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Determination of nitrous acid emission factors from a gasoline vehicle using a chassis dynamometer combined with incoherent broadband cavity-enhanced absorption spectroscopy

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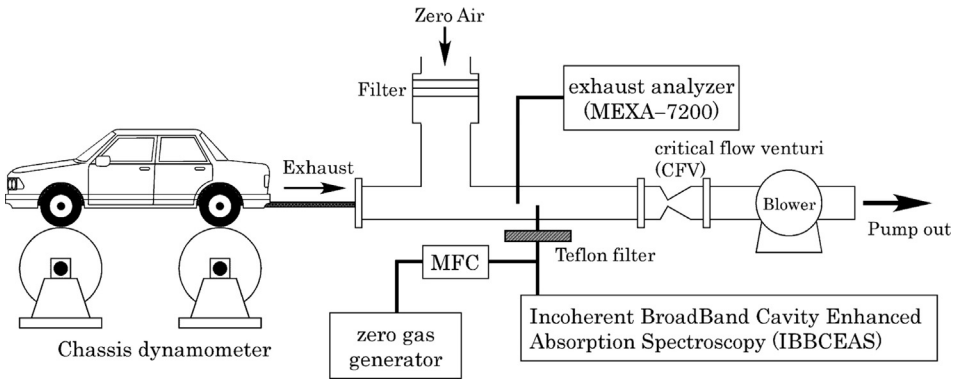
HIGHLIGHTS

- Measurements of nitrous acid (HONO) in gasoline exhaust made using a chassis dynamometer
- HONO was detected using incoherent broadband cavity-enhanced absorption spectroscopy.
- HONO concentrations when catalysts were hot were higher than those prior to heating.
- The calculated HONO/NOx ratio was consistent with previous studies.
- HONO emission factors were determined under different driving cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrous acid (HONO) is a well-known source of hydroxyl radicals in the troposphere. Vehicle exhaust is considered to be one of the primary emission sources of HONO. In this study, measurements of HONO in gasoline vehicle exhaust were carried out using a chassis dynamometer combined with incoherent broadband cavity-enhanced absorption spectroscopy. When catalysts were warm, concentrations of HONO were higher than those prior to catalysts warming. Other species, such as CO, and total hydrocarbons (THCs), showed the opposite pattern. There were no correlations evident between HONO and other trace species concentrations immediately after emission. The HONO/NOx ratio, a good proxy for the formation of HONO in atmosphere, ranged from 1.1 to 6.8×10^{-3}, which was consistent with previous studies. HONO emission factors (EFs) were calculated to be 0.01–3.6 mg kg^{-1} fuel, which was different from the vehicle's specifications and those reported under different driving cycles. Annual HONO emissions in Japan were estimated using the calculated EFs and other statistical data.

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1. Introduction

Nitrous acid (HONO) is an important source of hydroxyl radicals (OH) during the daytime because HONO is photolyzed by near-UV light:

$$HONO + h\nu(\lambda < 400\,nm) \rightarrow NO + OH \quad (1)$$

Ambient measurements of HONO concentrations exhibit a diurnal variation (Harris et al., 1982; Sjödin, 1988; Winer and Biermann, 1994). Concentrations peak during the nighttime and decreases after the sun rises. HONO is the dominant OH radical source during the early morning (Winer and Biermann, 1994; Alicke et al., 2002; Vogel et al., 2003). Hydroxyl radicals initiate the oxidation of trace species, such as CO, NOx, SO_2 and volatile organic compounds, resulting in the formation of photochemical oxidants such as ozone, aldehydes, peroxyacyl nitrates and secondary organic aerosols. Therefore, understanding the HONO budget and HONO's associated chemical processes supports our understanding of tropospheric photochemistry. HONO in the atmosphere also has adverse effects on human health. For example, irritation to mucous membranes at HONO concentrations of a few hundred ppbv has been reported (Rasmussen et al., 1995; Beckett et al., 1995). A recent study demonstrated that adult exposure to a few ppbv of HONO was correlated with decreased lung function and increased respiratory symptoms (Jarvis et al., 2005). However, a similar exposure experiment involving infants suggested that HONO was not, on its own, associated with respiratory symptoms (van Strien et al., 2004). The adverse health effects of exposure to low HONO concentrations remain a contentious research area.

Quantifying primary emissions and secondary formation of HONO is important for studying its photochemistry. Recently, various HONO primary emission sources and secondary formation processes have been reported. For example, microbial activities in soil during the daytime (Su et al., 2011), photolysis of NO_3^- within or at the surface (Zhou et al., 2001, 2003), aircraft exhaust (Lee et al., 2011), traffic (Kurtenbach et al., 2001), reaction of excited NO_2 with H_2O in the gas phase (Amedro et al., 2011), and photosensitized reduction of NO_2 on organic surfaces (George et al., 2005; Rohrer et al., 2005; Stemmler et al., 2006; Beine et al., 2008) have all been reported. However, recent field measurements have shown discrepancies between measurements and modeling of daytime HONO concentrations (Czader et al., 2012; Vogel and Vogel, 2013). More studies, not only on emission sources but also ambient measurements (Kleffmann et al., 2003; Wu et al., 2014; Xu et al., 2015) and modeling (Couzo et al., 2015; Gall et al., 2016) have been performed to investigate these discrepancies.

