Measurement of Nitrous Acid in Motor Vehicle Exhaust

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Nitrous acid (HONO) is an important tropospheric air pollutant. Photolysis of HONO produces hydroxyl radicals that promote ozone formation. HONO may also adversely affect human health. Sources of HONO include both direct emission from combustion processes and secondary atmospheric formation from nitrogen oxides (NO_x). The relative contribution of these sources to ambient HONO concentrations is not well known. In this study, HONO and NO_x emissions from on-road vehicles were measured at the Caldecott Tunnel during summer 1995. The Caldecott Tunnel is located on a heavily used highway in the San Francisco Bay area. The mean and median model years of vehicles observed during this study were 1989.3 and 1990, respectively. Nitrous acid was collected on sodium carbonate-coated glass annular denuders; NO_x concentrations were measured using chemiluminescent analyzers. Average HONO concentrations in the tunnel exhaust and background air were 6.9 ± 1.4 and 0.7 ± 0.3 ppb, respectively. The average HONO/NO_x ratio in motor vehicle exhaust was (2.9 ± 0.5) × 10^{-3}. The HONO/NO_x ratio in vehicle exhaust measured at the Caldecott Tunnel was higher than that reported previously for well-maintained, catalyst-equipped vehicles, but was lower than that for older vehicles with limited emission controls. Nighttime ambient HONO/NO_x ratios are typically much larger than the HONO/NO_x ratio measured at the Caldecott Tunnel, which suggests that ambient HONO concentrations are governed mainly by secondary formation.

Introduction

Nitrous acid (HONO) is an important air pollutant. In the troposphere, nitrous acid photolysis is a direct source of hydroxyl radicals (OH•):

$$HONO + h\nu \ (\lambda < 400 \ nm) \rightarrow NO + OH^{\bullet} \qquad (1)$$

Hydroxyl radicals initiate and drive the oxidation of volatile organic compounds in the atmosphere; these reactions promote the formation of ozone as well as other secondary air pollutants, including formaldehyde, peroxyacetyl nitrate, and nitric acid. Nitrous acid concentrations exhibit a diurnal cycle with maximum levels at night and low daytime concentrations (*1–3*). Daytime HONO concentrations typically do not exceed 1 ppb since photolysis limits its accumulation, whereas nighttime HONO concentrations up to 15 ppb have been measured (*3*). As a result of the nighttime buildup of HONO, early morning HONO photolysis can be the dominant source of OH• when the photolysis of ozone and formaldehyde is negligible. Smog chamber modeling has shown peak ozone concentration and the rate of ozone formation to be sensitive to early morning HONO photolysis (*4*), with a pronounced effect for atmospheres where ozone formation is hydrocarbon-limited (*1*).

In addition to its role in tropospheric chemistry, HONO may adversely affect human health and environmental quality. Recent studies have demonstrated that short-term exposures to elevated concentrations of nitrous acid may be irritating to mucous membranes in healthy subjects and may alter lung function in asthmatic subjects (*5, 6*). Long-term effects of repeated exposures to low concentrations of HONO have not been explored. Another potential health concern arises because nitrous acid is a precursor to nitrosamines in the presence of secondary amines (*7*). Many nitrosamines are powerfully carcinogenic in animals and are probably carcinogenic in humans (*8*). It has also been suggested that HONO may contribute significantly to acid deposition (*9, 10*).

Sources of HONO include both direct emission from combustion processes and secondary atmospheric formation from nitrogen oxides. However, the relative contribution of these sources to elevated nighttime HONO concentrations has not been determined definitively. The mechanism for atmospheric HONO formation has been discussed in the literature (*2, 11–13*), although uncertainties remain. Environmental chamber and ambient air studies demonstrate HONO formation in the presence of nitric oxide (NO), nitrogen dioxide (NO_2), and water. Several homogeneous gas-phase routes to HONO formation exist, but it is unlikely that any are significant net sources of HONO in the atmosphere (*11*). Instead, the following two heterogeneous reactions are commonly proposed as pathways for HONO formation:

$$2NO_2 + H_2O \rightarrow HONO + HNO_3 \qquad (2)$$

$$NO_2 + NO + H_2O \rightarrow 2HONO \qquad (3)$$
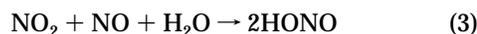
Calvert et al. (*11*) have proposed a mechanism for nighttime HONO formation involving the reaction of N_2O_3 with moist aerosols and suggest this reaction can explain the quantities of HONO observed in urban environments. In the atmosphere, heterogeneous formation of HONO has been shown to occur on aerosols and ground surfaces (*12, 13*). Chamber studies demonstrate that the formation rate of HONO is proportional to NO_2 and water vapor concentration and is sensitive to the nature of the reaction chamber surface and to the surface to volume ratio (*4, 14–16*).

