Trace Nitrogenous Species in Urban Atmospheres

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Recent results concerning the identification and measurement of nitrogenous air pollutants in the California South Coast Air Basin (CSCAB) are presented. In planning or evaluating studies of the human health effects of these pollutants, it is important to consider the entire range of species which may be present. We provide estimates of typical exposures to nitrogenous air pollutants during a single day oxidant event in the CSCAB.

A critical requirement in obtaining a better understanding of the nature and magnitude of health effects associated with nitrogenous air pollutants is to extend the quantitative data base concerning the atmospheric burden of such pollutants. Thus, it is important to have detailed information on the concentrations and temporal and geographical distributions not only of nitrogen dioxide—which, as a criteria pollutant, has been a prime focus of regulatory action—but also of the host of other toxic or potentially toxic nitrogenous copollutants. Many of these have been observed in laboratory or environmental chamber systems but until recently have not been unequivocally identified and measured in ambient air. Reliably determined atmospheric concentrations of the nitrogenous air pollutants are one important criterion for judging the relevancy of clinical and laboratory studies of their biological effects to health impacts resulting from human exposure to ambient polluted atmospheres.

We present here recent results from our laboratory concerning the spectrum of nitrogenous species potentially contributing to health effects of *photochemical air pollution and* indicate our present understanding of typical concentrations and exposures for nitrogenous species (Tables 1 and 2) in one severely impacted airshed: the Cali-

fornia South Coast Air Basin (CSCAB). It should be emphasized that while some of the nitrogenous species we discuss may be labeled "trace" from a purely quantitative point of view and are not currently designated as "criteria" pollutants, their individual and/or synergistic contributions to overall health effects may nevertheless be significant.

The atmospheric chemistry of oxides of nitrogen is complex. It involves part-per-billion (ppb) to part-per-trillion (ppt) concentrations of a number of highly reactive species which participate in a variety of homogeneous and heterogeneous thermal and photochemical reactions. Conventional methods of analysis, as applied to the criteria pollutants, lack the requisite sensitivity and specificity for the detection and characterization of such "trace" species. Thus, it remained for the development, starting in the early 1970s (1), of long-pathlength ($>$ 1 km) spectroscopic methods to permit the *in situ* identification and quantitation of gaseous species such as nitric acid (HNO_3), by Fourier transform infrared (FT-IR) absorption spectroscopy (2), and nitrous acid (HONO) and the nitrate radical (NO_3) by rapid-scan ultraviolet/visible differential absorption spectroscopy (3). Our use of these instruments led to the first unequivocal spectroscopic identification of these three species in the CSCAB and determination of their ambient levels at several source and receptor sites (4–7). These new ambient air data, together with information derived from studies of

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Table 1. Concentration ranges for gaseous nitrogenous pollutants observed in the CSCAB.

Compound	Range of peak concentrations ppb	Time of peak concentration	Approximate one-day exposure, ppb-hr[a]
Nitric acid (HNO$_3$)	<50	Midafternoon	250
Peroxyacetylnitrate (PAN)	<40	Midafternoon	150
Nitrogen dioxide (NO$_2$)	100-800	Morning/afternoon	1500
Nitrous acid (HONO)	1-8	Early morning	20
Nitrate radical (NO$_3$)	0.005-0.350	Early evening	<0.5

[a]Estimated for a 24-hr period including a moderate air pollution event; exposures exhibit wide day-to-day and site-to-site variations within the CSCAB.

Table 2. Compounds observed in simulated atmospheres with ranges of concentrations predicted for polluted urban atmospheres.

Compound	Range of peak concentrations ppt	Time of peak concentration	Approximate one-day exposure, ppb-hr[a]
Peroxynitric acid (HO$_2$NO$_2$)	50-200	Midafternoon	<1
Peroxyalkyl nitrates (RO$_2$NO$_2$)	10-50	Midafternoon	<0.2
Dinitrogen pentoxide (N$_2$O$_5$)	100-1000	Late afternoon and early evening	5-15[b]
Nitrotoluenes/ nitrobenzenes	?	?	
Nitroarenes	?	?	

[a]Estimated for a 24-hr period including a moderate air pollution event; exposures exhibit wide day-to-day and site-to-site variations within the CSCAB.
[b]Early evening exposure deduced from observed NO$_3$ at Riverside (5).

simulated atmospheres, provide a basis for more reliably assessing the nature and magnitude of the nitrogenous pollutant dose experienced by receptor populations.

The reactive nitrogen oxides of principal interest are NO, NO$_2$, N$_2$O$_5$ and NO$_3$. The ambient concentrations and diurnal profiles of NO and NO$_2$ in a variety of urban airsheds are well documented and the atmospheric chemistry and health effect implications of these pollutants have been widely discussed (8–10). We will therefore consider here only the higher oxides of nitrogen, NO$_3$ and N$_2$O$_5$.

