analyzed on high-purity quartz fiber filters as opposed to the traditional glass fiber filters.

The analysis of the composite dust sample for the 5-week St. Louis monitoring program is shown in Table 8. The composite dust sample was collected over the 5-week program with a cyclone sampler operating to collect particles of mean diameter greater than 2.5 micrometers. The results are given as weight percent of the total dust sample.

Several rainfall samples were also collected in St. Louis and analyzed for nitrogen-containing species. The results of these analyses are shown in Table 9. The quantity of rain which fell over the city is reported in the table in inches.

## TABLE 4. SUMMARY OF AIR QUALITY DATA – ST. LOUIS

| Date | Day | Weather Conditions | | | Aerosol Mass Loading | Pollutants | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 23-Hour Average | | | | | | | 1-Hour Maximum | | | | | |
| | | General[a] | Temp. C | RH% | $\mu g/m^3$ | $O_3$, ppm | NO, ppm | $NO_x$, ppm | $NH_3$, ppm | PAN, ppm | $HNO_3$[b], ppm | $HNO_3$[c], ppm | $O_3$, ppm | NO, ppm | $NO_x$, ppm | $NH_3$, ppm | PAN, ppm | $HNO_3$, ppm |
| 7-18 | W | S | 28 | 75 | 114.1 | 0.049 | 0.012 | 0.061 | 0.010 | 0.001 | 0.012 | 0.007 | 0.110 | 0.043 | 0.114 | 0.014 | 0.003 | 0.044 |
| 7-19 | Th | R,S | 27 | 92 | 80.7 | 0.038 | 0.016 | 0.061 | 0.008 | 0.002 | 0.005 | 0.004 | 0.107 | 0.061 | 0.121 | 0.011 | 0.007 | 0.022 |
| 7-20 | F | S | 29 | 79 | 51.5 | 0.027 | 0.013 | 0.047 | 0.008 | 0.002 | 0.002 | 0.000 | 0.083 | 0.034 | 0.070 | 0.011 | 0.006 | 0.012 |
| 7-22 | Sun | S | 27 | 82 | 32.6 | 0.072 | 0.019 | 0.037 | 0.002 | 0.001 | 0.001 | 0.007 | 0.146 | 0.026 | 0.050 | 0.016 | 0.003 | 0.003 |
| 7-23 | M | S,R | 26 | 84 | 42.8 | 0.041 | 0.005 | 0.034 | 0.004 | 0.001 | 0.006 | 0.009 | 0.086 | 0.020 | 0.067 | -- | 0.002 | 0.055 |
| 7-24 | T | S | 27 | 86 | 37.0 | 0.037 | 0.011 | 0.048 | 0.006 | 0.001 | 0.004 | 0.011 | 0.113 | 0.039 | 0.081 | 0.011 | 0.004 | 0.016 |
| 7-25 | W | S | 27 | 80 | 53.9 | 0.044 | 0.021 | 0.056 | 0.005 | 0.001 | 0.002 | 0.002 | 0.128 | 0.070 | 0.108 | 0.009 | 0.004 | 0.017 |
| 7-26 | Th | R,C | 26 | 69 | 33.4 | 0.032 | 0.013 | 0.035 | 0.004 | 0.001 | 0.000 | 0.004 | 0.066 | 0.024 | 0.060 | 0.005 | 0.001 | 0.000 |
| 7-27 | F | C | 27 | 67 | 50.9 | 0.028 | 0.013 | 0.038 | 0.004 | 0.001 | 0.000 | 0.004 | 0.067 | 0.042 | 0.069 | 0.006 | 0.004 | 0.000 |
| 7-30 | M | R | 25 | 76 | 68.2 | 0.023 | 0.026 | 0.057 | -- | -- | 0.001 | 0.006 | 0.050 | 0.054 | 0.089 | -- | -- | 0.006 |
| 7-31 | T | PC,R | 24 | 72 | 39.2 | 0.032 | 0.015 | 0.034 | 0.004 | 0.001 | -- | 0.002 | 0.068 | 0.047 | 0.084 | 0.005 | 0.002 | -- |
| 8-1 | W | C | 21 | 72 | 41.9 | 0.022 | 0.016 | 0.028 | 0.002 | 0.001 | -- | 0.003 | 0.033 | 0.030 | 0.049 | 0.003 | 0.002 | -- |
| 8-2 | Th | C | 22 | 66 | 43.5 | 0.022 | 0.014 | 0.034 | 0.003 | 0.001 | -- | 0.005 | 0.051 | 0.033 | 0.061 | 0.005 | 0.002 | -- |
| 8-3 | F | S | 23 | 61 | 53.7 | 0.034 | 0.011 | 0.035 | 0.002 | 0.002 | 0.000 | 0.004 | 0.087 | 0.037 | 0.077 | 0.004 | 0.004 | 0.000 |
| 8-4 | Sat | S | 25 | 68 | 79.9 | 0.052 | 0.007 | 0.033 | 0.003 | 0.003 | 0.004 | 0.008 | 0.124 | 0.051 | 0.096 | 0.006 | 0.006 | 0.015 |
| 8-5 | Sun | S | 26 | 76 | 63.0 | 0.045 | 0.009 | 0.039 | 0.003 | 0.002 | 0.003 | 0.001 | 0.092 | 0.034 | 0.091 | 0.006 | 0.003 | 0.018 |
| 8-6 | M | PC | 25 | 72 | 74.9 | 0.042 | 0.011 | 0.038 | 0.002 | 0.001 | 0.002 | 0.002 | 0.078 | 0.035 | 0.075 | 0.004 | 0.003 | 0.029 |
| 8-7 | T | S | 27 | 84 | 61.4 | 0.038 | 0.012 | 0.037 | 0.002 | 0.002 | 0.005 | 0.004 | 0.076 | 0.030 | 0.067 | 0.005 | 0.004 | 0.020 |
| 8-8 | W | S | 30 | 82 | 51.5 | 0.023 | 0.014 | 0.036 | 0.003 | 0.002 | 0.003 | 0.004 | 0.043 | 0.031 | 0.059 | 0.006 | 0.004 | 0.021 |
| 8-9 | Th | R | 24 | 95 | 47.9 | 0.004 | 0.024 | 0.051 | 0.003 | 0.002 | 0.001 | 0.000 | 0.011 | 0.060 | 0.089 | 0.007 | 0.004 | 0.011 |
| 8-10 | F | S,R | 24 | 82 | 66.4 | 0.041 | 0.015 | 0.041 | 0.002 | 0.005 | 0.004 | 0.002 | 0.163 | 0.083 | 0.106 | 0.004 | 0.019 | 0.024 |
| 8-12 | Sun | S,R | 26 | 85 | 40.6 | 0.037 | 0.026 | 0.047 | -- | 0.003 | 0.001 | 0.007 | 0.138 | 0.101 | 0.133 | -- | 0.006 | 0.005 |
| 8-13 | M | R | 23 | 93 | 63.3 | 0.016 | 0.026 | 0.054 | 0.005 | 0.002 | 0.008 | 0.000 | 0.058 | 0.051 | 0.094 | 0.008 | 0.004 | 0.042 |
| 8-14 | T | R,S | 21 | 82 | 42.0 | 0.035 | 0.013 | 0.029 | 0.002 | 0.002 | 0.000 | 0.000 | 0.063 | 0.021 | 0.059 | 0.004 | 0.004 | 0.004 |
| 8-15 | W | PC | 23 | 76 | 90.5 | 0.041 | 0.034 | 0.062 | 0.003 | 0.003 | 0.009 | 0.001 | 0.096 | 0.103 | 0.147 | 0.009 | 0.009 | 0.080 |
| 8-16 | Th | R,S | 23 | 83 | 79.6 | 0.029 | 0.016 | 0.044 | 0.002 | 0.003 | 0.003 | 0.000 | 0.065 | 0.042 | 0.078 | 0.005 | 0.008 | 0.017 |

(a) S = Sunny, R = Rain, C = Clear, PC = Partly Cloudy, Cl = Cloudy.

(b) Continuous Coulometric.

(c) Integrated Colorimetric.

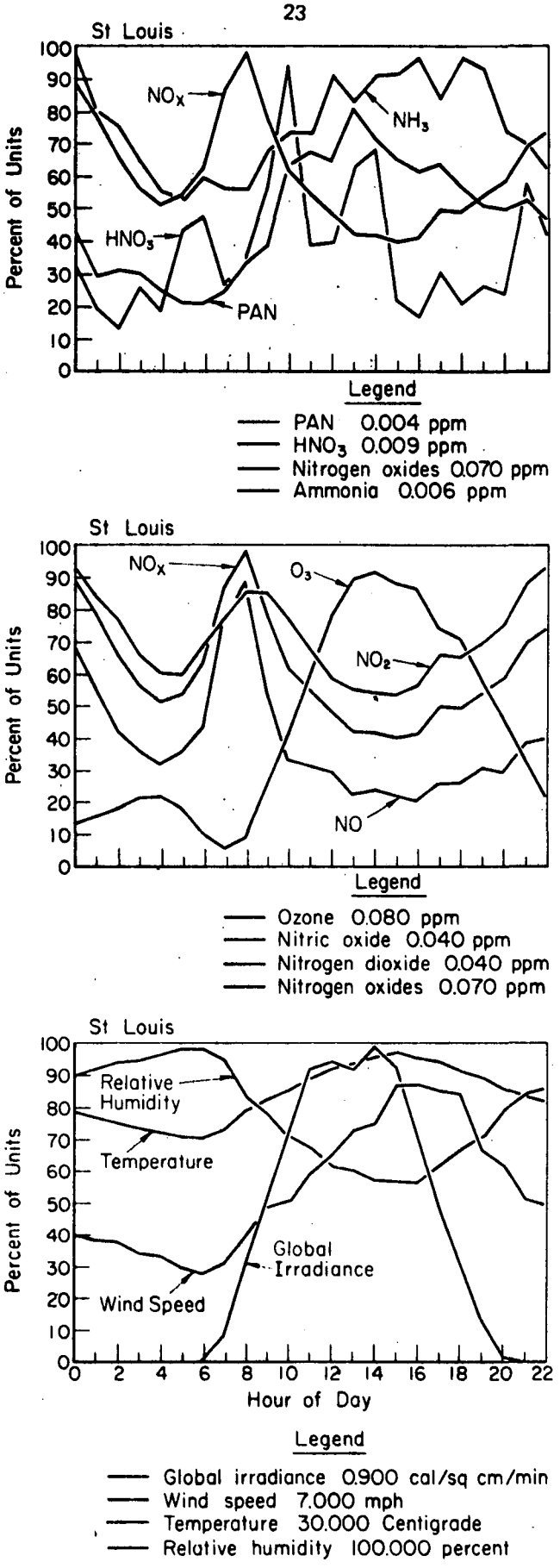



**FIGURE 2. AVERAGE DIURNAL AIR QUALITY AND METEOROLOGICAL PROFILE, ST. LOUIS**

## TABLE 5. SUMMARY OF ST. LOUIS HYDROCARBON DATA[a]

Hydrocarbon values in ppbC; carbon monoxide values in ppb.

| Date | 7-18-73 | | | | 7-19-73 | | | | 7-20-73 | | | | 7-23-73 | | | | 7-24-73 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Number[b] | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| Component | | | | | | | | | | | | | | | | | | | | |
| Methane | 2420 | 2541 | 2390 | 2053 | 2057 | 2326 | 2271 | 2235 | 2310 | 2418 | 1984 | 1570 | 2445 | 2235 | 2094 | 2079 | 2107 | 2129 | 2285 | 2117 |
| CO | 1674 | 2008 | 1266 | 578 | 1405 | 1746 | 2134 | 1634 | 1536 | 2047 | 594 | 390 | 882 | 1018 | 817 | 528 | 1010 | 1423 | 1113 | 930 |
| $C_2H_2$ | 21 | 24 | 18 | 5 | 17 | 26 | 38 | 27 | 27 | 23 | 12 | 10 | 12 | 14 | 4 | 4 | 15 | 21 | 13 | 12 |
| $C_2H_4$ | 29 | 29 | 17 | 7 | 30 | 28 | 40 | 26 | 24 | 30 | 15 | 11 | 20 | 18 | 8 | 9 | 20 | 26 | 17 | 15 |
| Olefins | 80 | 88 | 54 | 34 | 77 | 92 | 103 | 73 | 75 | 100 | 60 | 39 | 73 | 53 | 35 | 36 | 66 | 74 | 62 | 41 |
| Aromatics | – | – | – | – | – | – | – | – | 140 | 273 | 166 | 109 | 129 | 353 | 220 | 217 | 155 | 198 | 78 | 46 |
| Nonmethane Hydrocarbons | 570 | 454 | 452 | 140 | 295 | 435 | 555 | 424 | 513 | 818 | 530 | 376 | 448 | 657 | 448 | 420 | 486 | 579 | 387 | 284 |
| $C_2H_4/C_2H_2$ | 1.38 | 1.22 | 0.93 | 1.42 | 1.79 | 1.06 | 1.03 | 0.96 | 0.88 | 1.32 | 1.22 | 1.08 | 1.62 | 1.31 | 1.91 | 2.09 | 1.30 | 1.25 | 1.31 | 1.26 |

(a) Courtesy of the U.S. Environmental Protection Agency.
(b) Sample No. 1 = 6-8 a.m.; 2 = 8-10 a.m.; 3 = 10 a.m.-12 p.m.; 4 = 12-2 p.m.

**TABLE 6. ST. LOUIS VERTICAL SAMPLING**

(Above the St. Louis University Site)

| Date | Altitude, ft | Temperature, C | $NO_x$, ppm | $NO_2$, ppm | NO, ppm |
|---|---|---|---|---|---|
| 7/30/73 | Ground Level | 32.0 | 0.060 | 0.036 | 0.024 |
| | 1500 | 27.7 | 0.100 | 0.030 | 0.070 |
| | 2100 | 25.3 | 0.080 | 0.020 | 0.060 |
| | 3500 | 22.5 | 0.060 | 0.010 | 0.050 |
| | 4500 | 19.2 | 0.045 | 0.010 | 0.035 |
| 7/31/73 | Ground Level | 26.5 | 0.022 | 0.014 | 0.008 |
| | 1000 | 23.6 | 0.041 | 0.009 | 0.032 |
| | 2500 | 12.1 | 0.040 | 0.014 | 0.026 |
| | 4000 | 15.7 | 0.030 | 0.007 | 0.023 |
| | 5500 | 15.9 | 0.022 | 0.003 | 0.019 |
| 8/1/73 | Ground Level | 21.8 | 0.020 | 0.011 | 0.010 |
| | 1000 | – | 0.045 | 0.007 | 0.038 |

## TABLE 7. ST. LOUIS AEROSOL DATA

| Date | $NH_4^+$ mg | $NH_4^+$ $\mu g/m^3$ | $NO_2^-$, mg | $NO_3^-$ mg | $NO_3^-$ $\mu g/m^3$ | C, mg | H, mg | N, mg | Mass Loading, $\mu g/m^3$ |
|---|---|---|---|---|---|---|---|---|---|
| 7/18/73 | 11.6 | 7.0 | .012 | .60 | .35 | 24.8 | 7.1 | 9.3 | 114.1 |
| 7/19/73 | 7.4 | 4.5 | .009 | .75 | .45 | 19.7 | 5.8 | 6.7 | 80.7 |
| 7/20/73 | 1.2 | .77 | .004 | .70 | .45 | 16.6 | 3.0 | 1.6 | 51.5 |
| 7/22/73 | 3.9 | 2.3 | .010 | .40 | .24 | 11.7 | 0.3 | 3.6 | 32.6 |
| 7/23/73 | 4.4 | 2.7 | .007 | .45 | .27 | 14.9 | 3.3 | 4.5 | 42.8 |
| 7/24/73 | 2.8 | 1.7 | .011 | .62 | .38 | 15.5 | 3.2 | 2.5 | 37.0 |
| 7/25/73 | 2.8 | 1.7 | .011 | .45 | .28 | 16.1 | 2.8 | 2.7 | 53.9 |
| 7/26/73 | 1.3 | .77 | .010 | .40 | .24 | 14.0 | 2.1 | 1.7 | 33.4 |
| 7/27/73 | 1.9 | 1.2 | .014 | .75 | .46 | 18.5 | 2.9 | 2.2 | 50.9 |
| 7/30/73 | 2.8 | 1.8 | .006 | .55 | .34 | 18.2 | 2.1 | 2.8 | 68.2 |
| 7/31/73 | 1.7 | 1.1 | .009 | .50 | .31 | 11.6 | 0.0 | 1.9 | 39.2 |
| 8/1/73 | 2.6 | 1.6 | .006 | .43 | .27 | 11.6 | 2.2 | 2.6 | 41.9 |
| 8/2/73 | 2.1 | 1.3 | .002 | .38 | .24 | 13.9 | 2.6 | 2.1 | 43.5 |
| 8/3/73 | 1.7 | 1.1 | .009 | .80 | .51 | 14.6 | 2.4 | 1.7 | 53.7 |
| 8/4/73 | 6.1 | 3.8 | .007 | 1.00 | .63 | 22.3 | 4.6 | 5.0 | 79.9 |
| 8/5/73 | 7.5 | 4.8 | .002 | .45 | .28 | 11.5 | 5.1 | 5.3 | 63.0 |
| 8/6/73 | 7.4 | 4.6 | .004 | .60 | .37 | 13.7 | 3.1 | 6.1 | 74.9 |
| 8/7/73 | 8.2 | 5.2 | .005 | .90 | .56 | 18.1 | 5.8 | 7.1 | 61.4 |
| 8/8/73 | 1.6 | 1.0 | .005 | .60 | .39 | 13.0 | 1.9 | 1.3 | 51.5 |
| 8/9/73 | 0.2 | .13 | .001 | .83 | .53 | 14.5 | 2.1 | .7 | 47.9 |
| 8/10/73 | 2.0 | 1.3 | .002 | .50 | .31 | 22.6 | 3.6 | 2.4 | 66.4 |
| 8/12/73 | 1.6 | 1.0 | .000 | .28 | .18 | 12.7 | 1.4 | 1.6 | 40.6 |
| 8/13/73 | 4.8 | 3.1 | .000 | .40 | .26 | 17.9 | 2.5 | 4.1 | 63.3 |
| 8/14/73 | 4.1 | 2.6 | .000 | .30 | .19 | 13.9 | 1.8 | 4.1 | 42.0 |
| 8/15/73 | 8.9 | 5.6 | .003 | .70 | .43 | 29.2 | 5.7 | 7.9 | 90.5 |
| 8/16/73 | 11.2 | 6.8 | .000 | .78 | .48 | 25.3 | 6.6 | 10.8 | 79.6 |
| Average | 4.3 | 2.7 | .006 | .58 | .36 | 16.8 | 3.2 | 4.0 | 57.8 |

**TABLE 8. ANALYSIS OF COMPOSITE ST. LOUIS DUST SAMPLE**

Particle diameters >2.5 $\mu$m.

| Specie | Concentration, weight percent |
|---|---|
| $NH_4^+$ | 0.55 |
| $NO_2^-$ | 0.001 |
| $NO_3^-$ | 2.65 |
| Total Carbon | 14.6 |
| Total Hydrogen | 1.8 |
| Total Nitrogen | 1.5 |

**TABLE 9. ST. LOUIS RAINFALL ANALYSIS**

| Date | Inches of Rain | $NH_4^+$, ppm | $NO_2^-$, ppm | $NO_3^-$, ppm |
|---|---|---|---|---|
| 7/9/73 | 0.10 | <1 | 0.08 | 2.0 |
| 7/24/73 | 0.21 | 2 | 0.13 | 2.0 |
| 7/30/73 | 0.18 | <1 | 0.13 | 3.6 |
| 8/9/73 | 0.97 | 1 | 0.36 | 1.0 |
| 8/10/73 | Trace | <1 | 0.23 | 3.8 |
| 8/13/73 | 1.18 | <1 | 0.23 | 2.4 |
| 8/16/73 | 0.03 | 1 | 0.37 | 2.3 |

## West Covina, California

A detailed summary of the air-quality data for the 29 sampling days in West Covina, California, is given in Table 10. The field program in West Covina was carried out in August and September of 1973. The gas-phase data are shown in the table both as daily (23 hour) averages and as 1-hour maximum averages. The weather during most of the West Covina field sampling program was qvercast in the morning until about noon, after which clear or partly cloudy conditions prevailed. An exception to this pattern occurred on the last 3 days of the study when desert or "Santa Anna" winds reversed the wind flow over the Los Angeles basin, bringing high temperatures and very low relative humidities to the area.

Figure 3 profiles the *average* diurnal air quality and meteorology during the field sampling in West Covina. The individual daily profiles are included as Appendix B in a separate volume of this report. Also included in Appendix B are Los Angeles Air Pollution Control District (LAAPCD) data from Azusa for carbon monoxide, nitrogen oxides, and total hydrocarbons covering the period of our West Covina monitoring program.

