Geophysical Research Abstracts, Vol. 7, 01054, 2005
SRef-ID: 1607-7962/gra/EGU05-A-01054

Temporal variations of HNO_3 and particulate nitrate in Tokyo urban air

Y. Morino,(1) Y. Kondo, (1) N. Takegawa, (1) Y. Miyazaki, (1) K. Kita, (2) Y. Komazaki, (1) T. Miyakawa, (1) N. Moteki, (1) and D. R. Worsnop(3) , and S. N. Pandis (4)

(1) Research Center for Advanced Science and Technology, University of Tokyo, Tokyo, Japan, (2) Department of Environmental Science, Graduate School of Science, Ibaraki University, Japan, (3) Center for Aerosol and Cloud Chemistry, Aerodyne Research, Inc., Billerica, Massachusetts, USA, (4) Department of Chemical Engineering, Carnegie-Mellon University, Pittsburgh, Pennsylvania, USA (morino@atmos.rcast.u-tokyo.ac.jp / Fax: 81-3-5452-5148)

Nitric acid (HNO_3) formed via photo-oxidation of NO_x is one of the most important acidic gases in urban air. Aerosol nitrate (NO_3^-), which is one of the major aerosols in urban air, is formed from HNO_3 and ammonia (NH_3). Ground-based in-situ measurements of gas-phase HNO_3 and particulate NO_3^- were made with high precision (10-20%) and time resolutions of about 1 and 10 minutes, respectively, near the urban center of Tokyo during 2-3 weeks periods in 2003-2004, in order to assess parameters controlling their abundances. HNO_3 and total nitrate TN (= HNO_3 + NO_3^-) were observed to undergo distinct diurnal variations, reaching maximum values during midday and minimum values during the nighttime, confirming photo-oxidation of NO_x to be major source of HNO_3. The daytime HNO_3 mixing ratio also showed strong seasonal variation, highest in summer (3 parts per billion by volume (ppbv)) and lowest in winter (0.1 ppbv). This variation is caused mainly by the seasonal variation of the HNO_3/TN ratios rather than that of the photo-oxidation of NO_x. The HNO_3/TN ratio strongly depends on temperature and relative humidity. The partitioning of nitrate (HNO_3 and NO_{3-}) is calculated using box models: one is thermodynamic equilib-

rium box model, and the other is non-equilibrium box model. The non-equilibrium box model includes effects of vertical mixing; relatively-NO_3^--rich air is transported from colder upper boundary layer to the warmer surface. In general, the equilibrium model reproduces the observed HNO_3/TN ratios well, indicating that the partitioning of nitrate is largely controlled by local thermodynamic equilibrium. However, NO_3^- (HNO_3) is under-predicted (over-predicted) by the equilibrium model typical at midday in summer and autumn. The non-equilibrium model greatly reduces the discrepancy, indicating that vertical mixing largely affects the partitioning of nitrate on the surface during the daytime.