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# Detection of Excess Ammonia Emissions from In-Use Vehicles and the Implications for Fine Particle Control

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The emission rate for ammonia from in-use vehicles is calculated based on measurements made inside a Los Angeles roadway tunnel. Using fleet distributions by vehicle age and type, known catalyst distributions, and fuel economy by model year and vehicle type and attributing all ammonia to vehicles equipped with three-way catalysts or three-way catalysts plus oxidizing catalysts (dual-bed catalysts), we estimate an average ammonia emission rate of 72 mg $km^{-1}$ for these vehicles, or 61 mg $km^{-1}$ driven by the vehicle fleet as a whole. These emissions can emanate from vehicles running under rich air−fuel conditions, with three-way catalytic converters designed to reduce $NO_x$ to $N_2$ and $O_2$ in addition forming $NH_3$. Resulting calculations estimate ammonia emissions of 24−29 t of $NH_3$ $day^{-1}$ from the vehicle fleet for the South Coast Air Basin (SoCAB) that surrounds Los Angeles. This represents an increase in the daily emissions of ammonia attributable to motor vehicles in the SoCAB from 2% of basin wide emissions before the introduction of catalyst-equipped automobiles to 15% based on the current experiment. The air basin wide emission rate of ammonia from motor vehicles is compared to ammonia emissions from livestock waste decomposition at local dairies, and the implications for control of fine particle ammonium nitrate concentrations are discussed.

## Introduction

Ammonia emissions to the atmosphere arise from a great many sources including decay of livestock waste (*1*−*5*), use of chemical fertilizers (*6*−*10*), emissions from sewage treatment plants, and biological processes in soils (*11*−*15*). Ammonia also is emitted in small amounts from most combustion processes. Precatalyst cars, for example, emit ammonia at a low rate (*16*−*18*) and accounted for only about 3.3 ton $day^{-1}$ of the total of 150 ton $day^{-1}$ of $NH_3$ emissions in the South Coast Air Basin (SoCAB) that surrounds Los Angeles in 1974 prior to the introduction of catalyst-equipped cars (*19*).

A large number of reports in recent years show that the actual hydrocarbon vapor and CO emissions from the motor vehicle fleet in Los Angeles are higher than that intended under the Clean Air Act provisions designed to achieve compliance with air quality standards for ozone and CO. Remote sensing of the vehicle exhaust composition applied to many thousands of individual cars has shown that emissions of CO from the vehicle fleet are increased substantially by a small fraction of very high emitting vehicles and that in-use vehicle emissions are often much higher than the standards imposed on new vehicles (*20*, *21*). Measurements made in the Van Nuys highway tunnel in Los Angeles in 1987 by Ingalls et al. (*22*) likewise show that fleet-average hydrocarbon and CO emissions at that time were approximately 2−3 times higher than predicted by then-current regulatory computer-based models that track the emissions expected given the introduction of catalyst-equipped autos into the southern California vehicle fleet. For this reason, atmospheric models that predict ozone formation in the Los Angeles area commonly use hydrocarbon and CO emissions inventory data for motor vehicles that have been scaled upward by a factor of 2−3 times the values previously expected from the motor vehicle fleet (*23*).

The excess hydrocarbon and CO emissions from in-use catalyst-equipped motor vehicles strongly suggest that many cars in Los Angeles are running with rich air−fuel mixtures. That in turn raises the possibility that the local ammonia emissions from three-way catalytic converters within the in-use motor vehicle fleet likewise could be much higher than expected for properly operating vehicles tested under the customary Federal Test Procedure urban driving cycle. It is known that malfunctioning three-way catalyst-equipped cars unintentionally can manufacture ammonia when they are running rich (*18*), and it is also possible that driving conditions other than those envisioned by the Federal Test Procedure may lead to fuel-rich operation as well. In a recent aerosol modeling study of southern California, Lurmann et al. (*24*) find significant underpredictions of gas-phase ammonia (predicting 19 ppb $NH_3$ as compared to 29 ppb observed), which motivates the search for further ammonia emissions in southern California.