The aerosol data from the West Covina sampling program are shown in Table 11. The concentrations of ammonium, nitrite, nitrate, and total carbon, hydrogen, and nitrogen are presented in micrograms per cubic meter along with the total daily mass loading data.

A composite dust sample (particle diameters $>2.5$ $\mu$m) was also collected by cyclone in West Covina. The results of the composite dust sample analysis are shown as weight percent in Table 12.

## TABLE 10. SUMMARY OF AIR QUALITY DATA – WEST COVINA

| Date | Day | Weather Conditions | | | Aerosol Mass Loading | Pollutants | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 24-Hour Average | | | | | | | 1-Hour Maximum | | | | |
| | | General[a] | Temp, C | RH% | µg/m³ | $O_3$, ppm | NO, ppm | $NO_x$, ppm | $NH_3$, ppm | PAN, ppm | $HNO_3$[b], ppm | $HNO_3$[c], ppm | $O_3$, ppm | NO, ppm | $NO_x$, ppm | $NH_3$, ppm | PAN, ppm | $HNO_3$, ppm |
| 8-24 | F | S | 21 | 89 | 115.8 | 0.054 | 0.071 | 0.180 | 0.000 | 0.003 | 0.009 | 0.010 | 0.173 | 0.202 | 0.296 | 0.002 | 0.004 | 0.020 |
| 8-26 | Sun | C | 18 | 93 | 54.9 | 0.035 | 0.046 | 0.081 | -- | -- | 0.001 | 0.002 | 0.068 | 0.089 | 0.166 | -- | -- | 0.003 |
| 8-27 | M | S | 20 | 89 | 65.1 | 0.039 | 0.029 | 0.103 | 0.008 | -- | 0.000 | 0.000 | 0.142 | 0.065 | 0.143 | 0.013 | -- | 0.000 |
| 8-28 | T | PC | 19 | -- | 81.7 | 0.050 | 0.061 | 0.152 | 0.007 | -- | 0.002 | 0.003 | 0.210 | 0.274 | 0.360 | 0.013 | -- | 0.011 |
| 8-29 | W | PC | 20 | -- | 98.9 | 0.060 | 0.060 | 0.171 | 0.005 | -- | 0.003 | 0.000 | 0.264 | 0.205 | 0.272 | 0.008 | -- | 0.015 |
| 8-30 | Th | PC | 19 | -- | 96.1 | 0.044 | 0.020 | 0.120 | 0.005 | -- | 0.002 | 0.000 | 0.171 | 0.045 | 0.173 | 0.007 | -- | 0.009 |
| 8-31 | F | C | 18 | -- | 87.0 | 0.043 | 0.021 | 0.113 | 0.004 | 0.001 | 0.000 | 0.001 | 0.157 | 0.051 | 0.161 | 0.006 | 0.003 | 0.000 |
| 9-3 | M | S | 18 | -- | 64.5 | 0.042 | 0.007 | 0.062 | 0.002 | 0.002 | 0.002 | 0.005 | 0.132 | 0.042 | 0.099 | 0.003 | 0.006 | 0.015 |
| 9-4 | T | Cl | 17 | -- | 79.7 | 0.021 | 0.013 | 0.082 | 0.002 | 0.003 | 0.001 | -- | 0.088 | 0.032 | 0.125 | 0.003 | 0.006 | 0.005 |
| 9-5 | W | PC,S | 18 | -- | 77.6 | 0.048 | 0.020 | 0.090 | 0.002 | 0.007 | 0.000 | 0.000 | 0.171 | 0.052 | 0.127 | 0.003 | 0.015 | 0.000 |
| 9-6 | Th | S | 20 | 66 | 118.1 | 0.083 | 0.080 | 0.204 | 0.002 | 0.013 | 0.012 | 0.018 | 0.271 | 0.324 | 0.445 | 0.005 | 0.036 | 0.040 |
| 9-7 | F | S | 18 | 87 | 135.8 | 0.047 | 0.114 | 0.239 | 0.004 | 0.008 | 0.011 | 0.003 | 0.180 | 0.346 | 0.487 | 0.005 | 0.027 | 0.022 |
| 9-8 | Sat | Cl,S | 18 | 79 | 76.6 | 0.055 | 0.045 | 0.093 | 0.002 | 0.007 | 0.004 | 0.009 | 0.147 | 0.065 | 0.143 | 0.003 | 0.017 | 0.015 |
| 9-9 | Sun | Cl,S | 19 | 83 | 63.6 | 0.036 | 0.055 | 0.105 | 0.002 | 0.005 | 0.001 | -- | 0.103 | 0.068 | 0.127 | 0.003 | 0.010 | 0.005 |
| 9-10 | M | Cl | 17 | 90 | 64.7 | 0.017 | 0.056 | 0.122 | 0.002 | 0.003 | 0.002 | -- | 0.040 | 0.090 | 0.160 | 0.003 | 0.008 | 0.013 |
| 9-11 | T | Cl,S | 18 | 79 | 81.8 | 0.041 | 0.025 | 0.096 | 0.002 | 0.007 | 0.002 | 0.006 | 0.184 | 0.048 | 0.129 | 0.003 | 0.023 | 0.010 |
| 9-12 | W | Cl,S | 17 | 88 | 105.5 | 0.031 | 0.058 | 0.151 | 0.002 | 0.006 | 0.002 | 0.000 | 0.151 | 0.176 | 0.253 | 0.003 | 0.027 | 0.019 |
| 9-13 | Th | Cl,S | 17 | 85 | 94.1 | 0.048 | 0.020 | 0.071 | -- | 0.010 | 0.001 | 0.010 | 0.154 | 0.062 | 0.121 | -- | 0.025 | 0.007 |
| 9-14 | F | Cl,S | 17 | 80 | 123.7 | 0.064 | 0.013 | 0.075 | -- | 0.018 | 0.005 | 0.026 | 0.209 | 0.022 | 0.126 | -- | 0.040 | 0.024 |
| 9-17 | M | -- | 16 | 77 | 127.4 | 0.070 | 0.020 | 0.109 | -- | 0.018 | 0.007 | 0.016 | 0.234 | 0.071 | 0.135 | -- | 0.042 | 0.031 |
| 9-18 | T | S | 16 | 82 | 145.8 | 0.058 | 0.046 | 0.152 | -- | 0.020 | 0.010 | 0.018 | 0.213 | 0.092 | 0.227 | -- | 0.046 | 0.034 |
| 9-19 | W | PC | 17 | 82 | 137.3 | 0.052 | 0.044 | 0.140 | -- | 0.016 | 0.004 | 0.019 | 0.227 | 0.133 | 0.202 | -- | 0.044 | 0.015 |
| 9-20 | Th | -- | 16 | 85 | 116.5 | 0.048 | 0.041 | 0.112 | -- | 0.012 | 0.004 | 0.008 | 0.210 | 0.110 | 0.199 | -- | 0.040 | 0.016 |
| 9-21 | F | -- | 18 | 76 | 122.7 | 0.050 | -- | -- | -- | 0.010 | -- | 0.000 | 0.170 | -- | --- | -- | 0.025 | -- |
| 9-24 | M | C | 16 | 71 | 73.1 | 0.032 | 0.121 | 0.163 | -- | 0.007 | -- | 0.007 | 0.132 | 0.439 | 0.409 | -- | 0.019 | -- |
| 9-25 | T | S | 19 | 63 | 106.3 | 0.051 | 0.037 | 0.103 | -- | 0.012 | 0.002 | 0.011 | 0.176 | 0.277 | 0.403 | -- | 0.029 | 0.010 |
| 9-26 | W | S | 22 | 50 | 198.2 | 0.040 | 0.177 | 0.252 | -- | 0.008 | 0.000 | 0.007 | 0.150 | 0.407 | 0.470 | -- | 0.013 | 0.000 |
| 9-27 | Th | S | 23 | 37 | 123.7 | 0.031 | 0.147 | 0.221 | -- | 0.006 | 0.000 | 0.009 | 0.152 | 0.453 | 0.706 | -- | 0.008 | 0.000 |
| 9-28 | F | C | 23 | 44 | 105.6 | 0.052 | 0.175 | 0.256 | -- | 0.009 | 0.002 | 0.014 | 0.173 | 0.557 | 0.691 | -- | 0.025 | 0.009 |

(a) S = Sunny, R = Rain, C = Clear, PC = Partly Cloudy, Cl = Cloudy.

(b) Continuous Coulometric.

(c) Integrated Colorimetric.

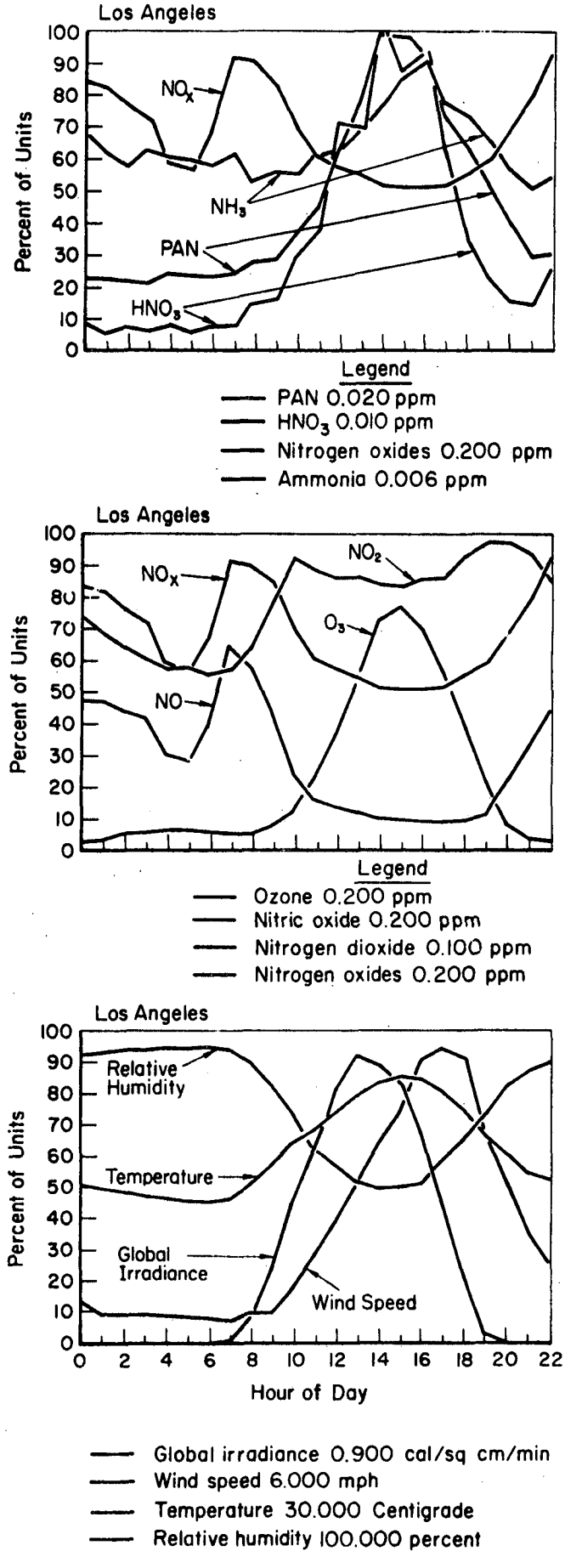



**FIGURE 3. AVERAGE DIURNAL AIR QUALITY AND METEOROLOGICAL PROFILE, WEST COVINA**

## TABLE 11. WEST COVINA AEROSOL DATA

| Date | $NH_4^+$ mg | $NH_4^+$ $\mu g/m^3$ | $NO_2^-$, mg | $NO_3^-$ mg | $NO_3^-$ $\mu g/m^3$ | C, mg | H, mg | N, mg | Mass Loading, $\mu g/m^3$ |
|---|---|---|---|---|---|---|---|---|---|
| 8/24/73 | 3.5 | 2.4 | .012 | 5.7 | 3.9 | 29.8 | 5.5 | 5.8 | 115.8 |
| 8/26/73 | 1.3 | .99 | .004 | 3.3 | 2.5 | 10.6 | 2.9 | 2.5 | 54.9 |
| 8/27/73 | 2.5 | 1.7 | .008 | 1.8 | 1.2 | 16.5 | 1.3 | 2.8 | 65.1 |
| 8/28/73 | 2.5 | 1.6 | .008 | 2.6 | 1.7 | 26.8 | 3.5 | 3.8 | 81.7 |
| 8/29/73 | 4.8 | 3.2 | .007 | 2.2 | 1.5 | 35.4 | 6.1 | 6.6 | 98.9 |
| 8/30/73 | 8.2 | 5.4 | .009 | 2.2 | 1.4 | 28.1 | 5.2 | 8.0 | 96.1 |
| 8/31/73 | 8.0 | 5.2 | .055 | 1.0 | 0.7 | 24.7 | 4.9 | 8.0 | 87.0 |
| 9/3/73 | 4.8 | 3.2 | .027 | 1.3 | 0.8 | 17.5 | 3.8 | 5.7 | 64.5 |
| 9/4/73 | 10.5 | 6.9 | .016 | 0.6 | 0.4 | 19.7 | 5.0 | 9.3 | 79.7 |
| 9/5/73 | 8.1 | 5.6 | .003 | 0.6 | 0.4 | 22.3 | 5.0 | 7.0 | 77.6 |
| 9/6/73 | 4.9 | 3.3 | .047 | 1.5 | 1.0 | 39.7 | 6.3 | 7.1 | 118.1 |
| 9/7/73 | 10.5 | 7.2 | .063 | 2.0 | 1.3 | 41.8 | 9.3 | 14.0 | 135.8 |
| 9/8/73 | 8.1 | 5.6 | .011 | 0.5 | 0.3 | 18.8 | 6.1 | 8.0 | 76.6 |
| 9/9/73 | 4.3 | 2.9 | .004 | 0.9 | 0.6 | 14.7 | 3.5 | 5.5 | 63.6 |
| 9/10/73 | 4.7 | 3.2 | .007 | 1.2 | 0.8 | 16.5 | 3.0 | 6.3 | 64.7 |
| 9/11/73 | 3.9 | 2.6 | .015 | 1.0 | 0.7 | 26.1 | 5.1 | 5.3 | 81.8 |
| 9/12/73 | 6.3 | 4.4 | .009 | 1.6 | 1.1 | 29.2 | 6.4 | 9.1 | 105.5 |
| 9/13/73 | 11.0 | 7.7 | .019 | 1.3 | 0.9 | 25.2 | 6.1 | 10.8 | 94.1 |
| 9/14/73 | 15.0 | 10.4 | .043 | 0.5 | 0.4 | 36.0 | 8.7 | 13.3 | 123.7 |
| 9/17/73 | 16.1 | 11.1 | .027 | 1.1 | 0.8 | 36.3 | 8.8 | 13.9 | 127.4 |
| 9/18/73 | 17.5 | 12.1 | .018 | 1.2 | 0.8 | 43.4 | 12.0 | 17.2 | 145.8 |
| 9/19/73 | 14.5 | 10.0 | .023 | 1.3 | 0.8 | 39.4 | 9.7 | 14.3 | 137.3 |
| 9/20/73 | 12.6 | 8.7 | .018 | 1.2 | 0.8 | 32.6 | 7.3 | 11.3 | 116.5 |
| 9/21/73 | 8.9 | 6.1 | .014 | 2.0 | 1.4 | 34.8 | 7.9 | 10.3 | 122.7 |
| 9/24/73 | 2.4 | 1.7 | .076 | 2.3 | 1.6 | 21.4 | 2.3 | 3.7 | 73.1 |
| 9/25/73 | 3.8 | 2.6 | .027 | 5.9 | 4.0 | 31.7 | 5.0 | 7.5 | 106.3 |
| 9/26/73 | 2.3 | 1.4 | .045 | 6.3 | 4.0 | 50.2 | 7.2 | 6.5 | 198.2 |
| 9/27/73 | 1.2 | 0.7 | .027 | 4.2 | 2.7 | 40.0 | 5.8 | 4.6 | 123.7 |
| 9/28/73 | 2.5 | 1.6 | .050 | 5.2 | 3.2 | 35.4 | 3.8 | 4.5 | 105.6 |
| Average | 2.5 | 4.7 | .024 | 2.2 | 1.7 | 28.9 | 5.7 | 7.9 | 101.4 |

**TABLE 12. ANALYSIS OF COMPOSITE WEST COVINA DUST SAMPLE**

| Specie | Concentration, weight percent |
|---|---|
| $NH_4^+$ | 0.63 |
| $NO_2^-$ | 0.001 |
| $NO_3^-$ | 4.8 |
| Total Carbon | 12.6 |
| Total Hydrogen | 1.8 |
| Total Nitrogen | 2.2 |

## ANALYSIS AND INTERPRETATION

This section contains a statistical analysis and interpretation of the field sampling results.

## ANALYSIS AND INTERPRETATION

### St. Louis, Missouri

In this discussion of the St. Louis results, we will first review the trends in the air quality data, then the aerosol results, and finally comment in some detail on the distribution and balance of nitrogen compounds in the St. Louis atmosphere. Obviously, the data presented here were collected over only a limited number of days during the summer of 1973. Any generalization of our results to other seasons or other years must be regarded with some degree of skepticism.

#### Air Quality Data

The general behavior of the St. Louis air quality data appears to follow the classical pattern of urban photochemical smog formation. Referring to the average profiles in Figure 2, a large increase in both NO and $NO_2$ is noted between 6:00 a.m. and 8:00 a.m. After that time, NO drops rapidly and $NO_2$ decreases, although somewhat more slowly, as $O_3$ increases to a peak at 2:00 p.m. During the late afternoon and evening, ozone drops off as its rate of production from photochemical reactions falls below its rate of removal. Throughout this late afternoon period, the reaction of $O_3$ with NO, which is continually emitted in auto exhaust, is an important mechanism for the removal of both species. Only when $O_3$ has been reduced to a very low level is NO permitted to increase substantially. The period between 10:30 and 11:30 p.m. is missing from the profiles due to the routine shutdown of the mobile laboratory for calibration and maintenance at this time each day. However, the performance of the various pollutants can be inferred from the trends prior to the 10:00 p.m. average and after the midnight average. An interesting feature of the data is the gentle rise in $O_3$ between midnight and 4:00 a.m. A likely explanation of this behavior is that, with the rapid decrease of NO over this time period, $O_3$ transported into the area is not scavenged by NO so that the ozone concentration at our sampling site increases. As NO begins to rise again after 4:00 a.m., ozone drops off steadily to its lowest level at 7:00 a.m. Whether this nighttime ozone is from natural sources (e.g., transport from the stratosphere) or from photochemical smog processes will be discussed shortly.

The average level of ozone provides ample evidence of photochemical smog activity during the course of our study. Indeed, ozone exceeded the 1-hour maximum standard of 0.08 ppm on half of the monitoring days.

The increases in NO and $NO_2$ late at night are not surprising when one considers the stable meteorological conditions existing at that time (note the wind-speed profile in Figure 2) combined with the fairly heavy traffic occurring in metropolitan areas until late at night during the summer months. These are conditions under which one would expect the accumulation of primary pollutants.

The interference with the chemiluminescent $NO_2$ determination by PAN and $HNO_3$, discussed in the Experimental Methods section, is not likely to have a major impact on the average $NO_2$ concentration due to the very low average PAN and $HNO_3$ levels encountered in St. Louis. However, during the afternoon hours when PAN and $HNO_3$ are high, up to one-half of the observed $NO_2$ might actually be PAN and $HNO_3$ on the average. Since the profile for $NO_2$ does not fluctuate in the same manner as the PAN and $HNO_3$ curves, however, the interference is probably not this great. The variability in the $HNO_3$ response factor mentioned in the Experimental Methods discussion may explain the nonquantitative interference.

The average concentrations of PAN, $HNO_3$, and $NH_3$ are profiled in Figure 2. The average concentration of PAN in St. Louis was quite low during the period of our study. PAN reached its peak during the day at 1:00 p.m., consistent with its association with photochemical smog reactions. After 1:00 p.m., the concentration of PAN drops rather slowly, falling during the evening and throughout the night. Since both PAN and $O_3$ are accumulating products of photochemical smog processes, it is instructive to compare their profiles. As might be expected, both $O_3$ and PAN begin to increase

at about the same time in the morning and, generally speaking, peak out together during the early afternoon. During the late afternoon and evening, the concentration of ozone decreases much faster than PAN, no doubt reflecting the rapid removal of ozone by the reaction with NO discussed earlier. As was noted earlier for ozone, PAN also increases slightly between 1:00 and 3:00 a.m. While this increase appears to be only marginal in the 26 day - average profile, on several individual daily profiles (Appendix A) very marked rises in early morning PAN and $O_3$ are observed. The association of an increase in PAN with the increase in ozone indicates a photochemical smog source rather than a natural source for this nighttime ozone. The coinciding increase in the concentrations of these two photochemically generated contaminants early in the morning gives very definite indication of the long-distance transport of a reacted air mass which passes over St. Louis during the early morning hours. The subject of long-distance pollutant transport is currently under investigation by Battelle-Columbus and several other organizations under the auspices of the U.S. Environmental Protection Agency.

