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Dispersion and photochemical evolution of reactive pollutants in street canyons

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HIGHLIGHTS

- Dispersion and photochemical evolution of reactive pollutants in street canyons.
- Photochemical ages of NO_x and VOC as a function of concentration ratios.
- Favorable O_3 chemical production in a more aged air mass.
- Sensitivities to NO_x and VOC emission rates, photolysis rate, and ambient wind speed.
- A diagram capturing the relative importance between O_3 and OH oxidation processes.

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ABSTRACT

Dispersion and photochemical evolution of reactive pollutants in street canyons with canyon aspect ratios of 1 and 2 are investigated using a computational fluid dynamics (CFD) model coupled with the carbon bond mechanism IV (CBM–IV). Photochemical ages of NO_x and VOC are expressed as a function of the NO_2-to-NO_x and toluene-to-xylene ratios, respectively. These are found to be useful for analyzing the O_3 and OH oxidation processes in the street canyons. The OH oxidation process (O_3 oxidation process) is more pronounced in the upper (lower) region of the street canyon with a canyon aspect ratio of 2, which is characterized by more (less) aged air. In the upper region of the street canyon, O_3 is chemically produced as well as transported downward across the roof level, whereas O_3 is chemically reduced in the lower region of the street canyon. The O_3 chemical production is generally favorable when the normalized photochemical ages of NO_x and VOC are larger than 0.55 and 0.28, respectively. The sensitivities of O_3 chemical characteristics to NO_x and VOC emission rates, photolysis rate, and ambient wind speed are examined for the lower and upper regions of the street canyon with a canyon aspect ratio of 2. The O_3 concentration and the O_3 chemical production rate divided by the O_3 concentration increase as the NO_x emission rate decreases and the VOC emission rate and photolysis rate increase. The O_3 concentration is less sensitive to the ambient wind speed than to other factors considered. The relative importance of the OH oxidation process compared to the O_3 oxidation process increases with increasing NO_x emission rate and photolysis rate and decreasing VOC emission rate. In this study, both O_3 and OH oxidation processes are found to be important in street-canyon scale chemistry. The methodology of estimating the photochemical ages can potentially be adopted to neighborhood scale chemistry.

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1. Introduction

In urban areas, pollutants are emitted from various types of sources and they are then transformed and transported in the atmosphere. A freshly emitted air mass mixes with the background air, and primary pollutants in the air mass are oxidized by hydroxyl radical (OH), hydroperoxy radical (HO_2), organic peroxy radicals (RO_2), and ozone (O_3). Mixing and photochemical processes interacting with each other change the characteristics of an air mass.

Flow in an urban street canyon is largely isolated from flow in the overlying atmosphere and pollutants from vehicles are emitted directly into the street canyon, thus exhibiting the distinct characteristics of an air mass. In a street canyon, the time scale of the photochemical evolution of an air mass is short and the length scale of the pollutant dispersion is small. Computational fluid dynamics (CFD) models have been used to examine the photochemical evolution of air masses in street canyons. Using CFD models that include simple photochemical reactions, Baker et al. (2004) and

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Baik et al. (2007) showed that the O_3 concentration is lower in a street canyon than above it because O_3 is largely depleted by the emitted NO. Baik et al. (2007) performed the budget analysis of the O_3 concentration and showed that the magnitude of the chemical reaction term is comparable to that of the advection or turbulent diffusion term. Using the field Monte Carlo method, Garmory et al. (2009) emphasized that the variances of some radical species in the carbon bond mechanism IV (CBM–IV) are significant near the rooftop level where the mixing process is active. These previous studies showed only the importance of O_3 oxidation in determining the dispersion of NO, NO_2, and O_3. Recently, Kwak and Baik (2012) developed a CFD model coupled with the CBM–IV. They found that the role of OH oxidation in the dispersion of reactive pollutants in a street canyon is crucial. Kim et al. (2012) also insisted that the OH oxidation of volatile organic compound (VOC) needs to be included in street-canyon scale chemistry. These two recent studies imply that the photochemical evolution of pollutants in a street canyon is significantly affected by the OH oxidation process as well as the O_3 oxidation process.

Many observational studies have been undertaken to investigate the photochemical evolution of air masses in urban areas. Several VOC concentration ratios have been used to estimate the evolution of air masses regarding photochemical processes (Calvert, 1976; Roberts et al., 1984; McKeen et al., 1996). A photochemical age, defined as the time-integrated exposure of an air mass to OH radical from the point of emission to the point at which observations are made, is based on the different reactivities of VOCs to OH (Kleinman et al., 2003). For example, de Gouw et al. (2005) and Apel et al. (2010) used the ratio between observed toluene (as a non-photochemically produced species) and observed benzene (as a long-lived species) following Roberts et al. (1984) and showed that more photochemically aged plumes have smaller toluene-to-benzene ratios in New England and in the outflow of the Mexico City metropolitan area, respectively. Despite its usefulness, the photochemical age has weaknesses resulting from certain assumptions. The photochemical age is valid under the assumptions on emission of VOCs from a single source location, reaction of VOCs only with OH radical, non-diffusive transport of VOCs, and clean background air with negligible VOC concentrations (Rudolph and Johnen, 1990; Kleinman et al., 2003).