During the fall 1987 Southern California Air Quality Study (SCAQS), Winer and Biermann (*3*) measured nighttime
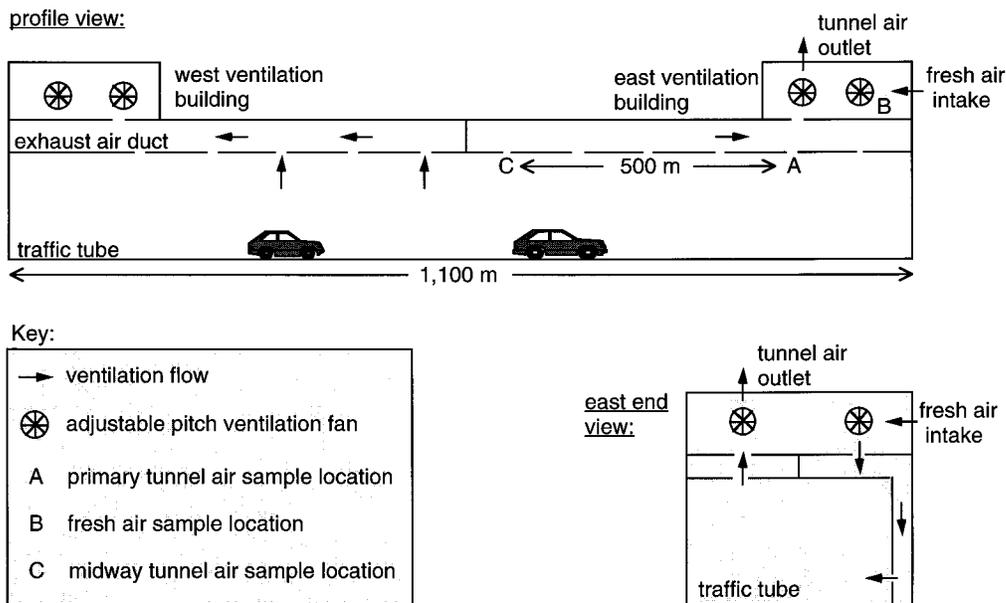
FIGURE 1. Schematic diagram of the Caldecott Tunnel showing ventilation air flows and air sampling locations (figure not drawn to scale).

HONO concentrations as high as 15 ppb. Using a regression analysis, they estimated the contributions to ambient HONO concentrations due to conversion of NO_2 in the atmosphere and direct nitrous acid emissions. Their analysis assumed a first-order dependence on NO_2 concentration, but did not consider the effects of water vapor concentration or aerosol loading on the rate of nitrous acid formation. A pseudo-first-order rate constant for NO_2 conversion of $1.0 \pm 0.7\%$ per hour and a nitrous acid fraction of $(8 \pm 6) \times 10^{-3}$ in direct NO_x emissions were calculated by Winer and Biermann (3). These authors stated that as much as one-third to one-half of the observed HONO concentrations could be attributed to direct emissions from combustion sources.

Pitts et al. (17) measured HONO emissions in the diluted tailpipe exhaust of eight light-duty, spark-ignition vehicles using differential optical absorption spectrometry (DOAS). Measured HONO/NO_x ratios were in the range of $1-8 \times 10^{-3}$, with a trend toward higher HONO emissions for older vehicles with limited emission control devices. A maximum ratio of 8×10^{-3} was measured for a 1974 model year vehicle without a catalyst, running on leaded gasoline. Sjödin and Ferm (18) measured HONO in the exhaust of a diesel bus in city traffic using an annular denuder technique. In this case, the average HONO/NO_x ratio in diesel exhaust was approximately 6×10^{-4}. Measurements at Ford Motor Co. quantified HONO emissions from well-maintained, catalyst-equipped vehicles by Fourier transform infrared (FTIR) spectroscopy. Of 92 measurements from gasoline-fueled vehicles, HONO emissions were below detection limits for 33, and the average HONO/NO_x ratio for the remaining 59 was 9×10^{-4} (11). This study indicated that newer, well-maintained vehicles emit very small amounts of nitrous acid.