The average nitric acid profile shown in Figure 2 is, to our knowledge, the first report of nitric acid in an urban atmosphere. The average concentration of nitric acid was rather low in St. Louis and was somewhat variable, as noted by the several peaks in the profile. An examination of the profiles shows little correlation between $HNO_3$ and any other parameter. Discussion of $HNO_3$ will be reserved for the statistical analysis of the data treated later in this section.

Ammonia is another compound which has rarely been determined continuously in urban atmospheres. The ammonia profile exhibits a slight but definite diurnal pattern with the average concentration of $NH_3$ about 5 ppb. The decrease in ammonia between midnight and 3:00 a.m. does not reflect the true behavior of $NH_3$, but rather is an artifact of the $NH_3$ calibration procedure. Desorption of $NH_3$ from the instrument after calibration is a lengthy process requiring several hours. For this reason, the calibration was generally performed on Sunday evenings when data were not being collected. Unfortunately, the desorption process continued after midnight on three Sunday nights so that erroneously high $NH_3$ values resulted. These high ammonia values show up in the average profile of Figure 2 between midnight and 3:00 a.m. The more correct pattern of $NH_3$ over this time period, as judged from the individual daily ammonia profiles in Appendix A, is a gradual decrease and leveling off from about 6:00 p.m. in the evening until ammonia begins to rise again at about 9:00 a.m. the next morning. It must be emphasized, again, that this is the average pattern and that individual profiles may differ substantially from the average. The pattern of $NH_3$ is similar in a general way with the profiles of wind speed and temperature. Since both the sources and sinks of ammonia are presumed to be biological in nature, temperature especially may play a part in the diurnal pattern of ammonia.

It is interesting to note that there appears to be little correlation between the nitric acid and ammonia profiles. It has often been suggested that these two species may react rapidly with one another in urban atmospheres to form $NH_4NO_3$, thereby maintaining both gaseous species at extremely low concentrations. While there is little evidence of such rapid removal processes here, the possibilities will be reviewed later in sections detailing the West Covina results.

On three consecutive days in St. Louis, above-ground concentrations of NO, $NO_2$, and $NO_x$ were monitored using the Battelle-Northwest twin-engined airplane. The results of this vertical sampling study are given in Table 6. The vertical sampling was conducted approximately above our St. Louis University ground site. The ground-level concentrations shown in the table are averages over the airplane sampling interval taken from our ground station. Both the ground station and airborne $NO_x$ instruments were spanned with the same cylinder of calibration gas. On July 30, the temperature profile gives no indication of inversion conditions. The NO concentration at 1500 feet is almost three times the ground level NO; from 1500 to 4500 feet the concentration decreases at a fairly constant rate. At 4500 feet the NO concentration is still higher than the ground station level. The concentration of $NO_2$ is slightly lower at 1500 feet than on the ground. Above 1500 feet the $NO_2$ level decreases regularly up to 3500 feet and then remains constant at 10 ppb.

On both July 31 and August 1, we observed the same pattern of higher $NO_x$ levels aloft. The temperature profile for the 31st indicates a temperature inversion between 2500 and 4000 feet. The decrease in temperature between 1000 and 2500 feet was also rather dramatic.

The surprising feature of these vertical data is the high level of $NO_x$ found at 1000 feet and above. On the 30th and 31st, the $NO_x$ levels did not approach ground concentrations until 3500 feet or higher. During one flight the plane flew through a partially dispersed stack plume which we observed visually. At the same time, the $NO_x$ measurements increased beyond the range of the monitoring instrument (10 ppm). It may well be that these high vertical $NO_x$ readings are caused by the dispersing plume from a stack in the vicinity of our St. Louis University site.

**Aerosol Composition**

The average particulate mass loading during our St. Louis field study was approximately 58 $\mu g/m^3$ as determined by high-volume sampling. It was pointed out earlier that high-purity quartz fiber filters were employed for high-volume sampling. Referring to Table 7, we note that carbon on the average, makes up about 19 percent of the total aerosol mass, hydrogen about 3.7 percent, and nitrogen roughly 4.7 percent. These three elements alone make up 27 percent of the average aerosol mass. It is assumed that water, metals, oxygen, and sulfur comprise most of the remaining mass. Of the nitrogen compounds determined specifically, ammonium at 2.7 $\mu g/m^3$ accounts for 4.7 percent of the mass, nitrate at 0.36 $\mu g/m^3$ makes up about 0.6 percent, and the contribution of nitrite to the total mass of aerosol is negligible.

Table 13 gives the comparison between the average total aerosol analysis and the composite dust (particle diameter $>$ 2.5 $\mu m$) analysis. Both ammonium and total nitrogen are seen to be associated primarily with smaller particles. This is consistent with other reports[31] of $NH_4^+$ as a submicron aerosol from a gas-phase source. Carbon and hydrogen are also more dominant in the small particles. Surprisingly, nitrate is much more prevalent in the larger particles. This is contrary to studies[31] which have found nitrate predominately in the submicron aerosol range, indicating a gaseous source. Indeed, not only is the distribution of nitrate at variance with earlier studies, but the absolute concentration of nitrate also appears anomalously low.[59] A discussion of a collaborative study to confirm the accuracy of our nitrate analyses is discussed with the West Covina results. We attribute these nitrate anomalies to the inefficient removal of gaseous or submicron nitric acid aerosols by quartz fiber filters as opposed to basic-surfaced glass fiber filters. The average nitric acid we measured in St. Louis (0.003 ppm), if all removed by the high-volume filter, would account for almost 8 $\mu g/m^3$ additional nitrate, bringing our nitrate values into correspondence with earlier reports. Although we would not expect all of the nitric acid to be removed by high-volume samplers, removal of even a small fraction would drastically affect the apparent distribution and absolute concentration of nitrate aerosol. A brief laboratory study seems to confirm the fact that glass fiber filters remove nitric acid from air streams, while high-purity quartz filters do not. Because of the possible health effects of respirable nitrate aerosols, this is a rather important subject area, in which research is continuing at Battelle-Columbus.

**TABLE 13. ST. LOUIS AEROSOL COMPOSITION (WEIGHT PERCENT)**

| | $NH_4^+$ | $NO_2^-$ | $NO_3^-$ | C | H | N |
|---|---|---|---|---|---|---|
| Average Total Aerosol Composition | 4.7 | – | 0.62 | 19.0 | 3.6 | 4.6 |
| Large Particle ($>$ 2.5 $\mu m$) Composition | 0.55 | 0.001 | 2.6 | 14.6 | 1.8 | 1.5 |

A recent CRC-EPA program at Battelle-Columbus has reported[32] $NH_4^+$, $NO_3^-$, carbon, and hydrogen in two particle-size ranges for aerosols collected in Columbus, Ohio, and New York City. These results are shown in Table 14. The large-particle compositions from both Columbus and New York are very similar to our St. Louis results shown earlier in Table 13. Comparison of the small-particle

**TABLE 14. SIZE CLASSIFICATION OF VARIOUS AEROSOL COMPONENTS BY CITY (WEIGHT PERCENT)**

| | Columbus | | New York | |
|---|---|---|---|---|
| Aerosol Diameter (μm) | < 2 | > 2 | < 2 | > 2 |
| Constituent | | | | |
| Carbon | 17 | 17 | 26 | 16 |
| Hydrogen | 6 | 1 | 6 | 1 |
| Nitrate | 1 | 2 | 4 | 3 |
| Ammonium | 6 | 0 | 7 | 0 |

composition is not straightforward, since the St. Louis data are for total aerosol only, with small-diameter particles not separated as a class. However, similar trends in the three cities can be inferred from the large-particle/total mass distribution. In all three cities, ammonium was associated almost totally with small particles, while in both Columbus and St. Louis nitrate appeared at higher percentages in the large-particle range. In New York, the nitrate aerosol distribution favors the small particles, but only slightly. A comparison of the St. Louis and West Covina C, H, N data for the two size ranges is reserved for the West Covina aerosol discussion.

The objective of this program involves ultimately a determination of the fate of nitrogen oxides in the atmosphere. One important step toward this goal is a determination of the total nitrogen which can be accounted for as aerosol. Since "total aerosol nitrogen" analyses were performed on the filter samples collected for the study, it is possible to determine a filter nitrogen balance to ascertain to what extent known nitrogen compounds can account for the total aerosol nitrogen. This is important, since it will enable us to determine whether some unsuspected nitrogen-containing aerosol might be a significant sink for the nitrogen oxides.

The filter nitrogen balance results are presented in Table 15. For some days, more than one filter has been analyzed so that the total number of filter samples shown is greater than the data from earlier tables. The values in the table are in milligrams of nitrogen per filter. The two important columns are (1) the sum of the ammonium and nitrate nitrogen and (2) the independently determined total nitrogen figures. The final column shows the percentage of the total aerosol nitrogen which can be accounted for as ammonium and nitrate. While the figures fluctuate from day to day, the average is about 82 percent. Thus, only 18 percent of the total aerosol nitrogen is unaccounted for. This amounts to an average of less than one ppb of aerosol nitrogen unaccounted for. This figure is negligible when the total nitrogen balance in urban atmospheres is considered. The concentration of nitrite found in our aerosol samples was extremely low and is also considered to be negligible in terms of overall nitrogen balance.

From the filter nitrogen data just discussed there is no indication that any previously unsuspected nitrogen-containing aerosol is playing a significant role in the fate of nitrogen oxides in the St. Louis atmosphere. Certainly, over the longer term after an air mass is well beyond the bounds of an urban area, conversion of both primary and secondary gaseous nitrogen products to nitrogen aerosols is no doubt very important. However, over the short interval during which an air mass resides in a metropolitan area, these filter data suggest that we must look for gaseous nitrogen reaction products or physical removal processes to explain any nitrogen imbalance.

TABLE 15. ST. LOUIS FILTER NITROGEN BALANCE

| Date | Filter | $NH_4^+$-N, mg | $NO_3^-$-N, mg | $\Sigma NH_4^+$-N + $NO_3^-$-N, mg | Total N, mg | $\frac{\Sigma NH_4^+\text{-N} + NO_3^-\text{-N}}{\text{Total N}} \times 100$ |
|---|---|---|---|---|---|---|
| 7/18 | 2 | 9.02 | .14 | 9.16 | 9.3 | 98.5 |
| 7/19 | 1 | 4.04 | .11 | 4.15 | 6.4 | 64.9 |
| | 2 | 5.76 | .17 | 5.93 | 6.7 | 88.5 |
| 7/20 | 1 | .93 | .16 | 1.09 | 1.6 | 68.0 |
| 7/22 | 2 | 3.03 | .09 | 3.12 | 3.6 | 86.7 |
| 7/23 | 2 | 3.42 | .10 | 3.52 | 4.5 | 78.2 |
| 7/24 | 2 | 2.18 | .14 | 2.32 | 2.5 | 92.8 |
| 7/25 | 2 | 2.18 | .10 | 2.28 | 2.7 | 84.4 |
| 7/26 | 1 | .78 | .07 | .85 | 1.9 | 44.6 |
| | 2 | 1.01 | .09 | 1.10 | 1.7 | 64.7 |
| 7/27 | 2 | 1.48 | .17 | 1.65 | 2.2 | 75.0 |
| 7/30 | 2 | 2.18 | .12 | 2.30 | 2.8 | 82.3 |
| 7/31 | 1 | 1.32 | .11 | 1.43 | 1.9 | 75.3 |
| 8/1 | 1 | 1.71 | .02 | 1.73 | 2.8 | 61.8 |
| | 2 | 2.02 | .10 | 2.12 | 2.6 | 81.4 |
| 8/2 | 2 | 1.63 | .09 | 1.72 | 2.1 | 81.7 |
| 8/3 | 2 | 1.32 | .18 | 1.50 | 1.7 | 88.3 |
| 8/4 | 2 | 4.74 | .23 | 4.97 | 5.0 | 99.3 |
| 8/5 | 2 | 5.83 | .10 | 5.93 | 5.3 | 111.9 |
| 8/6 | 1 | 5.76 | .14 | 5.90 | 6.1 | 96.6 |
| | 2 | 7.23 | .10 | 7.33 | 7.2 | 101.8 |
| 8/7 | 2 | 6.38 | .20 | 6.58 | 7.1 | 92.7 |
| 8/8 | 2 | 1.24 | .14 | 1.38 | 1.3 | 106.2 |
| 8/9 | 2 | .16 | .19 | .35 | .7 | 49.6 |
| 8/10 | 2 | 1.56 | .11 | 1.67 | 2.4 | 72.7 |
| 8/12 | 2 | 1.24 | .06 | 1.30 | 1.6 | 81.2 |
| 8/13 | 2 | 3.73 | .09 | 3.82 | 4.1 | 93.2 |
| 8/14 | 2 | 3.19 | .07 | 3.26 | 4.1 | 79.5 |
| 8/15 | 2 | 6.92 | .16 | 7.08 | 7.9 | 89.6 |
| 8/16 | 2 | 8.71 | .18 | 8.89 | 10.8 | 82.3 |
| | | | | | Average | 82.5% |

**Distribution and Balance of Nitrogen Compounds**

The ultimate aim of this program is to determine the fate of nitrogen oxides emitted to the atmosphere. This objective requires that the distribution of trace nitrogen compounds in the atmosphere be determined and that relationships among the nitrogen species and between these species and other atmospheric parameters be derived.

Essentially, the distribution of gaseous nitrogen compounds has been given as averages in Table 4, as composited time-dependent profiles in Figure 2, and as individual daily profiles in Appendix A.

On an average basis, the sum of PAN and nitric acid concentrations represent only a very small fraction of the total average $NO_x$. Since it was shown in the previous section that total aerosol nitrogen is also extremely low in comparison to the average level of $NO_x$, we are left with two hypotheses relating to the fate of nitrogen oxides in urban atmospheres. In the first hypothesis, it is assumed that nitrogen oxides are being removed from urban atmospheres at a fairly rapid rate and we have not determined the dominant removal processes. The second hypothesis holds that the reactions removing nitrogen oxides from the atmosphere are rather slow and are not important over the short time interval during which an air parcel resides in an urban area. By this argument, we should not expect to find high concentrations of nitrogen-containing products, since $NO_x$ scavenging processes would be too slow to allow significant quantities of reaction products to accumulate.

In order to test the validity of these two hypotheses, it is necessary to determine the fraction of $NO_x$ removed from the atmosphere and then attempt to "balance" the nitrogen oxides reactants with their chemical reaction products. The nitrogen balance will define the extent to which chemical reaction products can account for the removal of nitrogen oxides from an air mass. If poor nitrogen balances result, we must consider the possibility of unknown chemical reaction products or physical removal mechanisms as potential sinks for the nitrogen oxides.

**Statistical Interpretation.** Various statistical techniques will be employed to determine relationships among the many chemical and meteorological parameters measured during the field study. In particular, relationships will be sought to define the conditions under which loss of nitrogen oxides occurs. An understanding of the conditions necessary for $NO_x$ removal from the atmosphere should in itself indicate the types of sinks and removal mechanisms which are important.

The initial scanning of the data was accomplished using the Automatic Interaction Detector (AID) statistical program.[60] In essence, this technique identifies which independent variables are the best predictors of a given dependent variable. In quantitative terms, the best predictor is that independent variable which maximizes an F-ratio. In intuitive terms, the F-ratio is the ratio of the statistical variability of y that is accounted for by the variability of x, to the variability of y that is not accounted for by the variability of x. The AID program simply computes the F-ratios associated with each independent variable and splits the data using the variable that yields the maximum F-ratio.

Brief descriptions of the AID graphic-tree output and the initial series of AID runs are given in Appendix C. The significance of the AID splits is related to the size of the data base, the extent (graphically, the width) of the split, the number of times splitting occurs on any one independent variable, and, ultimately, the between sum of squares to total sum of squares ratio. Table 16 lists several dependent variables and the first three independent or predictor variables for each. The sign of the predictor variables is also listed; positive indicates that high values of the predictor variable predict high values of the dependent variables and negative indicates that low values of the independent variable predict high values of the dependent variable.

While the results of the AID runs are interesting in themselves, the real usefulness of the AID analysis lies in its ability to sort a large volume of data quickly and indicate which relationships appear to be most important. Of primary concern in this program are the variables $NO_x$, PAN, and $HNO_3$.

**TABLE 16. ST. LOUIS AID RESULTS**

First Three Predictor Variables

| Dependent Variable | Three Primary Predictor Variables | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| $NO_x$ | $O_3$ (-) | $HNO_3$ (+) | Humidity (-) |
| PAN | $O_3$ (+) | Wind Direction (-) | $NO_2$ (+) |
| $HNO_3$ | $NO_2$ (+) | Wind Direction (-) | $O_3$ (+) |
| $NH_3$ | Temperature (+) | $NO_x$ (+) | $NO_2$ (-) |
| $NH_4^+$ | Total Aerosol Nitrogen (+) | – | – |
| $NO_3^-$ | $NO_2$ (+) | $NO_2$ (-) | Total Aerosol Nitrogen (-) |
| Total Aerosol Nitrogen | $NH_4^+$ (+) | Wind Speed (-) | – |
| Mass Loading | Total Aerosol Nitrogen (+) | $HNO_3$ (+) | $NO_2$ (+) |

Ozone appears as a primary predictor variable for all three of these compounds. Ozone and $NO_x$ appear to be negatively correlated, while a positive relationship is maintained between ozone and the two $NO_x$ reaction products, PAN and $HNO_3$. These are precisely the types of relationships one would expect from kinetic mechanisms used for atmospheric modeling. High levels of ozone are expected to increase the rate of removal of $NO_x$ and the rates of production of PAN and $HNO_3$ from $NO_x$. The positive relationship between $NO_2$ and both PAN and $HNO_3$ is also predictable from kinetic models, since $NO_2$ is vitally important in the generation of $O_3$ and is necessary for the formation of both PAN and $HNO_3$. The negative sign accompanying wind direction as a PAN and $HNO_3$ predictor indicates that winds from the northeastern and southeastern quadrants (0° to 180°) lead to higher levels of PAN and $HNO_3$ than do other wind directions. Since the most heavily industrialized sections of St. Louis and East St. Louis, Illinois, lie to the east of our monitoring site, this result is not surprising.

The positive relationship between temperature and $NH_3$ was discussed earlier as possibly relating to the biological nature of the ammonia cycle. The positive $NH_4^+$-total aerosol nitrogen relationship is understandable, since $NH_4^+$ makes up the greatest fraction of the aerosol nitrogen mass. Other relationships indicated in the table are more or less explainable, based on our current understanding of atmospheric chemical processes. Since they are not directly pertinent to the objectives of this project, however, they will not be discussed here.

It was pointed out earlier that the main utility of the AID program is to indicate potentially important relationships and thereby serve as a guide for further data analysis. Based on the results of the AID analyses, several regressions have been run to further define the nature of the relationships primarily among $NO_x$, $O_3$, PAN, $HNO_3$, and relative humidity.

The first set of regression parameters is shown in Table 17 for the hourly average data for 23 hours each day. In this and subsequent regression tables, the first two columns show the Y and X coordinate variables, while the third column lists the correlation coefficient (R). In Table 17 the only relationships which stand out are those between $O_3$ and NO, $NO_2$, and $NO_x$. While none of these correlation coefficients is particularly high, a negative slope is apparent in all three cases. The statistical significance of the $O_3$-$NO_2$ result is only marginal, however.

**TABLE 17. ST. LOUIS REGRESSIONS**

All Hourly Averages.

| y | x | R |
|---|---|---|
| $NO_x$ | R.H. | 0.35 |
| $NO_x$ | $O_3$ | -0.54 |
| $NO_x$ | $HNO_3$ | 0.21 |
| $O_3$ | NO | -0.51 |
| $O_3$ | $NO_2$ | -0.33 |
| $O_3$ | $HNO_3$ | 0.04 |

An interesting comparison, and in some cases a strengthened statistical relationship, is obtained when only the daytime data are used in deriving the regression equations. Table 18 shows the same correlation terms given in Table 17, along with some additional regressions for the daily 6:00 a.m. to 6:00 p.m. time interval. Comparison of the three most important $NO_x$ predictor variables (from the AID analysis) in Table 17 for all hours of the day with the same variables in Table 18 for daylight

**TABLE 18. ST. LOUIS REGRESSIONS**

Data From 6 a.m. to 6 p.m.

| y | x | R |
|---|---|---|
| $NO_x$ | R.H. | 0.51 |
| $NO_x$ | $O_3$ | -0.58 |
| $NO_x$ | $HNO_3$ | 0.22 |
| $O_3$ | NO | -0.61 |
| $O_3$ | $NO_2$ | -0.32 |
| $O_3$ | PAN | 0.48 |
| $O_3$ | $HNO_3$ | 0.00 |
| $HNO_3$ | Global | -0.02 |
| $HNO_3$ | $NO_2$ | 0.41 |
| $HNO_3$ | PAN | 0.26 |

hours only shows that only the correlation coefficient for $NO_x$-relative humidity changed substantially. This may only reflect the fact that there was very little variation in relative humidity during the nighttime hours. The highest level of correlation, again, is between $O_3$ and NO with a coefficient of -0.61. The inverse relationship between $O_3$ and NO is expected because of the very rapid reaction between these two trace pollutants. If either $O_3$ or NO is present in air at a high level, the other must necessarily be present at a rather low level. The often used photostationary-state assumption defines the inverse relationship between $O_3$ and NO as follows:

$$O_3 = K \frac{NO_2}{NO}$$

where K is a function of ultraviolet light intensity. Obviously, the assumption collapses at night. The validity of the assumption is also questionable under low light intensities and at low concentrations due to the slower reaction rates.

