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Impact of NO_x reduction on long-term ozone trends in an urban atmosphere

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Abstract

We investigated the relationships between ambient O_3 concentrations and the concentrations of its precursors, NO_x and NMHC, in Osaka, Japan. The levels of O_x' (where $[O_x']=[O_3]+[NO_2]-0.1\times[NO_x]$ where the last term accounts for primary emissions of NO_2) were uniform within the city even in the photochemically active season. We suggested that NO oxidation by peroxy radicals was a minor contributor, and that oxidation of locally emitted NO by background O_3 in the city was the primary control on NO_2 concentrations. Ozone concentrations increased linearly from 1985 to 2002 at a rate of 0.6 ppbv/yr, even though O_x' concentrations remained constant after the mid 1990s. The trend for O_x' concentrations could not be explained in terms of an increase in local O_3 production, and the trend was found to reflect background O_3 concentrations in Japan. There was a clear relationship between the NO_2/O_x' ratio and NO_x concentration: the ratio decreased with decreasing NO_x concentration. As a consequence, O_3 increased with decreasing NO_x concentration. The reduction of NO_x emissions was deemed to be an important factor for the recent trend of increasing O_3 concentrations in Osaka City.

Keywords: Air quality; Oxidant; Photochemical air pollution; Trend analysis; Urban air pollution

1. Introduction

Photochemical ozone (O_3) is a key determinant of the atmospheric oxidation state and a contributor to global warming (Houghton et al., 2001). The increase in global O_3 levels is of special concern (Akimoto et al., 1994; Lelieveld et al., 2004; Vingarzan, 2004). High emissions of precursors from large metropolitan sites strongly affect global O_3 levels (Akimoto, 2003). Besides the global effect, O_3 is also a major constituent of photochemical smog which affects local air quality (Finlayson-Pitts and Pitts, 2000). O_3 air pollution remains a serious problem in most large cities (Baldasano et al., 2003). Therefore, understanding the behavior of O_3 at urban sites is essential for preserving air quality in the urban areas and around the globe.

Atmospheric O_3 in the lower troposphere is produced by photolysis of nitrogen dioxide (NO_2) and subsequent

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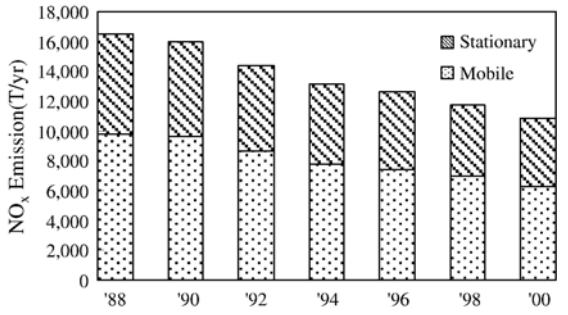

Fig. 1. NO_x emissions from mobile and stationary sources in Osaka City, 1988–2000 (Environment and Sewerage Bureau, Osaka City Government, 2003).

recombination between atomic and molecular oxygen in the presence of a third-body molecule (M):

$$NO_2 + h\nu \rightarrow NO + O \quad (1)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (2)$$

$$\text{net reaction}: \quad NO_2 + O_2 \overset{h\nu,M}{\rightarrow} NO + O_3, \quad (3)$$

where $h\nu$ denotes light with a wavelength shorter than 420 nm. Nitrogen dioxide is formed by the oxidation of nitric oxide (NO) emitted from combustion sources. Two major channels are known for the NO_2 formation in urban atmospheres: NO oxidation by peroxy radicals (radical channel) produced by photooxidation of non-methane hydrocarbons (NMHC) and that by O_3 (O_3 channel):

$$NO + ROO\cdot \rightarrow NO_2 + RO\cdot \quad (4)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (5)$$

where $ROO\cdot$ represents hydro- and alkyl-peroxy radicals and $RO\cdot$ represents the related oxy radicals (NO oxidation by oxygen is significant only at the point of emission when NO concentrations exceed 1 ppmv). The radical channel through reaction (4) results in net O_3 production when reaction (3) follows, thus the production of O_3 is expressed as a function of NO_x(=NO+NO_2) and NMHC concentrations (Sillman, 1999). The O_3 production rate is nonlinearly related to the concentrations of the precursors and is dependent on the NMHC/NO_x ratio as well (Sillman, 1999). Besides, numerous NMHC species exist in the ambient atmosphere (Lewis et al., 2000), and their reactivities and efficiencies with respect to O_3 production differ widely (Atkinson, 1990; Carter et al., 1995). These facts make it difficult to understand urban O_3 behavior. On the other hand, the O_3 channel through reaction (5) produces no net O_3 as this channel provides an inverse of reaction (3).

In urban areas where O_3 precursors are present at sufficient concentrations, the radical channel has been assumed to dominate. However, the O_3-precursor relationship would differ depending on which channel dominates in a particular geographic area. Moreover, the O_3 channel still occurs in areas with high NO_x emissions even when the radical channel dominates. Because NO_x emissions vary in time and space, the contribution of the O_3 channel has prevented accurate evaluation of O_3 levels and variations at certain sites, and comparison of O_3 levels at sites with different NO_x levels (Kley et al., 1999).

Osaka City, with a population of 2.6 million within an area of 220 km^2, is the largest metropolitan site in western Japan. Regulations of emissions from mobile and stationary sources in the city have been strengthened stepwise (Environment and Sewerage Bureau, Osaka City Government, 2003). As a result, NO_x emissions from both mobile and stationary sources have successfully been reduced (Fig. 1). This situation provides a good opportunity to investigate the relationships between O_3 and its precursors in an urban atmosphere. In this study, we assessed the dominant channel for NO_2 formation in the city. We examined recent trends in the concentrations of O_3 and its precursors to propose explanations for the recent worsening of the photochemical air pollution in the city.

2. Methodologies

2.1. Evaluation of the contributions of the ozone channel and the radical channel

To determine the dominant channel for NO_2 formation in a particular environment, it is useful to consider the oxidant concentration ($[O_x]$, where $[O_x]=[O_3]+[NO_2]$). Because O_x concentration is conserved by reactions (3) and (5) and increased by reaction (4) (White, 1977; Kimura, 1978), an increase in O_x concentrations implies the occurrence of the radical channel. However, at sites where NO_x emissions are high, primary NO_2 emissions can introduce positive bias on O_x concentrations. Several studies have pointed out that the primary NO_2/NO_x ratios vary, depending on the vehicle type (Wakamatsu et al., 1990; Kimura and Aikawa, 1991; Clapp and Jenkin, 2001; Carslaw and Beevers, 2004a,b). Therefore, we estimated a typical value for the ratio in the area from ambient monitoring data. As shown in Fig. 2, the ratio of NO_2 to NO_x at a roadside site in Osaka City gradually converges at about 0.1 as NO_x