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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #2

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General observation

This paper investigates the seasonal (summer/winter) and spatial (urban, urban/roadside, semi-rural and rural sites) distributions of water-soluble organic species in aerosol samples (PM2.5) collected in the Pearl Delta River (PRD) region in China. The organic compounds studied are the low molecular weight dicarboxylic acids and related polar compounds (ketocarboxylic acids and dicarbonyls) as well as fatty acids and benzoic acid.

The main conclusions of this work are the following: 1) The molecular composition of dicarboxylic acids in the PRD region (i.e. dominance of oxalic acid followed by phtalic acid) is similar to that reported in other urban cities of China. In addition to primary production from vehicular emissions, the enhanced secondary photochemical production is a significant source of dicarboxylic acids in the PRD region in summer. 2) The relatively high concentrations of total fatty acids show that anthropogenic activities (meat cooking, vehicular emissions) are important pollution sources in the PRD atmosphere; Conversely, the strong even carbon number predominance (maximum for hexadecanoic acid) also suggests a substantial influence of biological sources, while the photochemical degradation of unsaturated fatty acids is an important process as demonstrated by the values of the C18:1/C18:0 ratio ($\sim$ 0.5). 3) The seasonal and spatial distributions observed, i.e. higher concentration in organic acids for the downwind sites (i.e. PU an RT in winter, GZ and ZQ in summer), higher abundance of total quantified water-soluble organic carbon (TQWOC) in organic carbon (OC) in summer, higher concentration in fatty acids in urban sites compared to the background site, are consistent with regard to the meteorological conditions (air mass transport: north-easterly wind in winter, south-westerly wind in summer), the photochemical processes occurring in the atmosphere, and the level of urbanisation of the site. Finally, this study clearly points out that the distribution of these organic compounds in the PRD region is driven by a combination of anthropogenic, biological and photochemical sources, as well as the long range transports.

Overall the paper is well written and concise and is within the scope of Atmospheric Chemistry and Physics. The results presented are of good quality and the methodological approach used is valid. It is true that the conclusions reached are not really new or original compared to previous studies on the distribution of dicarboxylic acids and related polar compounds in aerosols samples of urban environments. However, the study area (PRD region) is of great interest because it is one of the rapidest economic growth regions in China, and the data deserve to be known from the community.

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In conclusion, I recommend that this paper will be accepted for publication in Atmospheric Chemistry and Physics after taking into consideration the comments/corrections listed below.

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 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 $\pm$ 327, 656 $\pm$ 346, 384 $\pm$ 171 and 490 $\pm$ 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.

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

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for comparing the distributions of these selected variables across sites and seasons.

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 Fig. 3.

Other comments:

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

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.

Minor comments/corrections

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

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

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.

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

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

Abstract, page 26678: the authors provide average data sometimes with SD, some-

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times without SD and sometimes with the min. and max. values. Please homogenise throughout the abstract and elsewhere in the text.

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 title of the paper.

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.

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

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

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

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.”

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

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.

Experiment (2.2), page 26682, lines 12 and 21: Please provide the detection limits in the same unit than samples (i.e. μg m-3).

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

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in Table 1, nor in Table 2. There is just the evocation of the correlation between C2 and sulfate (page 26689, line 27).

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

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%.

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

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.

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 $\pm$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 $\pm$ 0.8 (HT in summer) to 13.9 $\pm$ 4.4 μg m-3 (PU in winter) (Table 1).

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.

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

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

Results and discussion, page 26684, lines 5-6 and line 14: remove “total quantified

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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).

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

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

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

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

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

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.

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

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.

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

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

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

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repetitions). Also, I would have liked to see some perspectives for future works.

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

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

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

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