An important relationship appears to exist between $NO_x$ and $O_3$, since this regression equation yields the second highest correlation coefficient. However, because of the opposite effects NO and $NO_2$ have on ozone concentration as seen in the photostationary-state equation, an explanation of the relationship between $O_3$ and the sum of NO and $NO_2$ is not straightforward. Possibly, a negative relationship exists because $O_3$ is normally quite low in the morning when NO and, consequently, $NO_x$ are high; in the afternoon when $O_3$ accumulates, the high morning levels of $NO_x$ have dispersed and the $NO_x$ present is largely $NO_2$. The problem of interpreting these $O_3$-NO-$NO_2$-$NO_x$ relationships is further complicated by the fact that hydrocarbon data are not included here. Indeed, we know from smog chamber and atmospheric data that the hydrocarbon to $NO_x$ ratio (HC/$NO_x$) is an important determinant of the potential $O_3$ concentration. To further analyze the $O_3$-$NO_x$ relationship at this point would require the addition of hydrocarbon data and a discussion of kinetic models. Such a discussion would shed very little light on the fate of nitrogen oxides and is not warranted here.

A third set of regressions has been run on the St. Louis data and is shown in Table 19. The first four regressions include the maximum hourly averages for $O_3$, PAN, and $HNO_3$ versus the 6:00-9:00 a.m. averages for either NO or $NO_x$. The most interesting feature of this series of regressions is the reasonable correlation found between maximum $HNO_3$ and morning $NO_x$.

**TABLE 19. ST. LOUIS REGRESSIONS**

Maximum Hourly $O_3$, PAN, $HNO_3$
vs.
6:00-9:00 a.m. Average NO or $NO_x$

| y | x | R |
|---|---|---|
| $O_3$ | NO | 0.16 |
| $O_3$ | $NO_x$ | 0.25 |
| $NO_x$ | PAN | 0.31 |
| $NO_x$ | $HNO_3$ | 0.62 |
| $O_3$ | PAN | 0.50 |
| $O_3$ | $HNO_3$ | 0.06 |

Two additional regressions also shown in Table 19 are for the maximum hourly average $O_3$ versus maximum hourly average PAN and $HNO_3$. The $O_3$-$HNO_3$ correlation is virtually nonexistent; however, the $O_3$-PAN regression yields a correlation coefficient of 0.5. The slope of the $O_3$-PAN regression is 5.1 compared with a value of approximately 3 found for many U.S. cities in studies by Lonneman.[61]

**Nitrogen Balance.** In keeping with the objectives of the program, we have determined the atmospheric distribution of trace nitrogen compounds which are thought to be important to the fate of nitrogen oxides and investigated the interrelationships and time dependencies of the various compounds for clues as to the ultimate disposition of the nitrogen oxides. From the distributions it was clear that the sum of all the measured products of nitrogen oxide reactions could account for only a fraction of the average $NO_x$ concentration so that either (1) we were not observing all of the important $NO_x$

removal mechanisms or (2) the $NO_x$ removal mechanisms are relatively slow, so that the loss of $NO_x$ over the short term is only a small fraction of the total $NO_x$ concentration. Subsequently, AID and correlation analyses have indicated that $O_3$, relative humidity, and $HNO_3$ are the three most important predictors of $NO_x$ concentration of all the parameters determined in this study. From the correlation studies, $O_3$ appeared to be an especially important predictor of both the $NO_x$ and PAN concentrations. Two cautionary notes must be sounded here, however. First, the statistical relationships cannot be translated into chemical relationships; they can only indicate the importance of trends in the data. Inferring chemical meaning or cause-and-effect relationships from the statistical analysis requires extreme caution. Second, it must be kept in mind that the major factors affecting the $NO_x$ concentration are related to the intensity of source emissions, inversion conditions, convection, and advection. In our examination of the trends in $NO_x$ concentration for clues as to the $NO_x$ removal processes, these gross determinants of $NO_x$ concentration are no doubt masking some of the relationships we seek. What is needed is a means of computing the fraction of $NO_x$ which has been removed from the air mass at any point in time. Such "$NO_x$ loss" values would yield much more meaningful relationships since the masking effect of emission rates and dispersion would be eliminated. In addition, the "$NO_x$ loss" values can be compared with the sum of the measured $NO_x$ reaction products to determine a nitrogen balance. The closeness of the balance will reveal to what extent we are accounting for the $NO_x$ which has been removed from an air mass by either chemical or physical processes.

In deriving "$NO_x$ loss" values, we will make use of the inert tracer technique described in an earlier section of this report. The tracers we plan to use are carbon monoxide and acetylene, both of which were measured gas chromatographically by the Environmental Protection Agency mobile laboratory situated alongside our mobile lab in St. Louis. Values for CO and $C_2H_2$, integrated over 2-hour periods from 6:00 a.m. to 2:00 p.m., are available for 5 days during which our mobile laboratory took samples in St. Louis. These data were presented earlier in Table 5. Detailed hydrocarbon data provided by EPA are given in Appendix A.

With CO as the tracer, the equation used to calculate "$NO_x$ loss" is

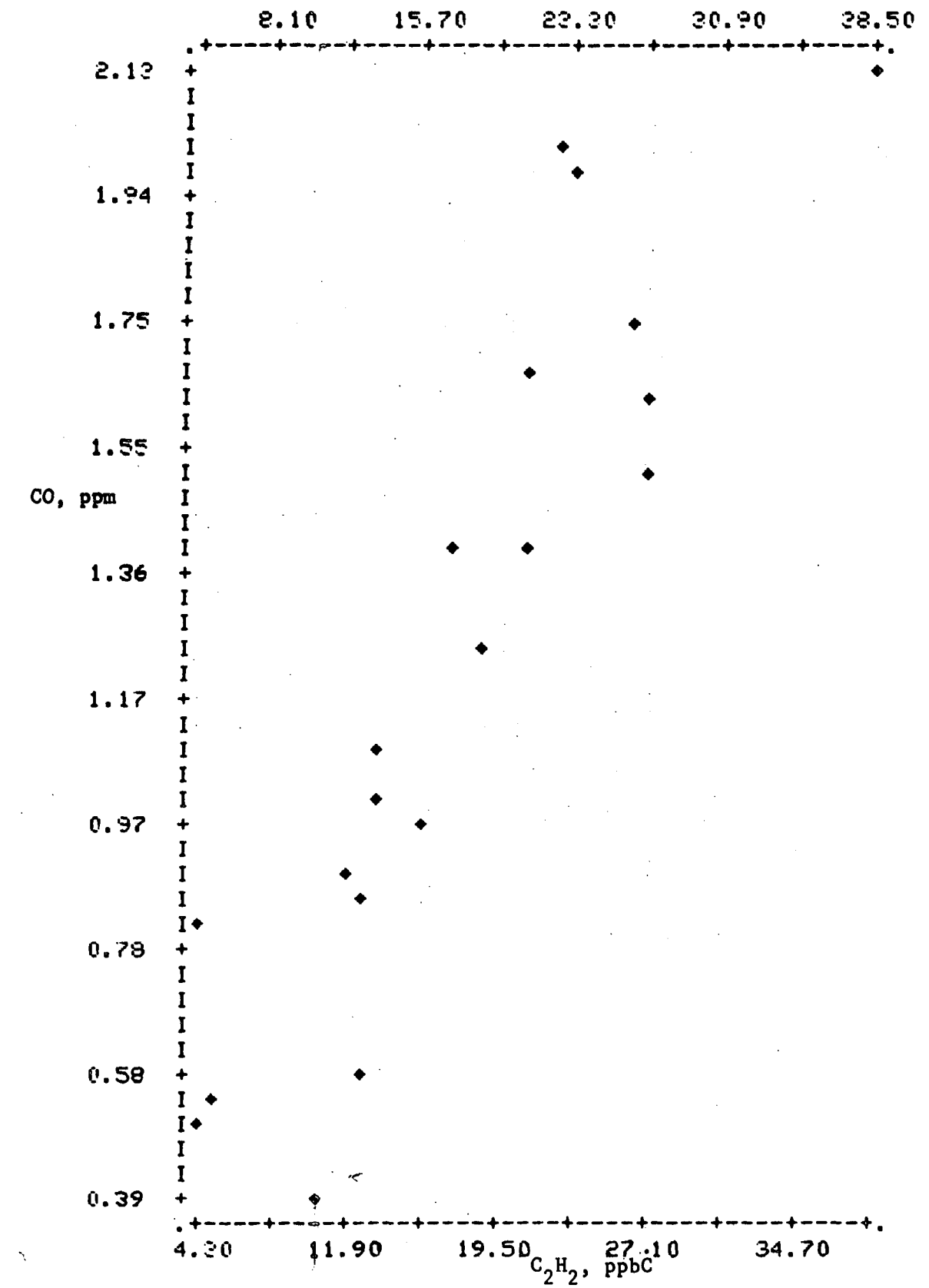
$$\frac{(CO)_{measured}}{(CO/NO_x)_{emission\ inventory}} - (NO_x)_{measured} = NO_x \text{ loss} \quad , \tag{1}$$

where the first term represents a theoretical or predicted $NO_x$ concentration based on emission ratios and the measured CO at any given time. The difference between the predicted $NO_x$ and the measured $NO_x$ is defined as $NO_x$ loss. The equation can be used in this form to calculate "$NO_x$ loss" from individual sets of measured CO and $NO_x$ data. However, in using the equation as it stands, we overestimate the $NO_x$ loss due to the presence of background CO, which is in no way associated with St. Louis emissions sources. For the most accurate determination of "$NO_x$ loss", we must eliminate any CO which is not associated with the emission inventory estimates. A convenient way of doing this involves rearrangement of Equation (1) as follows:

$$\left[\frac{(CO/NO_x)_m}{(CO/NO_x)_{E.I.}} - 1\right] (NO_x)_m = NO_x \text{ loss} \quad . \tag{2}$$

The equation in this form makes use of the measured $CO/NO_x$ ratio, which we will obtain from the slope of the CO versus $NO_x$ regression line. The slope of this regression line allows us to eliminate the CO intercept which contains CO contributions that are invariant to changing source emissions — e.g., background CO or incorrect CO calibration factors. The intercept can be viewed as CO from a source not associated with $NO_x$. Since all the important CO sources (with auto exhaust by far the most important) are associated also with $NO_x$ emissions, extrapolating $NO_x$ to zero (the CO intercept) yields an average CO concentration which is not included in the emission inventory and which, therefore, must be excluded from the "$NO_x$ loss" computation.

To demonstrate first that CO and acetylene have the same auto exhaust origin, we turn to Figure 4, where CO in ppm is plotted against $C_2H_2$ in ppb C. The correlation coefficient of 0.89 shows




| | | | |
|---|---|---|---|
| CORRELATION (R) - | 0.88552 | R SQUARED - | 0.78415 |
| SIGNIFICANCE R - | 0.00001 | STD ERR OF EST - | 0.25439 |
| INTERCEPT (A) - | 0.30975 | STD ERROR OF A - | 0.12796 |
| SIGNIFICANCE A - | 0.01214 | SLOPE (B) - | 0.05375 |
| STD ERROR OF B - | 0.00665 | SIGNIFICANCE B - | 0.00001 |

FIGURE 4. ST. LOUIS REGRESSION: CO VERSUS $C_2H_2$

very good correlation between these two pollutants. The intercept of the curve – at 0.31 ppm CO – will be important to our subsequent discussion, since it is this fraction of CO which is not associated with auto exhaust and which we shall consider as background CO. It is interesting to note that Kopczynski, et al.[62], have measured nonurban CO in the St. Louis area at 0.295 ppm. It is very likely this nonurban CO which comprises our background or intercept CO. The geologic background from natural processes alone is thought[63] to contribute 0.1-0.2 ppm CO.

The important plot of CO versus $NO_x$ is shown as Figure 5. The CO intercept of 0.41 ± 0.20, again, is quite similar to the intercept from Figure 4 and the nonurban CO reported by Kopczynski, et al.[62] The most important feature of this curve is the slope, however. It is this slope which will be used in the calculation of the average "$NO_x$ loss". Also necessary for the calculation are the most recent emissions inventory values* for CO and $NO_x$, which are given in Table 20 for the city of St. Louis and the St. Louis Air Quality Control Region (AQCR).

**TABLE 20. EMISSIONS INVENTORIES FOR ST. LOUIS REGION**

Tons per Day.

| | St. Louis City | AQCR |
|---|---|---|
| CO | 299,088 | 3,852,746 |
| $NO_x$ | 35,545 | 433,547 |

Substituting the measured $CO/NO_x$ ratio from the slope of Figure 5, the molar $CO/NO_x$ ratio from the St. Louis AQCR, and the average measured $NO_x$ into Equation (2),

$$NO_x \text{ loss} = \left[\frac{14.6 \pm 3.2}{14.6} - 1\right] (0.056)$$

$$NO_x \text{ loss} = 0.000 \pm 0.012 \text{ ppm.}$$

If we use the St. Louis city emission inventory ratio, we obtain

$$NO_x \text{ loss} = \left[\frac{14.6 \pm 3.2}{13.8} - 1\right] (0.056)$$

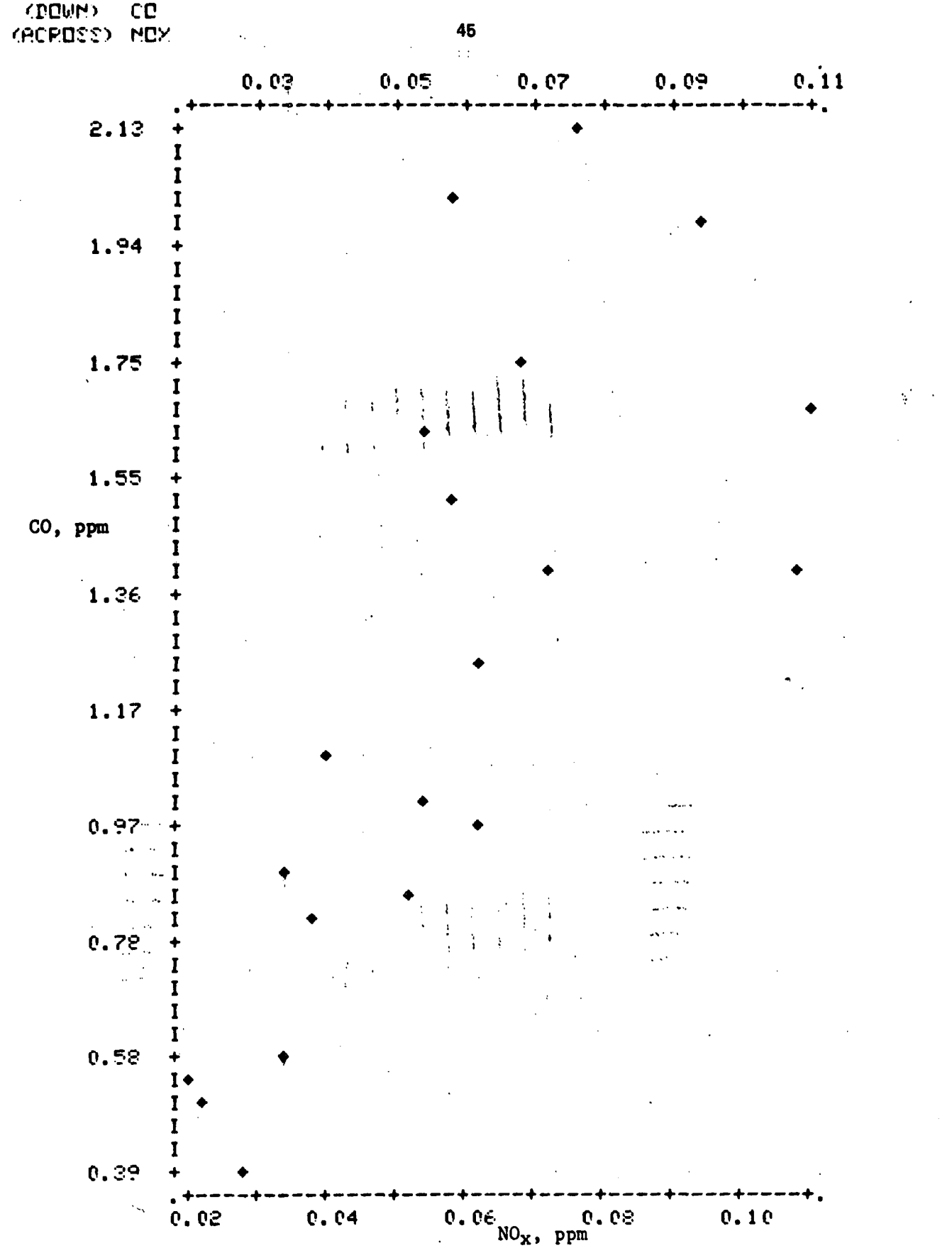
$$NO_x \text{ loss} = 0.003 \pm 0.012 \text{ ppm.}$$

It is apparent that the average $NO_x$ loss is very small in comparison with the average concentration of $NO_x$. The average sum of PAN and $HNO_3$ over the same 5-day period was 0.007 ppm, well within the 0.012 ppm deviation. Thus, the nitrogen balance is quite good.

As a secondary check on $NO_x$ balance, we can use $C_2H_2$ as a tracer and recalculate the "$NO_x$ loss". The pertinent equation is

$$NO_x \text{ loss} = \left[\frac{(C_2H_2/NO_x)_m}{(C_2H_2/NO_x)_{E.I.}} - 1\right] (NO_x)_m \quad . \qquad (3)$$

* Courtesy of C. Masters, U.S. Environmental Protection Agency.




| | | | |
|---|---|---|---|
| CORRELATION (R) - | 0.73454 | R SQUARED - | 0.53955 |
| SIGNIFICANCE R - | 0.00011 | STD ERR OF EST - | 0.37155 |
| INTERCEPT (A) - | 0.41178 | STD ERROR OF A - | 0.19789 |
| SIGNIFICANCE A - | 0.02600 | SLOPE (B) - | 14.62534 |
| STD ERROR OF B - | 3.18452 | SIGNIFICANCE B - | 0.00011 |

**FIGURE 5. ST. LOUIS REGRESSION: CO VERSUS $NO_x$**

It must be remembered that acetylene is present in the atmosphere at much lower concentrations than CO, so the error in its measurement is correspondingly larger. The measured $C_2H_2/NO_x$ ratio for the 5 days of available data is obtained from the slope of Figure 6 and found to be 0.20 ± 0.06. The emission inventory ratio needed for our calculation presents us with a problem, however, since inventories are not broken down for individual hydrocarbons. We can circumvent this problem by using the $C_2H_2/NO_x$ ratio for auto exhaust after correction for the nonexhaust fraction of $NO_x$ for St. Louis. Using Kopczynski, et al.'s[62], value of 28 for the $CO/NO_x$ ratio in St. Louis auto exhaust, we calculate that about 60 percent of our measured $NO_x$ is attributable on the average to auto exhaust. The background CO again has been subtracted to improve the accuracy of the calculation.