Excess ammonia emissions from the vehicle fleet could pose a serious problem for air quality control in Los Angeles because ammonia emissions react in the atmosphere with the nitric acid produced in photochemical smog to yield fine particle ammonium nitrate (*19*, *25*−*27*). The Los Angeles area already experiences the highest fine particle concentrations in the United States. Light scattering by fine particles is the cause of the well-known Los Angeles visibility problem (*28*−*30*), and aerosol nitrate concentrations often dominate the fine particle concentrations on the worst days of the year (*31*−*33*).

To determine whether excess ammonia emissions are being released to the atmosphere in large quantities from three-way catalyst-equipped automobiles and light trucks in Los Angeles, measurements of ammonia emissions from a fleet of more than 7000 vehicles were made in a Los Angeles highway tunnel. The purpose of this paper is to report the results of that experiment and to discuss the implications for air pollution control in the Los Angeles area.

## Experimental Methods

**Collection of Samples.** Measurements of motor vehicle exhaust were made within the Van Nuys Tunnel, where Sherman Way, a major east−west thoroughfare with three lanes of traffic in each direction, passes under the runway of the Van Nuys Airport. Samples were collected on Tuesday, September 21, 1993, from 0600 to 1000 PDT during the morning traffic peak. In the tunnel, the traffic flow in opposite directions is separated by a wall, with eight open doorways

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in that wall that allow minimal access between the two bores of the tunnel. Samples were collected in the east-bound tunnel at a traffic turn-out, 147 m from the tunnel entrance and 75 m from the tunnel exit. A second set of sampling equipment was located on the tarmac of the airport, directly above the site where the roadway enters the tunnel. A video camera was used at the traffic turn-out within the tunnel to record the vehicles as they passed the sampling site. Vehicle counts, distributions by vehicle age and vehicle type, and estimates of vehicle speeds were obtained from this videotape. Vehicle speed was estimated by timing the images of vehicles passing over a known distance in the tunnel from the videotape. At no point in the videotapes did traffic conditions cause congestion in the tunnel, and vehicle speeds were generally uniform over the length of the experiment. Each vehicle viewed on the video tape was assigned to a vehicle class, and all light-duty vehicles were further assigned to a model year by an acknowledged expert in the field of vehicle identification.

**Measurement Methods.** The sampling methods used during the Van Nuys Tunnel experiment are the same as those used for atmospheric sampling by Fraser et al. (*34*) and will only be briefly summarized here.

Low volume particulate matter samplers were used to collect fine ($d_p \leq 1.6\,\mu$m) and total airborne particulate matter and certain inorganic gas-phase species. Measurements of gas-phase ammonia and particle-phase ammonium ion were accomplished by use of open-faced stacked filter systems in which particulate matter is first collected on a Teflon prefilter followed by collection of gas-phase ammonia on oxalic acid-impregnated glass fiber backup filters. These filters were extracted in distilled−deionized water, and the aqueous ammonium concentrations were measured by an indophenol colorimetric procedure (*35*).

To measure fuel consumption inside the tunnel based on the amount of carbon-containing fuel burned, internally electropolished stainless steel canisters were used to collect gas-phase air pollutants. The 6-L canisters were deployed to the field under high vacuum and used to collect both 4-h integrated and instantaneous grab samples both inside and outside the tunnel. Gas chromatography with flame ionization detection (GC-FID) was used to determine the concentrations of methane, carbon monoxide, carbon dioxide, and total non-methane volatile organic compounds (*36*). Sulfur hexafluoride (released as an artificial tracer in order to determine dilution inside the tunnel) was measured by gas chromatography with electron capture detection (GC-ECD).

**Calculation of Emission Rates.** To measure vehicle emissions per unit of fuel consumed, pollutant concentrations outside the tunnel first are subtracted from those inside the tunnel in order to calculate the increment to total carbon concentrations due to vehicle exhaust inside the tunnel. The total carbon concentration increase inside the tunnel is directly related to fuel consumption, and the ratio of individual pollutants to this total carbon concentration increase can be used directly to calculate emissions per unit of fuel burned using fuel carbon content and density. Fuel-specific emission rate calculations in the present paper are based on the density and carbon content of gasoline, as only 2.8% of the vehicles within the tunnel were diesel-powered. The carbon weight fraction of gasoline is taken to be 0.87, and the density of gasoline is taken to be 750 g $L^{-1}$ in these calculations. The oxygen content in southern California gasoline at the time of this experiment is approximately 0.2 wt %. Translation of these emissions rates per unit of fuel burned into emission factors based on vehicle-miles traveled requires measurement of the dilution of vehicle exhaust inside the tunnel as well as traffic flows through the tunnel. Because the Van Nuys Tunnel studied here is short relative to its cross-sectional area (length to cross-sectional area of one bore yields a ratio of approximately 3 $m^{-1}$), the fuel consumption-based emission factor is preferred because it eliminates any possible uncertainties in measuring the extent of vehicle exhaust dilution within the tunnel, including uncertainties due to the effect of any air exchange through the openings between the two sections of the tunnel in which traffic flows in opposite directions.

