

海洋エアロゾルおよびバイオマス燃焼エアロゾル中のジカルボン酸、ケトカルボン酸、 α -ジカルボニルの分布とエアロゾル窒素・炭素の安定同位体組成に関する大気化学的研究

Atmospheric chemical studies on the distributions of dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls in marine and biomass burning aerosols and stable isotopic composition of aerosol nitrogen and carbon

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The ubiquitous presence and significant contribution of dicarboxylic acids and related compounds (ketocarboxylic acids and α -dicarbonyls) to aerosol mass is well recognized in the atmosphere. Although we do have limited knowledge about their chemical formation and degradation, and sources, these compounds are produced via atmospheric photochemical processes. Therefore, they can provide information on the chemical evolution of water-soluble organic aerosols, which is poorly understood. Dicarboxylic acids can contribute to the CCN activity, which affects cloud microphysical properties and hence precipitation patterns and cloud albedo. To better understand the source and formation mechanisms of dicarboxylic acids and related compounds in the atmosphere, marine aerosol samples ($n = 84$) (total suspended particles: TSP) were collected at Gosan site in Jeju Island, South Korea from April 2003 to April 2004 whereas biomass burning aerosol samples (daytime: 6 and nighttime: 9) in the particle size $< 2.5 \mu\text{m}$ were collected from a Amazonian pasture site in Rondônia, Brazil, during an intensive biomass burning period of 16-26 September 2002. The usefulness of $\delta^{13}\text{C}$ of total carbon (TC) and $\delta^{15}\text{N}$ of aerosol nitrogen such as total nitrogen (TN), remained nitrogen (remained N, mostly NH_4^+) and removed nitrogen (removed N, mostly NO_3^-), which has rarely been addressed in the literature, was examined to explain their sources and chemical processing in the atmosphere, and biomass burning mechanism. Furthermore, organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), and water-soluble inorganic ions were studied here.

Among the molecular organics detected, oxalic acid (C_2) was found to be the most abundant, followed by malonic acid (C_3) in marine aerosols and by succinic acid (C_4) in biomass burning aerosols. The mean concentrations of total dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls are 784, 41, and 15 ng m^{-3} in the marine aerosols from Gosan site whereas those are 2180, 167, and 56 ng m^{-3} in biomass burning aerosols from Amazon. The 2-16 times higher concentra-

tions of diacids and related compounds in biomass burning aerosols than those reported in urban aerosols indicate that biomass burning is a very important source for dicarboxylic acids and related compounds at the regional and global scales.

The annual mean contributions of dicarboxylic acids, ketocarboxylic acids and dicarbonyls to WSOC are 12, 1, and 0.4% in marine aerosols, respectively. They are several times higher than those reported in East Asian countries from which air masses are transported to Gosan, indicating an importance of photochemical processing of aerosols during a long-range transport. Higher ratios of dicarboxylic acids and related compounds to biomass burning tracers (levoglucosan and K^+) in biomass burning aerosols, as well as higher ratios of oxalic acid to other dicarboxylic acids and related compounds normalized to biomass burning tracers were found in daytime than in nighttime, suggesting an importance of photochemical production and degradation in the smoke layers. Higher mass concentrations of SO_4^{2-} , NH_4^+ and CH_3SO_3^- normalized by K^+ , levoglucosan, or elemental carbon (EC) in daytime also suggest their photochemical production in biomass burning plumes.

Marine aerosols showed the highest mean $\delta^{15}\text{N}$ values of TN ($+16.9 \pm 4.5\%$) and remained N ($+20.2 \pm 5.2\%$) in summer (June-August) and the lowest mean $\delta^{15}\text{N}$ values ($+12.9 \pm 3.4\%$, $+11.3 \pm 5.1\%$, respectively) in winter (December-February). This can partly be explained by an enhanced contribution of ^{15}N -enriched emissions from agricultural straw burning in a harvest season (summer and autumn) in China. The mean $\delta^{15}\text{N}$ of removed N showed an opposite trend: the lowest ($+9.2 \pm 3.7\%$) in warm season (March-August) and the highest ($+14.8 \pm 3.8\%$) in cold season (September-February). These results can be explained by changes in source regions and emission strengths from different sources of nitrogenous species, and difference in secondary aerosol nitrogen formation between the warm and cold seasons.

In biomass burning aerosols, the $\delta^{15}\text{N}$ values of total nitro-

gen (TN) ranged from +23.5‰ to +25.7‰, however, there was no diurnal trend. Consecutive day and night samples showed that $\delta^{13}\text{C}$ values of total carbon (TC) were lower in daytime samples, which can be interpreted as resulting from higher contributions of refractory TC depleted in ^{13}C mainly due to flaming combustion. Higher values of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ for biomass burning particles than those of unburned vegetation reflect positive isotopic enrichment either during the formation of particles or after the emission of particles in the atmosphere.

This study demonstrates that there are differences in the molecular distributions of dicarboxylic acids and related compounds between biomass burning and marine aerosols. The chemical evolution of water-soluble organics and water-

soluble inorganic ions was observed in both the marine and biomass burning atmospheres during a long-range transport. It is clarified that biomass burning is a very important source for dicarboxylic acids and related compounds at the regional and global scales. The $\delta^{15}\text{N}$ of total nitrogen (TN), remained nitrogen (mostly NH_4^+) and removed nitrogen (mostly NO_3^-) was found to be an effective tool to backtrack the sources of nitrogenous species and their atmospheric processing at Gosan. It is demonstrated that the $\delta^{13}\text{C}$ of total carbon (TC) can successfully explain the source of organic carbon formed during biomass burning processes. It is also proved that the $\delta^{13}\text{C}$ of TC and $\delta^{15}\text{N}$ of TN can together provide information on their sources and isotopic fractionation that occur during biomass burning.

和文要旨

大気中の水溶性有機エアロゾルの起源と生成機構を明らかにするために、韓国済州島・Gosan サイトにて2003年4月から2004年4月にかけて採取した海洋エアロゾル試料 (TSP, 84試料) を GC, GC/MS にて分析し、シュウ酸をはじめとした低分子ジカルボン酸, ケトカルボン酸, α -ジカルボニルの濃度分布・季節変化を明らかにした。また、バイオマス燃焼の有機エアロゾルへの影響を評価するために、アマゾン牧草地においてエアロゾル試料 (PM 2.5) を採取し、低分子ジカルボン酸などを測定した。更に、エアロゾル炭素・窒素の同位体比を測定し、エアロゾルの起源・大気中での化学プロセスに関する情報を解析した。水溶性有機炭素 (WSOC), 有機炭素 (OC), 元素状炭素 (EC), 無機イオンも測定した。