Pitts et al. (19) measured elevated levels of HONO in the indoor environment during experiments where a gas-fired kitchen range was in use. Measured ratios of HONO/NO_2 during these experiments ranged from 0.15 to 0.30 and were several times larger than those observed in polluted outdoor atmospheres. Use of kerosene and propane space heaters also led to higher indoor HONO concentrations. Brauer et al. (20) reported elevated HONO levels in residential buildings that exceeded concurrently measured outdoor concentrations. Indoor HONO concentrations were again related to the use of combustion appliances.

In summary, the relative contributions of direct emissions and atmospheric formation to the levels of HONO observed in ambient air remain uncertain. Mechanisms of HONO formation are not well understood, and definitive measurements of HONO emissions from combustion sources are scarce. Past studies of motor vehicle HONO emissions involved small numbers of individual vehicles and reported HONO/NO_x ratios ranging over more than 1 order of magnitude from $<10^{-3}$ to about 10^{-2}. The objective of this study was to measure HONO emissions from a large sample of on-road vehicles representative of the present-day mix of engine types and vehicle emission control technologies.

Experimental Section

Field Sampling Site. Vehicle emissions were measured in the Caldecott Tunnel, which is located in the San Francisco Bay area on California State Highway 24. The tunnel carries traffic through the Berkeley Hills, connecting Oakland and Berkeley with inland communities in Contra Costa County. The tunnel consists of three two-lane traffic bores each about 1100 m in length. The center bore was selected as the sampling location for this study. Weekday traffic through the center bore is switched from westbound in the morning to eastbound during the afternoon to accommodate the commuter fleet. The roadway grade in the tunnel is a constant 4.2% with eastbound traffic traveling uphill. Fully transverse ventilation is provided by adjustable pitch fans housed in ventilation buildings at the east and west ends of the tunnel, as shown in Figure 1. Longitudinal ventilation is induced by the flow of vehicles through the tunnel and by prevailing westerly winds. Measurements of carbon monoxide concentrations along the length of the tunnel showed that pollutant concentrations were higher at the east end during uphill driving events (eastbound traffic). Thus, the east end of the center bore was selected as the sampling location for this study.

Pollutant Measurements. Pollutant concentrations were measured from August 1 to August 22, 1995. Mea-

surements were made on weekdays during the afternoon peak traffic period between 1600 and 1800 h, when traffic traveled in the uphill direction. HONO and NO_x concentrations were measured simultaneously in the tunnel exhaust air about 50 m before the tunnel outlet (sample location A in Figure 1) and at the ventilation fresh air intake fan (location B). On August 18, 21, and 22, HONO and NO_x concentrations were measured simultaneously half-way along the tunnel (location C) and near the tunnel outlet (location A). These latter measurements were performed with the mechanical ventilation system switched off so that air flow through the tunnel was solely longitudinal, in the same direction as vehicles traveling through the tunnel.

Nitrous acid concentrations were measured using the annular denuder method, which is described in detail elsewhere (*21–24*). The sampling system used in this study comprised two glass annular denuders coated with sodium carbonate (Na_2CO_3) and glycerol. The denuders were placed in series with a fluorinated ethylene–propylene copolymer-coated aluminum cyclone at the inlet to remove coarse particles. The second denuder was used to correct for the formation of HONO on denuder surfaces by heterogeneous reaction involving NO_x and water. Since the reactivity of the Na_2CO_3 coating toward NO_2 is very low, NO_2 concentrations will be approximately the same in both denuders, and any HONO sampling artifact will occur equally on both the primary and secondary denuders (*21*). Nitrous acid samples were collected over 90-min sampling periods at a constant flow rate of 15 L min^{-1}. At this flow rate, the cyclone cutpoint diameter was 2 μm.

