Partitioning of HNO3 and Particulate Nitrate in Tokyo: Effect of Vertical Mixing

Yu Morino[1]; Yutaka Kondo[2]; Nobuyuki Takegawa[3]; Yuzo Miyazaki[4]; Kazuyuki Kita[5]; Yuichi Komazaki[6]; Takuma Miyakawa[7]; Nobuhiro Moteki[8]

[1] RCAST, Univ. Tokyo; [2] RCAST, Univ. of Tokyo; [3] RCAST, Univ of Tokyo; [4] Earth and Planetary Physics, Univ. of Tokyo; [5] Ibaraki Univ.; [6] none; [7] Earth and Planetary Sci., Univ. of Tokyo; [8] Earth and Planetary Sci., Tokyo Univ

Nitric acid (HNO3) formed via photo-oxidation of NOx is one of the most important acidic gases in urban air. Aerosol nitrate (NO3-), which is one of the major aerosols in urban air, is formed from HNO3 and ammonia (NH3). Ground-based in-situ measurements of gas-phase HNO3 and particulate NO3- 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. HNO3 and NO3-; were observed to undergo distinct diurnal and seasonal variations driven mainly by the temporal variations in the HNO3 production rate and HNO3-NO3-; partitioning. Higher temperature and lower RH were observed to increase the HNO3/NO3-; ratios, as predicted by the thermodynamic theory. Temporal changes in the HNO3 - NO3-; partitioning controlled the HNO3 and NO3-; concentrations more strongly than those in the total nitrate, TN = HNO3 + NO3-;, although largest TN values in daytime summer was due to the enhanced HNO3 production. The NO3-;/TN ratio showed strong diurnal and seasonal variations, HNO3 becoming a dominant part of TN during midday, except for winter, when the NO3-;/TN ratio was higher than 0.9 throughout the day. The partitioning between HNO3 and NO3-; was calculated by equilibrium and one-dimensional (1-D) models. By comparing the results from the two models, the vertical mixing was found to effectively shift the partitioning to NO3-; at the surface due to transport of air from above, richer in NO3-; and poorer in HNO3. The NO3-;/TN ratios calculated by the 1-D model in the whole observed ranges of temperature (1-34 C) and RH (18-95%) greatly improved agreement with those observed over the equilibrium model for daytime conditions. The results suggest the importance of the vertical mixing on the HNO3-NO3-; partitioning.