The $C_2H_2/NO_x$ ratio for St. Louis auto exhaust has been determined by Kopczynski, et al.[62], to be 0.38. Making the usual assumption that auto exhaust is the only source of $C_2H_2$, we can correct the $C_2H_2/NO_x$ exhaust ratio for nonexhaust sources of $NO_x$, so the ratio will be representative of all St. Louis sources. The corrected ratio is 0.38 x 0.60 or 0.23. Substituting this value for the emissions inventory ratio in Equation (3) yields

$$NO_x \text{ loss} = \left[\frac{0.20 \pm 0.06}{0.23} - 1\right] (0.056) \quad ,$$

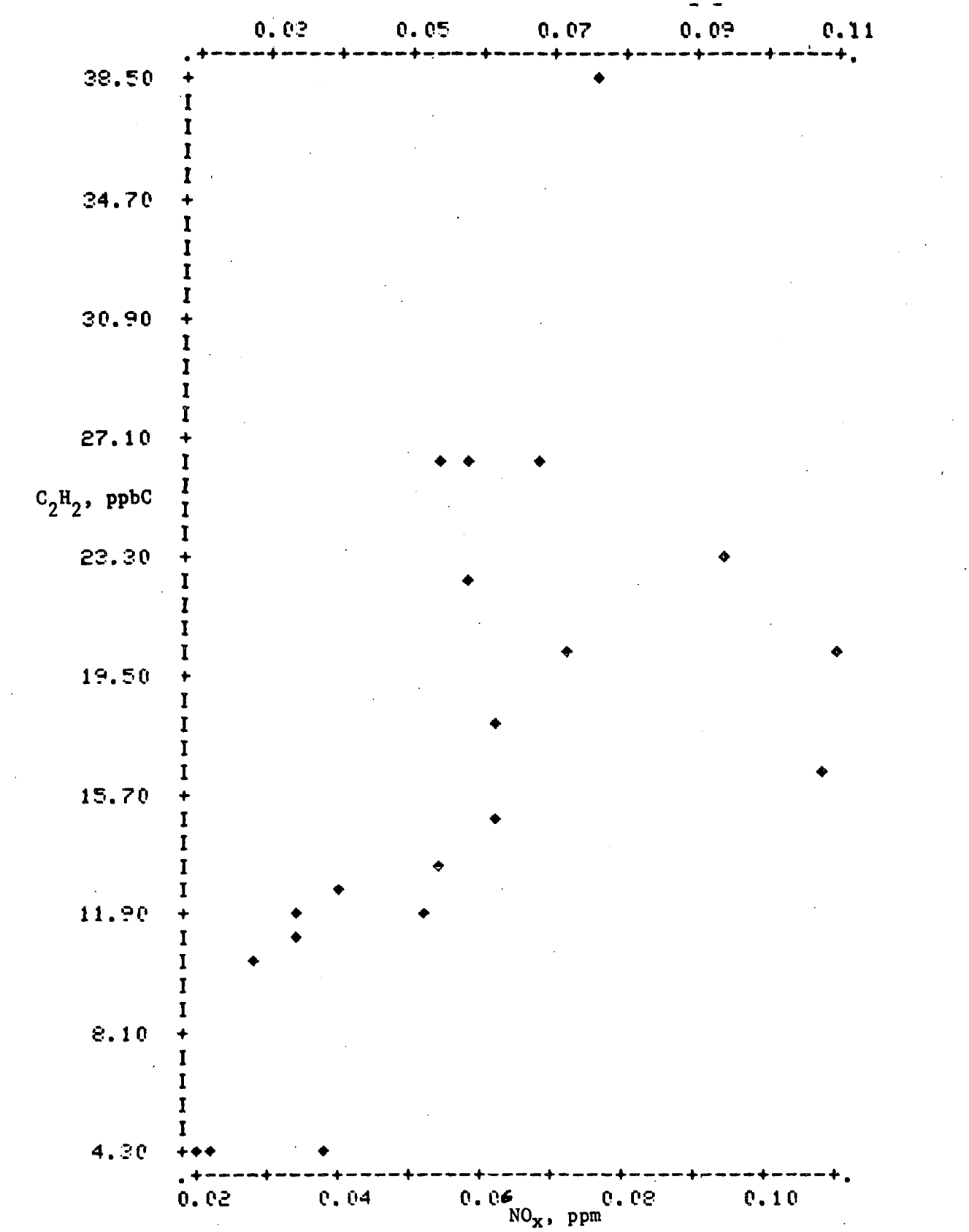
$$NO_x \text{ loss} = -0.007 \pm 0.015 \quad .$$

This calculated average "$NO_x$ loss" is in essential agreement with the earlier CO-tracer calculation in that the average loss of $NO_x$ is found to be negligible.

Prior to our determination of the absolute value of $NO_x$ loss, AID analyses were performed on relative "$NO_x$ loss" values to determine what factors might be influencing the removal of $NO_x$ from the St. Louis atmosphere. These AID runs incorporated the EPA hydrocarbon data given earlier in Table 5. The results of these runs were contradictory and somewhat confusing. It is obvious now that, with no true $NO_x$ loss, the AID program was splitting the dependent variable (relative $NO_x$ loss) primarily on noise. Consequently, these runs have no significance and are not presented here.

In summarizing the St. Louis results, we have found that the loss of nitrogen oxides from the St. Louis atmosphere was minimal on the average and that PAN and nitric acid, which were present at low levels, can account for what little $NO_x$ loss was observed. Nitrite and nitrate aerosol were found to be unimportant in terms of nitrogen balance.

These findings support the contention that the removal of $NO_x$ from the atmosphere is a relatively slow process requiring considerable residence or reaction time. The fact that our mobile laboratory was situated within the City of St. Louis meant that the air mass we were sampling normally experienced only a very short residence time over St. Louis under average wind conditions. If, indeed, the removal of $NO_x$ from the atmosphere is a slow process, a more favorable location for observing $NO_x$ loss and $NO_x$ reaction products should be downwind of an urban area where a well-aged air mass is encountered. This was, in fact, our siting arrangement in the Los Angeles field study, the results of which are discussed in the following section.




| | | | |
|---|---|---|---|
| CORRELATION (R) - | 0.61289 | R SQUARED - | 0.37563 |
| SIGNIFICANCE R - | 0.00203 | STD ERR OF EST - | 7.12815 |
| INTERCEPT (A) - | 5.90584 | STD ERROR OF B - | 3.79652 |
| SIGNIFICANCE B - | 0.06861 | SLOPE (B) - | 201.04901 |
| STD ERROR OF B - | 61.09468 | SIGNIFICANCE B - | 0.00203 |

**FIGURE 6. ST. LOUIS REGRESSION: $C_2H_2$ VERSUS $NO_x$**

## West Covina, California

In discussing the results of the West Covina field sampling effort, we will first review the trends in the air quality data, then the aerosol results, and, finally, comment in detail on the distribution and balance of nitrogen compounds in the West Covina atmosphere.

### Air Quality Data

During the 29 days of monitoring in the Los Angeles basin, the symptoms of photochemical smog were extensive, as evidenced by Table 10. Even though a great many days were heavily overcast until almost noon, the Federal standard of 0.08 ppm 1-hour average ozone was exceeded on 27 of the 29 sampling days. Of the two substandard days, one was a heavily overcast Monday and the other a clear Sunday.

In general, the concentrations of NO, $NO_x$, $O_3$, and PAN were considerably higher in West Covina than in St. Louis, even though the average solar intensity was greater for St. Louis. A comparison of the overall averages and the average 1-hour maxima for the two cities is given in Table 21.

**TABLE 21. ST. LOUIS-WEST COVINA COMPARISONS**

| | St. Louis | | West Covina | |
|---|---|---|---|---|
| | Overall Average | Average 1-Hour Maximum | Overall Average | Average 1-Hour Maximum |
| Solar Intensity (cal./cm$^2$/min.) | 0.314 | — | 0.242 | — |
| Wind Speed (m.p.h.) | 3.84 | — | 2.13 | — |
| Temperature (°C) | 25.19 | — | 18.46 | — |
| Relative Humidity (%) | 78.39 | — | 77.15 | — |
| $O_3$ (ppm) | 0.035 | 0.073 | 0.046 | 0.153 |
| NO (ppm) | 0.016 | 0.035 | 0.058 | 0.128 |
| $NO_2$ (ppm) | 0.029 | 0.037 | 0.078 | 0.097 |
| $NO_x$ (ppm) | 0.053 | 0.069 | 0.136 | 0.185 |
| $NH_3$ (ppm) | 0.005 | 0.006 | 0.004 | 0.005 |
| PAN (ppm) | 0.002 | 0.003 | 0.009 | 0.020 |
| $HNO_3$ (ppm) | 0.003 | 0.008 | 0.003 | 0.010 |

The behavior of the West Covina air quality data follows the same general pattern as was noted in St. Louis. Referring to the average air quality trends in Figure 3, a large increase in NO and $NO_x$ is observed between 5:00 and 7:00 a.m., followed by a rapid decrease in NO and corresponding increase in $NO_2$. Nitrogen dioxide peaks at about 10:00 a.m. and remains fairly close to this peak level until late in the afternoon. As in St. Louis, the average $NO_2$ concentration is high enough that the sum of the PAN and $HNO_3$ interferences can make up only a small fraction of the total $NO_2$. Again, however, when PAN and $HNO_3$ are high, as during the afternoon, up to 30 percent of the average measured $NO_2$

could actually be PAN and $HNO_3$. Elimination of this interference would cause an afternoon dip in the average $NO_2$ profile rather than the almost constant afternoon concentration observed. Since these $NO_2$ and $NO_x$ values will not be used in the subsequent nitrogen balance discussions and since correction of the data would be difficult due to the variable interference response, we have elected not to attempt a correction of the chemiluminescent $NO_2$-$NO_x$ data.

During the afternoon period, NO drops to a very low level and remains there throughout the afternoon, as ozone rises rapidly to a peak at about 3:00 p.m. It is noted in Figure 3 that $O_3$ follows the solar intensity profile quite closely with 1 to 2 hours' delay. The concentrations of PAN and $HNO_3$ appear to start increasing during the conversion of NO to $NO_2$ and follow the same pattern as the ozone profile. Both PAN and $HNO_3$ reach their maximum levels at about 2:00 p.m. and thereafter drop off through the evening. The concentration of PAN seems to decrease at about the same rate as $O_3$; however, $HNO_3$ drops off faster than either PAN or $O_3$. This implies either that the processes forming $HNO_3$ terminate more quickly than the $O_3$ or PAN formation processes or that $HNO_3$ removal mechanisms are more rapid.

Late in the afternoon (starting at approximately 5:00 p.m.), $O_3$ decreases rapidly as NO from evening rush-hour exhaust reacts with it to form $O_2$ and $NO_2$. During this period, $NO_2$ increases to its highest level at 7:00 p.m. Once $O_3$ has been depleted, NO rises rapidly starting at 7:00 p.m. Wind speed, also shown in Figure 3, peaks at about 5:00 p.m. on the average, and the mixing thus created prevents the concentrations of exhaust products from the evening rush hour from building up to the same high levels noted during the morning rush hour.

The average nitric acid profile in Figure 3 exhibits much less variability than the St. Louis pattern. Within the limits just discussed, it appears to follow the same trend as the $O_3$ and PAN concentrations, which strongly implicates photochemical smog reactions in the formation process. The profile is consistent with either of the two mechanisms shown below:

$$OH + NO_2 \xrightarrow{(m)} HNO_3$$

or

$$O_3 + NO_2 \rightarrow O_2 + NO_3$$

$$NO_3 + NO_2 \rightleftarrows N_2O_5$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 .$$

However, the results of some of our recent smog-chamber experiments[14] indicate the latter mechanism to be dominant.

The average ammonia profile, as shown in Figure 3, is similar to that of St. Louis both in concentration and pattern. The levels and patterns of ammonia in both St. Louis and West Covina are completely consistent with the Great Britain[23] and St. Louis[24] ammonia results discussed in an earlier section of this report. It is interesting to note that during the late morning and early afternoon hours, the average behavior of $NH_3$ and $HNO_3$ is similar. This does not tend to support the argument for a very rapid reaction between these two substances; however, it cannot rule out such a reaction since very rapid emissions or formation of $NH_3$ and $HNO_3$ could lead to the type of behavior observed. The facts that the concentration of $HNO_3$ drops off more rapidly than other smog products and that $NH_3$ is decreasing at the same time, further complicate the picture. At the present time, all one can say is that $NH_3$ and $HNO_3$ do coexist in the atmosphere and that the general time dependence of their concentrations is similar in the West Covina atmosphere.

**Aerosol Composition**

The average particulate mass loading during the West Covina field sampling study was 101 $\mu g/m^3$, as determined by high-volume sampling of air through high-purity quartz fiber filters. Of this total

aerosol mass, carbon comprises 19.4 percent, hydrogen 3.8 percent, and nitrogen 5.3 percent. These three elements alone make up 28.5 percent of the average aerosol mass; water, metals, oxygen, and sulfur presumably make up most of the remaining mass. The carbon and nitrogen percentages are in good agreement with the values reported by Hidy[64] of 19 percent carbon and 5 percent nitrogen. Of the nitrogen compounds determined specifically, ammonium accounts for 4.7 percent of the mass, nitrate about 1.7 percent, and the contribution of nitrite to the total mass is negligible, as in St. Louis.

Table 22 gives the comparison between the average total aerosol analysis and the composite dust (particle diameter > 2.5 μm) analysis for West Covina. The aerosol composition from West Covina can be compared with the composition of St. Louis aerosol shown earlier in Table 13. The weight percentages and relative distribution of size ranges is very similar for all components from the two cities with the exception of nitrate. The fraction of aerosol mass accounted for as nitrate rose sharply from St. Louis to West Covina. The $NO_3^-$ fraction increased by a factor of 2.7 for the total aerosol mass, while an increase of a factor of 1.8 occurred in the large-particle size range. High nitrate measurements in the Los Angeles area are not surprising; indeed, NASN[59] data have shown high nitrate in the Los Angeles basin for years. What is surprising at first glance is the relatively low nitrate concentration found in this study relative to Los Angeles nitrate values reported elsewhere. For example, in the study of Gordon and Bryan[33], nitrate concentrations on the order of 10-15 $\mu g/m^3$ were found from 1970 through 1972, compared with our average 1.7 $\mu g/m^3$ concentration. To check the accuracy of our nitrate analyses to insure that the analytical technique was not responsible for the low nitrate values, several filter sections from St. Louis and West Covina were sent to the California Air Industrial Hygiene Laboratory* (AIHL) and to Rockwell International* for comparative analysis. Collaborative ammonium analyses were also carried out at the same time by the AIHL group. The results of this collaborative

**TABLE 22. WEST COVINA AEROSOL COMPOSITION (WEIGHT PERCENT)**

| | $NH_4^+$ | $NO_2^-$ | $NO_3^-$ | C | H | N |
|---|---|---|---|---|---|---|
| Average Total Aerosol Composition | 4.7 | – | 1.7 | 19.4 | 3.8 | 5.3 |
| Large Particle (> 2.5 μm) Composition | 0.63 | 0.001 | 4.8 | 12.6 | 1.8 | 2.2 |

study are shown in Table 23. The ammonium results agree quite well, especially considering that the samples were analyzed several months apart. Three different nitrate procedures were employed for selected aerosol samples, two by Battelle and one by the AIHL. There is considerable scatter in the results from both St. Louis and West Covina, but the values determined by the three independent methods are definitely of similar magnitude. Rockwell International employed a newly developed polaragraphic technique for the nitrate analysis, and, although they were unable to report quantitative results, their determinations indicated nitrate values similar to or even lower than the Battelle values. These collaborative nitrate analyses allow us to eliminate the analytical procedure as a factor in the low nitrate results.

The Gordon and Bryan[33] study mentioned earlier employed the usual fiber glass filters for aerosol collections. As discussed in the St. Louis section, nitric acid may well interfere with aerosol nitrate determination on glass fiber filters due to removal of $HNO_3$ from the air by basic-surfaced glass fiber filters. Brief laboratory studies indicate that the neutral quartz filters employed in this study do not scrub nitric acid from the air. If the average level of nitric acid we determined in West Covina were removed by the filters, the nitrate values reported here would increase by about 8 $\mu g/m^3$. This would put our nitrate results within the range of values reported by other researchers. This possibility of $HNO_3$ interference with aerosol $NO_3^-$ on fiber glass filters is an important finding of this study and will be pursued in subsequent research.

* Our thanks to Dr. Bruce Appel at AIHL and Dr. Ed Parry at Rockwell for performing these analyses.

## TABLE 23. INTERLABORATORY COMPARISONS

Mg on Filter.

| Filter No. | $NH_4^+$ BCL ($NH_3$ Electrode) | $NH_4^+$ AIHL (Indophenol Blue) | $NO_3^-$ BCL # 1 (Brucine Sulfate) | $NO_3^-$ BCL # 2 (Chromatropic Acid) | $NO_3^-$ AIHL (2,4-Xylenol) |
|---|---|---|---|---|---|
| | | | **St. Louis** | | |
| 3 | 5.2 | 5.5 | 0.50 | – | 0.06 |
| 17 | 1.0 | 1.2 | 0.30 | – | 0.20 |
| 25 | 2.2 | 2.1 | 0.10(0.43) | – | 0.34 |
| 35 | 7.4 | 6.0 | 0.60 | – | 0.26 |
| | | | **West Covina** | | |
| 102 | 3.8 | 1.7 | <12.4 | 8.5 | 7.9 |
| 124 | 4.9 | 4.7 | 1.5 | 3.3 | 2.4 |
| 130 | 8.1 | 7.8 | 0.5 | 1.7 | 0.68 |
| 158 | 2.3 | 1.9 | 6.3 | 7.8 | 1.7 |

The average ammonium values reported here are quite similar to $NH_4^+$ concentrations reported [33] elsewhere for Los Angeles. Average gaseous ammonia concentrations are considerably above the average ammonium aerosol levels, so atmospheric conversion of $NH_3$ to $NH_4^+$ could well account for all the $NH_4^+$ aerosol mass.

Comparison of the elemental ratios hydrogen/carbon (H/C) and carbon/nitrogen (C/N) is shown for different aerosol size fractions in Table 24. The total aerosol H/C ratio is very similar for both cities at about 2.4. This is the same H/C ratio as pentane; obviously, if saturated hydrocarbons are making up any large fraction of the aerosol, they must be of higher molecular weight than pentane due to vapor pressure considerations. Higher molecular weight saturates must have a lower H/C ratio than 2.4, and

## TABLE 24. AEROSOL ELEMENTAL RATIOS FOR ST. LOUIS AND WEST COVINA (MOLAR RATIOS)

| | St. Louis | | West Covina | |
|---|---|---|---|---|
| Aerosol Size Range (μm) | Total | > 2.5 | Total | > 2.5 |
| Elemental Ratio | | | | |
| Hydrogen/Carbon | 2.3 | 1.5 | 2.4 | 1.7 |
| Carbon/Nitrogen | 4.8 | 11.4 | 4.3 | 6.7 |

oxygenated hydrocarbons of corresponding molecular weight will have even lower ratios. Thus, we are left in the position of being unable to explain the H/C ratio on the basis of hydrocarbons alone; additional hydrogen must be contributed by another specie. The four hydrogens on the ammonium group provide a ready explanation of the H/C ratio. If we subtract the average $NH_4^+$-hydrogen contribution from the total aerosol, the average H/C ratio becomes approximately 1.7. This is very close to the ratio of 1.6 found for primary auto exhaust aerosols in a Battelle-Columbus study.[65] Because of the possibility of carbon and hydrogen-containing aerosols from other nonautomotive sources influencing this ratio, however, agreement may only be fortuitous.

The carbon/nitrogen (C/N) ratio for the total St. Louis aerosol is 4.8. The West Covina ratio of 4.3 is somewhat lower than the St. Louis ratio. It is probable that this ratio is lower due to the higher $NO_3^-$-nitrogen in the West Covina atmosphere, although an alternative explanation would be that primary carbonaceous exhaust aerosol comprises a larger fraction of the total carbonaceous aerosol in West Covina than in St. Louis. In view of our downwind (well-aged air mass) sampling site in West Covina, this latter explanation appears unlikely.

The higher C/N ratios in the large particle-size range is undoubtedly caused by the much lower contribution of $NH_4^+$-nitrogen in this size fraction.

An important step in understanding the fate of nitrogen oxides in the atmosphere involves a determination of the fraction of $NO_x$ which may result in aerosol. Since "total aerosol nitrogen" analyses were performed on the filter samples, we can undertake a filter nitrogen balance to ascertain the extent to which known nitrogen compounds can account for the aerosol nitrogen. Daily West Covina filter nitrogen balances are shown in Table 25. The fraction of total aerosol nitrogen that can be accounted for by $NH_4^+$ and $NO_3^-$ averages 73.6 percent. Nitrite values are not shown in the table because of their negligible impact on the final nitrogen balance. The 26 percent total aerosol nitrogen that cannot be accounted for as $NH_4^+$ or $NO_3^-$ amounts to roughly 0.002 ppm average unexplained aerosol nitrogen in the West Covina atmosphere. If all of this unexplained aerosol nitrogen results from $NO_x$ reactions, then this figure is not negligible in terms of the fate of nitrogen oxides in West Covina. A comparison of the aerosol nitrogen balances for St. Louis, West Covina, Columbus, New York, and Pomona is shown in Table 26. The Columbus, New York, and Pomona data were taken from a previous Battelle-Columbus study.[32] The striking feature of these aerosol nitrogen balances is their similarity from city to city. The question of the identity of the unaccounted-for nitrogen is unresolved at this time. Possibly, the amine and pyridine-type compounds reportedly[36] found in atmospheric aerosol samples by electron spectroscopy chemical analysis (ESCA) will account for the remaining aerosol nitrogen. In an effort to determine whether these basic nitrogen species might be present in our samples, we collected six silver membrane filters in West Covina suitable for ESCA analysis. The filters have been sent to the Lawrence Berkeley Laboratory for analysis; however, at this writing the results are not yet available. For this reason, discussion of the ESCA results must be left for the second year of this study.

**Distribution and Balance of Nitrogen Compounds**

The distribution of gaseous nitrogen compounds in West Covina has been given as averages in Table 10, as composited time-dependent profiles in Figure 3, and as individual daily profiles in Appendix B.