**Volumetric Air Flow Rate through the Tunnel.** The volumetric air flow rate through the tunnel was measured by releasing 1.8 g of sulfur hexafluoride ($SF_6$) at the entrance of the tunnel for 29 min of the 4-h sampling period. By analogy to turbulent fluid flow through a pipe, the tracer is expected to be well mixed across the tunnel bore well before the air flow reaches the sampling location. $SF_6$ was then measured in two stainless steel canisters used to collect volatile organic compounds inside the tunnel; the primary canister was sampled for the entire 240-min experiment and thus contained within it a sample collected over the duration of the entire $SF_6$ release. A second canister was filled instantaneously during the $SF_6$ release period to measure the degree of short-term departure from the long-term average dilution rate. From the rate of $SF_6$ release and the resulting concentration far down the tunnel, it is possible to calculate the outside air flow rate through the tunnel. The mechanical ventilation system within the Van Nuys Tunnel was not in use during this experiment. Instead, the traffic in the tunnel creates a piston flow of air through the tunnel from its entrance to the exit. Given data on air volumes flowing through the tunnel, vehicle fleet average fuel efficiency can be calculated since the total carbon concentration increment inside the tunnel then can be converted to a total carbon flux, and vehicle counts and distances traveled are also known. Given data on vehicle fuel economy (km $L^{-1}$) and emission rates per unit fuel burned (mg $L^{-1}$), it is then possible to calculate emissions rates per vehicle-kilometer traveled.

## Results and Discussion

The traffic volume and the distribution of vehicle types and ages flowing through the tunnel were scored by viewing the video tape of the experiment by an acknowledged expert in the field of traffic evaluation. A total of 7060 vehicles were counted, including 4546 catalyst-equipped automobiles, 256 precatalyst gasoline-powered automobiles and light-duty trucks, 12 diesel-powered automobiles, 1936 catalyst-equipped light trucks and vans, 91 heavy-duty gasoline-powered trucks, 186 heavy-duty diesel trucks, and 33 motorcycles. The distribution of gasoline-powered light-duty vehicles as a function of model year is shown in Figure 1. Averaging model years for the gasoline-powered light-duty vehicles gives 1986.4 as the mean model year. This vehicle age distribution is similar to that seen in remote sensing studies in the Los Angeles area (*1*).

The concentrations of carbon dioxide, carbon monoxide, methane, non-methane hydrocarbons, sulfur hexafluoride, and ammonia measured inside and outside the tunnel are reported in Table 1 (*37*). These data are used to calculate emission rates based on fuel consumption as well as the volumetric air flow rate through the tunnel.

Results of the $SF_6$ tracer experiment show volumetric flow rates inside the tunnel of 157 $m^3\,s^{-1}$ during the instantaneous grab sampling period and 133 $m^3\,s^{-1}$ for the 29 min period of $SF_6$ release within the 4-h integrated sample, within reasonable agreement considering the expected fluctuations in tunnel ventilation rates. Using the longer period-average volumetric air flow rate calculated from the $SF_6$ release, the vehicle counts, the total carbon concentration increment measured in the tunnel that was due to vehicle exhaust emitted in the tunnel (difference between inside and outside samplers), and average fuel parameters (including fuel density