The gaseous nitrate radical, a product of the reaction of NO$_2$ with ozone, has been postulated to be present in the troposphere on the basis of laboratory studies but was only identified and measured in polluted urban air in 1979 (5). While the daytime concentration of NO$_3$ is strongly suppressed by its rapid photolysis, its concentration after sunset has been observed to be as high as 350 ppt. Some aspects of the chemistry of NO$_3$ in the polluted troposphere are not fully understood; however, it is well recognized that an equilibrium exists among NO$_3$, NO$_2$ and N$_2$O$_5$. Dinitrogen pentoxide has never been observed in ambient air due to the lack of a sufficiently sensitive spectroscopic technique. The compound hydrolyzes to produce nitric acid (11), and this may be a significant pathway for the loss of gas phase NO$_x$ and production of "acid rain." Laboratory studies (12) and our model predictions indicate that N$_2$O$_5$ concentrations may range from 0.1 to 1 ppb, being highest when elevated levels of NO$_x$ and O$_3$ are simultaneously present.

Three oxyacids of nitrogen—HONO, HNO$_3$ and peroxynitric acid (HO$_2$NO$_2$)—have been observed in the gas phase. Nitrous acid represents an important source of the reactive, chain-initiating, hydroxyl radical in the early morning atmo-

sphere (*13*). However, the source(s) of HONO in polluted air, whether primary, secondary or both, are not understood at this time. Our recent observations (*13*) of HONO concentrations ranging up to 8 ppb *near a freeway interchange in downtown Los Angeles* (Fig. 1) has several potential implications for health impacts. The direct health effects of inhaled HONO are unknown at this time, but the possibility of its involvement in *in vivo* nitrosation of secondary amines yielding carcinogenic nitrosamines merits serious consideration.

A separate implication for health effects research methodologies arises from our studies of nitrous acid. We have utilized a short-path version of our differential ultraviolet/visible absorption spectrometer to analyze the contents of the sample bag in a standard apparatus for collecting auto exhaust (*14*) from vehicles operating under load on a chassis dynamometer. We observed nitrous acid concentrations of several parts per million in bags filled by standard procedures in these experiments. Exposure of animals to dilute *auto exhaust delivered by similar systems is a* common approach to assessing the health effects of such exhaust, thus attention should be given to the implications of the probable exposure of experimental animals to substantial but unrecognized levels of HONO (which almost certainly arise from heterogeneous reactions of NO_x precursors in such facilities).

We have also employed the differential ultraviolet/visible absorption spectrometer in studies of heterogeneous formation of HONO in the dark in our 5800-L evacuable environmental chamber (*15*) and have directly observed HONO levels (*16*)
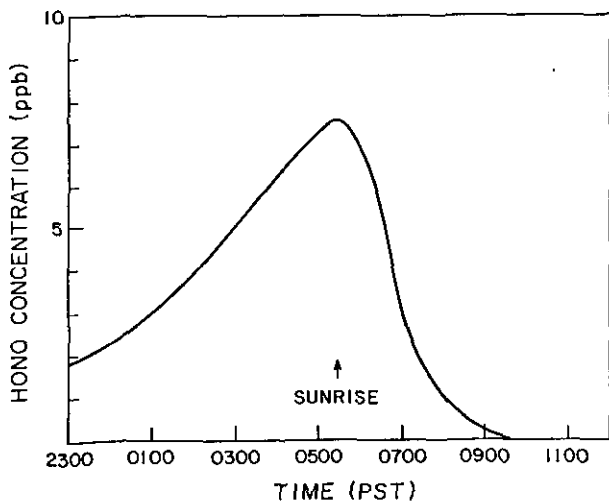
which are in agreement with those deduced from experimental measurements of the rate of radical production at the start of NO_x–air irradiations (*17*). From these studies we have suggested that *the hydrolysis of* NO_2 [Eq. (1)]

$$2\,NO_2 + H_2O \xrightarrow{\text{heterogeneous}} HONO + HNO_3 \qquad (1)$$

may be an important mechanism for the observed HONO production in the dark in our chambers. If this process also occurs in polluted atmospheres, then it would represent a source, of undetermined magnitude, for HNO_3 formation at night. During daylight hours, however, the main formation *mechanism for nitric acid in polluted atmospheres is the homogeneous reaction* (2).

$$OH + NO_2 \xrightarrow{\text{M}} HNO_3 \qquad (2)$$

This process may give rise to gas-phase nitric acid concentrations of up to 50 ppb (*6, 7*) in the midafternoon and *represents the largest homogeneous loss process for* NO_2 *from the photochemical* system. Clearly, in the wider context of overall ecosystem impacts (e.g., acid rain), the processes resulting in the conversion of gaseous NO_x into aqueous nitrate ion are of concern and further studies of the gas phase-aerosol phase interactions of NO_x are needed.