## TABLE 25. WEST COVINA FILTER NITROGEN BALANCE

| Date | Filter | $NH_4^+$-N, mg | $NO_3^-$-N, mg | $\Sigma NH_4^+$-N + $NO_3^-$-N, mg | Total N, mg | $\frac{\Sigma NH_4^+\text{-N} + NO_3^-\text{-N}}{\text{Total}} \times 100$ |
|---|---|---|---|---|---|---|
| 8/23 | 2 | 2.96 | 2.80 | 5.76 | 4.6 | 125.2 |
| 8/24 | 2 | 2.72 | 1.29 | 4.01 | 5.8 | 69.1 |
| 8/26 | 2 | 1.01 | .74 | 1.75 | 2.5 | 70.2 |
| 8/27 | 2 | 1.94 | .41 | 2.35 | 2.8 | 83.8 |
| 8/28 | 2 | 1.94 | .59 | 2.53 | 3.8 | 66.5 |
| 8/29 | 2 | 3.73 | .50 | 4.23 | 6.6 | 64.0 |
| 8/30 | 1 | 6.38 | .50 | 6.88 | 8.0 | 86.0 |
| 8/31 | 2 | 6.22 | .23 | 6.45 | 8.0 | 80.6 |
| 9/3 | 2 | 3.73 | .29 | 4.02 | 5.7 | 70.5 |
| 9/4 | 2 | 8.17 | .14 | 8.31 | 9.3 | 89.4 |
| 9/5 | 2 | 6.30 | .14 | 6.44 | 7.0 | 92.0 |
| 9/6 | 2 | 3.81 | .34 | 4.15 | 7.1 | 58.4 |
| 9/7 | 2 | 8.17 | .45 | 8.62 | 14.0 | 61.6 |
| 9/8 | 2 | 6.30 | .11 | 6.41 | 8.0 | 80.1 |
| 9/9 | 2 | 3.34 | .20 | 3.54 | 5.5 | 64.4 |
| 9/10 | 2 | 3.66 | .27 | 3.93 | 6.3 | 62.4 |
| 9/11 | 2 | 3.03 | .23 | 3.26 | 5.3 | 61.5 |
| 9/12 | 2 | 4.90 | .36 | 5.26 | 9.1 | 57.8 |
| 9/13 | 2 | 8.56 | .29 | 8.85 | 10.8 | 81.9 |
| 9/14 | 2 | 11.67 | .11 | 11.78 | 13.3 | 88.6 |
| 9/17 | 2 | 12.53 | .25 | 12.78 | 13.9 | 91.9 |
| 9/18 | 2 | 13.62 | .27 | 13.89 | 17.2 | 80.8 |
| 9/19 | 2 | 11.28 | .29 | 11.57 | 14.3 | 80.9 |
| 9/20 | 2 | 9.80 | .27 | 10.07 | 11.3 | 89.1 |
| 9/21 | 2 | 6.92 | .45 | 7.37 | 10.3 | 71.6 |
| 9/24 | 2 | 1.87 | .52 | 2.39 | 3.7 | 64.6 |
| 9/25 | 2 | 2.97 | 1.33 | 4.30 | 7.5 | 57.3 |
| 9/26 | 2 | 1.79 | 1.42 | 3.21 | 6.5 | 49.4 |
| 9/27 | 2 | 0.93 | .95 | 1.88 | 4.6 | 40.9 |
| 9/28 | 2 | 1.94 | 1.17 | 3.11 | 4.5 | 69.1 |
| | | | | | Average | 73.6% |

## TABLE 26. AEROSOL NITROGEN BALANCE

| City | Average Aerosol Nitrogen Accounted for as $NH_4^+$ and $NO_3^-$, percent |
|---|---|
| St. Louis, Mo. | 82.5 |
| West Covina, Calif. | 73.6 |
| Columbus, O. | 73.6 |
| New York, N.Y. | 75.8 |
| Pomona, Calif. | 70.7 |

In reviewing the West Covina results presented thus far, we note that, as in St. Louis, the sum of the measured nitrogen oxide reaction products makes up only a small fraction of the average $NO_x$. To understand the fate of nitrogen oxides we must first determine whether we are measuring all the products and observing all the processes which account for $NO_x$ removal from the atmosphere. Such a determination can only be made by ascertaining the balance between nitrogen oxides and their reaction products. The method used for deriving the nitrogen balance will be the same as that employed earlier for the St. Louis results. Before turning to the nitrogen balance, however, it is important to first examine the data for general trends and relationships which may improve our understanding of the conditions under which nitrogen oxides are removed from the atmosphere.

**Statistical Interpretation.** The initial scanning of the data was again accomplished using the Automatic Interaction Detector (AID) statistical routine. The graphic-tree outputs for the initial AID analyses of our West Covina data bank are given in Appendix C. A list of the dependent variables employed in the AID analyses and the three primary predictor variables for each is shown in Table 27. Several important similarities are apparent from comparison of this table with the corresponding St. Louis AID

**TABLE 27. WEST COVINA AID RESULTS (FIRST THREE PREDICTOR VARIABLES)**

| Dependent Variable | Three Primary Predictor Variables | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| $NO_x$ | $O_3$ (–) | Humidity (–) | $HNO_3$ (+) |
| PAN | $O_3$ (+) | NO (–) | $HNO_3$ (+) |
| $HNO_3$ | PAN (+) | $NO_2$ (+) | $O_3$ (+) |
| $NH_3$ | $O_3$ (+) | $NO_2$ (+) | PAN (–) |
| $NH_4^+$ (Excluding Total Aerosol N) | $NO_x$ (+) | $NH_3$ (–) | $HNO_3$ (–) |
| $NO_3^-$ | Wind Speed (–) | NO (+) | Temperature (–) |
| Total Aerosol Nitrogen | $NH_4^+$ (+) | $NO_2$ (+) | $NO_x$ (+) |
| Mass Loading | Wind Speed (–) | $HNO_3$ (+) | — |

results in Table 16. First, the three primary predictor variables for $NO_x$ are the same in both cities – namely, ozone, relative humidity, and nitric acid. The relationships of these variables to $NO_x$ are also in the same direction for both cities. While recognizing the inherent limitations of these statistical relationships, the similarity between the two cities still is so striking that it strongly implies similar processes occurring in both cities. Continuing with Table 27, we note that $O_3$ is one of the primary predictors of PAN and nitric acid concentrations, as it was in St. Louis. The relationship is also positive in both cities; that is, high ozone levels predict high concentrations of PAN and $HNO_3$. The negative correlation between $O_3$ and $NO_x$, along with the positive correlation between $O_3$ and the $NO_x$ reaction products, PAN and $HNO_3$, is completely consistent with current kinetic mechanisms of photochemical smog processes. As might be expected, PAN and $HNO_3$ are strong positive predictors of one another.

The remainder of Table 27 is interesting in itself and in comparison with the St. Louis results; however, these results are not directly pertinent to the fate of nitrogen oxides and will not be discussed further here. It must be emphasized that the aerosol results in the table are derived from daily aerosol collections and, consequently, are based on a much more limited number of observations than the gas-phase results.

Using the AID results as a guide toward potentially important relationships, a series of regressions was undertaken for further documentation of some of the relationships just discussed. Results from these regression analyses are shown in Table 28. Only 6:00 a.m. to 6:00 p.m. data were used in the first series of tabulated regressions in order to examine relationships during the irradiated portion of the day. The relationships between $NO_x$ and its three most important predictor variables are in the same directions as the corresponding St. Louis regressions given in Table 18, although the West Covina correlation coefficients are not nearly as strong as those for St. Louis, In fact, the correlation coefficients are so low as to be almost meaningless. This no doubt reflects the fact that the major determinants of $NO_x$ concentration are variables such as traffic density and meteorology.

**TABLE 28. WEST COVINA REGRESSIONS**

6 a.m. - 6 p.m. Data

| y | x | R |
|---|---|---|
| $NO_x$ | R.H. | 0.13 |
| $NO_x$ | $O_3$ | -0.26 |
| $NO_x$ | $HNO_3$ | 0.10 |
| $O_3$ | NO | -0.41 |
| $O_3$ | $NO_2$ | 0.30 |
| $O_3$ | PAN | 0.78 |
| $O_3$ | $HNO_3$ | 0.63 |
| $HNO_3$ | Global | 0.40 |
| $HNO_3$ | $NO_2$ | 0.47 |
| $HNO_3$ | PAN | 0.71 |

The correlations between $O_3$ and PAN, $O_3$ and $HNO_3$, and PAN and $HNO_3$ are relatively strong, reinforcing the contention that PAN and $HNO_3$ formation are related to ozone and therefore that ozone must play a role in determining the fate of nitrogen oxides. It is also interesting to note in the table that the $O_3$-$NO_2$ coefficient is positive in West Covina, while it was negative in St. Louis. This sign reversal may reflect some interaction effect not yet fully understood.

A second series of regressions is shown in the upper portion of Table 29 where the maximum hourly average concentrations of $O_3$, PAN, and $HNO_3$ have been run against the 6:00-9:00 a.m. averages of either NO or $NO_2$. These correlation coefficients are very low, undoubtedly because the interaction of hydrocarbons has not been taken into account. Hydrocarbon data may well be incorporated into the data analysis during the second year of this program.

Two regressions shown in the lower portion of Table 29 are for maximum daily 1-hour PAN and $HNO_3$. The $O_3$-PAN coefficient is relatively high, as in St. Louis. In contrast to St. Louis, the $O_3$-$HNO_3$ coefficient is also rather high. The slope (m) of the regression lines is also given in this table. The slope found for the $O_3$-PAN curve is 2.7, in good agreement with the value of 3 found by Lonneman [61] for several U.S. cities. The $O_3$-$HNO_3$ slope is also very close to this value of 3. The fact that the $O_3$-PAN and $O_3$-$HNO_3$ slopes are so similar but the average PAN concentration is considerably higher than $HNO_3$

**TABLE 29. WEST COVINA REGRESSIONS**

Maximum Hourly $O_3$, PAN, $HNO_3$
6-9 A.M. NO, $NO_x$

| y | x | R | m |
|---|---|---|---|
| $O_3$ | NO | 0.13 | 0.06 |
| $O_3$ | $NO_x$ | 0.27 | 0.12 |
| $NO_x$ | PAN | -0.03 | -0.24 |
| $NO_x$ | $HNO_3$ | 0.15 | 1.65 |
| $O_3$ | PAN | 0.76 | 2.73 |
| $O_3$ | $HNO_3$ | 0.58 | 2.92 |

further confirms the view that PAN persists longer in an air mass than $HNO_3$ and that the scavenging processes for $HNO_3$ are probably more rapid than those for PAN.

**Nitrogen Balance.** From the statistical treatment of the West Covina data just discussed, it is clear that a determination of the amount of $NO_x$ removed from the atmosphere is necessary in order to reduce the masking effect which the major determinants of $NO_x$ concentration are having on the subtle processes which remove $NO_x$ from the atmosphere. The method which will be used to calculate "$NO_x$ loss" from the West Covina atmosphere is the same procedure used in St. Louis. However, in West Covina, accurate gas chromatographic measurements of the tracers CO and $C_2H_2$ are not available at this time. These measurements, taken simultaneously with our monitoring data by the General Motors mobile laboratory situated next to our laboratory in West Covina, will be made available shortly and will be incorporated in our data base for use in our continuing data analysis effort. Meanwhile, with the consent of the CAPA-9 Project Committee, we have proceeded with the West Covina data analysis using tracer data (CO) from the nearest available monitoring station, the LAAPCD site in Azusa, California. The Azusa data on CO, $NO_x$, and hydrocarbons is included in Appendix B of this report.

Initially, two options were available to us for analyzing the CO and $NO_x$ data for "$NO_x$ loss"; (1) we could use the CO data from Azusa in conjunction with our own $NO_x$ data from West Covina or (2) we could use Azusa data for both CO and $NO_x$. The first option was ruled out by correlational analysis of the $NO_x$ data from the two sites. The correlation coefficient for the data from the two sites was low enough ($R = 0.4$) that it indicated time lags and, possibly, different local source intensities for the two sites. The use of CO data from one site as a tracer for $NO_x$ concentrations at the other station appeared dubious. This is not too surprising, since the sites are roughly 5 miles apart. We decided, therefore, to use the CO and $NO_x$ data from Azusa to calculate "$NO_x$ loss". This "$NO_x$ loss" could then be compared with the $NO_x$ reaction products' concentrations which we had determined in West Covina in order to derive a nitrogen balance. The rationale for making this comparison is as follows: CO and $NO_x$ at the two different sites do not correlate well because they are primary pollutants and are strongly influenced by local source fluctuations (traffic patterns, etc.). However, factors such as PAN concentration, $HNO_3$ concentration, and extent of $NO_x$ loss are properties characteristic of large-scale air masses and as such should be intercomparable over spatial distances as small as 5 miles. One potential problem with these comparisons may be time lag; there is no assurance that air masses will reach the two monitoring stations at the same time. We must remain aware of the possible time lag problem in our subsequent discussions of the data.

One possibly beneficial side effect accruing from our use of the Azusa $NO_x$ data results from the fact that the LAAPCD employs colorimetric rather than chemiluminescent methods for $NO_x$ analysis. This eliminates the tricky problem of correcting our chemiluminescent $NO_x$ data for variable PAN and $HNO_3$ interferences. It is interesting to note that the average $NO_x$ concentration at Azusa during the

course of this study was 0.122 ppm, while the average West Covina $NO_x$, as determined by chemiluminescence, was 0.136 ppm. While the agreement is already quite good, if we assume quantitative interference with the $NO_2$ chemiluminescent determination by PAN and nitric acid, then the corrected West Covina $NO_x$ average is 0.124 ppm, in even better agreement with the Azusa data.

One negative aspect of our use of the Azusa data involves the nondispersive infrared (NDIR) procedure used by LAAPCD for carbon monoxide. This technique has been shown[66] to be less sensitive, less accurate, and more prone to interference than gas chromatographic techniques. Indeed, the sensitivity of the technique is such that LAAPCD reports CO concentrations in ppm as whole numbers only. This is certainly sufficient for most monitoring purposes; however, our calculation of "$NO_x$ loss" is so sensitive to the CO concentration that we must again turn to regression analysis for the most precise determination of the crucial $CO/NO_x$ ratio.

The regression plot of CO versus $NO_x$ is shown as Figure 7. The use of integer CO values is obvious from the stratification of the plot. The numbers within the coordinate system refer to the number of points falling on the same spot. Nine or more coinciding points are represented by the number nine. The total number of points in the plot is close to 700.

The correlation coefficient of 0.73 shown in the statistical tabulation in the figure is quite reasonable for two primary pollutants which are both associated to some degree with auto emissions. Interestingly, this is the same coefficient found for the St. Louis $CO\text{-}NO_x$ regression. The most important information to be derived from this plot is its slope, 18.4 ± 0.6 in consistent units, and its intercept, 1.43 ± 0.06 ppm CO. Fitting this slope and the most recent $CO/NO_x$ emissions inventory ratio for Los Angeles[67] into Equation (2) yields:

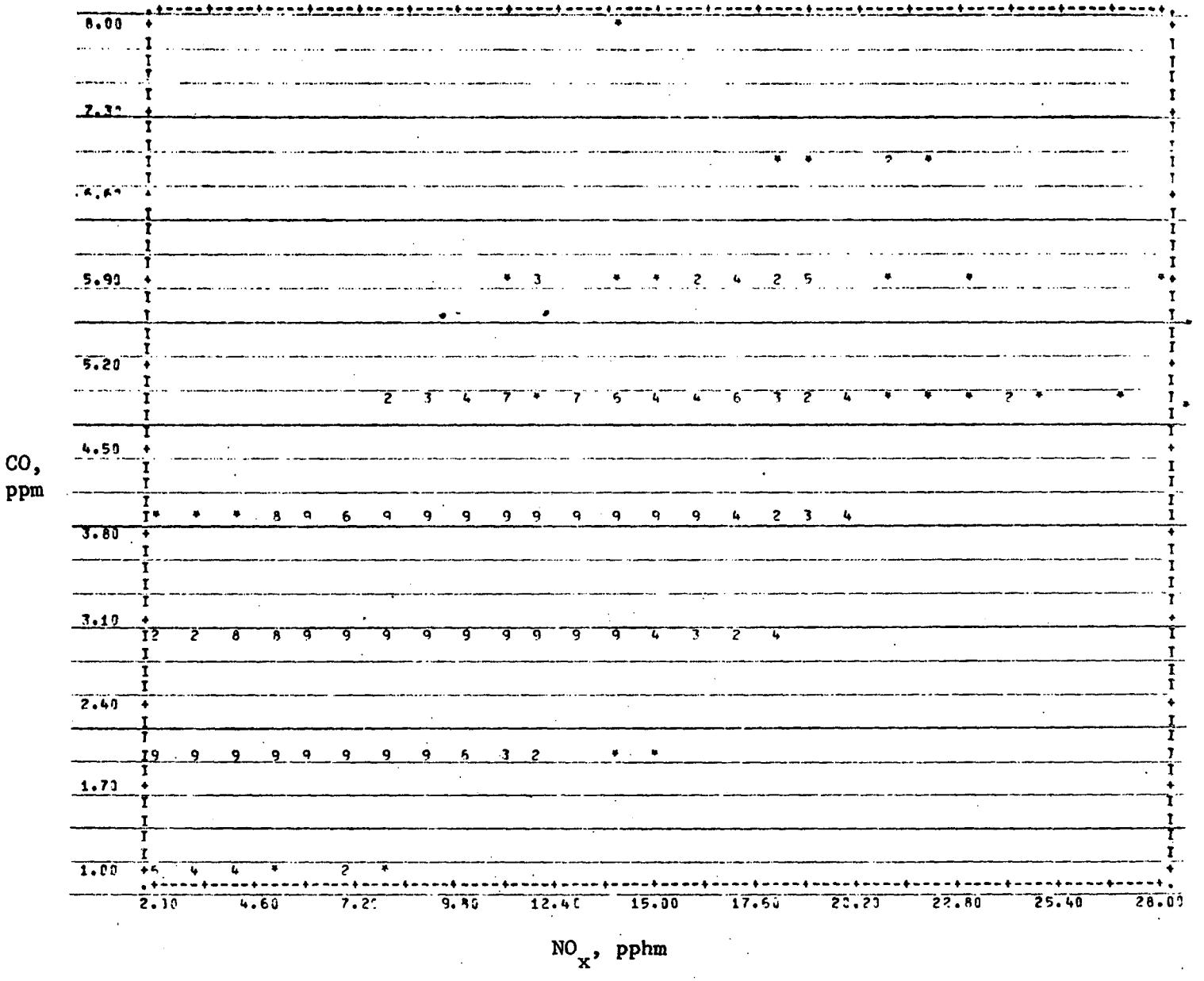
$$NO_x \text{ loss} = \left[\frac{(CO/NO_x)_m}{(CO/NO_x)_{E.I.}} - 1\right] NO_{x_m} \quad , \tag{2}$$

$$NO_x \text{ loss} = \left[\frac{18.4 \pm 0.6}{14.3} - 1\right] (0.122) \quad ,$$

$$NO_x \text{ loss} = 0.035 \pm 0.006 \text{ ppm} \quad .$$

Thus, 0.035 ± 0.006 ppm is the average $NO_x$ loss during our monitoring effort in West Covina. The 6-ppb deviation is merely the statistical deviation about the slope calculation. There are several sources of error which may be having a much greater impact on the accuracy of the "$NO_x$ loss" value. First, the calculation depends on the accuracy of emission inventories which are over 2 years old. Second, it depends on the elimination of a CO intercept value which is no longer just a geologic background CO term, but which now presumably incorporates insensitivity and inaccuracy of the analytical technique along with the background CO. An important argument in favor of eliminating the CO intercept requires thinking of the extrapolation to zero $NO_x$ (the CO intercept) in physical terms. Since virtually all CO sources included in the emissions inventory are also $NO_x$ sources (over 90 percent of Los Angeles CO comes from auto exhaust, while less than 70 percent of the $NO_x$ is from automobiles), the CO remaining when all $NO_x$ sources are eliminated (extrapolation to zero $NO_x$) must not be part of the emissions inventory ratio and therefore must not be included in the $(CO/NO_x)_m$ ratio regardless of its origin.

In terms of a nitrogen balance, we can account for an average of 0.012 ppm of the missing $NO_x$ by the sum of PAN and nitric acid; $NO_3^-$ along with the remainder of the unidentified aerosol nitrogen can account for an additional few parts per billion. At best, however, the measured $NO_x$ reaction products can account for less than 20 ppb of the missing $NO_x$ on the average. Because of the many factors which may be influencing the accuracy of the "$NO_x$ loss" calculation, we cannot at this time make an unqualified judgment as to the "goodness" of the nitrogen balance. If the assumptions made here are justified, then the balance must be close (certainly, three-fourths of the $NO_x$ is not lost immediately after emission, as has been suggested), but a more exact balance must await the inclusion of the more accurate CO and $C_2H_2$ data in the second year of this investigation.




