Temporal variation of secondary air pollutants $\text{H}_2\text{O}_2$ and $\text{HNO}_3$ in Seoul, Korea

Hui-Kang Kim, Choong Min Kang, Hyun Gu Yeo, Kwang Jin Kim and Young Sunwoo

Kon-Kuk University, Department of Environmental Engineering
93-1 Mojin-dong, Kwangjin-ku, Seoul, Korea 143-701
E-Mail: ysunwoo@kkucc.konkuk.ac.kr

Abstract

Concentrations of gas-phase secondary air pollutants, hydrogen peroxide and nitric acid, were analyzed for one week every season during 1997 in Seoul, Korea at six sites already measuring such pollutants as ozone and nitric dioxide. Both $\text{H}_2\text{O}_2$ and $\text{HNO}_3$ had the highest values in the summer with $\text{H}_2\text{O}_2$ showing more variability due to a few anomalous values. Diurnal variations of $\text{HNO}_3$ and $\text{HNO}_2$ showed mostly ‘textbook’ behavior with respect to photochemistry other than some ill-behaved situations suggesting the importance of other factors such as meteorology and emissions. Correlations with other pollutants and meteorological factors also were mostly consistent with photochemical production conditions.

1 Introduction

The city of Seoul has experienced an explosive growth in the number of automobiles during the past decade. Consequently, the photochemical smog problem in the city has reached severe proportions with several ozone warnings being declared each summer. With predicted continuing increases in emission sources for the near future there is an urgent need to evaluate the concentrations and spatial/temporal variations of secondary air pollutants for this metropolis.
Air pollutant monitoring stations set up throughout the capital and in neighboring satellite cities have been continuously measuring O₃, NOₓ, SO₂, CO and TSP for several years. Some of these sites are maintained by the Ministry of Environment while the rest are run by the city of Seoul. Starting from the spring of '97, measurements of secondary pollutants such as aldehydes, HNO₃ and H₂O₂ were carried out for one week each season at six of these sites, four within the city and two on the outskirts of the city boundaries. These data, along with those from the monitoring network are being analyzed to study the seasonal variation of secondary pollutants in Seoul. For this paper we looked at the photochemical production characteristics and distribution patterns of HNO₃ and H₂O₂.

2 Methodology

In order to study the photochemical production and distribution of secondary air pollutants in the capital region six sites were selected and gas-phase HNO₃ and H₂O₂ concentrations were measured for seven days in each season. Figure 1 shows the locations of the six sampling sites. Based on the Han River flowing east to west through the center of Seoul three of the sites were chosen north of the river while the other three are located on the south side. Other than the westernmost site of Puchon and the easternmost site of Kuri the other four sites are each located in one of the four administrative sectors (i.e. northeast, southeast, southwest and northwest used for the ozone warning system) within Seoul proper. The sampling dates for the four seasons were as follows: Feb. 14-20 for the winter, May 17-23 for spring, Aug. 12-18 for summer, and Oct. 9-15 for autumn. No measurement data were available for one day each in winter and spring due to precipitation. The last day of each sampling period was designated as an intensive measurement span for HNO₃ and HNO₂ where three samples were taken at each site, in the morning, afternoon, and nighttime. Finally, meteorological data used in the analysis of measurement results were taken from the Seoul city meteorological office. Unfortunately, on-site meteorological data were not available.

The sampling of atmospheric H₂O₂ was carried out using the cold trap method explained in Sakugawa and Kaplan[1]. This method selectively samples water vapor and H₂O₂ (m.p. -0.4 °C) by using a dry ice/acetone slush to keep the temperature between -70 ~ -60 °C which allows the passage of such major atmospheric gases like N₂, NO, O₂, O₃,
CO$_3$, CO$_2$ and highly volatile organics. A sampling time of three hours was used with an inflow rate of 1 liter/min while taking measurements three times each day. In addition, gas-phase HNO$_3$ was measured using an annular denuder system (Keuken et al.[2], Shaw et al.[3]) consisting of a Teflon-coated cyclone, dual denuders, a filter pack and pump. Here, the first and second denuders were coated with NaCl and Na$_2$CO$_3$ solutions, respectively, to selectively sample HNO$_3$ and HNO$_2$. The sampling time was for ten daylight hours. The analysis of hydrogen peroxide was carried out using a fluorometer after several pretreatment steps while an ion chromatograph was used for HNO$_3$. 

