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Long-term trend in NO_2 and NO_x levels and their emission ratio in relation to road traffic activities in East Asia

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ABSTRACT

Long-term trend in emission ratio of NO_2 to NO_x was analyzed in relation to traffic activities using ambient monitoring data (such as NO, NO_2, NO_x, and O_3) collected from 7 urban roadside (U-RS) and 7 urban background (U-BG) locations in Seoul, Korea over a 14-year period (1996–2009). In general, the temporal trend of NO_2 concentrations is less distinctive than that of NO_x, whether being downward or upward. However, if their differences are checked statistically, only a few cases were significant. The mean emission ratio of NO_2 to NO_x values varied slightly across the 7 U-RS sites during the study period, ranging from 0.11 to 0.19. In general, there was no significant annual trend in the relative fraction of NO_2 in NO_x emission ($f(NO_2)$) at U-RS, with an exceptional downward trend at one site (slope of $-0.008\ y^{-1}$). On the other hand, diurnal variations of $f(NO_2)$ were likely affected by driving conditions and fuel type of vehicles. The overall results of this study suggest that NO_x emission control strategies such as diesel particulate filter (DPF) or diesel oxidation catalyst (DOC) should have direct influences on $f(NO_2)$ values at U-RS sites.

1. Introduction

Out of various manmade sources of nitrogen oxides ($NO_x = NO + NO_2$), traffic activity exerts a dominant control on the concentration levels of NO_x in the urban environment (US EPA, 2000; Pandey et al., 2008). The atmospheric NO_x, especially NO_2 does adversely impact human health and the natural environment (Case et al., 1979; Barck et al., 2005). Thus, hourly or annual mean concentrations of NO_2, involved in the formation of ground-level ozone (O_3), are one of the principal focuses of air quality assessment. NO_2 concentration can be affected primarily by its emission and secondarily by its formation via reaction (NO with O_3). It was thus suggested that a national air quality standard of NO_2 is hardly attainable at urban roadsides due to the constant input from road vehicles (Carslaw and Beevers, 2004). Legislative standards for total emissions of NO_x from vehicles have been reinforced in the developed countries to improve air quality in the urban environments (Grice et al., 2009 and references therein).

The total emissions of NO_x (and its concentrations) at roadside sites in Europe are significantly decreasing due to its emission control efforts. However, that was not the case for urban locations during specific periods (Carslaw and Beevers, 2004; Carslaw, 2005). The temporal trend of NO_2 and NO_2/NO_x road traffic emissions ratio (or the secondary formation of NO_2) was investigated at the roadside sites in Europe (Hueglin et al., 2006; Anttila et al., 2011; Mavroidis and Chaloulakou, in press). The significant contribution of primary road traffic emission to the smaller negative trend of NO_2 concentration was reported at the roadside stations in Switzerland (Hueglin et al., 2006). In contrast, the secondary NO_2 formation (via the chemical reaction) was a dominant contributor to the increasing NO_2/NO_x concentration ratio in Athens, Greece (Mavroidis and Chaloulakou, in press). This difference is attributed mainly to the vehicle fuel type and exhaust-treatment technologies. Note that quantification of the NO_2 fraction in NO_x emission has been recently assessed and the methods for that are discussed below.

Meanwhile, a distinction between NO and NO_2 fractions in NO_x emission has not been sufficiently emphasized in the literature. Although the emission inventory for NO_x has also been well established, relatively little is known about the partitioning between NO and NO_2 in vehicle emissions. Therefore, quantitative information on the latter term in the exhausts of different vehicle types under typical or “real-world” driving conditions can offer valuable insights into the emission control efforts (Hilliard and Wheeler, 1979; Latham et al., 2001; Jimenez et al., 2000,

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Kurtenbach et al., 2001). It was found that the emission control efforts such as the implementation of Natural Gas Vehicle Supply (NGVS) program and the use of low emission diesel engines can affect the long-term (downward) trends of urban roadside (U-RS) NO_2 concentration (Shon and Kim, 2011).

The method used to estimate the proportion of NO_2 in NO_x emission (f(NO_2)) from road traffic in the literature can be categorized into two groups. One is a direct NO or NO_2 emission measurement from on-road test vehicles or chassis dynamometer. According to the direct method, the road emission of NO_x in the form of NO_2 or NO was significantly different depending on vehicle fuel type, exhaust after-treatment system, vehicle speed, engine loads, etc. (Latham et al., 2001; Collier et al., 2005; Stones et al., 2006; Alvarez et al., 2008; Grice et al., 2009 and references therein). For instance, it has been reported that f(NO_2) decreases with increasing speed above 50 km h^{-1} (Latham et al., 2001). The f (NO_2) values for diesel vehicles (a median of 28.3%) were higher than those for petrol vehicles (<5%) (Collier et al., 2005). It has been reported that the exhaust-treatment system such as diesel particulate filter (DPF) enhances NO_2 fraction in NO_x emission up to 70% (Alvarez et al., 2008; Millstein and Harley, 2010). In contrast, an exhaust gas recirculation (EGR) system had no significant effect on f (NO_2) (Grice et al., 2009 and references therein).

