Development of a Fast Analytical Instrument for the Detection of NO, NO₂ and O₃ and Application at a Mountain Roadside

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ABSTRACT: We developed an analytical method for the detection of nitric oxide (NO), nitrogen dioxides (NO₂) and ozone (O₃) simultaneously with high time resolution (1 s). The fast analytical method was applied for the observation at the Fuji mountain roadside at an altitude of 2300 m. We successfully observed the concentrations of NO and NO₂ in emissions from each vehicle at a roadside, and the O₃ concentration decreased due to the reaction with NO. Relative amounts of NOₓ emissions and primary NO₂ emission ratios of each vehicle driven on the road were estimated by the concentrations observed with high time resolution.

KEY WORDS: environment, energy, resources, emissions, emission gas, nitrogen oxides, in situ observation, fast analyzer, mountain road [D2]

1. Introduction

The concentration of tropospheric O₃ has increased. Because O₃ is cause adverse effects on human health, natural vegetation and agricultural produce, an effective strategy to decrease it is needed (1). Nitrogen oxides (NOₓ) are also toxic and are O₃ precursors. NOₓ emissions from the continent region of China have been decreasing since 2015 (2). The regulation regarding NOₓ emissions from vehicles is advancing, and specifically, the emissions from diesel-powered vehicles have decreased (3). However, the regulation is considered by the emissions of vehicles driving in certain patterns, and the emissions were measured in the laboratory. Therefore, the emissions do not reflect the real environmental conditions when vehicles are driven on real roads (4).

Recently, the importance of emission regulation on real roads has been recognized, which included the driving conditions at high altitudes, such as 1000 m in Japan, 1350 m in EU, and 2400 m in China. Even though the ratio of the road located over the 1000 m altitude is sufficiently small, the amounts of NOₓ emitted by vehicles should be monitored and recognized, especially on tourists, in order to protect their health, and on national parks, to conserve the natural environment (5). In the Cape Breton Highlands National Park in Canada, the NOₓ concentration, which was high in the valley where the road gradients are large, was observed (6). However, NOₓ concentrations are observed mostly in the city area, and there are few examples to measure it in national parks at such high altitudes (6).

In the Fuji-Hakone-Izu National Park in Japan, the Fuji mountain road which starts from the foot of the mountain to the 5th station at an altitude of 2300 m. A traffic control period in the Fuji mountain road was set in summer to solve traffic congestion and conserve the natural environment. Consequently, the NOₓ concentration in the traffic control period was found to be higher than the NOₓ concentration out of the traffic control period (7, 8). One of the reasons suggested was that even though the total...
number of vehicles was small to prevent normal cars from entering the mountain road, the number of large vehicles, such as sightseeing and public buses, increased. This could indicate that large vehicles emit a large amount of NOx, especially at high altitudes; therefore, if the emissions of each vehicle driven on a road are identified and the knowledge is accumulated, these could help to consider the traffic control period and to conserve the natural environment.

There are some examples of measuring the NOx concentration in exhausts by inspecting cars at high altitudes. Wang et al. measured NOx concentrations in exhausts at an altitude between 1000 and 2400 m using an exhaust gas analyzer. They also reported that the amount of NOx emissions increased with the increase in altitude. However, Nagpure et al. measured the amount of NOx emissions using the same method and observed no significant difference between the amount of NOx emissions and the increase in altitude (5). These studies could obtain detailed NOx concentrations with altitude, but they obtained it from only one inspection vehicle.

A remote sensing device is one of those used for estimating the amounts of NOx emissions of each vehicle at a roadside. This device can measure the concentrations of hydrocarbons, carbon monoxide (CO), and carbon dioxide (CO2) using the infrared absorption method and the NO and NO2 using the ultraviolet absorption method with high time resolution. Bishop et al. (2016) measured the NO concentration at an airport with a time resolution of 0.5 s using the remote sensing device. They reported that the buses at the airport driven at long distances emitted more NO, even if they were newly manufactured (10). However, the detection limit of the method was 24 ppm, and it is difficult to measure the NO concentrations emitted by general buses along roads. The O3 concentration in the atmosphere is also small (typically dozens of ppb) compared with those of NOx emitted by large vehicles and it is difficult to measure the O3 concentration with high time resolution.

Through this study, a fast instrument was developed and employed at a high altitude to investigate the possibility of conducting NOx and O3 observations in order to estimate the relative NOx emission and the primary NO2 emission ratio for each vehicle driven on a road.