Glass annular denuders (Model 2000-30B) used in this study were obtained from University Research Glassware, Chapel Hill, NC. Denuders were 242 mm in length with a 1-mm annulus and a 25-mm flow straightener on one end to establish laminar flow ahead of the annulus. Denuders were coated with a 50:50 v/v mixture of 2% by weight Na_2CO_3 in water and 2.5% by weight glycerol in methanol. The addition of glycerol to the coating material reduces the oxidation of nitrite to nitrate which can occur when ozone is present (*21, 22*). After application of the coating solution, the denuders were dried with nitrogen gas. Each day an extra denuder was prepared and used as a blank to check for sources of nitrite contamination.

Immediately following each sample period, denuders were rinsed with 10 mL of deionized water, and the extracts were refrigerated. The extracted samples were analyzed for nitrite ion using a Dionex Model 2010i ion chromatograph with a conductivity detector. A Dionex AG10 anion exchange column with a 0.025 mM Na_2CO_3/0.025 mM $NaHCO_3$ eluent solution was used to obtain optimal peak separation during analysis. The detection limit for nitrite ion in solution was 5×10^{-7} M, or 0.23 μg of nitrite/10 mL of sample. Given the sampling conditions described above, the detection limit for nitrous acid was 0.1 ppb. Samples collected on primary denuders (the first denuder in series) in the tunnel were analyzed within 3 days of collection. Remaining samples and blanks were analyzed once all primary denuder samples had been analyzed. Re-analysis of selected samples several weeks after collection indicated that nitrite was stable in stored samples.

Denuder collection efficiency for nitrous acid was determined by sampling air streams prepared in the laboratory with several different concentrations of nitrous acid. Using two denuders in series, collection efficiency was calculated as

$$\eta = \left(\frac{m_1}{m_1 + m_2}\right)100 \qquad (4)$$

where η is the collection efficiency (%) and m_1 and m_2 are the masses of nitrite collected on the first and second denuder, respectively. Nitrous acid was generated by passing a humidified air stream containing gaseous hydrochloric acid (HCl) through a bed of solid sodium nitrite (*25*). HCl was generated using a high-emission permeation tube (VICI Metronics, Santa Clara, CA) in a constant temperature oven at 100 °C. Collection efficiency was determined for four different nitrous acid concentrations (5–23 ppb) that spanned the range of nitrous acid concentrations observed in the Caldecott Tunnel. The denuder collection efficiency was 100% for each nitrous acid concentration tested; nitrite was never detected in the secondary denuders. The laboratory collection efficiency experiments were performed with the same flow rate and sampling interval used in the field.

As part of SCAQS, Appel et al. (*26*) conducted a field intercomparison of the annular denuder and spectroscopic DOAS methods for measurement of HONO. Measured HONO concentrations from the two techniques were highly correlated ($r = 0.94$), with the annular denuder results averaging about 7% lower than those of DOAS, a difference that was less than the estimated uncertainty in the DOAS procedure.

In addition to HONO, other gaseous pollutants were measured at the Caldecott Tunnel. NO_x concentrations in the tunnel exhaust air (location A in Figure 1) were measured using a Thermo Environmental Instruments (TECO) Model 42 chemiluminescent analyzer. A Bendix Model 8101C chemiluminescent analyzer was used to measure NO_x concentrations in the ventilation intake air. Carbon dioxide concentrations were measured in the tunnel with a TECO Model 41H gas filter correlation spectrometer. Ozone concentrations were measured in the ventilation intake air using a TECO Model 49 ultraviolet photometric analyzer. All gas analyzers were calibrated daily immediately prior to each afternoon sampling period.

Traffic Monitoring. The vehicle fleet traveling through the center bore was monitored during each sampling period. Vehicle counts indicated an average traffic volume of 4220 ± 260 vehicles per hour. Traffic consisted almost entirely of light- and medium-duty vehicles; heavy-duty vehicles are only permitted in the outer bores of the Caldecott Tunnel. On average, the vehicle fleet in the center bore comprised 67% cars and 33% pickups and small vans, with less than 0.2% heavy-duty traffic. A license plate survey was conducted to characterize the age distribution of vehicles traveling through the Caldecott Tunnel. A Hi-8 format video camera was used to record license plates of vehicles driving through the tunnel. License plates were keyed to DMV vehicle registration data. The average and median model years of the observed vehicle fleet were 1989.3 and 1990, respectively. Pre-1975 model year vehicles comprised about 2% of the fleet; the oldest vehicle model year observed was 1964. Greater than 99% of all vehicles traveling through the center bore were gasoline-fueled.