Vehicle exhaust is considered to be an important source of primary HONO emissions. Measurements of HONO emissions from vehicles have been made using chassis dynamometers (Pitts et al., 1984; Calvert et al., 1994), a stationary engine test (Kessler and Platt, 1984), inside traffic tunnels (Kirchstetter et al., 1996; Kurtenbach et al., 2001) and at a highway junction (Rappenglück et al., 2013). These studies have provided values for HONO/NOx ratios. Because the formation of HONO is related to NOx as mentioned above, the HONO/NOx ratio should be a good proxy for the formation of HONO in the atmosphere. By contrast, a HONO emission factor (EF) has only been reported by Kurtenbach et al. (2001). Vehicle EFs quantify the amount of pollutant emitted per unit (e.g. mass of fuel consumed, mileage or energy). Pollutant EFs from vehicles are used to prepare effective air quality plans for minimizing the impacts of road transport on public health and the environment. The effects of modifying EFs on ambient air quality can be modeled, allowing for estimation of the magnitude of air quality improvement that can be gained through decreased emissions. Generally, EFs change over time for various reasons. For example, vehicle deterioration, changes to emission control standards and development of new vehicle and fuel technologies are all possible factors affecting EFs (Carslaw and Rhys-Tyler, 2013; Dallmann et al., 2012). As such, it is essential to consistently update EFs for pollutants emitted from vehicles.

In this study, concentrations of HONO in gasoline vehicle emissions were measured using a chassis dynamometer with incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS), one of the few techniques available for accurately quantifying HONO concentrations. The technique also has some advantages over other measurement techniques, including: high species selectivity, chemical interferences are avoided, high temporal resolution and sensitivity and measurements are relatively simple to make. It is especially important to use a measurement technique with high species selectivity that suffers from little chemical interference because there are many different species emitted in vehicle exhaust. From the measurements made, HONO EFs for gasoline vehicles were calculated. Using a chassis dynamometer makes it possible to derive EFs under different ideal driving conditions. It is also possible to determine emissions for vehicles with different specifications, such as registration, displacement and mileage, under the same emission control standard and driving conditions. From the determined EFs, annual HONO emissions in Japan were estimated by combining the EFs with other data on vehicles across the country.

2. Experimental

2.1. Vehicles and driving conditions

Measurements of HONO and other trace species concentrations in gasoline exhaust were conducted using a chassis dynamometer with a constant volume sampler (CVS, CVS-7200, HORIBA, Japan) at the National Institute for Environmental Studies (NIES) in Tsukuba, Japan. Six different passenger vehicles made by a Japanese company, and in compliance with the 2005 Japanese emission control standard, were studied. Detailed specifications of the vehicles are presented in Table 1. As shown in Table 1, three different light vehicles, made by different companies, were included. Each vehicle was set on the chassis dynamometer and driven by a programmed robot (ADS-1100, HORIBA, Japan). Four different driving cycles, listed in Table 2, were carried out during the experiments (Sekimoto et al., 2013). For the JC08C cycle, the vehicle was cooled inside the room where the experiments took place overnight and measurements began at the beginning of the day. After the first measurement, the vehicle was allowed to cool over 6 h, after which the second measurement started. The third measurement was performed similarly. For other driving cycles, the vehicle was allowed to warm up by running on the dynamometer for 20 min at a speed of 60 km h^{-1} prior to the measurements being made. For each driving cycle, measurements were repeated three times and the results were averaged. Throughout the experiments the temperature and relative humidity were maintained at 298 K and 50%, respectively.

A schematic diagram of the vehicle exhaust dilution system used and its connection to the measurement system is presented in Fig. 1. The tail pipe of the vehicle was connected to the CVS and the exhaust was diluted using zero air generated from a dilution air refinement system (DAR-2200, HORIBA, Japan). The total flow rate of the CVS ranged from 3.5 to 20 m^3 and varied according to the critical flow venturi (CFV in Fig.1). Generally, diluted vehicle exhaust is continuously sampled at a constant flow rate by the CVS and stored in a bag made of chemically-inactive material (e.g. perfluorovinyl polymer). But in this study, direct measurements of the diluted exhaust gas were carried out. A polytetrafluoroethylene (PTFE) tube with an outer diameter of 12 mm

Table 1
Specifications of the gasoline vehicles used in this study.

Vehicle	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Weight (kg)	950	990	1030	650	830	950
Mileage (km)	75,831	50,557	2597	21,057	22,454	25,179
Registration/year	2004	2012	2016	2015	2015	2014