



## Characteristic behavior of peroxyacetyl nitrate (PAN) in Seoul megacity, Korea

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### ABSTRACT

We measured the concentrations of peroxyacetyl nitrate (PAN) and other photochemically reactive species, including O<sub>3</sub>, NO<sub>2</sub>, and non-methane hydrocarbons (NMHCs), in the Seoul Metropolitan area (SMA) during May through June in 2004 and 2005. PAN was determined using a fast chromatograph with luminol-based chemiluminescence detection. Mixing ratios of PAN ranged from below the detection limit (0.1 ppbv) to 10.4 ppbv with an average of 0.8 ppbv. O<sub>3</sub> concentrations ranged from 0 to 141 ppbv. The average PAN/O<sub>3</sub> ratio of 0.07 was higher than that observed in cities of Europe and North America (0.02) where control strategies have been enforced to reduce hydrocarbon emissions through extensively reformulated gasoline programs. Strong positive correlations between daily PAN and O<sub>3</sub> maxima during the day demonstrate that similar photochemical factors controlled the production of these two chemicals. However, relationships between PAN and its precursors, NO<sub>2</sub> and NMHCs, suggest that PAN production was more sensitive to NO<sub>2</sub> than NMHCs levels whereas O<sub>3</sub> production was limited by the overall availability of NMHCs. It is likely that the compositions of NMHCs in SMA were favorable for PAN production because of the low fractions of oxygenated compounds in automobile fuels. PAN maxima were observed around noon, which was 2–3 h earlier than the much broader O<sub>3</sub> maxima that occurred in the midafternoon. After reaching the maximum, PAN concentrations rapidly dropped within a few hours, which could be largely due to thermal destruction and to limited production under the typically low NO<sub>2</sub> levels that occurred in the early afternoon. The heterogeneous destruction of particulate matter could be an additional sink for PAN in SMA.

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### 1. Introduction

Peroxyacetyl nitrate (PAN) and ozone (O<sub>3</sub>) are the most important secondary air pollutants formed by a series of photochemical reactions between hydrocarbons and nitrogen oxides in urban atmospheres that experience strong sunlight (Haagen-Smit, 1952). These key species have been the subject of numerous studies related to their role in vegetation damages and in air pollution. It is unlikely that PAN poses a significant human health problem at the levels that occur even in polluted urban environments (Vyskocil et al., 1998). However, PAN is highly phytotoxic and can damage vegetation at concentrations as low as 5 ppbv (Sun and Huang, 1995; Cape, 2003), and high levels of PAN harmful to vegetation are prevalent in large cities (Sun and Huang, 1995; Gaffney et al., 1999; Glavas and Moschonas, 2001; Rubio et al., 2004). To prevent vegetation damage, the World Health Organization set an air quality guideline of 5 ppbv over 8 h for PAN (WHO, 1987).

Although the behaviors of PAN and O<sub>3</sub> in urban atmospheres are very similar and often are significantly correlated with each other, researchers consider PAN to be a more reliable indicator of photochemical air pollution than O<sub>3</sub> because it originates solely from photochemical reactions within the troposphere (Nielsen et al., 1981; Tsalkani et al., 1987; Schrimpf et al., 1995). PAN is, therefore, the key species used to evaluate the degree of urban pollution and its photochemical age (Gaffney et al., 1989; Gaffney et al., 1997). Thus, measurements of the temporal variability of PAN are crucial to determining the oxidative reactions involved in the formation of secondary air pollutants such as O<sub>3</sub> and aerosol species (Marley et al., 2007). PAN also is a very good proxy for changes in urban chemistry. For example, Marley et al. (2007) demonstrated that the considerable decrease in PAN concentrations in Mexico city during the past 10 years reflected the effectiveness of control strategies for reducing hydrocarbon emissions.

Seoul Metropolitan area (SMA) has a well-documented history of high photochemical pollution. The number of days exceeding the O<sub>3</sub> air quality standard has rapidly increased since 1996 (Kim et al., 2005). Researchers have attributed the more frequent high ozone episodes in SMA to growing numbers of automobiles,

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despite the successful reduction of emissions from industrial sources (Jo et al., 2000; Lee et al., 2006a,b). A critical evaluation of the photochemical state of SMA has been hindered by the very limited number of available PAN observations (Kim et al., 2001). Thus, measurements of PAN and other photochemically reactive species are needed on a long-term basis.

In this study, we carried out the first concurrent measurements of PAN, O<sub>3</sub>, and their precursors in SMA during May through June in two consecutive years (2004 and 2005). In SMA, the highest O<sub>3</sub> and PM<sub>10</sub> concentrations occur in June. The objectives of this study were to understand the photochemistry that controls PAN production and its sensitivity to nitrogen oxides and hydrocarbon levels and to identify key constituents and parameters involved in its photochemical formation.

## 2. Methodology

We conducted intensive field experiments at the Korea University (KU, 37.58°N, 127.00°W) campus, located in the northeastern part of SMA, Korea (Fig. 1). As KU sampling site is located 80 m south from a four-lane main road, it is likely that local influence from traffic emission prevails only during the southerly wind or any stagnant weather conditions.