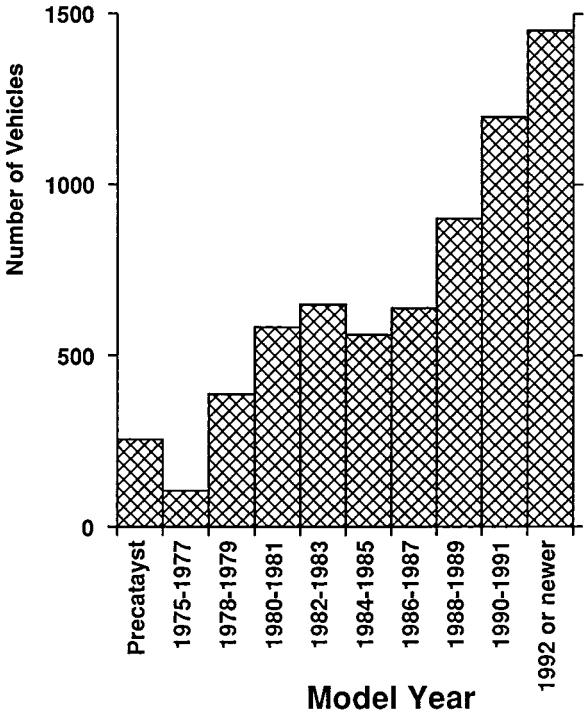


**FIGURE 1. Distribution of light-duty vehicles in the Van Nuys Tunnel by model year.**

**TABLE 1. Gas-Phase Concentrations Measured Inside and outside the Van Nuys Tunnel**

| pollutant | units | background concn | tunnel concn |
|---|---|---|---|
| CO | ppm V | 0.8 | 10.7 |
| $CO_2$ | ppm V | 365 | 468 |
| methane | ppm V | 2.0 | 2.0 |
| non-methane hydrocarbons ($\leq C_{10}$) | ppb C | 302 | 1927 |
| other organics (TO12−NMHC) | ppb C | 72 | 328 |
| $SF_6$ | ppt V | 5.8 | 160 |
| ammonia | $\mu$g m$^{-3}$ | 1.9 | 34 |

and carbon weight fraction), the fleet-average fuel efficiency was calculated to be 6.3 km L$^{-1}$ gasoline-equivalent fuel (14.7 mi gal$^{-1}$). By comparison, if a vehicle fleet with the same distribution of vehicle ages and types performed according to city driving fuel efficiency data published by the U.S. Environmental Protection Agency (*38*), the calculated fuel efficiency for the entire fleet (including heavy-duty trucks) would have been 8.6 km L$^{-1}$ (20.3 mi gal$^{-1}$). The fuel efficiency data published by the EPA are roughly 20% higher than the observed fuel economy on the road (*39*), resulting in an expected fuel economy in acutal use of about 6.9 km L$^{-1}$ (16.2 mi gal$^{-1}$), a little higher than the 6.3 km L$^{-1}$ measured for traffic in the tunnel. It is recognized that the driving conditions in the tunnel do not match those used during the Federal Government's fuel economy tests and that experimental conditions make it difficult to measure the dilution rate in the tunnel and thus the fuel economy of the fleet in the tunnel. Therefore, the emission factors given later in this paper in mg L$^{-1}$ of fuel burned based on a carbon balance in the tunnel should be considered to be the primary results of this study while emissions stated in mg km$^{-1}$ driven (which require knowledge of exact fuel economy) should be viewed at best as estimates.

That the vehicle fleet in the Van Nuys Tunnel on average was running rich is borne out not only by the low measured fuel economy but also by the high measured CO and volatile organic compounds (VOC) emissions rates, which were 130 g L$^{-1}$ (20.8 g km$^{-1}$) for CO and 9.1 g L$^{-1}$ (1.5 g km$^{-1}$) for VOC when averaged over the entire vehicle fleet in the tunnel. These emissions rates are higher than reported from other tunnel studies conducted in other cities but are within the range seen in southern California. In 1994, emission rates of 78 g L$^{-1}$ CO and 4.2 g L$^{-1}$ VOC were measured in the Caldecott Tunnel the San Francisco Bay Area (*40*). In 1992, measurements made in the Ft. McHenry Tunnel in Baltimore yielded emissions rates of 4.0 g km$^{-1}$ CO and 0.4 g km$^{-1}$ VOC (*41*). But recent remote sensing studies of the southern California vehicle fleet, however, yielded emissions rates of 108 ± 25 g L$^{-1}$ CO (*1*), which are statistically indistinguishable from the CO emissions rates measured in the present study. By comparison, emissions rates measured in the Van Nuys Tunnel during the 1987 SCAQS experiments were 13 g km$^{-1}$ for CO and 1.7 g km$^{-1}$ non-methane hydrocarbons (NMHC) (*22, 42*). While the emissions rates presented here for CO and VOC are high, it is unlikely that this is due to artifacts of the experimental design. The emissions rates per unit of fuel burned are highly accurate, dependent only on the ratio of the concentration of the pollutant of interest in the tunnel to the total carbon concentration in the tunnel.