Figure 1. Sampling sites.
3 Results and Discussion

The seasonal variation of both gas-phase H₂O₂ and HNO₃ in the Seoul area are shown in Figure 2. The H₂O₂ values represent averages of the six sites and the three daily measurements while the HNO₃ values are just averaged over the six sites. Hydrogen peroxide values ranged from 0.003~1.626 ppbv while HNO₃ had a minimum of 0.088 in the fall and a maximum of 0.943 ppbv during the summer.

3.1 Seasonal Variation of H₂O₂ and HNO₃

The hydrogen peroxide measurements showed relatively little variability within each season with a minimum of 0.0053 ppbv in the winter season but in the summer, a maximum standard deviation of 0.8 ppbv was recorded. The relative standard deviation (or coefficient of variation: standard deviation/mean) in the summer (2.13) was twice that of the other seasons (0.96, 0.88, 1.05 for winter, spring and autumn, respectively). The cause of this high variation in the summer is the maximum value of 1.626 ppbv on August 13 which appears to be an anomaly as none of the other days in any of the four seasons have averages above 0.4 ppbv. However, the peak was a result of a region-wide episode on the 13th as maximum single-sample values of 2.43, 5.32, 5.93, 0.077, 5.31, and 4.49 ppbv were measured at the six sites, with the spatial maximum appearing at the Kwanghwamun site in downtown Seoul. Some sites had high values for the entire day while most of the other sites had the “extreme” value only during the afternoon sampling period. The 0.077 ppbv was measured at Chamshil in southeastern Seoul and the Ssangmun value of 5.31 ppbv was measured in the morning period followed by an afternoon value of only 0.024 ppbv.

This single-day August episode is more puzzling because none of the other “indicators of photochemical activity” such as O₃ and HNO₃ nor its precursors showed any unusually high concentrations on this day. These maximum values are significantly higher than many previous urban measurements (Das and Aneja[4]) but are in the range of the very high values seen in Southern California in the U.S. (Sakugawa and Kaplan [5]).

The overall range of values was much smaller for gas-phase nitric acid when compared to that of hydrogen peroxide. The variability is naturally smaller because of the fewer samples, however, the highest variability came in the spring for HNO₃ with a relative standard deviation
of 1.62. The seasonal variation for the overall average was not drastic like H$_2$O$_2$ involving “order of magnitude” differences but rather a moderate variation of approximately a factor of four for the seasonal mean from a low of 0.1 18 ppbv in the fall to the highest value of 0.491 ppbv in the summer.

3.2 Diurnal Variation of HNO$_3$ and HNO$_2$

The diurnal variations of HNO$_3$ and HNO$_2$ for each season and for each sampling site are displayed in Figure 3. These are results from the above-mentioned one-day intensive measurement period for each season. The sampling time was 08:00~12:00 for the morning, 13:30~17:30 for the afternoon, and 19:00~09:00 for the nighttime intervals. The figure shows that excluding a few instances, the diurnal maximum for HNO$_3$ occurs in the afternoon and the minimum at night due to the influence of photochemical processes. However, it is also quite apparent that other factors, such as meteorology and emissions, are also playing major roles in the temporal variation of nitric acid in the greater Seoul area.

