



## Field measurement of nitromethane from automotive emissions at a busy intersection using proton-transfer-reaction mass spectrometry



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### HIGHLIGHTS

- Field measurements focusing on automotive emissions of nitro compounds were performed.
- Nitromethane was usually observed with air pollutants emitted from automobiles.
- The mixing ratios of nitromethane fluctuated with the cycle of traffic signals.
- Nitromethane emissions were mainly from diesel vehicles with older aftertreatment.
- Most of the mixing ratios of nitroarenes fluctuated within the detection limits.

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### ABSTRACT

Field measurements of seven nitro-organic compounds including nitromethane and ten related volatile organic compounds were carried out using proton-transfer-reaction mass spectrometry at a busy intersection of an urban city, Kawasaki, Japan from 26th February to 6th March, 2011. Among the nitro-organic compounds, nitromethane was usually observed along with air pollutants emitted from automobiles. The mixing ratios of nitromethane varied substantially and sometimes clearly varied at an approximately constant interval. The interval corresponded to the cycle of the traffic signals at the intersection and the regular peaks of nitromethane concentrations were caused by emissions from diesel trucks running with high speed. In addition to the regular peaks, sharp increases of nitromethane concentrations were often observed irregularly from diesel trucks accelerating in front of the measurement site. For other nitro-organic compounds such as nitrophenol, nitroresol, dihydroxynitrobenzene, nitrobenzene, nitrotoluene, and nitronaphthalene, most of the data fluctuated within the detection limits.

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### 1. Introduction

We demonstrated recently on-line measurements of gaseous nitro-organic compounds in automotive exhaust during a transient cycle on a chassis dynamometer system using proton-transfer-reaction mass spectrometry (PTR-MS) (Inomata et al., 2013; Sekimoto et al., 2013). Three diesel trucks, each with a different type of exhaust gas treatment system (aftertreatment), and a gasoline passenger car were tested. Among the mono nitro-organic

compounds detected, nitromethane, a Group 2B carcinogen (“possibly carcinogenic to humans”; International Agency for Research on Cancer (IARC), 2000), was commonly observed and found to be related to the emissions of carbon monoxide, benzene, and acetone, which are thought of as primary products of combustion in an engine. Emissions of other nitro-organic compounds, such as nitrophenol, C<sub>7</sub>-, C<sub>8</sub>-, C<sub>9</sub>-, and C<sub>10</sub>-nitrophenols, and dihydroxynitrobenzene (DHNB), were observed in the gaseous phase, but they likely depended on the vehicle, in particular on the type of aftertreatment. Among nitrophenols, especially 4-nitrophenol, 2-nitrophenol, 2,4-dinitrophenol, and 3-methyl-4-nitrophenol in diesel exhaust particles have attracted attention because of their vasodilatory, estrogenic, and anti-androgenic activities (Taneda et al., 2004).

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Nitromethane has been detected using gas chromatography/mass spectrometry (GC/MS) in urban ambient air in Brazil and Algeria at concentrations ranging between 1 and 9 parts per billion by volume (ppbv) (Grosjean et al., 1998; Yassaa et al., 2001). Both 4-nitrophenol and 2-nitrophenol were detected in the gas phase as well as in rain and cloud water. The concentration range observed in the gas phase at polluted sites, summarized by Harrison et al. (2005), was 3–60 parts per trillion by volume (pptv). Recently, Zhang et al. (2010) investigated the seasonal variation of nitrophenols in particulate matter (PM) collected in Germany. They suggested that 2-nitrophenol is produced photochemically (because the concentration maximum occurs in summer), whereas 4-nitrophenol is emitted from primary sources. With regard to DHNB, 4-nitrocatechol, which is one component of DHNB, was also detected in PM by Zhang et al. (2010), and again they suggested that 4-nitrocatechol too is produced photochemically, for the same reason. More recently, Mohr et al. (2013) measured nitrated phenols such as nitrophenol, methylnitrophenol, nitrocatechol, methylnitrocatechol, and dinitrophenol in ambient aerosols mainly from biomass burning using a micro-orifice volatilization impactor high-resolution chemical ionization mass spectrometry in the United Kingdom. Kahnt et al. (2013) reported annual variations of nitrophenols, 4-nitrocatechol, methylnitrocatechols, and dimethylnitrocatechol in PM<sub>10</sub> measured by liquid chromatography combined with negative ion electrospray ionization mass spectrometry in Belgium. Because of the low volatility of DHNB, it was observed only in the particulate phase; however, gaseous NDHB would be detectable by PTR-MS because of the method's high sensitivity.

With regard to nitro aromatic hydrocarbons, some nitro polycyclic aromatic hydrocarbons such as 1-nitropyrene are known to be probable human carcinogens (IARC, 1989). Among relatively volatile nitro aromatic hydrocarbons, nitrobenzene is categorized in Group 2B (IARC, 1996), whereas both 1- and 2-nitronaphthalenes are categorized in Group 3 (“not classifiable as to its carcinogenicity to humans”) (IARC, 1989). Very recently, we observed emissions of not only nitrophenol and DHNB but also nitrobenzene and nitronaphthalene in the diesel exhaust of a diesel passenger car with diesel oxidation catalyst and diesel particulate filter using PTR-MS (see A1 of the Supplementary Material).

