Supplementary material to: Seasonal and spatial variability of the OM/OC mass ratios and region-wide high correlation between oxalic acid and zinc in Chinese urban organic aerosols

L. Xing[1], T.-M. Fu[1], J.J. Cao[2], S.C. Lee[3], G.H. Wang[2], K.F. Ho[4], M.-C. Cheng[5], C.-F. You[5], T.J. Wang[6]

[1]Department of Atmospheric and Oceanic Sciences and Laboratory for Climate and Ocean-Atmosphere Studies, School of Physics, Peking University, Beijing, China, 100871

[2]State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, China, 710075

[3]Research Centre of Urban Environmental Technology and Management, Department of Civil and Structural Engineering, Hong Kong Polytechnic University, Hong Kong, China

[4]School of Public Health and Primary Care, The Chinese University of Hong Kong, Hong Kong, China

[5]Department of Earth Sciences, National Cheng Kung University, Tainan 701, Taiwan

[6]School of Atmospheric Sciences, Nanjing University, Nanjing, China, 210093

Correspondence to: T.-M. Fu (tmfu@pku.edu.cn)

Abstract

We calculated the organic matter to organic carbon mass ratios (OM/OC mass ratios) in $PM_{2.5}$ collected from 14 Chinese cities during summer and winter of 2003 and analyzed the causes for their seasonal and spatial variability. The OM/OC mass ratios were calculated two ways. Using a mass balance method, the calculated OM/OC mass ratios averaged 1.92±0.39 year-round, with no significant seasonal or spatial variation. The second calculation was based on chemical species analyses of the organic compounds extracted from the $PM_{2.5}$ samples using dichloromethane/methanol and water. The calculated OM/OC mass ratio in summer was relatively high (1.75±0.13) and spatially-invariant, due to vigorous photochemistry and secondary organic aerosol (OA) production throughout the country. The calculated OM/OC mass ratio in winter (1.59±0.18) was significantly lower than that in summer, with lower values in northern cities (1.51 ±0.07) than in southern cities (1.65 ±0.15). This likely reflects the wider usage of coal for heating purposes in northern China in winter, in contrast to the larger contributions from biofuel and biomass burning in southern China in winter. On average, organic matter constituted 36% and 34% of Chinese urban $PM_{2.5}$ mass in summer and winter, respectively. We reported, for the first time, a region-wide high correlation between Zn and oxalic acid in Chinese urban aerosols in summer. This is consistent with the formation of stable Zn oxalate complex in the aerosol phase previously proposed by Furukawa and Takahashi (2011). We found that many other dicarboxylic acids were also highly correlated with Zn in the summer Chinese urban aerosol samples, suggesting that they may also form stable organic complexes with Zn. Such formation may have profound implications for the atmospheric abundance and hygroscopic properties of aerosol dicarboxylic acids.

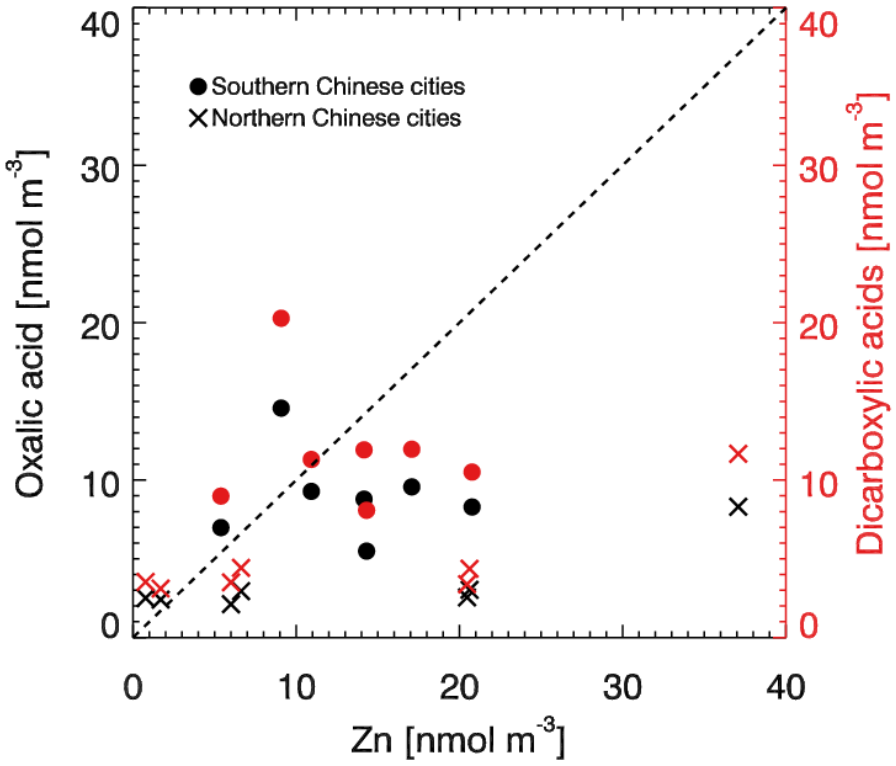

Figure S1. Zn versus oxalic acid molar concentrations (black) in aerosol samples collected from 14 Chinese cities in winter 2003. Also shown in red are the molar concentrations of Zn versus the the sum of the molar concentrations of the 12 dicarboxylic acids (terephthalic acid, 4-ketopimelic acid, oxalic acid, dodecanedioic acid, malonic acid, malic acid, phthalic acid, azelaic acid, glutaric acid, fumaric acid, adipic acid, and sebacic acid) that were highly correlated with Zn in the summertime Chinese urban aerosol samples. The dashed line indicates 1:1 molar concentrations.