The other is an indirect method using ambient air monitoring data such as NO, NO_2, NO_x and O_3 (Clapp and Jenkin, 2001; Jenkin, 2004; Abbott, 2005, Carslaw and Beevers, 2005; Carslaw, 2005; Grice et al., 2009). The fundamental principle for this method is the same between the previous studies in terms of using ambient air monitoring data, but there is slight difference in detailed application. For instance, the methods of Clapp and Jenkin (2001) and Jenkin (2004) were developed on the basis of the linear relationship between oxidants, OX ($=NO_2+O_3$) and NO_x (i.e., in the form of $[OX]=A[NO_x]+B$; $A=f(NO_2)$) at one location. In contrast, for those of Abbott (2005), Carslaw and Beevers (2005), Carslaw (2005), Grice et al. (2009), and Anttila et al. (2011), f(NO_2) was estimated by considering the differences in NO_2 concentrations between urban background (U-BG) and U-RS site pairs based on the mass balances of NO_x and O_3.

The studies of vehicle emission in relation to partitioning between NO and NO_2 have been carried out intensively in Europe and North America. However, to our knowledge, no such attempts have been made in Asia. In this study, the spatio-temporal patterns of f(NO_2) emission ratio from road traffic in Seoul, Korea were analyzed based on ambient air monitoring data obtained from 7 U-RS and 7 U-BG sites in Seoul for a little over decadal period (1996–2009). As a means to assess the relation between NO_x concentration and f(NO_2), the long-term trends of their (NO_2/NO_x) concentration ratio (along with the concentrations of NO_x and O_3) and meteorological parameters were also analyzed at both U-RS and U-BG sites. The results of this study can provide valuable insights into NO_2 emission factor that is site-specific for air pollution modeling in the urban area. (Note that the emission factor of NO_2 is generally allocated without such consideration.). The results of our previous study focusing on the long-term NO_2 levels and NO_x emissions from urban roadside

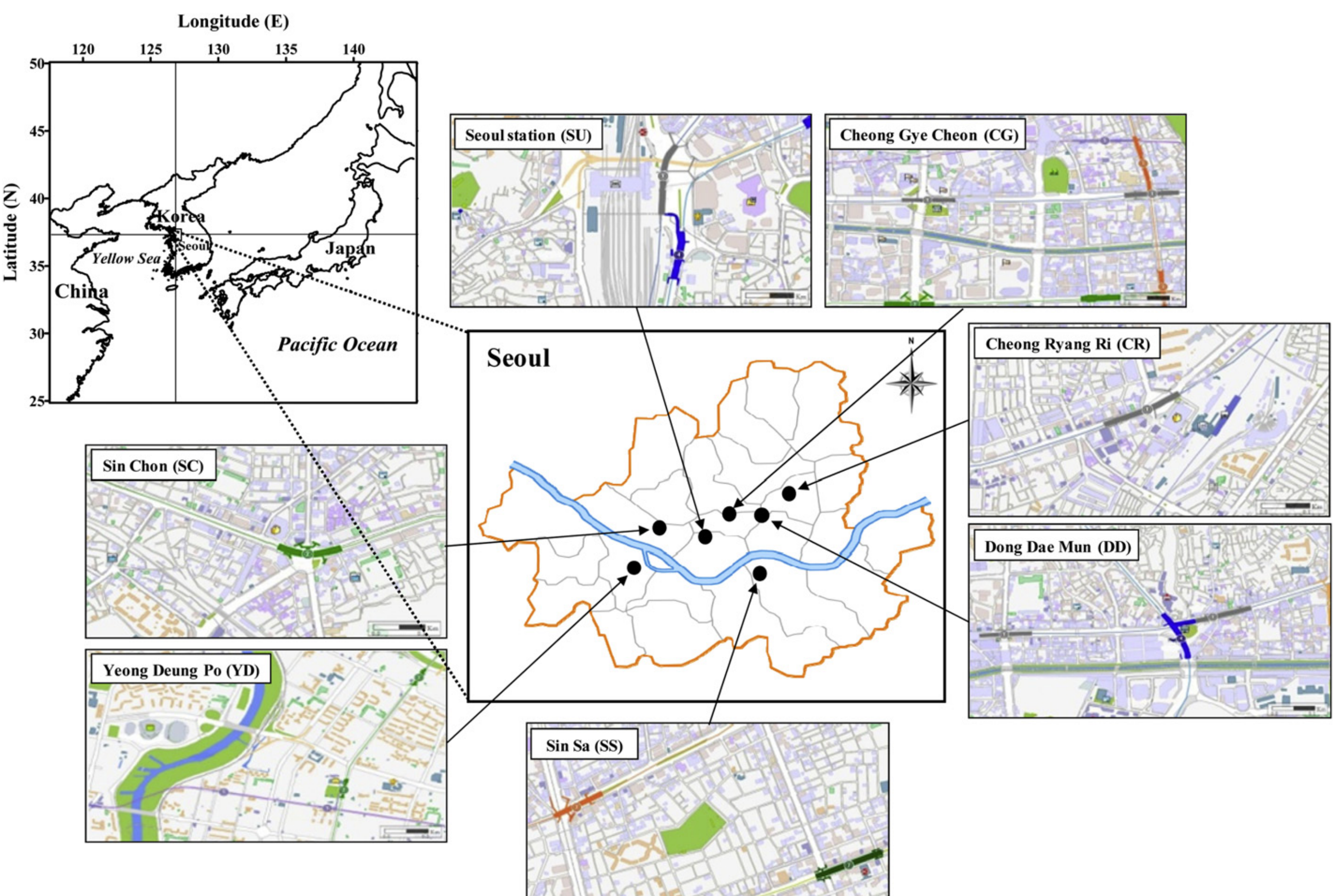

Fig. 1. Geographical locations of U-RS and U-BG sites in Seoul, Korea.