Typical vehicle speeds at the tunnel exit, measured using a hand-held radar gun, ranged from 40 to 50 mph. Traffic within the center bore was generally smooth-flowing once vehicles entered the tunnel. High-power enrichment is not expected for vehicles in the Caldecott Tunnel. The

TABLE 1
Measured HONO and NO$_x$ Concentrations at the Caldecott Tunnel

	tunnel concentrations[a]		background concentrations[b]		
sample date	HONO (ppb)	NO$_x$ (ppm)	HONO (ppb)	NO$_x$ (ppb)	Δ[HONO][c]/Δ[NO$_x$] (%)
Aug 1	7.9	2.1	1.4	50	0.32
Aug 2	9.2	2.3	1.0	89	0.38
Aug 7	6.1	2.1	0.7	79	0.27
Aug 8	8.4	2.4	0.8	84	0.33
Aug 9	7.1	2.3	0.7	75	0.29
Aug 10	5.4	2.1	0.3	80	0.24
Aug 11	5.2	2.0	0.4	51	0.24
Aug 14	8.0	2.1	0.6	47	0.36
Aug 15	5.3	1.9	0.5	69	0.25
Aug 16	5.1	2.0	0.5	91	0.25
Aug 17	8.3	2.4	0.7	94	0.33
Aug 18	5.6	2.2	n/a[d]	n/a	0.24
Aug 21	6.6	2.1	n/a	n/a	0.29
Aug 22	7.7	2.4	n/a	n/a	0.30
average	6.9 $\pm$ 1.4	2.2 $\pm$ 0.2	0.7 $\pm$ 0.3	74 $\pm$ 15	0.29 $\pm$ 0.05

[a] Tunnel air samples were collected in the exhaust duct near the tunnel outlet (sample location A in Figure 1). [b] Background air samples were collected at the fresh air ventilation intake (sample location B in Figure 1). [c] Δ[HONO] and Δ[NO$_x$] refer to the difference between tunnel and background concentrations. [d] Background HONO and NO$_x$ concentrations were not measured on these days because the sampling equipment was moved to location C (see Figure 1); average background levels from other sampling days were used to compute Δ[HONO] and Δ[NO$_x$].

TABLE 2
Comparison of HONO/NO$_x$ Measured at Different Sampling Locations along the Length of the Tunnel

	sample location					
	near tunnel exit[a]			middle of tunnel[b]		
sample date	HONO (ppb)	NO$_x$ (ppm)	HONO/NO$_x$ (%)	HONO (ppb)	NO$_x$ (ppm)	HONO/NO$_x$ (%)
Aug 18	5.6	2.2	0.26	3.5	1.3	0.28
Aug 21	6.6	2.1	0.32	3.5	1.2	0.29
Aug 22	7.7	2.4	0.32	4.1	1.5	0.28

[a] Measurements at sample location A in Figure 1, about 50 m from the exit portal of the tunnel. [b] Measurements at sample location C, located midway along the tunnel, about 500 m away from sample location A (see Figure 1).

specific power (power per unit vehicle mass) required for a vehicle to climb the 4.2% roadway grade and to accommodate gradual accelerations that are typical of driving conditions in the Caldecott Tunnel is well below the maximum specific power encountered during the Federal Test Procedure (*27*).

Results

Table 1 presents HONO concentrations measured in both the tunnel and background air as well as average NO$_x$ concentrations measured during each sample period. Average HONO concentrations were 6.9 $\pm$ 1.4 ppb in tunnel exhaust and 0.7 $\pm$ 0.3 ppb in background air. The average HONO/NO$_x$ ratio in motor vehicle exhaust was (2.9 $\pm$ 0.5) $\times 10^{-3}$. Nitrous acid concentrations have been corrected for the formation of HONO on denuder surfaces by heterogeneous reaction involving NO$_x$ and water. This correction was small for tunnel samples: on average, the nitrite mass collected on primary denuders was 14 times greater than the nitrite mass collected on secondary denuders when sampling tunnel exhaust. In all cases, nitrite was below the detection limit in denuders used as blanks.