### 2. Method

#### 2.1. Observation

The observations were conducted on October 6, 2019, at a roadside parking lot (2250 m a.s.l., 35.4°N, 138.7°E), which was located 5 km down from the 5th station of Mt. Fuji. Figure 1 presents the map of the observatory. The mountain road (Fuji Subaru Line) set a traffic control period in the summer, but the observation was conducted out of the traffic control period, and both of large and normal vehicles were driven on the road. The two-way road led from west to east with a clear view, and the observatory was located on the north side of the road. The slope was 5°. Figure 2 presents a schematic diagram and a picture of the observation point.

A pollution-monitoring car was parked at the roadside and was used for the observation. Air was sampled from inlets above the pollution-monitoring car, 4.5 m above the ground, and 10 m away from the center of the road. The sampled air was supplied to the instrument through a PTFE tubing with a diameter of 0.25 inch. The electricity was supplied by a generator for a public toilet, and the wind speed and direction were measured using a propeller.
anemometer (P45940EKO, EKO instruments). Precipitation (CTC-PIS, Adolf Thies), solar radiation (PCM-01, Prede), temperature and relative humidity (TR-72WF-H, T&K) were also measured. A camera was set close to the sample inlets and took pictures every 1 s at the road in front of the observatory and obtained the times and types of passing vehicles.

2.2. Instrument

Figure 3 presents a schematic diagram of the fast detection instrument of NO, NO$_2$ and O$_3$. The instrument consisted of a part of NO and NO$_2$ analyzers with chemiluminescence techniques and a part of a NO$_2$ analyzer with a laser induced fluorescence technique. The NO concentrations were measured by a chemiluminescence technique, which added O$_3$ to the sample air and produced an excited NO$_2$. The excited NO$_2$ went back to a ground state with luminescence and detected them by a photo multiplier tube (PMT: R928, Hamamatsu). The O$_3$ was produced by a discharge O$_3$ generator (FOG-RC15G, Ecodesign) with 1%, as per the product information, and supplied to a reaction cell of a NO analyzer with a flow rate of 10 ml/min, regulated by a flow controller. Oxygen gas (Air-water) was used for the O$_3$ generator. Conversely, the O$_3$ concentration was measured by adding NO (10% in N$_2$, Air-water), and chemiluminescence was observed. Both flow rates of the sample air were 500 ml/min. The NO$_2$ and O$_3$ in the exhaust of the instrument were eliminated by a scrubber with NO$_2$ and O$_3$ absorbents.

The fast NO and O$_3$ analyzers were calibrated by the method applied to observe concentrations at 1 s and were averaged and compared with concentrations obtained from the commercially available chemiluminescence NO$_2$ analyzer (CLAD-1000, Shimadzu) and UV absorption O$_3$ analyzer (model 1100, Dylec).

The detection limits of the fast NO and O$_3$ analyzers were 2.8 and 0.78 ppb for 1 s (S/N = 2), respectively.

NO$_2$ concentrations were measured by a laser induced fluorescence (LIF) technique. LIF is a highly sensitive method. The details of the system developed to detect NO$_2$ are reported elsewhere
e and only a brief description is provided here. The laser, the wavelength of which matched the characteristic wavelength of NO$_2$ resonance, was stimulated and used to measure the fluorescence of NO$_2$ from the electronically excited state between the 590 and 2800 nm wavelengths via a PMT. Therefore, there was no chemical interference in the NO$_2$ measurement as occurs with the chemiluminescence technique. The LIF instrument consists of a fluorescence detection cell, a pump, and optical parts. The 100-nm fluorescence cell is made of stainless steel and its inner surface was treated. To avoid scattered laser light, 400-mm arms, in which optical baffles are set, were used on both sides of the fluorescence cell. A PMT (R928, Hamamatsu) was used for fluorescence detection. An optical filter (LPF-600, CVI) was set between the PMT and the fluorescence cell to prevent scattered laser light and Rayleigh scattering by the sample air. Two spherical planoconvex lenses were used to improve the fluorescence detection efficiency. The signal from the PMT over the threshold was counted using a counter board (CSI-632106, Interface) and logged by a programme developed in house. A GaN semiconductor laser (DHOM-M-445, Ultra laser) was used as a light source, which has a wavelength of 445 nm with a power of 1 W in continuous mode. The absorption cross section of NO$_2$ at 445 nm is large (6.0×10$^{-19}$ cm$^2$ molecule$^{-1}$, FWHM = 0.83 nm, T = 273 K) enough to detect low atmospheric

![Figure 4](image1.png)

**Fig. 4** Concentrations of (a) NO, (b) NO$_2$ and (c) O$_3$ with (d) wind speed and (e) wind direction at a roadside on the Fuji mountain road, Japan, on October 6, 2019. The (f) time and type of vehicles that passed in front of the observatory are also shown. Peaks I to IV are presented in the figure.

