

Interactive comment on “ Summer and winter

variations of dicarboxylic acids, fatty acids and benzoic acid in PM_{2.5} in Pearl Delta River Region, China” by K. F. Ho et al.

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Main comment My main concern about this paper is the lack of statistical analyses/tests applied on the dataset. Statistics could strengthen (and validate) the spatial/temporal differences observed. I have several remarks:

1) The average values presented in Table 1 ($n = 8$ in winter and $n = 7$ in summer) often have high standard deviations (SD). So, when the authors compare these average values, they have to take care that they are (or are not) statistically different. For

C13563

example the authors argue that “The concentrations of the organic pollutants in winter were generally higher in PU and HT than in GZ and ZQ”. If we look at the data, the concentrations of total organic acids in winter reported in Table 1 are 644 ± 327 , 656 ± 346 , 384 ± 171 and 490 ± 241 ng m⁻³ for PU, HT, GZ and ZQ, respectively. Indeed, the trend described by the authors is correct. Nevertheless, with regard to the relatively high SD, are the average values reported at PU and HT really higher than those measured at GZ and ZQ? The authors could use a parametric test such as one-way analyses of variance (ANOVA). Since the number of samples is not very high ($n = 7$ or 8) and SD are high, I think a non parametric test (Mann Whitney) could be more appropriated here.

Response: Non parametric tests (Mann Whitney) were applied to evaluate the statistically different between the concentrations of different data set in different seasons. And for example “The concentrations of the organic pollutants in winter were generally higher in PU and HT than in GZ and ZQ” was revised as “The concentrations of the organic pollutants in winter were statistically higher in PU than in GZ”.

2) It is difficult to highlight spatial and temporal variations from Table 1. The information provided by this table is too disseminated and scatter because of the high number of variables. Hence, the authors should add a figure showing only some variables of Table 1 (the ones for which variations clearly appeared between sites and seasons: concentration of total dicarboxylic acids, concentration of total fatty acids, TQWOC/OC ratio, C3/C4 ratio, . . .). This new figure would allow emphasizing the spatial/temporal variations in a more synthetic way. Maybe box-and-whisker plots should be employed for comparing the distributions of these selected variables across sites and seasons.

Response: Box pots of TQWOC, sum of fatty acids, TQWOC/WSOC, and TQWOC/OC ratios have been added as Figure 3 (in revised manuscript).

3) The significance (p value) of the correlation coefficients (r) reported in Table 2 should be included. Are all r values significant? Same thing for the two r values presented in

C13564

Fig. 3.

Response: The statistical significance (p value) of the correlation coefficients has been reported and presented in Table 2, Figure 3, and section 3.4 (section 3.5 in revised manuscript).

Other comments: 4) Are the results obtained from the 2-day air mass back trajectory analyses (i.e. northeasterly wind in winter, south-westerly wind in summer) representative of seasonal wind regimes in the PRD area?

Response: Meteorological conditions over this region and a large part of Asia are strongly influenced by Asian monsoon circulations. During the winter, prevailing surface winds are northerly and northeasterly. By contrast, southerly and southwesterly winds are predominant in the summer. Such meteorological conditions make the coastal region of southern China an ideal place to measure the chemical composition of polluted continental outflow in the winter and clean South China Sea air during summer (Guo et al., 2010). It is similar to the air flows presented in Figure 2.

Reference Guo, H., Simpson, I. J., Ding, A. J., Wang, T., Saunders, S. M., Wang, T. J., Cheng, H. R., Barletta, B., Meinardi, S., Blake, D. R., Rowland, F. S., 2010. Carbonyl sulfide, dimethyl sulfide and carbon disulfide in the Pearl River Delta of southern China: Impact of anthropogenic and biogenic sources. *Atmospheric Environment* 44, 3805-3813.

5) Did the authors perform isotopic measurements on some of the samples presented in this study? If they did not, I do not ask them to carry out such analyses of course. But if they have some isotopic measurements, it should be interesting to include them to the dataset. Indeed, the stable carbon isotopic composition of individual organic acids could bring complementary information about the sources and the transformation processes occurring in the atmosphere of the PRD region.

Response: We agreed with the suggestions of the reviewer. However, we didn't per-

C13565

form isotopic measurements on the samples presented in this study.

Minor comments/corrections

Abstract, page 26678, line 2: add "at four different sites" between "collected" and "in Pearl River Delta"

Response: Revised as suggested.

Abstract, page 26678, line 15 and 16: replace "are" by "were".

Response: Revised as suggested.

Abstract, page 26678, line 20: "pollutant". This word is employed several times in the paper. I am not sure if we can talk about "pollutant" for these organic species because they can have a biological origin.

Response: In the revised abstract, the word "pollutant" is changed to "organic specie". And in the paper, the word "organic pollutants" are changed to "organic species"

Abstract, page 26678, line 26: add "in" between "concentrations" and "Guangzhou"

Response: Revised as suggested.

