

学位論文題名

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

(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)

学位論文内容の要旨

Abstracts

Aerosol samples ($n=84$) were collected continuously from April 2003 to April 2004 at Gosan site in Jeju Island, South Korea. They were studied for diacids, ketoacids and α -dicarbonyls, as well as organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), and water-soluble inorganic ions. While the WSOC fraction accounted for $\sim 25\%$ mass concentration of SO_4^{2-} in spring and summer, $\sim 18\%$ were found in autumn and winter. Average WSOC to OC ratios ranged from 0.5 to 0.6, with the highest value in winter. Higher ratios than those reported in East Asia, from which air masses are transported to Gosan, suggest the photochemical processing of aerosols during a long-range transport. Oxalic (C_2) acid followed by malonic (C_3) acid was the most abundant in all seasons. The mean concentration (784 ng m^{-3}) and relative abundances (81, 8.4, and 15%) of total diacids in detected molecular organics, OC and WSOC were found the highest in summer, whereas those (47 ng m^{-3} and 10, 0.5, and 0.8%) of ketoacids and those (23 ng m^{-3} and 7, 0.3, and 0.5%) of dicarbonyls showed the highest in winter. These results suggest that the sources of diacids are different from the sources of ketoacids and dicarbonyls. There are differences in the seasonal variations of diacids and related compounds, which is also an indication of their different sources. This study demonstrates an enhanced photochemical production and degradation in summer than in other seasons. Higher positive correlations between combustion tracers (K^+ and EC) and diacids and related compounds in winter were observed than those in summer, pointing to higher emission of diacids and related compounds or their precursors from fossil fuel/biomass burning in winter. More tight, positive correlations of secondary tracers (SO_4^{2-} and NO_3^-) with diacids and related compounds in winter than those in summer are explained by their more specific sources in winter.

The atmospheric aerosol samples ($n=84$) collected at Gosan site were also analyzed for the measurements of total nitrogen (TN) and its isotopic ratio ($\delta^{15}\text{N}$) as well as nitrogen species (NH_4^+ and NO_3^-). Measurements were also conducted for remained N and removed N on HCl fume treatment. A pronounced seasonal variation was found in the $\delta^{15}\text{N}$ of TN,

remained N (mostly composed of NH_4^+) and removed N (mostly composed of NO_3^-). The highest mean $\delta^{15}\text{N}$ values of TN ($+16.9\pm4.5\text{‰}$) and remained N ($+20.2\pm5.2\text{‰}$) are detected in summer (June-August), whereas the lowest mean $\delta^{15}\text{N}$ values ($+12.9\pm3.4\text{‰}$, $+11.3\pm5.1\text{‰}$, respectively) are in winter (December-February). This can partly be explained by an enhanced contribution of ^{15}N -enriched emissions from agricultural straw burning in China in a harvest season (summer and autumn). The mean $\delta^{15}\text{N}$ of removed N showed an opposite trend: the lowest ($+9.2\pm3.7\text{‰}$) in warm season (March-August) and the highest ($+14.8\pm3.8\text{‰}$) 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. Higher ratios of $\text{Ca}^{2+}/\text{Na}^+$ and the lowest ratios of $\text{Na}^+(\text{Cl}^- + \text{NO}_3^-)$ are found to associate with lower $\delta^{15}\text{N}$ values of removed N as a result of less isotopic enrichment ($\varepsilon_{\text{product-reactant}}$) during the reaction between HNO_3 and dust particles. This study demonstrates that $^{15}\text{N}/^{14}\text{N}$ ratio is a good process tracer of nitrogenous species during long range transport in the atmosphere.

