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学 位 論 文 審 査 の 要 旨

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学 位 論 文 題 名

Seasonal distributions of low molecular weight dicarboxylic acids, ketoacids and α-dicarbonyls in ambient aerosols collected at Cape Hedo, Okinawa, an outflow region of Asian dusts
（沖縄辺戸岬で採取したエアロゾル中の低分子ジカルボン酸と関連有機化合物の組成分布の季節変化）

Ambient aerosol samples were collected for one year in Cape Hedo, Okinawa, the southernmost main island of Japan and studied for water-soluble dicarboxylic acids, ketoacids, and α-dicarbonyls to better understand the formation/transformation pathways of organic aerosols during long-range atmospheric transport. Here, we report the seasonal variations of diacids and related compounds in Okinawa, the outflow region of Asian dusts in the western North Pacific. We found that oxalic acid is the most abundant diacid species followed by malonic (C_3) and succinic (C_4) acids whereas glyoxylic acid is a dominant ketoacid. Total diacids and ketoacids maximized in spring when air masses originated from the Asian Continent under westerly winds. In contrast, α-dicarbonyls showed maximum concentrations in winter. The C_3/C_4 ratios were found to increase in summer, suggesting an enhanced photochemical aging of organic aerosols. Both phthalic acid (Ph)/C_9 and C_6/C_9 ratios peaked in winter, suggesting an enhanced transport of organic pollutants from East Asia. The average total diacid-C/total carbon ratio (5.4%) is higher than that (3.1%) from the East China Sea but lower than that from the remote Pacific including tropics (8.8%), suggesting that Okinawa aerosols are more aged than East Asian aerosols. This study demonstrates that the ambient aerosols from Cape Hedo are strongly influenced by the outflow of Asian pollutants in winter/spring and by photochemical processes of marine-derived organic matter in summer.

In addition, we analyzed organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), total nitrogen (WSTN) and organic nitrogen (WSON), and major inorganic ions. The average concentration of OC is higher in growing seasons; spring (2.36 μg m^{-3}) and summer (1.79 μg m^{-3}). Similarly, the highest concentrations of EC and WSOC were found in spring (av. 0.41 μg m^{-3} and 0.95 μg m^{-3},

respectively) followed by winter (0.37 and 0.90 μg m^{-3}) whereas the lowest concentrations were found in summer (0.19 and 0.52 μg m^{-3}, respectively). Higher concentrations of WSON were observed in early summer (av. 0.26 μg m^{-3}) probably due to the emission from marine biota. The relatively high OC/EC (av. 7.6) and WSOC/OC (44%) ratios suggest the secondary formation of organic aerosols. A strong positive correlation between Ca^{2+} and TSP in spring suggests a significant contribution of Asian dusts whereas the higher concentrations of NO_3^- and nss-SO_4^{2-} in winter suggest an important influence from anthropogenic sources including biomass burning, vehicular emission and coal combustion. Moreover, stable carbon ($\delta^{13}C$) and nitrogen isotope ratios ($\delta^{15}N$) were determined for total carbon (TC) and nitrogen (TN). The annually averaged $\delta^{13}C$ and $d^{15}N$ ratios are -22.1‰ and +12.2‰, respectively. The seasonally averaged $\delta^{13}C$ and $d^{15}N$ ratios are higher in spring (-22.5‰ and +14‰, respectively) whereas these ratios are lower in summer (-22.9‰, +11.1‰). However, no correlation was obtained between nss-Ca/TSP and $\delta^{13}C$, suggesting that during long-range atmospheric transport organic aerosols are intermixed with various sources. A strong correlation between TC and TN in spring (r^2=0.78) and winter (0.70) suggests that TC and TN have similar sources. Contributions of NO_3^- to TN are higher (45%) than those (18%) of NH_4^+, suggesting that vehicular exhaust and biomass burning emissions are more important nitrogen sources than the emissions from agricultural wastes and animal excreta.