STATISTICS..

| | | | | | |
|---|---|---|---|---|---|
| CORRELATION (R) - | .72795 | R SQUARED - | .52861 | SIGNIFICANCE R - | .000 |
| STD ERR OF EST - | .77171 | INTERCEPT (A) - | 1.43275 | STD ERROR OF A - | .060 |
| SIGNIFICANCE A - | .0:051 | SLOPE (B) - | .18377 | STD ERROR OF B - | .005 |
| SIGNIFICANCE B - | .0:001 | | | | |

**FIGURE 7. SCATTERGRAM OF L.A.-DATA FATE OF $NO_x$**

In the foregoing discussion, we have computed an average "$NO_x$ loss" for our 5 weeks of monitoring in the Los Angeles basin and have used this average loss term to determine the average nitrogen balance in the West Covina atmosphere. In order to elucidate the factors which are influencing atmospheric $NO_x$ loss, it would be quite instructive to examine the time dependence of the removal of $NO_x$ from the atmosphere. Presumably, a knowledge of this time dependence of the removal processes might indicate the nature of the removal mechanisms. Once the temporal variation in "$NO_x$ loss" is available it can be compared statistically with the fluctuation in our other measured chemical and meteorological parameters. Plots of the calculated "$NO_x$ loss" for the entire West Covina monitoring program are shown in Figure 8. These plots were made with the raw CO and $NO_x$ data and must be corrected to account for the error introduced by the CO analytical problems mentioned earlier. Unfortunately, we have no way of correcting each individual hourly average; we must apply a general correction derived from the CO intercept of Figure 7. To compute the average error caused by the CO intercept, we rearrange Equation (1) to split the CO term into slope and intercept contributions:

$$NO_x \text{ loss} = \frac{[CO]_{slope} + [CO]_{intercept}}{(CO/NO_x)_{Emission\ Inventory}} - [NO_x]_{measured} \quad , \tag{4}$$

$$\text{Intercept correction} = \frac{[CO]_{intercept}}{[CO/NO_x]_{E.I.}} = \frac{1.43}{14.3} \quad , \tag{5}$$

$$\text{Intercept correction} = 0.100 \text{ ppm} \quad .$$

This CO intercept correction factor may now be subtracted from each hourly "$NO_x$ loss" value to account for the *average* inaccuracy in the CO concentration. Obviously, the CO inaccuracy is going to fluctuate from hour to hour and day to day; applying this correction will account for the average inaccuracy, but we must still expect to see positive and negative variation in the corrected "$NO_x$ loss" profile. The correction has been made in Figure 8 merely by drawing a new baseline at 0.100 ppm $NO_x$ loss. Variation in $NO_x$ loss should be judged starting from this corrected baseline. It is interesting to note that for many of the days shown in Figure 8 the new 0.100 ppm baseline seems to correspond quite well with what might be described as the natural baseline that the curves themselves indicate. On days of milder photochemical smog (as judged by the lower $O_3$ levels in Table 10), such as September 4, 9, and 10, the natural baseline appears to be very similar to the artificial 0.100 ppm baseline we have drawn. Further evidence of the appropriateness of this correction factor will be discussed shortly.

Using the corrected hourly average "$NO_x$ loss" values just computed as the dependent variable, we can run an AID analysis on our entire West Covina data bank to indicate which variables are correlated well with $NO_x$ removal from the atmosphere. The graphic-tree outputs from these AID runs are included in Appendix C. A tabulation of the AID results is given in Table 30. In the first AID run, PAN was unquestionably the best predictor of "$NO_x$ loss", with nitric acid and ozone also important variables. Since PAN, nitric acid, and ozone were shown earlier to be highly correlated in West Covina, the first split, occurring on PAN, removes some of the potency from the $HNO_3$ and $O_3$ predictor capacities. However, PAN is such a strong predictor that it does appear again in split number three. The significance of the split on temperature, which is negative in sign, is unclear at this time.

In the second AID run, PAN was omitted as an independent variable in order to determine what other factors were correlated with $NO_x$ loss. Nitric acid and ozone were the most important predictor variables, with the inverted temperature correlation appearing again. Solar intensity, which is well correlated with $O_3$, also appeared as an important splitter. In the third AID analysis both PAN and $HNO_3$ were removed from the data set. Ozone appeared as the most important predictor of $NO_x$ loss in this run, as expected from the two earlier analyses.

Using the AID results for guidance, several regression analyses have been carried out to further document the statistical relationship between "$NO_x$ loss" and the important predictor variables. The regression results are shown in Table 31. Slopes (m) and intercepts (b) are included in the table. All of the correlation coefficients given in the table are reasonably high, with the exception of those for $NO_{x\ avg}$, temperature, relative humidity, and $NO_{3\ avg}^-$.