High concentrations of gas-phase ammonia were measured inside the tunnel (34 $\mu$g m$^{-3}$) as compared to background concentrations outdoors above the tunnel entrance (1.9 $\mu$g m$^{-3}$), leading to a measured emission rate of ammonia per unit of fuel burned of 380 mg L$^{-1}$ gasoline-equivalent fuel. Given that the emissions of ammonia from dual-bed or three-way catalysts can be much higher than from either noncatalyst vehicles, oxidation catalyst-equipped vehicles, or diesel engines (*16*−*18*) and knowing that the fleet distribution in the tunnel is made up mostly of vehicles with a dual-bed or three-way catalyst (dual-bed and three-way catalyst-equipped vehicles make up 81% of the vehicles in the tunnel), we will assume that dual-bed and three-way catalysts running rich are the main source of ammonia emissions. Using measured fuel economy data based on model year (*38*), the fraction of vehicles from each model year and each vehicle type that are equipped with three-way catalysts (*43, 44*), and the observed age distribution of vehicles and vehicle type, a rough estimate of the fraction of fuel burned in the tunnel attributable to vehicles with dual-bed or three-way catalysts is possible. The resulting estimate is that 76% of the fuel burned inside the tunnel is burned by vehicles equipped with dual-bed or three-way catalysts. Using this result and attributing all ammonia in the tunnel to dual-bed and three-way catalyst vehicles, we estimate that the ammonia emission rate for these dual bed and three-way catalyst-equipped vehicles in on-road operation averages 72 mg km$^{-1}$ (or about 480 mg L$^{-1}$ after rough adjustment for the greater than average fuel economy of the three-way and dual-bed catalyst vehicles). If the ammonia emissions were attributed equally across all vehicles in the tunnel, the emission rate is calculated to be 61 mg km$^{-1}$.

The most recent comprehensive ammonia emission inventory for light-duty gasoline-powered vehicles in southern California (*45*) was based on a literature review. Ammonia emission rates cited for vehicles in proper operation range from 0.4 to 10.9 mg km$^{-1}$ for diesel vehicles, 2.5−5.0 mg km$^{-1}$ for noncatalyst vehicles, 2.5−5.7 mg km$^{-1}$ for oxidation catalyst-equipped cars, 2.6−20.1 mg km$^{-1}$ for cars with dual-bed catalysts, and 3.6−60.8 mg km$^{-1}$ for three-way catalyst-equipped vehicles. Average values adopted for use in the emission inventory for properly operating vehicles were 2.0, 3.3, 3.6, 9.4, and 16.1 mg km$^{-1}$ for diesel, noncatalyst, oxidation catalysts, dual-bed, and three-way catalyst-equipped vehicles, respectively. Malfunctioning three-way catalyst-equipped light-duty vehicles are estimated in that

emission inventory to emit ammonia at a rate of 67.0−166.6 mg $km^{-1}$, with an average emission rate of 115.9 mg $km^{-1}$. The fraction of malfunctioning vehicles was estimated to vary with vehicle age, ranging from 15% for 1981 and newer vehicles to 82% for 1979 and older model light-duty vehicles. Roadside survey data were used to estimate the fraction of "improperly" operating vehicles in order to arrive at the weighted average emissions factor recommended, but no actual measurements of ammonia emissions were used to gauge how many vehicles fell into the properly operating versus improperly operating category. The weighted-average emissions rate of $NH_3$ for the light-duty vehicle fleet used in that emission inventory thus is fairly low, averaging 33.0 mg $km^{-1}$ for all catalyst-equipped vehicles. In contrast, our measurements suggest a fleet-average emission rate that is roughly double the previous estimates that are in current use.

