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主 論 文 の 要 旨

論 文 題 目 Acidity of aerosol particles: Estimation based on a chemical thermodynamic model and development of a direct measurement method
(エアロゾル粒子の酸性度：化学熱力学モデルに基づいた推定および直接測定方法の開発)

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論 文 内 容 の 要 旨

Aerosol particles are suspended solid or liquid particles in the atmosphere that impact many chemical and physical processes and human health. Aerosol particles consist of various substances including hygroscopic components such as sulfate, nitrate and ammonium. Depending on relative humidity (RH) of the air, aerosol particles absorb water vapor and grow their size. Thus, the aerosol particles often contain liquid water of high ionic strength. Aerosol acidity is the pH of the liquid water in the aerosol particles. It is a critical parameter that strongly affects the gas/particle phase partitioning of inorganic semivolatile species and the multiphase chemical processes. However, it is difficult to measure aerosol pH directly because of small solution quantity and the high ionic strength of atmospheric aerosol particles. In the earlier studies, aerosol pH is inferred based on the aerosol sample extracts, but it cannot adequately indicate real aerosol pH due to much lower ionic strength of extracts than that in aerosols. Recently, the chemical thermodynamic models are often used to estimate aerosol pH during short-term and high concentration events in some areas. However, long-term studies based on a high-quality data set including gaseous ammonia are scarce.

In this study, aerosol pH is estimated by using a benchmark chemical thermodynamic model, the Extended Aerosol Inorganics Model (E-AIM), based on two-years data obtained from continuous observations of water-soluble gaseous species (NH_3 and HNO_3) and ionic constituents of particles in Nagoya during 2017–2018. Moreover, based on the same data, the factors affecting aerosol pH are investigated by various sensitivity tests conducted using E-AIM model. The estimation results show that aerosol pH presented a seasonal variation of low in summer (an average of 2.31 ± 0.39) and high in winter (an average of 3.05 ± 0.15). The sensitivity test results indicate that (1) such seasonal variation of aerosol pH appears only in the low SO_4^{2-} concentration area like Nagoya, (2) the liquid water content of aerosol particles is related to temperature, resulting in the influence of temperature on aerosol pH, and (3) ammonium, which can neutralize SO_4^{2-}, is also an important driving factor for aerosol pH.

In order to provide comparable data for relating the chemical thermodynamic estimations with atmospheric aerosol particles, a direct measurement method of aerosol pH is needed. Herein, according to hygroscopic equilibrium under high RH conditions, a direct measurement method for the pH of hygroscopic particles was developed by utilizing a pH testing paper. The color response accuracy for 6 kinds of pH testing papers were examined under various ionic strengths to select the best performing paper under higher ionic strength of various salt mixtures. Then the KNO_3 saturated solution is used to provide the constant RH at 92%, enabling hygroscopic constituents in the aerosol sample to form an aqueous droplet which has realistic high ionic strength in the atmosphere. After selected the best pH test paper using the droplet tests, it is further examined for the measurement capability of atmospheric aerosols. The results indicate that this method needs more than about 12 μg per sample spot of fine aerosols to form the detectable size of the deliquesced droplet.

By comparing the measurement results of the pH testing paper method and the estimation results from the E-AIM model, the effect of gaseous NH_3 on the pH testing paper method was examined. The NH_3 concentration in the chamber should be controlled to obtain more reliable data. Moreover, this comparison also indicates that the pH definition based on a molality scale is the most suitable when the E-AIM model is used to estimate aerosol pH.

The results of this thesis revealed the seasonal variation and driving factors of aerosol pH in Nagoya, which is expected to be a representative for other less-polluted urban areas and a future situation for the currently polluted but improving areas. Furthermore, approaches shown in this study, including the application of E-AIM model and the pH testing paper method, can provide more realistic pH data on various acidity-dependent chemical processes on aerosol particles.