Measurements of PAN, CO, NO<sub>x</sub>, and O<sub>3</sub> were made at the top floor of the six-story Science Building from 15 May to 29 June, 2004 and from 1 May to 30 June, 2005. In Seoul, high ozone episodes are most frequently observed in June (Kim et al., 2005; Shon et al., 2007). Meteorological parameters, including UV radiation, temperature, relative humidity, wind direction, and wind speed, also were continuously measured at this site. A Teflon common inlet (1 inch diameter) was used to bring ambient air from 1.5 m above the roof into a glass manifold in the lab, where samples were distributed through PFA lines to measurement instruments. A blower pumped air into the manifold at 500 LPM; air dwelled in the manifold for 0.6 s, which was short enough to minimize ad-

verse effects during sampling. Air from the glass manifold was delivered to a 2 cm<sup>3</sup> Teflon sample loop attached to six-port two-position switching valve (Cheminert C22, Valco Instruments (Houston, TX, USA) by a vacuum pump operating at 100 ml/min. The valve position was controlled by a window-based PC program via a RS-232 serial port.

The concentration of PAN was measured every 5 min in 2004 and 2.5 min in 2005 using fast gas chromatography (GC) with luminol detection (Gaffney et al., 1998; Gaffney et al., 1999; Marley et al., 2004). A luminol cell was connected to the end of 10 m capillary GC column (DB-1, J&W Scientific (Folsom, CA, USA)). The chemiluminescence signal was detected by a gated photon counter (HC135-01, Hamamatsu, Bridgewater, NJ, USA) set at 750 V and operated at room temperature and then recorded by PC through the RS-232 port.

Measurement of PAN was calibrated against standards synthesized using a nitration of peracetic acid in *n*-tridecane whenever the luminol solution was changed (Gaffney et al., 1984; Gregory et al., 1990). For the calibration, a few microliter aliquots of the PAN/*n*-tridecane solution were injected through an injection port into a 5 l Tedlar bag and then filled with zero air (99.999%). After letting the air in the bag equilibrate for 2 min, it was connected to the sampling line and injected into the GC system. Immediately after being injected to the GC system, the air in the same bag was introduced to a commercial NO chemiluminescence instrument (42C, Thermo Electron Corporation, Franklin, MA, USA) with Mo converter. The NO instrument was calibrated against NO standard gas, assuming complete conversion of PAN to NO in Mo converter (Winer et al., 1974; Grosjean and Harrison, 1985). The above calibration procedure took less than 5 min to prevent the possible thermal decomposition of PAN (Kourtidis et al., 1993). The degree of PAN decomposition could be easily identified by comparing relative peak sizes of PAN and NO<sub>2</sub> as they are detected simultaneously in the GC/Luminol instrument. There was no noticeable increase in NO<sub>2</sub> during the calibration. As the nominal detection

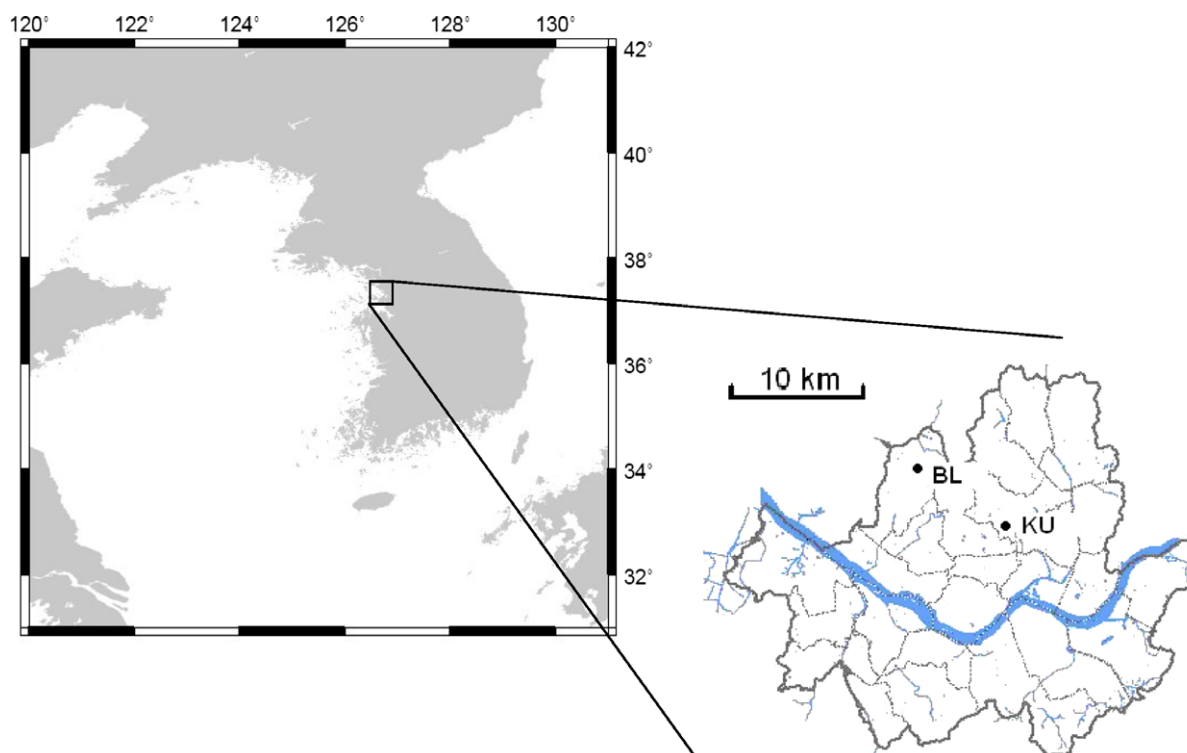


Fig. 1. Locations of sampling sites in Seoul Metropolitan area with county boundaries and rivers. KU and BL indicate Korea University and Bulgwang PAMS site for the measurement of PAN and VOCs, respectively.

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