From the present experiment, which looks at the vehicle fleet as a whole passing through the Van Nuys Tunnel, it is not possible to tell whether the very high ammonia emissions are due to a large number of cars running rich or to a smaller number of cars running very rich. That one or the other of these cases must be true is substantiated by the high CO and non-methane hydrocarbons emissions rates measured for the fleet in the tunnel. Fuel-rich operation can be caused by failures of oxygen sensors used to monitor and adjust the air−fuel ratio that is critical in the proper operation of three-way catalyst systems, by other types of vehicle malfunctions, or possibly by driving conditions not represented by the Federal Test Procedure urban driving cycle.

Control of ammonia emissions is important to control of fine particle ammonium nitrate levels in the South Coast Air Basin that surrounds Los Angeles. Peak 24-h average fine particle concentrations in the SoCAB measured during 1993 ranged from 75.3 to 139.2 $\mu g\ m^{-3}$ across the four air monitoring sites (Azusa, Central Los Angeles, Long Beach, and Rubidoux) studied by Christoforou et al. (*33*), far higher than the newly adopted 24-h average fine particle National Ambient Air Quality Standard of 65 $\mu g\ m^{-3}$. Fine particle nitrate ion is the largest single contributor to those fine particle concentrations, accounting for 21−45% of the peak day concentrations, while fine particle ammonium ion contributed another 8−13% of the fine particle mass depending on the site considered. As a reasonable approximation, ammonium nitrate forms when the product of the gas-phase ammonia times nitric acid vapor concentrations in the atmosphere reaches the value of the equilibrium dissociation constant for $NH_4NO_3$ (*19*). Beyond that point, further additions of $NH_3$ from vehicle exhaust will shift the atmospheric condition toward more $NH_4NO_3$ formation. Assume that the measured emission factor for ammonia from the Van Nuys Tunnel can be scaled by fuel usage to obtain a range of estimates for daily ammonia emissions to the atmosphere of the SoCAB from the vehicle fleet as a whole. Daily fuel use in the basin by highway vehicles is approximately $14 \times 10^6$ gal of gasoline and $3 \times 10^6$ gal of diesel fuel per day (*46*). Total fuel use when multiplied by the fuel-specific emissions factor from the tunnel study results in a total emission rate of ammonia in the SoCAB of 24 t $day^{-1}$. Alternatively, estimated traffic in the air basin (*46*) amounts to $293 \times 10^6$ vehicle-miles traveled daily ($471 \times 10^6$ km $day^{-1}$), which at 61 mg of $NH_3$ $km^{-1}$ yields an $NH_3$ emissions flux from the entire vehicle fleet of about 29 t $day^{-1}$. The modest difference between 24 t $day^{-1}$ $NH_3$ computed from the fuel use data versus 29 t $day^{-1}$ computed from VMT is no larger than the uncertainty in the $NH_3$ emissions factor based on vehicle distance traveled, which is known no more accurately than the range of the two measures of tunnel dilution obtained from the two $SF_6$ measurements. We believe that the fuel consumption-based emissions value is more accurate since that calculation relies on daily fuel useage and the carbon balance in the tunnel, both of which are more precisely known than the estimates of daily VMT and $NH_3$ emissions per kilometer driven, respectively.

These estimates can be compared with the most important traditional source of ammonia emissions in the air basin, ammonia release from livestock waste decomposition at dairies, which has been estimated at roughly 27−30 t of $NH_3$ $day^{-1}$ out of a total inventory of about 165−218 t $day^{-1}$ (*25*, *45*). Thus, at this point, catalyst-equipped cars could be one of the most important $NH_3$ sources in the air basin. As further fleet turnover causes newer vehicles equipped with three-way catalysts to replace older precatalyst vehicles or oxidation-only catalyst vehicles, these ammonia emissions may increase somewhat. Ammonium nitrate concentrations can be reduced by controlling $NO_x$ emissions, $NH_3$ emissions, or both (*27*); conversely, increased emissions of $NH_3$ or $NO_x$ will increase ammonium nitrate levels. If ammonium nitrate concentrations are to be reduced in the SoCAB, each of the major $NH_3$ sources should be examined to see if that source can be controlled. The major $NH_3$ sources now apparently include three-way and dual-bed catalyst-equipped light-duty vehicles operated under rich air−fuel ratio conditions.

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