Abstract, page 26678, line 27: add "the" between "whereas" and "highest"

Response: Revised as suggested.

Abstract, page 26678: the authors provide average data sometimes with SD, sometimes without SD and sometimes with the min. and max. values. Please homogenize throughout the abstract and elsewhere in the text.

Response: Thanks for the valuable suggestion. We have standardized to express average data with SD throughout the abstract and manuscript.

Abstract, page 26678: there is no mention of benzoic acid. The authors could add a sentence about the distribution of benzoic acid in the abstract since it appears in the

C13566

title of the paper.

Response: A sentence about the distribution of benzoic acid has been added in the abstract.

Introduction, page 26679: Perhaps the first paragraph (i.e. Pearl River Delta region) may be placed just before the last one. Therefore, the introduction would begin with information on particulate matter and organic acids.

Response: Revised as suggested.

Introduction, page 26679, line 23: replace "Dicarboxylic acids" by "Dicarboxylic acids and related polar compounds".

Response: Revised as suggested.

Experiment (2.1), page 26681, lines 9-10: replace "Fifteen samples" by "Fifteen samples (i.e. 8 samples in winter, 7 samples in summer)".

Response: Revised as suggested.

Experiment (2.1), page 26681, line 17: "Approximately 5%". The authors should rather give a number of field blanks here.

Response: "Approximately 5% of field blanks were collected. . . ." has been revised as "One field blank was collected. . . ."

Experiment (2.1), page 26681, lines 22-23: replace "in summer; but northern air mass flow was dominated during winter, then PU and HT were the downwind sites in winter." by "in summer. On the contrary, northern air mass flow dominated during winter, thus PU and HT were the downwind sites in winter."

Response: Revised as suggested.

Experiment (2.1), page 26681, line 22: replace "ketoacids" by "ketocarboxylic acids"

Response: Revised as suggested.

C13567

Experiment (2.2), page 26682, lines 5-6: replace "at 120°C, 250°C, 450°C, and 550°C" by "at 120, 250, 450 and 550°C". Same thing for line 9.

Response: Revised as suggested.

Experiment (2.2), page 26682, lines 12 and 21: Please provide the detection limits in the same unit than samples (i.e. $\mu\text{g m}^{-3}$).

Response: Revised as suggested.

Experiment (2.3), page 26682-26682: Is the part describing the analysis of inorganic species necessary? The inorganic compounds are not presented in this paper, neither in Table 1, nor in Table 2. There is just the evocation of the correlation between C2 and sulfate (page 26689, line 27).

Response: This section has been added according to the comments of other reviewer.

Experiment (2.4), page 26683, line 4: replace "were" by "are".

Response: Revised as suggested.

Experiment (2.4), page 26683, line 16: recoveries for short chain ketocarboxylic acids and dicarbonyls were all > 70%? I thought they were lower than 70%.

Response: Recoveries of authentic standards spiked to a pre-combusted quartz fiber filter were 71 % for oxalic acid and better than 80 % for malonic, succinic and adipic acids. Recoveries of glyoxylic acid, pyruvic acid and methylglyoxal were 88 %, 72 % and 47 %, respectively. Spiked experiment of diacid standards to the filter sample (QFF 166) showed higher recoveries of oxalic acid (86 %) and malonic acid (94 %). Duplicate analyses of filter sample showed that analytical errors are within 15% for major species. Procedural blanks showed small peaks of oxalic and phthalic acids in the GC chromatograms; however, they were less than 0.66 % (oxalic acid) and 5.6 % (phthalic acid) of the aerosol samples. Concentrations of the acids reported here are corrected for the procedural blanks, but are not corrected for the recoveries (Kawamura

C13568

and Yasui, 2005).

Experiment (2.4), page 26683: please add a sentence on the determination of TQWOC (sum of dicarboxylic, ketocarboxylic and dicarbonyls).

Response: Revised as suggested. The definition of TQWOC has been added in Section 2.4.

Results and discussion: Instead of mixing in the paragraph 3.1 concentrations of OC, EC and WSOC with the molecular composition of dicarboxylic acids, the authors could separate in two paragraphs: 3.1 for concentrations of OC, EC and WSOC, and 3.2 for Molecular composition.

Response: Revised as suggested.

Results and discussion: Generally, the values cited in the text do not correspond to values reported in Table 1. For example, none of the values given for OC, EC and WSOC in the text (page 26683, lines 23-24) are found in Table 1 because they correspond to average global values. However, is it really relevant to provide these average concentrations, for which SD is very high (5.6 ± 5.6 for EC)? As an alternative the authors may give in the text the data shown in Table 1. For example for OC they could write: OC ranged from 1.8 ± 0.8 (HT in summer) to $13.9 \pm 4.4 \mu\text{g m}^{-3}$ (PU in winter) (Table 1).

Response: The average concentrations (correspond to values reported in Table 1) were reported as suggested.