The highest oxyacid of nitrogen, peroxynitric acid (HO_2NO_2), is thought to be of minor chemical significance in polluted urban atmospheres because of its short lifetime with respect to thermal decomposition (*18, 19*). Peroxynitric acid has *never been observed in polluted air,* but our model calculations indicate that its midafternoon peak concentration during an air pollution event may be in the range 50–200 ppt. Whether such concentrations of HO_2NO_2 could have health effects associated with them remains to be investigated.

In addition to the inorganic species discussed above, several classes of organic-nitrogen air pollutants are observed in real and simulated atmospheres. For example, peroxyacetyl nitrate (PAN), a potent phytotoxicant and eye irritant (*20*), has a relatively long thermal decomposition lifetime, in contrast to peroxynitric acid [reaction (3)], and may act as an overnight "reservoir"

$$CH_3CO_3NO_2 \xrightleftharpoons{} CH_3CO_3 + NO_2 \qquad (3)$$
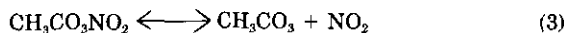
for NO_2 and the CH_3CO_3 radical, a species which *can react with fresh emissions of NO to produce* hydroxyl radicals (*21*). Hence, PAN can be regarded as a chemical link between consecutive

FIGURE 1. Concentration-time profile of nitrous acid, August 1, 1980, Los Angeles, CA.

days of photochemical oxidant formation. Concentrations of PAN have been observed to reach levels of up to 40 ppb in the midafternoon period of an air pollution event (6, 7). Other members of the class of peroxyacyl nitrates (e.g., peroxybenzoyl nitrate, another powerful eye irritant) have also been reported in real or simulated atmospheres (22, 23). As indicated, these species tends to persist during the night leading, in the case of PAN at least, to potentially significant integrated doses for exposed populations (Table 1).

Other organic nitrogen compounds formed from gaseous NO_x may be of sufficiently low volatility that they appear primarily in the particulate phase. Thus, for example, nitroaromatics such as nitrotoluenes and nitrocresols are formed during irradiation of NO_x–air mixtures containing toluene (24), a major constituent of unleaded gasoline. Little, if anything, is known about the possible health effects of long term inhalation of such compounds. However, the possible impact of these and other related nitrogenous compounds (e.g., alkyl nitrates and nitrites) should be considered in conjunction with proposals for weakening NO_x emission standards for mobile or stationary sources.

Additionally, there is growing evidence that polycyclic aromatic hydrocarbons (PAH) such as pyrene and the well-known carcinogen benzo(a)-pyrene may be rapidly nitrated in the atmosphere. Such nitrations have been shown to occur in the laboratory (25, 26) when PAH deposited on glass fiber filters are exposed to ambient levels of NO_2 (0.25 ppm) and HNO_3 (10 ppb). Similar reactions also occur for PAH absorbed on soot particles or other substrates (27–30). These nitroarenes, some of which are strong, direct mutagens in the Ames test (31, 32), seem to be widely distributed in the environment (33–35), and their health effects are currently the subject of intensive research.

An emerging aspect of the presence of certain trace nitrogenous species in the troposphere is their participation in acid deposition phenomena. These include not only acid rain but also highly acidic fogs, which have been recently observed in southern California (36). In these measurements, fogs with pHs below 2 were collected, with a ratio of nitrate to sulfate of ~2. The occurrence of such strongly acidic fogs in heavily populated urban areas may have significant health implications.

In conclusion, whether or not any or all of the "trace" nitrogeneous species known or suspected to be present in ambient polluted air may have health impacts out of proportion to the fraction of the total pollution burden they represent remains

to be shown. Certainly, however, many of these compounds must be considered in predictive and phenomenological assessments of the total "oxidant" dose presented to impacted populations. Hence, it is important to initiate or expand studies directed to the elucidation of possible direct health effects associated with these recently measured pollutants, and to be particularly concerned with their synergistic capacities for forming other toxic or carcinogenic compounds.

Other regulatory implications of the presence of these nitrogeneous pollutants are apparent. While we have emphasized the nature of the nitrogeneous air pollutant burden in photochemical smog, it should also be recognized that several of these species, especially those produced in thermal reactions, will result from NO_x emissions into environments not subject to significant photochemical activity. In either case greater emissions of NO_x to the atmosphere will mean higher levels of NO_2, nitric and nitrous acids, as well as of other trace nitrogeneous species. Clearly, the total, complex impact of the nitrogeneous pollutants must be carefully evaluated when assessing real or potential health hazards, or in considering relaxation of present control strategies for NO_x.

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