Table 2 compares HONO and NO$_x$ concentrations in tunnel exhaust air near the outlet and at the middle of the tunnel, measured when the mechanical ventilation system was turned off. As expected for longitudinal air flow conditions, both HONO and NO$_x$ concentrations at the middle of the tunnel were lower than those measured near the outlet. The HONO/NO$_x$ ratios were the same at both locations, with average values of (3.0 $\pm$ 0.3) $\times 10^{-3}$ near the tunnel exit and (2.8 $\pm$ 0.1) $\times 10^{-3}$ at the middle of the tunnel.

Discussion

Consideration of Sampling Artifacts. The presence of ozone and sulfur dioxide (SO$_2$) can interfere with the measurement of HONO concentrations by the annular denuder method. Ozone oxidizes nitrite to nitrate on Na$_2$-CO$_3$-coated denuders (*28, 29*), creating a negative bias in the determination of HONO concentration. Nitrous acid measurements made at the Caldecott Tunnel, however, were not affected by this problem because the denuders were coated with glycerol to inhibit nitrite oxidation, and furthermore, ozone concentrations were low. The average ozone concentration measured in background air was 17 ppb. Any ozone drawn into the tunnel was quickly removed by reaction with nitric oxide, which was present at high concentrations (on the order of 2 ppm) inside the tunnel.

The presence of concurrently high levels of SO$_2$ and NO$_2$ can lead to a positive bias in the determination of HONO concentration. Febo et al. (*23*) demonstrated that noticeable amounts of nitrite forms on Na$_2$CO$_3$-coated denuders in the presence of both SO$_2$ and NO$_2$ when at least one of these species is present at concentrations above several hundred parts per billion. This sampling artifact was not an issue when sampling at the Caldecott Tunnel since both NO$_2$ and SO$_2$ concentrations were low. The average NO$_2$ concentration measured in the tunnel was 71 $\pm$ 17 ppb. Almost all of the measured motor vehicle NO$_x$ emissions

were in the form of NO, not NO_2. Concentrations of SO_2 were even lower than NO_2 concentrations since California gasoline has very low sulfur content. Gasoline samples collected during July 1995 in Concord, CA, were analyzed for sulfur content and numerous other fuel properties (*30*). Measured sulfur levels in gasoline ranged from 25 to 100 ppm by weight, with an overall average of 80 ppm. SO_2 concentrations in the tunnel were estimated using the following equation:

$$\frac{\Delta[SO_2]}{\Delta[CO_2]} = \frac{w_s}{w_c} \times \frac{12}{32.1} \qquad (5)$$

where $\Delta[SO_2]$ and $\Delta[CO_2]$ are the increases in SO_2 and CO_2 concentrations (ppm) in the tunnel above background levels; w_s and w_c are the gasoline weight fractions of sulfur and carbon, respectively. Measured CO_2 concentrations were 1063 ± 43 ppm in the tunnel and 363 ± 12 ppm in background air. Measured 24-h average ambient SO_2 concentrations were below 10 ppb throughout the Bay Area in 1995 (*31*). Weight fractions $w_s = 8 \times 10^{-5}$ and $w_c = 0.87$ were used (*30, 32*) in eq 5 to arrive at an upper bound estimate of 34 ppb for the SO_2 concentration inside the tunnel. Therefore, both SO_2 and NO_2 concentrations were well below levels at which artifact nitrite formation has been reported (*23*).

Interactions of HONO with Tunnel Surfaces. Nitrous acid is a reactive gas, and it has been shown to form on environmental chamber surfaces (*4, 14−16*). Therefore, the formation of HONO on tunnel surfaces and the loss of HONO by deposition to the walls of the tunnel may affect measured HONO concentrations. The loss of a species by deposition to a surface can be characterized using a deposition velocity (*33, 34*). The characteristic time, τ, for species loss by deposition is