Results and discussion, page 26683, lines 24-25: "The OC to EC ratio has been used to infer the origin of carbonaceous particles". Please add one or several references for this sentence.

Response: Two references (Cao et al., 2003b; Novakov et al., 2005) have been added as suggested.

C13569

Reference: Cao, J. J., Lee, S. C., Ho, K. F., Zou, S. C., Zhang, X. Y., Pan, J. G. (2003b), Spatial and seasonal distributions of atmospheric carbonaceous aerosols in Pearl River Delta Region, China, *China Particuol.* 1, 33–37.

Novakov, T., Menon, S., Kirchstetter, T. W., Koch, D., Hansen, J. E. (2005), Aerosol organic carbon to black carbon ratios: analysis of published data and implications for climate forcing, *J. Geophys. Res.* 110. D21205.

Results and discussion, page 26684, lines 1-2: please provide values for OC/EC ratios.

Response: The value of OC/EC ratios has been added as suggested.

Results and discussion, page 26684, line 3: define "SOA".

Response: "SOA" is defined as secondary organic aerosol and has been added in Section 3.1.

Results and discussion, page 26684, lines 5-6 and line 14: remove "total quantified water-soluble organic compounds (diacids+ketoacids+dicarbonyls)" and "total quantified water-soluble organic compounds". TQWOC should have been defined in the experimental section (2.4).

Response: Revised as suggested. The definition has been added in Section 2.4.

Results and discussion, page 26684, lines 15-29: Much information is given for the origin of phthalic acid but not that much for the origin of oxalic acid.

Response: Good point. Statements have been added to show the origin of oxalic acid: "The predominance of oxalic acid was recognized in previous studies also (Ho et al., 2007; Ho et al., 2010). The abundant presence of cis configuration (maleic acid and methylmaleic acid) in the urban atmosphere supports an oxidation of aromatic hydrocarbons (benzene and toluene) as a precursor of oxalic acid"

Results and discussion, page 26685, line 25: replace "consistent to" by "consistent with"

C13570

Response: Revised as suggested.

Results and discussion, page 26686, line 13: replace “represents to” by “emphasizes”

Response: Revised as suggested.

Results and discussion, page 26686, line 21: replace “ranged to” by “ranging”

Response: Revised as suggested.

Results and discussion, page 26688, line 4: I do not know if the word “poorest” is adequate here.

Response: The related statement has been revised to: “Poor air quality in Hong Kong in winter is due to the influence of local sources and polluted air mass transported from South China.”

Results and discussion, page 26688, lines 10-11: “The highest average concentrations of the TQWOC and total quantified fatty acids were found at PU in winter. . .” According to Table 1, the highest concentration of total fatty acids was recorded at ZQ in summer and not at PU in winter.

Response: Thanks for pointing out the mistake. The statement has been revised to: “The highest average concentration of the TQWOC was found at PU in winter, which is attributable to the mixed contribution of local and regional sources.”

Results and discussion, page 26688, line 25: add “at” between “except” and “PU”

Response: Revised as suggested.

Results and discussion, page 26689, lines 2-7: the explanation of primary and secondary productions of dicarboxylic acids in the atmosphere is not very clear. Please rephrase it.

Response: The related statements have been revised to: Low molecular weight dicarboxylic acids can be primarily produced from anthropogenic emissions. Photochemical

C13571

reactions in the atmosphere also play an important role in the formation of dicarboxylic acids. The dicarboxylic acids are secondarily generated in the atmosphere by photochemical chain reactions of unsaturated hydrocarbons or fatty acids as well as their oxidation products (Kawamura and Sakaguchi, 1999; Kawamura et al., 1996b), even though their formation mechanisms are poorly understood.

Results and discussion, page 26689, line 7: “Therefore. . .” The word “Therefore” is not appropriate here.

Response: “Therefore” has been deleted in this sentence.

Results and discussion, page 26689, lines 11 and 15: replace “HK” by “PU”.

Response: Revised as suggested.

Summary and conclusions: When I compare this part to the abstract, I have the feeling that it does not enough underline the main findings of the study (there are many repetitions). Also, I would have liked to see some perspectives for future works.

Response: The abstract and summary and conclusions have been revised. We believe that the parts have covered our main findings of this study. A statement for future works has been added in summary and conclusions: “In light of WSOC being the most abundant component of PM_{2.5}, future work is suggested to further speciate and quantify this fraction [e.g., humic-like substances (HULIS)] in PRD and other megacities in China.”

Table 1: add values of OC/EC, WSOC/OC, TQWOC, TQWOC/OC.

Response: The values of OC/EC, WSOC/OC, TQWOC, and TQWOC/OC have been added as suggested.

Figure 2: the picture (a) seems correspond to winter, and picture (b) to summer.

Response: Figure 2 has been revised as suggested.

C13572

Figure 3: in the caption, add "(TQWOC)" after "total quantified water-soluble organic compounds". In the figure, replace "total measured species" by "TQWOC".

Response: Revised as suggested.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 26677, 2010.

C13573