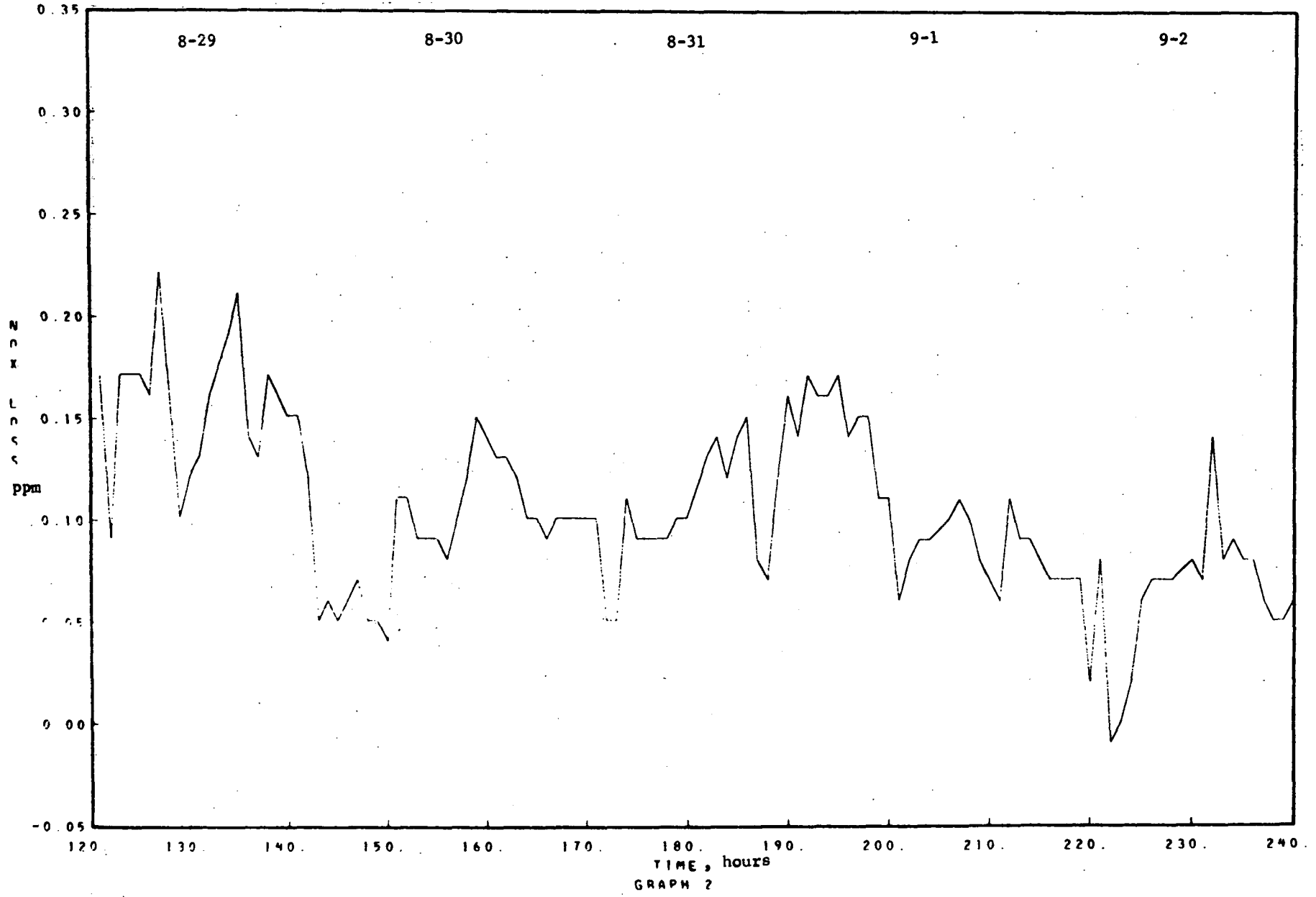



FIGURE 8A. WEST COVINA $NO_x$ LOSS

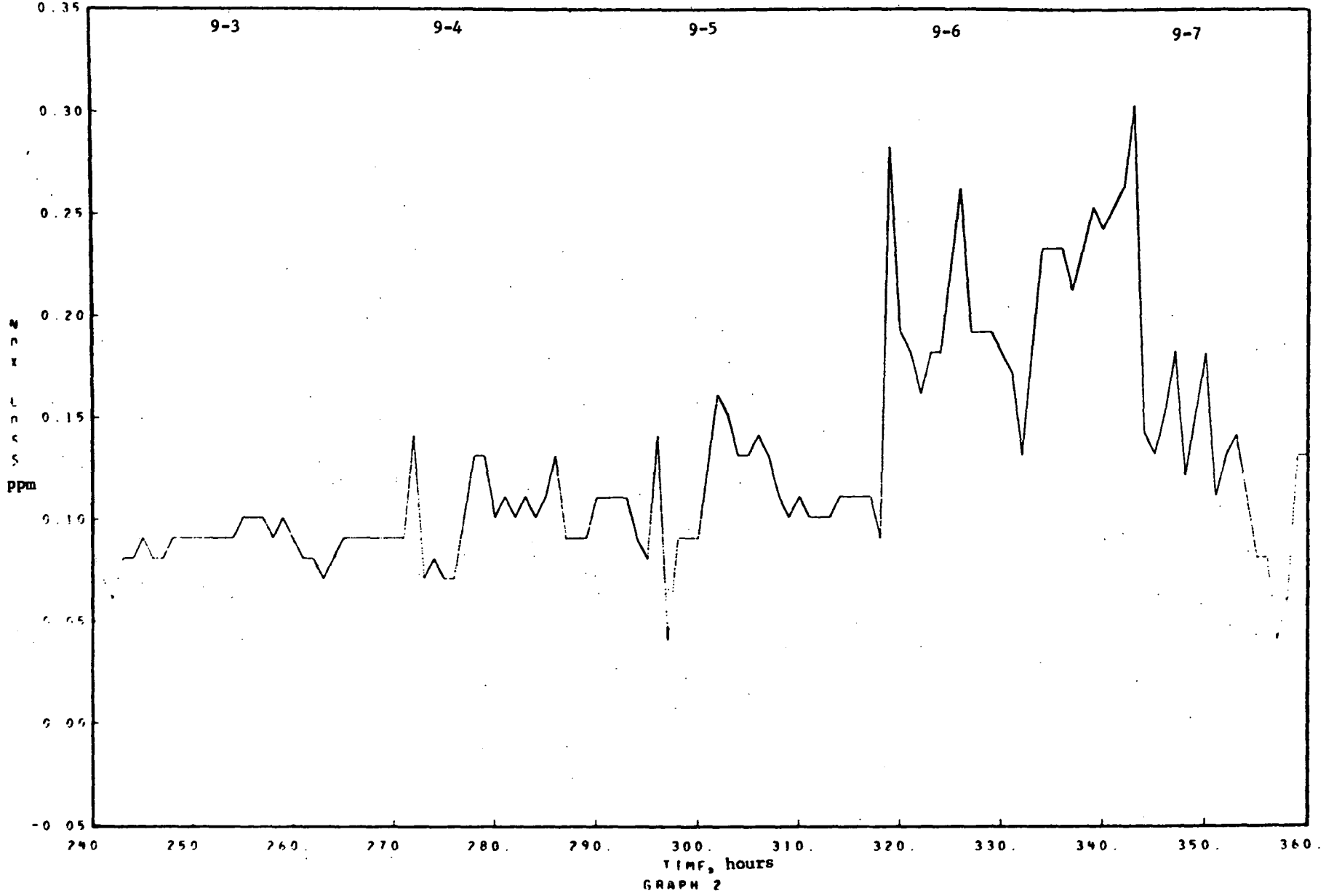



FIGURE 8B. WEST COVINA $NO_x$ LOSS

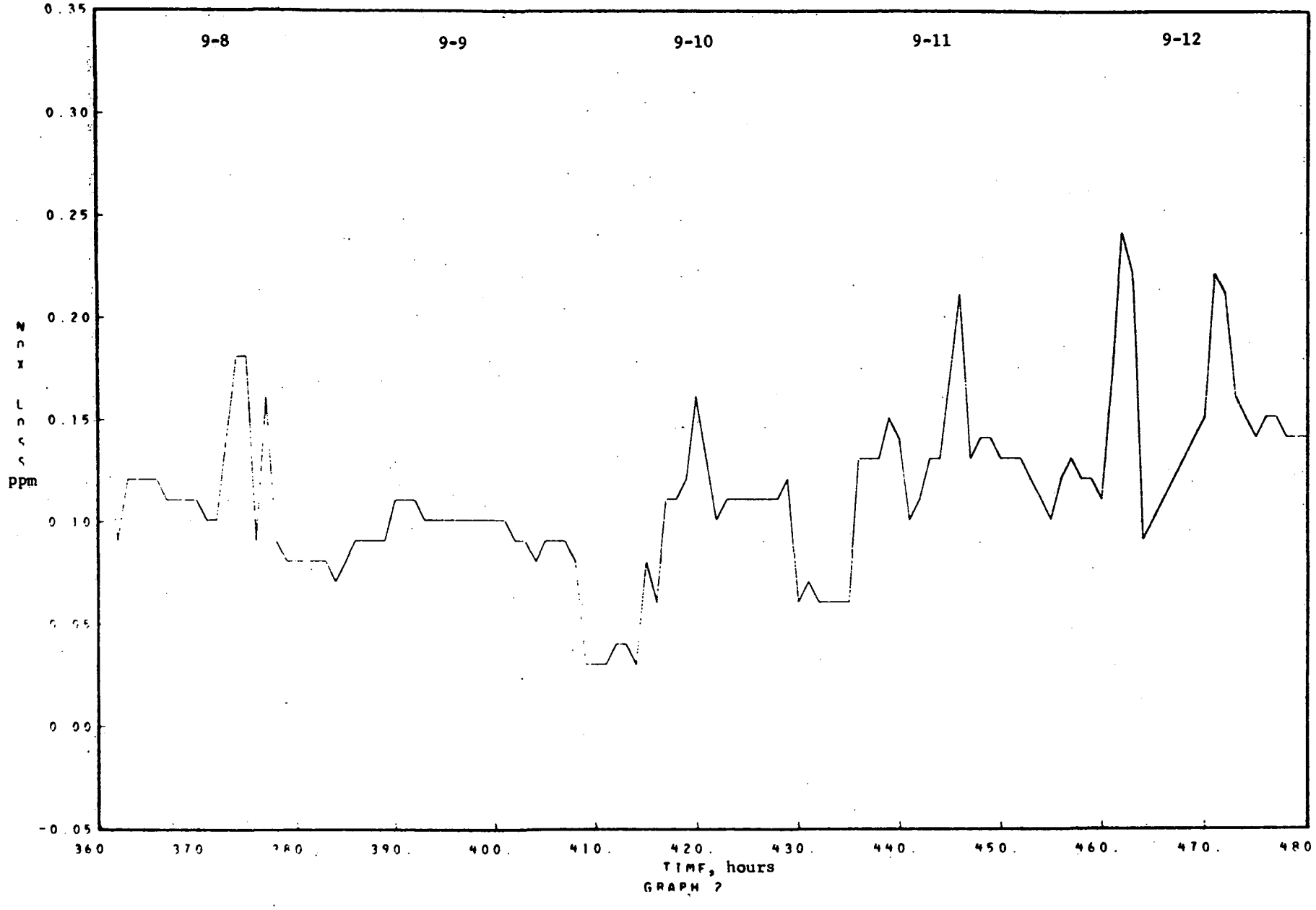



FIGURE 8C. WEST COVINA $NO_x$ LOSS

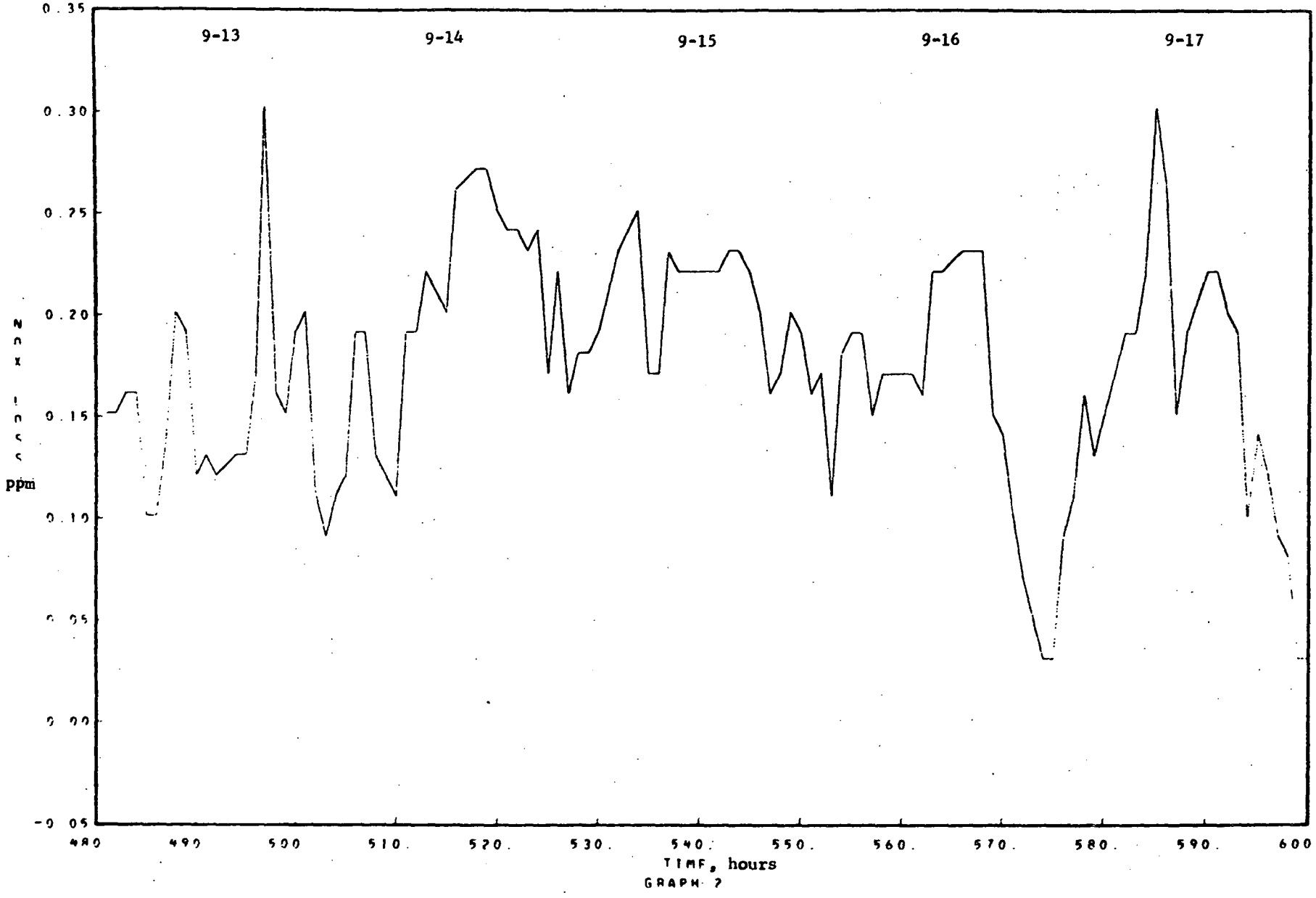



FIGURE 8D. WEST COVINA AND $NO_x$ LOSS

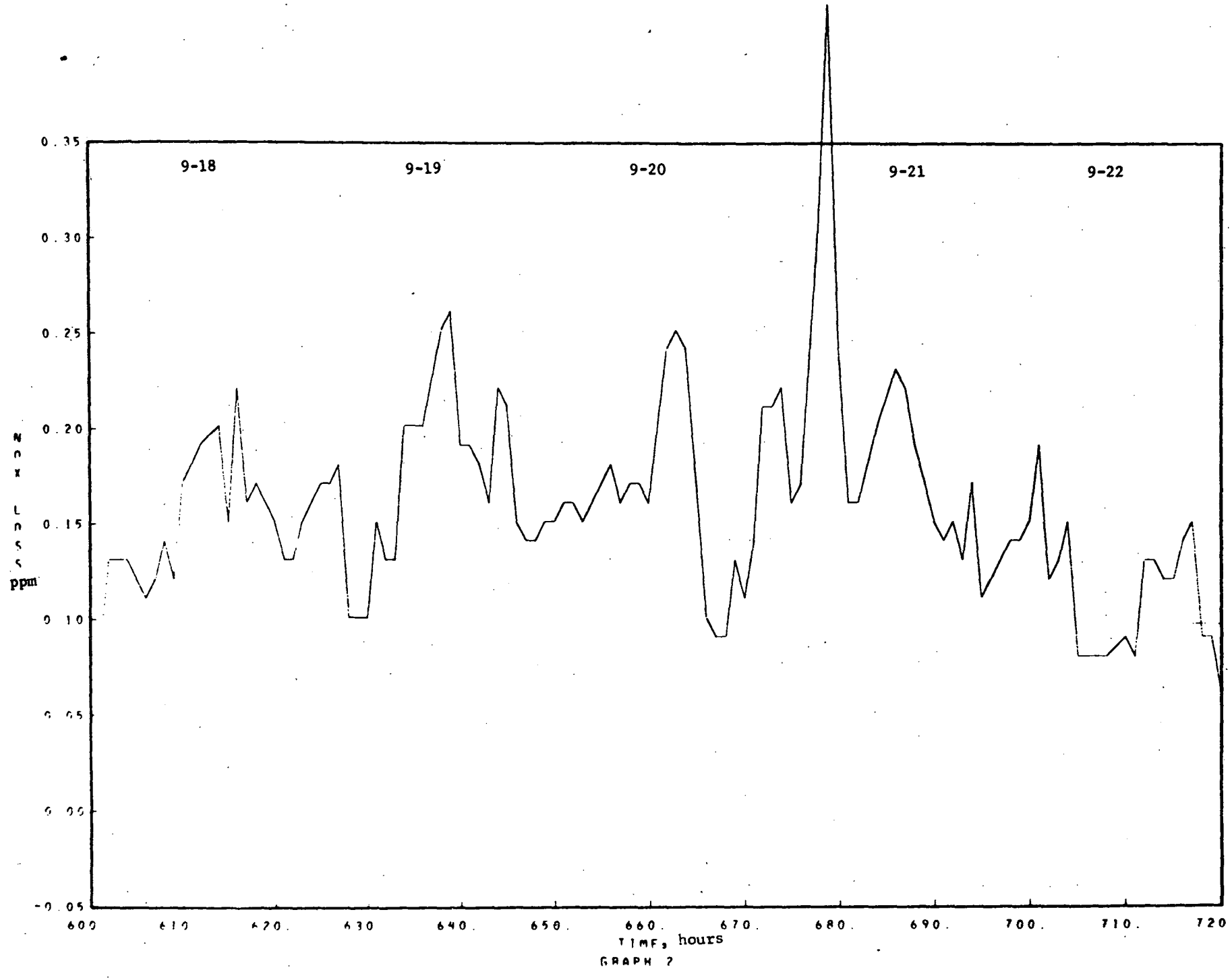



FIGURE 8E. WEST COVINA $NO_x$ LOSS

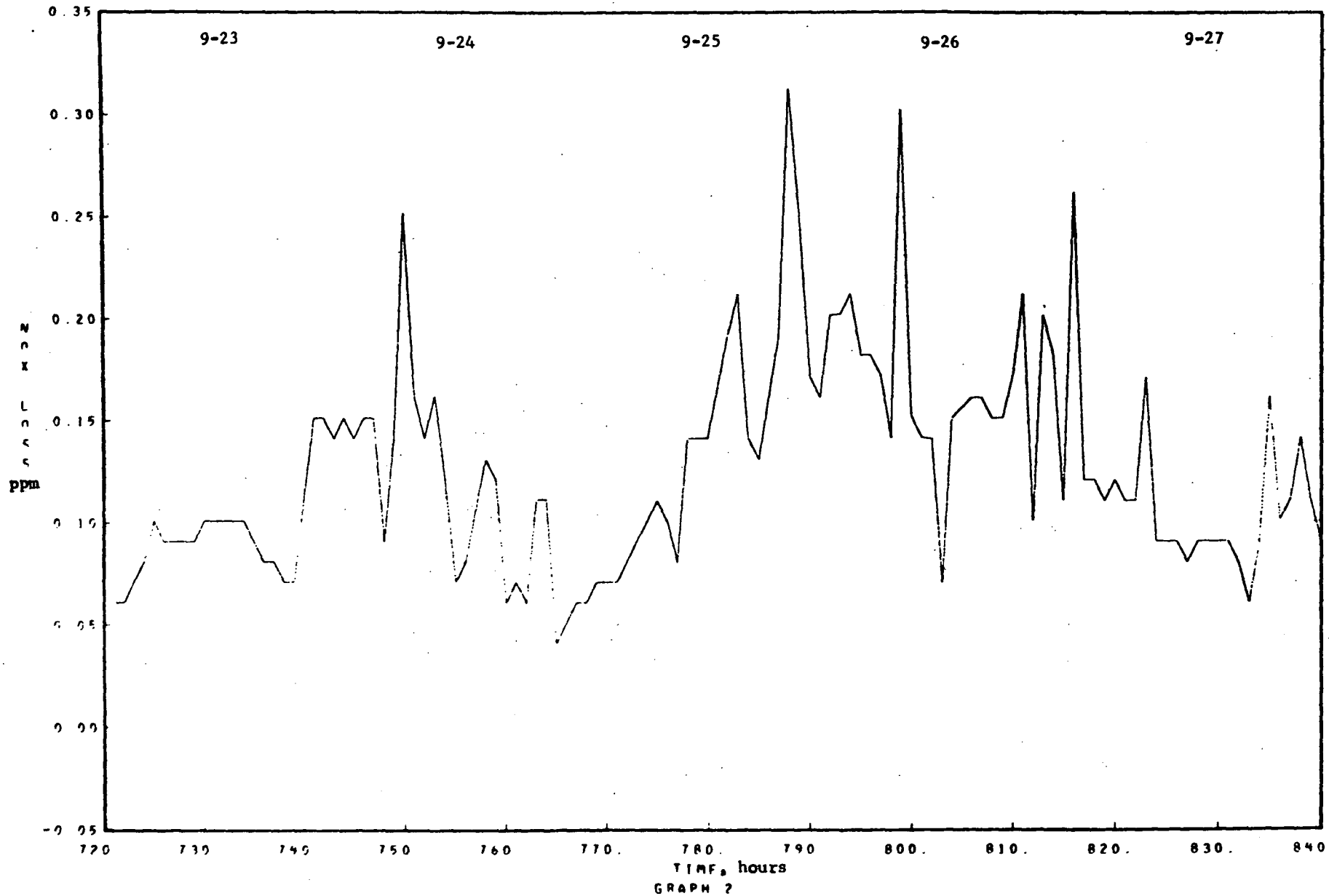



FIGURE 8F. WEST COVINA $NO_x$ LOSS

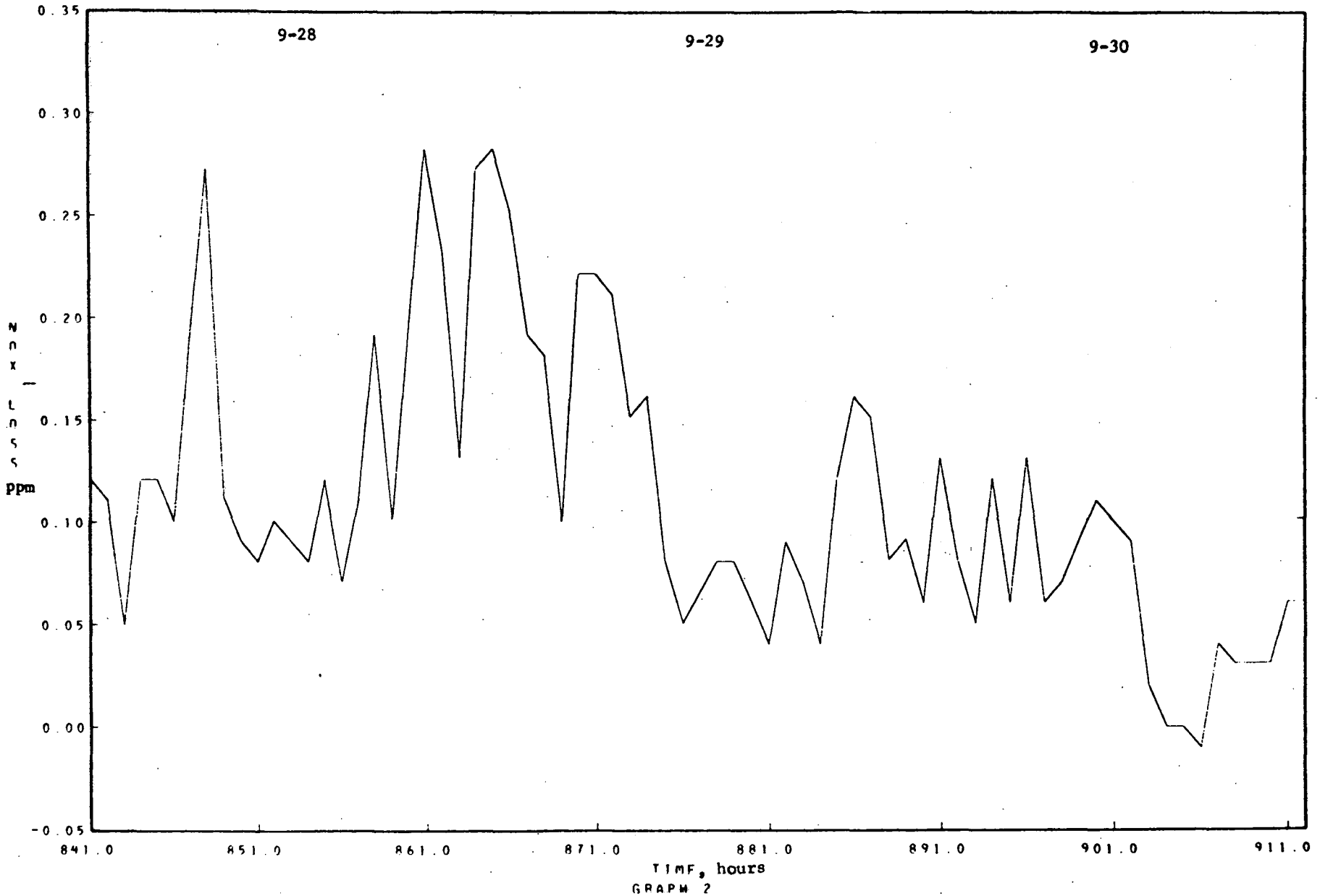



FIGURE 8G. WEST COVINA $NO_x$ LOSS

TABLE 30. RESULTS[a] OF AID ANALYSIS OF "$NO_x$ LOSS" DEPENDENT VARIABLE

| Run Number | Variable Omitted | Splitting Order and BSS/TSS of Split | |
|---|---|---|---|
| | | Split Number | |
| 1 | None | 1 | PAN(.18), $HNO_3$(.11), $O_3$(.08) |
| | | 2 | Temp(.09), WS(.08), WD(.07) |
| | | 3 | PAN(.10), WD(.08), RH(.07) |
| | | Split Number | |
| 2 | PAN | 1 | $HNO_3$(.13), $O_3$(.08), RH(.03) |
| | | 2 | Temp(.09), WS(.05), GI(.04) |
| | | 3 | GI(.03), WD(.02), Temp.(.02) |
| | | Split Number | |
| 3 | PAN, $HNO_3$ | 1 | Ozone(.07), Temp(.05), WS(.03) |
| | | 2 | Temp(.08), WS(.06), WD(.03) |
| | | 3 | RH(.04), $O_3$(.03), WS(.02) |

(a) WS is wind speed.
WD is wind direction.
RH is relative humidity.
GI is solar intensity.

TABLE 31. WEST COVINA "$NO_x$ LOSS" REGRESSIONS

Daily Average $NO_x$ Loss
versus
Daily Average or 1-Hr Maximum Data

| y | x | R | m | b |
|---|---|---|---|---|
| $NO_x$ loss | $O_3$ Avg | 0.63 | 1.57 | 0.059 |
| $NO_x$ Loss | $NO_x$ Avg | 0.34 | 0.20 | 0.101 |
| $NO_x$ Loss | $\Sigma$PAN + $HNO_3$ (coulometric) | 0.74 | 3.07 | 0.096 |
| $NO_x$ Loss | Max $O_3$ | 0.68 | 0.45 | 0.057 |
| $NO_x$ Loss | Max $\Sigma$PAN + $HNO_3$ | 0.73 | 1.03 | 0.097 |
| $NO_x$ Loss | Mass Loading | 0.76 | 0.00084 | 0.046 |
| $NO_x$ Loss | Temp | -0.08 | -0.0014 | 0.158 |
| $NO_x$ Loss | R.H. (%) | -0.15 | -0.00035 | 0.166 |
| $NO_x$ Loss | $NO_3^-$ ($\mu g/m^3$) | 0.07 | 0.002 | 0.128 |

The perhaps unexpectedly high correlation between average $NO_x$ loss and aerosol mass loading is probably best understood as a coincidental result; both mass loading and $NO_x$ loss are expected to be highest on photochemical smog days. It is interesting to note that the average "$NO_x$ loss" intercept, i.e., the apparent $NO_x$ loss when all the x-variables are extrapolated to zero, is 0.101 ppm "$NO_x$ loss" — in extremely good agreement with the artificial "$NO_x$ loss" baseline which we calculated earlier. This average intercept indicates an *apparent* $NO_x$ loss of 0.1 ppm, which is an average invariant to changes in the independent variables shown in the table. Obviously, an $NO_x$ loss invariant to all external changes is physically untenable and indicates some constant error in the calculation. We believe that this apparent $NO_x$ loss is merely a further manifestation of the CO intercept error and that the agreement between the two values is further confirmation of the validity of the calculated correction factor.

Speculation as to the significance of the slopes of these regression lines in intriguing; however, we do not believe such a discussion is warranted at this time due to the many sources of error which may be influencing these results. We would like to reserve such a discussion until after the data analysis and interpretation phases of the second-year program have been completed.

Some very important progress in understanding the fate of nitrogen oxides has now been made. We have separated out of the overall $NO_x$ concentration profile the gross factors influencing $NO_x$ variation, leaving us with time-dependent profiles of $NO_x$ that has been chemically or physically removed from the atmosphere. The variations in "$NO_x$ loss" have subsequently been analyzed, with the result that PAN, $HNO_3$, and $O_3$ are all highly correlated with the loss fluctuations. Along these lines, we have determined that the average $NO_x$ loss during our 5-week stay in West Covina was only a small fraction of the average total $NO_x$ concentration, on the order of 30-40 ppb. Although the error limits around this loss value could be as large as 50 percent because of the many factors affecting the calculation, the important point is that the average $NO_x$ loss is low. Another important finding is that the sum of PAN, nitric acid, and aerosol nitrogen can account for a major fraction, if not all, of the $NO_x$ loss.

One final view of the problem can be gained by examining the time dependence of the composited $NO_x$ loss profile. This 5-week averaged plot is shown in Figure 9. It should be observed first of all that the data form their own baseline at approximately 0.120 ppm $NO_x$ loss. This is 20 ppb higher than our artificial baseline derived from the CO intercept correction. This baseline may well be the more accurate, however, since it includes any contribution from dry deposition processes and any inaccuracies due to the emissions inventories; in our previous calculations, we had no way of estimating the effect of this latter source of error. If the actual average correction factor is indeed 0.120 ppm, then the average $NO_x$ loss is 0.035-0.020 or 0.015 ppm. This is almost exactly the average sum of PAN, $HNO_3$, and aerosol nitrate. Further substantiation of the actual nitrogen balance must await the more accurate tracer data to be available for the second-year investigation.

Of the two prominent humps displayed in the "$NO_x$ loss" curve, the second one can be accounted for entirely by the sum of PAN and $HNO_3$. This is illustrated by the profile in the lower portion of the figure. We can say, therefore, that the mechanism of afternoon loss of $NO_x$ is photochemically related and that the magnitude of the loss can be completely accounted for by measured $NO_x$ reaction products.

The explanation for the apparent early morning loss of $NO_x$ is unclear at this time. Obviously, for the "$NO_x$ loss" to increase as shown in the figure, the $(CO/NO_x)m$ ratio must have increased. Since it is during the period when this early morning hump appears that the CO and $NO_x$ emissions sources are undergoing their most dramatic change of the day, the possibility exists that the hump is artificial. The rationale is as follows: A major increase in the auto exhaust contribution to the air mass occurs between 5:00-8:00 a.m., judging from the average $NO_x$ profile in Figure 3. Since auto exhaust has a considerably higher $CO/NO_x$ ratio than the normal Los Angeles basin mixture (approximately 24 versus 14.3), our morning "$NO_x$ loss" peak may only be a result of a different emissions mix at that time of day and not truly reflect removal of $NO_x$ from the air mass. Indeed, if the additional morning auto exhaust burden (at a $CO/NO_x$ of 24) raises the normal $CO/NO_x$ ratio from 14.3 to 16.5, then the 6:00 a.m. morning peak would be completely eliminated. At this time there is no sure way to incorporate a variable emission inventory ratio into our calculations, although it seems very likely that the emissions ratio must vary during the day due to traffic patterns. At this point we can only suggest the variation in the $CO/NO_x$ emissions ratio as a probable cause of the apparent morning $NO_x$ loss.

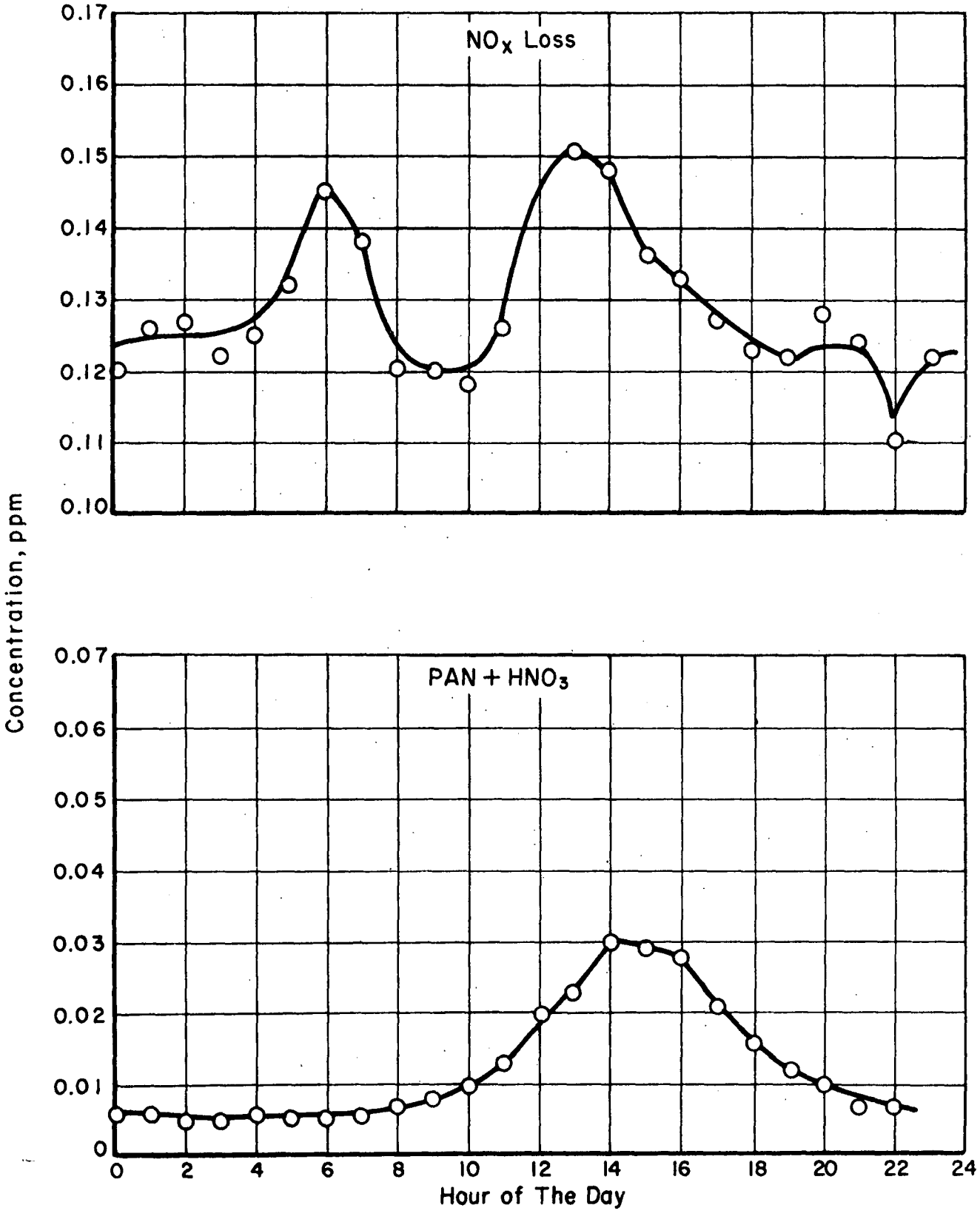



**FIGURE 9. WEST COVINA $NO_x$ LOSS AND PAN + $HNO_3$ PROFILES**

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