

Photochemical Ozone Production Rates and Limiting Factors over East Asia: Impact of Radical Chemistry Mechanism and Ozone-Control Implications

Y. Kanaya (1), F. Takiyama (1), X. Pan (1,4), P. Pochanart (1,5), H. Akimoto (1,2), Y. Yokouchi (2), S. Nozoe (2,6), S. Inomata (2), H. Irie (1,7), H. Takashima (1,8), Y. Komazaki (1), H. Tanimoto (2), and Z. Wang (3)

(1) Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Department of Environmental Geochemical Cycle Research, Yokohama, Japan (yugo@jamstec.go.jp), (4) Now at RIAM, Kyushu University, Fukuoka, Japan, (5) Now at National Institute of Development Administration, Bangkok, Thailand, (2) National Institute for Environmental Studies, Tsukuba, Japan, (6) Now at National Museum of Emerging Science and Innovation, Tokyo, Japan, (7) Now at Chiba University, Chiba, Japan, (8) Now at Fukuoka University, Fukuoka, Japan, (3) Institute of Atmospheric Physics, CAS, Beijing, China

Growth of tropospheric ozone, causing health and climate impacts, is concerned over East Asia, because emissions of precursors have dramatically increased. Photochemical production rates of ozone and limiting factors, primarily studied for urban locations, have been poorly assessed within a perspective of regional-scale air pollution over East Asia. Here we provide an overview of such assessment performed at several locations with regional representativeness based on the observation-based modeling approach using comprehensive observations of ozone precursors. Diagnosis of aged air masses at Fukue Island (32.75°N, 128.68°E) remotely located in western Japan (May 2009) is highlighted, where the highest 10% of hourly ozone concentrations reached 72–118 ppb during May influenced by Asian continental outflow. The average in-situ ozone production rate was estimated to be 6.8 ppb per day, suggesting that in-travel production was still active, while larger buildup must have occurred beforehand. Information on the chemical status of the air mass arriving in Japan is important, because it affects how further ozone production occurs after precursor addition from Japanese domestic emissions. The main limiting factor of ozone production was usually NO_x , suggesting that domestic NO_x emission control is effective in reducing further ozone production and the incidence of warning issuance (>120 ppb). VOCs also increased the ozone production rate, and occasionally (14% of time) became dominant. This analysis implies that the VOC reduction legislation recently enacted should be effective. The uncertainty in the radical chemistry mechanism governing ozone production had a non-negligible impact, but the main conclusion relevant to policy was not altered. When chain termination was augmented by including heterogeneous loss of HO_2 on aerosol particle surfaces, for which an uptake coefficient (γ) of 0.25 was assumed as we recently verified in the laboratory kinetic experiments using water extract of aerosol samples collected at the summit of Mt. Tai (36.26°N, 117.11°E), Shandong Province, China, the daily ozone production rate decreased from 6.8 to 5.2 ppb per day, and the fraction of hours when the VOC-limited condition occurred varied from 14% to 16%. In another case when $\text{HO}_2\text{-H}_2\text{O} + \text{NO}$ reaction producing HNO_3 at a yield of 0.07 was added, the production rate and the fraction of hours with the VOC-limited condition were virtually unchanged (6.7 ppb per day and 14%). These reaction pathways may correct the tendency that three-dimensional model simulations overestimate production and mixing ratios of ozone.

References:

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