![Figure 5](image2.png)

**Fig. 5** An enlarged figure of the concentrations of NO, NO$_2$ and O$_3$ at peaks I and II, and the time and type of vehicles that passed in front of the observatory. The dashed lines indicate the observed peak times, and the red lines indicate the baselines of the peaks used for the analysis at the section of discussion. Large vehicles passed in front of the observatory before 19 s and 26 s at peaks for each peaks I and II, respectively. Pictures of the large vehicles at peaks I (top) and II (bottom) are also presented.
concentration of NO$_2$; therefore, fluorescence was efficiently detected. The sample air was obtained at a flow rate of 500 mL/min. The zero-gas calibration was carried out for 5 min after every 30 min. The span calibration was performed after the observation at the observatory using a direct dilution system with standard gas (NO$_2$/N$_2$: 9.92 ppm; the NO$_2$ concentration was determined before the observation period at the laboratory). The detection limit of NO$_2$ was estimated to be 1.1 ppb (S/N = 2) in 1 s.

The delayed times between the arrival time at the sample inlet and detection time at the instrument were determined, and the observed times were calibrated and shown in Figures as the arrival time at the sample inlet.

3. Results

Figure 4 presents the observed NO, NO$_2$ and O$_3$ concentrations, wind speed and direction. The NO, NO$_2$ and O$_3$ concentrations were measured every 1 s, whereas the wind speed and direction were measured every 2 s. There was no precipitation upon the observation, and the average temperature, relative humidity and solar radiation were 10.4 °C, 86%, and 380 W m$^{-2}$, respectively.

Figure 4 presents the peaks from I to IV. NO peaks were observed at 8:26, 8:29 and 8:55, with the peak concentrations from 50 to 350 ppb. NO$_2$ peaks were also observed at 8:29 and 8:55, with the peak concentrations from 200 to 300 ppb. O$_3$ peaks were observed at the same time as NO and NO$_2$; however, the peaks were negative and decreased from 10 to 20 ppb. The wind direction was westerly, from the foot of the mountain to the mountaintop, and did not change during the observation. The wind speed was almost 0 to 3 m s$^{-1}$ and the average wind speed was 1.7 m s$^{-1}$. Figure 4 also presents the time and type of vehicles that passed in front of the observatory. Four large and thirteen standard-sized vehicles passed during the observation period. All the four large and eight of the standard-sized vehicles passed along a climbing lane and five of the standard-sized ones along a descending lane. According to previous studies, the amount of NO$_x$ emission from standard-sized vehicles is much smaller than that from large vehicles at the observatory (8). No significant increase in the NO$_x$ concentration was observed when a standard-sized car passed across the front of the observatory. Therefore, in this study, we focused and analyzed the large NO$_x$ peaks observed when large vehicles pass across the front of the observatory.

Fig. 7 An enlarged figure of the concentrations of NO, NO$_2$ and O$_3$ at peak IV, and the time and type of vehicles that passed in front of the observatory. The dashed lines indicate the observed peak times, and the red lines indicate the baselines of the peaks used for the analysis at the section of discussion. A large vehicle passed in front of the observatory before 11 s at peak IV. A picture of the large vehicle at peak IV is presented.

Figures 5 to 7 present the enlarged figures of peaks I to IV. NO, NO$_2$ and O$_3$ peaks in the figures were observed simultaneously. O$_3$ exhibited negative peaks because it reacted with NO, and the concentration of O$_3$ decreased due to the reaction (1).

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad (1)
\]

Table 1 presents the peak concentrations of NO, NO$_2$ and O$_3$ for peaks I to IV. The peaks were observed when the large vehicles passed in front of the observatory. Figures 5 to 7 presents the pictures of the large vehicles passing at the peaks.