PTR-MS is a technique that enables us to perform rapid analyses of volatile organic compounds (VOCs) with low detection limits (Lindinger et al., 1998; de Gouw and Warneke, 2007; Blake et al., 2009). Chemical ionization by proton transfer permits soft ionization of chemical species that have a proton affinity higher than that of the reagent species, i.e., water:



Note that protonated species ( $\text{VOC} \cdot \text{H}^+$ ) usually give ion signals at odd  $m/z$  values, but protonated mono-nitro-organic compounds usually give ion signals at even  $m/z$  values. However, protonated mono-nitro-organic compounds observed at even  $m/z$  tend to be buried due to an overlap of <sup>13</sup>C isotopologue signals of protonated organic compounds also observed at even  $m/z$ . The <sup>13</sup>C isotopologue signal can be easily calculated from the protonated organic compound signal. By subtracting the contributions of the <sup>13</sup>C isotopologue signals from the ion signals at even  $m/z$  values, we can more accurately reveal the emission properties of nitro-organic compounds.

Recently, several techniques have been used for on-line analysis of multiple VOCs in diesel vehicle exhaust; some examples include ion–molecule reaction mass spectrometry with  $\text{Hg}^+$  as the primary ion (Heeb et al., 2002), proton-transfer-reaction mass spectrometry (PTR-MS) (Jobson et al., 2005), selected-ion flow-tube mass spectrometry (Smith et al., 2004), supersonic jet/resonance-enhanced

multiphoton ionization time-of-flight mass spectrometry (Misawa et al., 2009), and single-photon ionization time-of-flight mass spectrometry (Yamamoto et al., 2012). However, previous studies did not focus on emissions of nitro-organic compounds. Given the demonstrated abundance of nitromethane and other nitro-organic compounds in our laboratory experiments with a chassis dynamometer system (Inomata et al., 2013; Sekimoto et al., 2013), we performed a field experiment to determine if nitromethane and other nitro-organic compounds associated with diesel engine exhaust emissions are measurable in urban air. These compounds are of interest because they adversely affect human health. We carried out field measurements of nitro-organic compounds at a busy intersection in Kawasaki city, a large city in Japan, in winter-time from 26th February to 6th March, 2011. We continuously monitored nitromethane, nitrophenol, nitrocresol, DHNB, nitrobenzene, nitrotoluene, and nitronaphthalene along with some related VOCs using PTR-MS. In the present paper, we show the behaviors of the emissions of these nitro-organic compounds with short intervals (7-s or 26-s) at the intersection, and discuss the observed data with the knowledge obtained from our laboratory experiments with a chassis dynamometer system (Inomata et al., 2013; Sekimoto et al., 2013).

## 2. Materials and methods

### 2.1. Measurement site

Field measurements of nitro-organic compounds were carried out at a roadside site of the Ikegami-Shincho intersection in Kawasaki city, Kanagawa prefecture, Japan (Fushimi et al., 2008; Fujitani et al., 2012) during 9 days from 26th February (Saturday) to 6th March (Sunday) in 2011. Maps of the measurement site are shown in Fig. A2 of the Supplementary Material. In Fig. 1, a schematic diagram of the intersection is described. At this intersection two large roads are crossing. One is an arterial road called “Industrial Road”, which connects Tokyo and Yokohama. An elevated road (“Metropolitan Expressway”) runs above it. The other is called “Satsuki-bashi Mizue-cho Line”, connecting downtown Kawasaki and the seashore area facing onto Tokyo bay. The seashore area,

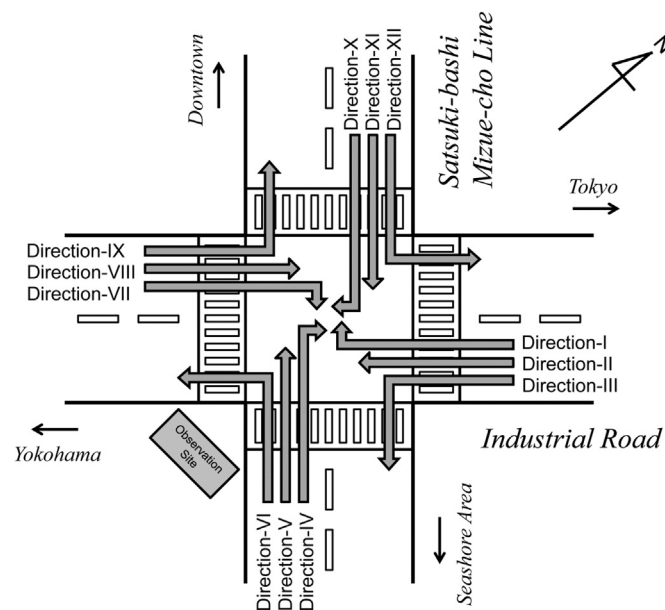


Fig. 1. A schematic diagram of Ikegami-Shincho intersection.

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