The case for nitrous acid is a little more straightforward for the
Figure 3. Diurnal variation of gas-phase HNO$_2$ and HNO$_3$. 
winter and spring seasons, monotonically decreasing from morning to night for all the sites due to rapid photolysis by sunlight (Keeler et al.[6]). Nighttime formation reactions bring the HNO₂ concentrations back up to its peak levels by early morning. However, the situation is a little different for some sites in the summer and for almost all the sites in the fall as the nighttime concentrations have the highest values. Interpretations and inferences using these measurements must be conducted with care because the data is only for a single day in the entire season. The fall sampling day was during a period of severe nocturnal inversions. HNO₂ is also a primary pollutant so this meteorological boundary layer condition may have affected the measurements. Site differentiation was rather difficult except for perhaps the summer season when the downtown Kwanghwamun site had relatively higher values separating it from the rest of the monitoring sites. Similar diurnal behavior of HNO₃ and HNO₂ has been reported in other studies (Lee et al.[7]).

3.3 Comparative Analysis of Gas-phase Pollutants

The measurements of hydrogen peroxide and nitric acid were compared to the gas-phase criteria air pollutant concentrations being continuously monitored at these sites. Figure 4 shows the week-long trend of H₂O₂ along with that of O₃ and NO₂ for all six sites during the summer of 1997. The plots are dominated by the high hydrogen peroxide values measured on August 13th. As was mentioned earlier, the ozone and nitrogen dioxide trend does not show any such “polluted” tendencies for this particular day. In general, the “long-term” ozone and nitrogen dioxide concentrations appear to be anti-correlated with ozone, increasing slightly during the week, and NO₂, slightly decreasing for almost all the sampling sites. The correlations of H₂O₂ with these two pollutants are very weak as even when we remove the unusually high values of August 13th linear regression analysis shows a correlation coefficient value of 0.135 for H₂O₂ with O₃ and -0.374 with NO₂ for the remaining data set.

The plots also include the day-to-day variation of HNO₃ and HNO₂ during the summer for the six sampling sites. As in the case of ozone, once again, due most likely to photochemical activity the nitric acid values also went up during the week while the nitrous acid concentrations overall decreased slightly. However, due to the complex nonlinearity of the processes involved, the linear correlation values were quite weak. Even O₃ and HNO₃ had a correlation coefficient of -0.09 for the summer season. Meanwhile, HNO₃ and HNO₂ had a ‘r’ value of
Figure 4. Temporal variation of H₂O₂ and HNO₃ compared with that of O₃, HNO₂ and NO₂ in the summer season for the six sites.
0.053 for the summer but in the winter season the correlation jumped to 0.724.

3.4 Effect of Meteorological Parameters

As expected, temperature showed the biggest correlation with H$_2$O$_2$ with a value of 0.555 for the entire data set. Solar radiation also had a positive relationship with a ‘r’ value of 0.243. Conversely, wind speed showed a strong negative correlation of -0.448 while relative humidity displayed almost no correlation with a value of -0.019. However, this is rather misleading because when one looks at the seasonal correlations relative humidity shows strong negative correlations for all seasons except winter with values ranging from -0.46 ~ -0.58. The other parameters were more or less consistent.

The effects of these meteorological parameters on HNO$_3$ concentrations are similar to that on H$_2$O$_2$ except for relative humidity which has a positive correlation of 0.244. The correlations for temperature, solar radiation and wind speed are 0.5, 0.423 and -0.518, respectively. These values are consistent with the conditions enhancing photochemical smog formation. The effect of relative humidity is different from hydrogen peroxide due to nitric acid formation reactions involving water vapor such as

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\begin{align*}
N_2O_5 + H_2O &\rightarrow 2HNO_3 \\
2NO_2 + H_2O &\rightarrow HNO_3 + HNO_2 \\
NO + NO_2 + H_2O &\rightarrow 2HNO_3
\end{align*}
\]

However, seasonal correlations showed some inconsistencies as was the case with hydrogen peroxide.

4 Summary

Analysis results of HNO$_3$ and H$_2$O$_2$ displayed significant proof of the effects of photochemical activity in Seoul and its surrounding areas. Measurements are continually being carried out each season and will last for two more years under the current project. Subsequent analysis, having more data to work with, will deal with detailed spatial analysis and intensive statistical treatments including factor analysis.
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References