A street canyon is a space in which the above assumptions are satisfactorily met. Thus, the photochemical age can be employed. In addition to the previously suggested OH oxidation process, the O_3 oxidation process needs to be included in the photochemical age in a street canyon. In this study, we express the photochemical age of NO_x (= NO + NO_2) as a function of the NO_2-to-NO_x ratio (NO_2/NO_x) representing the O_3 oxidation process and the photochemical age of VOC as a function of the toluene-to-xylene ratio (TOL/XYL) representing the OH oxidation process. Using these photochemical ages based on the concentration ratios, the O_3 and OH oxidation processes in a street canyon are examined. This is the first objective of the present study.

A street canyon with a canyon aspect ratio of 1 is typically considered to examine flow and dispersion in a street canyon. In fact, large amounts of pollutants emitted from the bottom of a street canyon with a canyon aspect ratio of 1 are ventilated directly through the roof level. Baik and Kim (1999) and Li et al. (2009) revealed that multiple vortices appear in street canyons with larger canyon aspect ratios. In a street canyon with a canyon aspect ratio of 2, two counter-rotating vortices appear and they act to suppress the upward transport of emitted pollutants, resulting in a small vertical pollutant flux at the roof level (Baik and Kim, 2002). Therefore, a street canyon with a canyon aspect ratio of 2 is a suitable choice to examine the photochemical evolution of an air mass and its related processes therein. Many factors such as NO_x and VOC emission rates, photolysis rate, and ambient wind speed can affect transport and chemical production of reactive pollutants in a street canyon. The second objective of this study is to examine O_3 chemical characteristics that are sensitive to these factors in the lower and upper regions of the street canyon.

2. Methods

2.1. Photochemical age

An air mass is aged over time through mixing with the background air and through photochemical reactions. Because of the different reactivities of chemical species, the concentrations of chemical species decrease at different rates in an air mass. Concentration ratios have been traditionally applied to studies in urban areas (Calvert, 1976) and rural areas (Roberts et al., 1984) to estimate unknown OH concentrations or the diluting effect of an air mass. In some previous studies, the concentration ratios were proposed as a photochemical aging indicator (Nelson and Quigley, 1983; Roberts et al., 1984).

To apply a photochemical age to street-canyon scale chemistry, we use two different concentration ratios, NO_2/NO_x and TOL/XYL.

$$NO + O_3 \rightarrow NO_2 + O_2, \quad \text{(R1)}$$

$$NO_2 \rightarrow NO + O, \quad \text{(R2)}$$

$$TOL + OH \rightarrow \text{products}, \quad \text{(R3)}$$

$$XYL + OH \rightarrow \text{products}. \quad \text{(R4)}$$

NO_2/NO_x is an indicator of O_3 oxidation of NO to NO_2. NO_2 is produced by the NO titration of O_3, as shown in (R1). As an air mass ages, NO_2/NO_x increases until the NO_2 production is balanced by the NO_2 loss shown in (R2). The O_3 oxidation of NO to NO_2 is more pronounced in street-canyon scale chemistry, whereas the OH oxidation of NO_x to NO_y (total reactive nitrogen) is more pronounced in regional scale chemistry. TOL/XYL is an indicator of OH oxidation of VOCs. Because TOL is less reactive than XYL with OH [see (R3) and (R4)], the TOL concentration slowly decreases over time in comparison to the XYL concentration. Therefore, TOL/XYL increases as an air mass ages. It is noteworthy that TOL and XYL are more reactive than alkanes, alkenes, and benzene, which were previously used in regional scale studies on the photochemical age. As a result, TOL/XYL is an appropriate indicator for application in street-canyon scale chemistry.

The photochemical ages of NO_x (t_{NO_x}) and VOC (t_{VOC}) are expressed as a function of NO_2/NO_x and TOL/XYL, respectively. Following Parrish et al. (2007), the photochemical ages can be derived as

$$t_{NO_x} = -\frac{1}{\langle k_{NO+O_3}\rangle\langle[O_3]\rangle}\left\{\ln\left(1-\frac{[NO_2]}{[NO_x]}\right)-\ln\left(1-\frac{[NO_2]_e}{[NO_x]_e}\right)\right\}, \quad (1)$$

$$t_{VOC} = \frac{1}{\langle k_{XYL+OH}-k_{TOL+OH}\rangle\langle[OH]\rangle}\left\{\ln\left(\frac{[TOL]}{[XYL]}\right)-\ln\left(\frac{[TOL]_e}{[XYL]_e}\right)\right\}. \quad (2)$$

Here, k_{NO+O_3}, k_{XYL+OH}, and k_{TOL+OH} are the reaction coefficients between NO and O_3, XYL and OH, and TOL and OH, respectively. $\langle\rangle$ denotes the time average from the point of emission to the point at which observations are made. $[NO_2]_e$, $[NO_x]_e$, $[TOL]_e$, and $[XYL]_e$ are the concentrations of NO_2, NO_x, TOL, and XYL at the point of emission, respectively.

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