Aerosol particles ($\text{PM}_{2.5}$) were collected during the day ($n=6$) and nighttime ($n=9$) from a tropical pasture site in Rondônia, Brazil during an intensive biomass burning period (16-26 September, 2002). Higher normalized (by K^+ , levoglucosan, or apparent elemental carbon, EC_a) mass concentrations of SO_4^{2-} and CH_3SO_3^- in daytime suggest their photochemical production, while the opposite trend for NO_3^- suggests its transfer to the aerosol phase at lower temperatures and higher humidities, as well as possibly production through hydrolysis of N_2O_5 on aqueous aerosol particles. About 4.2-7.5% of OC (5-13% of water-soluble organic carbon (WSOC)) could be characterized at the molecular level using GC-MS and GC-FID. Among the detected organic compound classes, the relative abundances of anhydrosugars and aromatics were higher in night samples, but sugars/sugar alcohols, diacids, oxoacids and α -dicarbonyls were more abundant in daytime samples. 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 contribution of refractory TC depleted in ^{13}C due to predominant flaming combustion. The $\delta^{15}\text{N}$ values of total nitrogen (TN) ranged from $+23.5\text{‰}$ to $+25.7\text{‰}$, however, there was no trend in day and night samples. 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.

The $\text{PM}_{2.5}$ aerosol samples were also analyzed for homologous series of dicarboxylic acids ($\text{C}_2\text{-C}_{11}$) and related compounds (ketocarboxylic acids and dicarbonyls) using gas chromatography and GC/mass spectrometry (GC/MS). Among the species detected, oxalic acid was found to be the most abundant, followed by succinic, malonic and glyoxylic acids. Average concentrations of total dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls in the aerosol samples were 2180 , 167 and 56 ng m^{-3} , respectively. These are 2-8, 3-11 and 2-16 times higher, respectively, than those reported in urban aerosols, such as in 14 Chinese megacities. Higher ratios of dicarboxylic acids and related compounds to biomass burning tracers (levoglucosan and K^+) were found in daytime than in nighttime, suggesting an importance of the photochemical production. On the other hand, higher ratios of oxalic acid to other dicarboxylic acids and related compounds normalized to biomass burning tracers (levoglucosan and K^+) in daytime provide an evidence for possible degradation of dicarboxylic acids ($\geq \text{C}_3$) in this smoke-polluted environment. Assuming that these diacids and related compounds are photochemically oxidized to oxalic acid in daytime, this process could account for, on average, 77% of the formation of oxalic acid. The remaining portion of oxalic acid may have been directly emitted from biomass burning as suggested by a good correlation with the biomass burning tracers (K^+ , CO and EC_a) and organic carbon (OC). However, photochemical production from other precursors could not be excluded.

学位論文審査の要旨

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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 widely believed to be produced by 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 concentrations 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 $\delta^{15}N$ values of TN ($+16.9\pm4.5\%$) and remained N ($+20.2\pm5.2\%$) in summer (June-August) and the lowest mean $\delta^{15}N$ values ($+12.9\pm3.4\%$, $+11.3\pm5.1\%$, 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 $\delta^{15}N$ of removed N showed an opposite trend: the lowest ($+9.2\pm3.7\%$) in warm season (March-August) and the highest ($+14.8\pm3.8\%$) 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 $\delta^{15}N$ values of total nitrogen (TN) ranged from $+23.5\%$ to $+25.7\%$, however, there was no diurnal trend. Consecutive day and night samples showed that $\delta^{13}C$ 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 $\delta^{13}C$ and $\delta^{15}N$ 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 $\delta^{15}N$ 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 $\delta^{13}C$ of total carbon (TC) can successfully explain the source of organic carbon formed during biomass burning processes. It is also proved that the $\delta^{13}C$ of TC and $\delta^{15}N$ of TN can together provide information on their sources and isotopic fractionation that occur during biomass burning.

The committee members agreed that this dissertation provides new data sets that are useful

for the community of atmospheric chemistry and relevant environmental sciences. In particular, this study demonstrated an importance of photochemical process in controlling the water-soluble organic aerosols. The new observations at marine and tropical forest sites together with isotopic measurements of carbon and nitrogen have contributed for better understanding the chemical evolution of organic aerosols in the atmosphere. The thesis has been well written. All the committee members agreed to grant the degree to Mr. Shuvashish Kundu.