4. Discussion

The NO$_2$ primary emission ratio (NO$_2$/NO$_x$: $\alpha$) of the emissions from each large vehicle is estimated via the fast observation of NO, NO$_2$ and O$_3$ at a roadside. When $\alpha$ is estimated via the observation at a roadside, the emitted NO from a...
vehicle reacts with O\(_3\) in the atmosphere, and the NO\(_2\) concentration increases as a reaction (1); therefore, this effect should be considered. The concentrations of NO, NO\(_2\) and O\(_3\) were observed with high time resolution when each vehicle passed, and the \(\alpha\) of each vehicle is estimated using Eqs. (2) to (4):

\[
\begin{align*}
[\text{NO}_2]_0 &= [\text{NO}_2] - \Delta [\text{O}_3] \\
[\text{NO}]_0 &= [\text{NO}] + \Delta [\text{O}_3] \\
\alpha &= \frac{[\text{NO}]_0}{[\text{NO}]_0 + [\text{NO}_2]_0} = \frac{[\text{NO}_2] - \Delta [\text{O}_3]}{[\text{NO}] + [\text{NO}_2]} 
\end{align*}
\]

Here, [NO\(_0\)] and [NO\(_2\)]\(_0\) denote the concentrations of NO and NO\(_2\) emitted by a vehicle before NO reactions with O\(_3\) in the atmosphere; [NO] and [NO\(_2\)], the concentrations of NO and NO\(_2\) observed at the observatory; and \(\Delta [\text{O}_3]\), the difference in the observed O\(_3\) concentrations and the concentrations before the vehicles passed the observatory. In this study, the \(\alpha\) of each vehicle is estimated by the peak area of the concentrations of NO, NO\(_2\) and O\(_3\), Table 1 presents the estimated \(\alpha\) at the peaks I to IV.

The \(\alpha\) of each large vehicle for the peaks I to IV was estimated at 0.07 ± 0.02, 0.28 ± 0.03, 0.46 ± 0.01, 0.44 ± 0.01, respectively. The \(\alpha\) was different in each large vehicles. The average \(\alpha\) in the observation was 0.31 ± 0.18. A typical \(\alpha\) of motor vehicles are widely accepted as 0.05–0.10 \(^{15,19}\) and a \(\alpha\) of diesel-powered vehicles are reported as 0.40 ± 0.20 \(^{20}\). The average \(\alpha\) agreed with those of previous studies. The method used to obtain \(\alpha\) for each vehicle driven on a road is developed by a fast observation of NO, NO\(_2\) and O\(_3\) concentrations.

Table 1 NO and NO\(_2\) concentrations, decrease in O\(_3\) concentration, primary NO\(_2\) emission ratio (\(\alpha\)), and relative NO\(_x\) emission at the peaks I to IV. Error of \(\alpha\) is estimated by uncertainties of concentration measurements (3\(\sigma\)).

|    | NO /ppb | NO\(_2\) /ppb | \(\Delta [\text{O}_3]\) /ppb | Arri-val time /s | Primary NO\(_2\) emission /s | Relati-time NO\(_x\) emission /s | Relati-time NO\(_x\) emission ratio (\(\alpha\)) |
|----|---------|--------------|----------------|-----------------|-----------------|-----------------|-----------------|
| I  | 129.5   | 25.1         | 19.3           | 19              | 0.07 ±0.02      | 1.0             |
| II | 45.3    | 39.2         | 14.2           | 26              | 0.28 ±0.03      | 1.1             |
| III| 328.8   | 272.3        | 22.0           | 10              | 0.46 ±0.01      | 9.7             |
| IV | 330.2   | 298.0        | 19.3           | 11              | 0.44 ±0.01      | 15.5            |

The amounts of relative NO\(_x\) emissions are compared with the four large vehicles during peaks I to IV. The relative NO\(_x\) emissions were estimated by NO\(_x\) concentrations multiplied by the arrival time during the peak observed, as presented in Figures 5 to 7, which include a perpendicular spread of emissions from the road. Also, there is an assumption that emissions spread vertically in the same way, not parallel to the road, because the vehicle emissions are continuous along the road, and the concentrations of NO\(_x\) are high in the dimension parallel to the road compared with other dimensions. Table 1 presents the relative NO\(_x\) emission for each large vehicle. The relative amount of NO\(_x\) emissions was found to be from 1.0 to 15.5, which were more than 10 times different. The vehicles with large \(\alpha\) have a large amount of NO\(_x\) emissions. The analytical method to obtain the relative NO\(_x\) emission for each vehicle on the road is developed. The NO\(_x\) emission per quantity of fuel for each vehicle can possibly be obtained when the CO\(_2\) concentration, as well as the NO\(_x\) and O\(_3\) concentrations, is measured with high time resolution.

