Seasonal changes in stable carbon isotopic compositions of LMW dicarboxylic acids, ketoacids and α-dicarbonyls in aerosols over the western North Pacific

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Low molecular weight (LMW) dicarboxylic acids such as oxalic acid (C_2) are most abundant organic compound class in atmospehric aerosols. Because they are water-soluble, dicarboxylic acids can enhance the hygroscopic properties of atmospheric particles. We collected marine aerosols every week from 2001 to 2013 at a remote island, Chichijima, in the western North Pacific. The filters were extracted with organic free pure water to isolate diacids and related compounds. The extracts were reacted with BF_3/n-butanol to derive carboxyl groups to butyl esters and aldehyde groups to dibutoxy acetals. The derivatives were determined by GC and GC/MS. We found that C_2 is the dominant diacid species followed by malonic (C_3) acid in the aerosols thoroughout the year whereas glyoxylic acid is the dominant ketoacid. Stable carbon isotopic ratios ($\delta^{13}C$) of small diacids, ketoacids and α-dicarbonyls (glyoxal and methylglyoxal) were measured in the marine aerosols using a capillary gas chromatography combined to on-line combustion/isotope ratio mass spectrometer (GC/IRMS) [1].

We found that $\delta^{13}C$ of C_2 increased from -20‰ in winter to -5‰ in summer. Malonic acid (C_3) also showed an increase of $\delta^{13}C$ from winter (-25‰) to summer (-15‰). The increase in $\delta^{13}C$ values is likely caused by isotopic fractionation that occurs during photochemical decomposition of carboxylic acids [2]. We propose that ^{12}C-^{12}C bonds of oxalic acid decompose preferentially over ^{12}C-^{13}C bonds during photolysis of oxalate-iron complex. Interestingly, methylglyoxal and glyoxylic acid, which are the precursor compounds of oxalic acid, generally showed higher $\delta^{13}C$ values than those of oxalic acid. Seasonal variation of $\delta^{13}C$ will be discussed in terms of Asian outflow of anthropogenic aerosols and photochemical aging.

[1] Kawamura and Watanabe (2004) *Anal. Chem.* **76**, 5762-5768 [2] Pavuluri and Kawamura (2012) *Geophys. Res. Lett.*, ***39***, L03802.