学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Identification of hydroxy and keto-dicarboxylic acids in remote marine aerosols: Implications for photochemical formation and transformation of water-soluble organic aerosols

（外洋エアロゾル中のヒドロキシおよびケトジカルボン酸の同定：水溶性有機エアロゾルの光化学的生成と変質への関係）

Identification of hydroxy- and keto-dicarboxylic acids (diacids) in remote marine aerosol samples is important to a better understanding of the photochemical process and chemical composition of organic particulate matter, as this chemical composition is essential for predicting the effects on climate, air quality, and human health. Therefore, aerosol (TSP) samples were collected from remote marine aerosols at Chichijima Island and were studied for hydroxy- and keto-diacids. A two-step derivatization technique was employed, using 14% $BF_3$/n-butanol for the butylation of carboxyl groups and acidic ketones followed by N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) for the trimethylsilylation of hydroxyl groups. Several new peaks were detected in the gas chromatogram after trimethylsilylation of the dibutyl ester fraction. Based on mass spectral interpretation with authentic standards, we successfully identified and quantified a homologous series of hydroxy-diacids (hC3di–hC6di), including tartronic acid, malic acid, 3-hydroxyglutaric acid, 2- hydroxyglutaric acid, 2-hydroxyadipic acid, 3-hydroxyadipic acid, and tartaric acid. Keto-diacids (kC4) includes oxaloacetic acid.

Seasonal variations of hydroxy- and keto-diacids at Chichijima Island shows maximum in spring followed winter and autumn. Molecular compositions of hydroxy- and keto-diacids show predominance of malic acid followed by tartronic acid. Total hydroxy- and keto-diacids maximized in spring when air masses originated from the Asian Continent with westerly winds. Concentrations of total hydroxydiacids contribute 5.6 % for total diacids. Significant positive correlation was observed between hydroxydiacids and diacids compounds in all four seasons suggest that hydroxydiacids and diacids have similar sources. This study demonstrates that the ambient aerosols from Chichijima Island are strongly influenced by the outflow of Asia pollutants in winter/spring and by photo-oxidation process they are converting into low molecular weight diacids through intermediates.

Furthermore, to better understand the photochemical processing of hydroxy- and keto-diacids, we conducted batch UV irradiation experiments on two types of samples collected from India, which symbolize anthropogenic (AA) and biogenic aerosols (BA), for time periods of 0.5 to 120 h. The results show that photochemical degradation of tartronic (hC3), malic (hC4), 2-hydroxyglutaric (2-hC5), and 2-hydroxyadipic acids (2-hC6) and keto form of oxaloacetic acid overcome their production in aqueous aerosols. Whereas, 3-hydroxyglutaric acid (3-hC5), tartaric acid, 3-hydroxyadipic acid (3-hC6), enol form of oxaloacetic acid showed a significant increase during the course of irradiation experiment. We also found a gradual decrease in the relative abundance of hC4 to total hydroxy diacids and an increase in the relative abundance of enol form of oxaloacetic acid during prolonged experiment. Based on the changes in concentrations and mass ratios of selected species with the irradiation time, we suggest that hydroxydiacids are the intermediates in degradation of small diacids. This study demonstrates that the ambient aerosols contain abundant precursors that produce diacids via intermediates such as hydroxy and keto diacids.