$$\tau = \left[v_d \left(\frac{S}{V} \right) \right]^{-1} \qquad (6)$$

where v_d is the deposition velocity and S/V is the surface to volume ratio. Chang et al. (*34*) calculated a deposition velocity of 0.07 cm s^{-1} for SO_2 in a tunnel with physical features similar to those of the Caldecott Tunnel. Assuming a comparable deposition velocity for HONO and given $S/V = 0.7$ m^{-1} for the Caldecott Tunnel, the characteristic time for removal of HONO via deposition to the walls of the tunnel is 35 min. Deposition velocities calculated in indoor environments for NO_2 are typically an order of magnitude smaller than deposition velocities for HONO (*33*). Based on empirical rate constants derived for HONO production in reaction chambers (*14, 15*), the rate of HONO formation in the Caldecott Tunnel is less than 1 ppb/h. Therefore, the rate at which HONO is generated by heterogeneous reactions of NO_2 on tunnel surfaces is likely to be much smaller than the rate of HONO removal by deposition. In contrast, the residence time of air in the tunnel is on the order of 3 min. Comparison of characteristic times suggests that the rate of HONO removal by deposition is about 10 times smaller than the rate of HONO removal by ventilation. Therefore, the concentration of HONO in the Caldecott Tunnel should not be significantly altered by deposition to tunnel walls.

Measurements in the Caldecott Tunnel support this conclusion. With the mechanical ventilation system switched off, HONO and NO_x concentrations were mea-sured simultaneously midway along the length of the tunnel (location C in Figure 1) and near the end of the tunnel (location A). If a significant fraction of the observed HONO formed heterogeneously on tunnel surfaces, or if significant amounts of HONO were removed at the tunnel walls, then under these conditions, the HONO/NO_x ratio should change with distance along the tunnel. Since the measured HONO/NO_x ratio at the middle of the tunnel was equal to the HONO/NO_x ratio near the tunnel outlet (see Table 2), it is unlikely that wall formation or deposition affected measured HONO concentrations to a significant extent.

Motor Vehicle HONO Emissions. The measured fraction of HONO in NO_x emissions from vehicles traveling through the Caldecott Tunnel lies within the range of HONO/NO_x ratios reported in previous studies. The HONO/NO_x ratio for vehicles measured in this study, $(2.9 \pm 0.5) \times 10^{-3}$, is more than three times higher than that reported for well-maintained, catalyst-equipped vehicles (*11*) and is lower than the maximum value of 8×10^{-3} reported for vehicles without catalysts (*17*). The model years of vehicles observed in this study range from present day (1995) to pre-1975. Given that vehicles observed at the Caldecott Tunnel represent a mix of engine types and vehicle emission control technologies, it is reasonable to expect the HONO/NO_x ratio to lie between the limits reported previously.

The results of this study are representative of a large sample of vehicles. More than 6000 vehicles drove through the tunnel during each 90-min sampling period, and emissions were measured on 14 different sampling days. A large sample size is needed because remote sensing data show that a small number of vehicles ($\sim$10% of the fleet) contribute about half of the total vehicle NO_x emissions (*35*).

In this study, HONO emissions were measured from vehicles operating in a hot stabilized driving mode. Vehicles traveling through the center bore were known to be operating with warmed-up engines and emission control systems because of the remote location of the Caldecott Tunnel (*36*). Vehicles were operating under moderate load in order to climb the 4.2% roadway grade. Note, however, that high-power enrichment was not expected for vehicles in the Caldecott Tunnel during the study period. These driving conditions were conducive to high NO_x emissions. This study did not include measurements of vehicle emissions that occur during cold start and idle operation. However, vehicles operating in these latter driving modes have low NO_x emissions. In the San Francisco air basin, stabilized running exhaust emissions are estimated to contribute more than two-thirds of the total light-duty vehicle NO_x emissions (*37*).