The NO, NO\(_2\) and O\(_3\) concentrations with time after emission from a vehicle in peak IV were calculated via a numerical calculation using the Runge–Kutta method. The numerical calculation is included for reactions (1), (5), and (6), as well as the diffusions.

\[
\begin{align*}
\text{NO}_2 + \text{hv} &\rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 &\rightarrow \text{O}_3
\end{align*}
\]

The reaction rate constant of reaction (1) is represented by \(kr\), the photolysis rate of NO\(_2\) is represented by \(j\), and the diffusion rate constants of NO, NO\(_2\) and O\(_3\) are represented by \(kd_1\), \(kd_2\), and \(kd_3\), respectively. The differential equations are shown below:

\[
\begin{align*}
\frac{d[\text{NO}]}{dt} &= -kr[\text{NO}] [\text{O}_3] - kd_1[\text{NO}] + j[\text{NO}_2] \\
\frac{d[\text{NO}_2]}{dt} &= kr[\text{NO}] [\text{O}_3] - kd_2[\text{NO}_2] - j[\text{NO}_3] \\
\frac{d[\text{O}_3]}{dt} &= -kd_3([\text{O}_3] - [\text{O}_2]) + j[\text{NO}_2]
\end{align*}
\]

The NO, NO\(_2\) and O\(_3\) concentrations with time after emission from a vehicle at peak IV. The black, red, and blue lines indicate the concentrations of NO, NO\(_2\) and O\(_3\) by calculation, and the black, red, and blue squares indicate the concentrations of NO, NO\(_2\) and O\(_3\) by observation.
The initial concentration of O\textsubscript{3} is used before observing a peak. The initial concentrations of NO and NO\textsubscript{2} are estimated as that \( \alpha \) becomes 0.44, and the calculated NO, NO\textsubscript{2} and O\textsubscript{3} concentrations reproduced the observed concentrations. Figure 8 presents the calculated NO, NO\textsubscript{2} and O\textsubscript{3} concentrations with time. The calculation results revealed that the concentrations of NO and NO\textsubscript{2} becomes half of the initial concentrations in 7 s after emission from a vehicle, and the concentrations were a few ppb after 60 s. The calculated O\textsubscript{3} concentration revealed a minimum at 7 s after emission and increased and became a background level before the vehicle passed. A numerical calculation with parameters determined by fast observation shows the details of the change of NO, NO\textsubscript{2} and O\textsubscript{3} concentrations after emission from a vehicle.

5. Conclusion

An analytical method for the detection of NO, NO\textsubscript{2} and O\textsubscript{3} concentrations at the same time with high time resolution (1 s) was developed. The chemiluminescence method to detect NO and O\textsubscript{3} and the LIF technique to detect NO\textsubscript{2} were used. The instrument is applied for observation at the Fuji mountain roadside at a height of 2300 m on October 6, 2019. The concentrations of NO and NO\textsubscript{2} that were emitted by each vehicle on the road were observed. The primary NO\textsubscript{2} emission ratios for each vehicle were estimated at the area of peaks of NO, NO\textsubscript{2} and O\textsubscript{3} by considering NO\textsubscript{2} production from a reaction of NO with O\textsubscript{3}. The primary NO\textsubscript{2} emission ratios for the four large vehicles observed in this study were 0.07 ± 0.02, 0.28 ± 0.03, 0.46 ± 0.01, 0.44 ± 0.01, and the average was 0.31 ± 0.18, which agrees with those of previous studies. The relative amount of NO\textsubscript{3} emissions was estimated, and it was found that the difference among the four vehicles was more than 10 times. The vehicles with a large \( \alpha \) have a large amount of NO\textsubscript{3} emissions. The details of the change in NO and NO\textsubscript{2} concentrations emitted by a vehicle and O\textsubscript{3} in the atmosphere with time were revealed by a numerical calculation. The methods to obtain \( \alpha \) and relative NO\textsubscript{3} emissions for each vehicle on a road are developed and applied at a mountain road.

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