Reconciliation with Ambient Data. Sjödin (*2*) measured ambient HONO concentrations in Göteborg, Sweden, at a location where the air pollution was dominated by motor vehicle emissions. Maximum HONO levels ranged from about 1 to 4 ppb. Measured HONO/NO_x ratios rose quickly after sunset and often exceeded 0.02. The maximum observed HONO/NO_x ratio was 0.06. Harrison and Kitto (*13*) measured HONO/NO_x ratios above rural grassland in Halvergate, England. Maximum nighttime HONO concentrations were about 1 ppb, and HONO/NO_x ratios ranged from about 0.015 to 0.085. Measurements made at Long Beach during fall 1987 SCAQS (*3, 26, 38, 39*) comprise one of the most extensive data sets available for ambient HONO concentrations. Figure 2 shows the diurnal variation in
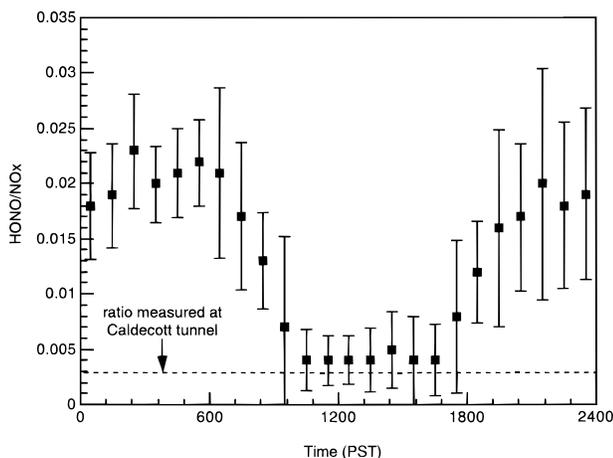
FIGURE 2. Plot of the diurnal variation in average HONO/NO$_x$ ratio measured in ambient air at Long Beach, CA, for 6 days during November−December 1987 SCAQS. When measured HONO concentrations were below the DOAS detection limit of 0.8 ppb, a HONO concentration of 0.4 ppb was used to calculate the HONO/NO$_x$ ratio for that hour. Error bars shown on this plot are ±1 SD ($N = 6$). The dotted line indicates the HONO/NO$_x$ ratio measured in vehicle exhaust at the Caldecott Tunnel.

HONO/NO$_x$ ratio measured in ambient air averaged over all 6 days of the fall monitoring campaign. Nighttime HONO/NO$_x$ ratios measured during SCAQS typically reached 0.02; the maximum ratio observed was 0.04 on December 3. The dotted line in Figure 2 indicates the HONO/NO$_x$ ratio measured in vehicle exhaust at the Caldecott Tunnel. Nighttime ambient HONO/NO$_x$ ratios measured during SCAQS were much larger than the HONO/NO$_x$ ratio of $(2.9 \pm 0.5) \times 10^{-3}$ measured at the Caldecott Tunnel.

The high HONO/NO$_x$ ratios measured in ambient air, together with measurements from the present study indicating that the HONO/NO$_x$ ratio in motor vehicle exhaust is low, suggest that ambient HONO concentrations are governed mainly by heterogeneous formation in the atmosphere. Apportionment of ambient HONO levels observed during SCAQS to direct emissions and secondary formation has been performed by Winer and Biermann (*3*) using the following model equation:

$$[HONO] = \alpha[NO_x] + k[NO_2]t \tag{7}$$

where [HONO] is the observed ambient HONO concentration at time t, α is the HONO/NO$_x$ ratio in combustion source emissions, [NO$_x$] and [NO$_2$] are the observed ambient NO$_x$ and NO$_2$ concentrations at time t, and k is the rate constant for pseudo-first-order reaction of NO$_2$ to form HONO. If a HONO/NO$_x$ ratio of 3×10^{-3} in motor vehicle exhaust is used in the apportionment (eq 7), then 5−15% of the HONO at Long Beach was emitted directly by motor vehicles, while most of the HONO was formed by secondary processes. The pseudo-first-order rate constant for NO$_2$ conversion to HONO was calculated to have ranged from 0.8 to 2.7% h^{-1}. This value is larger than previously reported in some studies (*2, 3*) but is comparable to values reported by Harrison and Kitto (*13*).

Since exhaust HONO/NO$_x$ ratios are dependent on vehicle age and emission control technology (*11, 17*), the HONO/NO$_x$ ratio in vehicle exhaust at Long Beach during 1987 SCAQS was probably higher than the ratio measured for vehicles at the Caldecott Tunnel in 1995. Stationary combustion sources are also known to emit HONO (*19, 20*) and may have contributed to the HONO levels observed at Long Beach. However, during the fall portion of SCAQS, NO$_x$ emissions from power plants with tall stacks would have been trapped above the nocturnal inversion layer (*40*). Furthermore, since the Long Beach monitoring site was located near a freeway, ambient NO$_x$ concentrations were dominated by motor vehicle emissions.

This analysis indicates that direct HONO emissions from motor vehicles can explain a portion of observed elevated nighttime HONO levels. However, the dominant source appears to be from secondary conversion of nitrogen oxides. The contribution of direct vehicle emissions to ambient HONO levels will likely decrease over time as new cars with three-way catalysts enter the fleet and old cars are retired.

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