

## Our response to the reviewers' comments

### Anonymous Referee #1

#### **General comments:**

This paper reports valuable measurements of alcohol and acid species in particle phase at three sites, representing three different atmospheric conditions. The size distribution analysis provides likely source information of primary and secondary WSOC components. However, the main focus of the paper is not very clear and some arguments are not supported by evidence. For example, the authors show that acids are more abundant at the marine site than at the continental sites, indicating transport and aging occurs at the marine site. Does the back trajectories show transport of air mass from main land to the Pacific Ocean? If yes, this should be discussed in the text. Another example is that fine mode glucose is thought to be from levoglucosan hydrolysis under relatively high acidity in aqueous phase, but the RH and acidity during the measurement periods are not shown. The literature (Seinfeld and Pandis, 1998 and Helle et al., 2007) could not support the argument as well since the conditions in these papers are very different from ambient conditions.

**Response:** We thank the review's comments, which is very helpful for improving our paper quality. An example of backward trajectories of air mass transported from Mainland China to the Okinawa site was added into the paper as the supporting information. We agree with the reviewer on the comments of levoglucosan hydrolysis, thus we deleted the related discussion.

#### **General comments:**

There are six figures in the paper, four of which are repeating size distributions of different species. Similar figures could be condensed into one in order to make room for other figures to show different kind of evidence.

**Response:** We think the figures are important, because size distributions of compounds showed in the figures are different from each other. Without these figures it would be very difficult for readers to understand our data and related discussion, as well as the implications. As such, the second reviewer requested us to add an additional figure illustrating the size distribution of *o*-phthalic acid (see our response later). Thus, these figures presented in the paper are necessary.

#### **General comments:**

The writing may need improvement as well. For example, in page 7, line 6, the sentence "we feel that their argument may be wrong" is informal. There are grammar mistakes as well (see "technical corrections").

**Response:** The sentence in page 7, line 6 was deleted as mentioned above. We have also corrected the grammar mistakes and revised some sentences. (see the details below)

#### **General comments:**

In general, the measurements are new and important to be added to current literature, but "what is new in this work" needs to be stated clearly and better explained. Polishing the writing will also improve the quality of the paper.

**Response:** We thank the comments and have polished the writing (see throughout the paper)

#### **Specific comments:**

1. Sugar and sugar alcohol are mentioned several times in the paper. What are the differences between "sugar" and "sugar alcohol"? Sugar contains C-OH groups, so is sugar alcohol as well?

**Response:** Sugar means saccharide (e.g., glucose, fructose, sucrose and etc) and anhydrosaccharides (e.g., levoglucosan, mannosan, and galactosan), which contains carbonyl and hydroxyl groups, while sugar-alcohols are reduced sugars, which contain hydroxyl group only (Simoneit et al., 2004), for example, glycerol, mannitol, inositol et al. Such a classification has broadly been used by many researchers and can be found in many papers, for examples, Ion et al., (2005); Kourtchev et al., (2008); and Yttri et al., (2007).

2. How are "primary WSOC" and "secondary WSOC" defined? Should list assumptions.

**Response:** Suggestion taken. We have made the definition in the text, see page 4, lines 79–85 in the revised paper.

3. Page 6, lines 8-9, is there evidence of biomass burning? Does back trajectories show air mass transports from urban to mountain and ocean sites?

**Response:** Biomass burning for house heating in rural inland China is very common in winter. Levoglucosan has been taken as a key tracer for biomass burning smoke. The abundant occurrence of levoglucosan in our samples especially in the urban samples is the evidence of biomass burning. An example of backward trajectories was added into the text as the supporting information for air mass long-range transported from Mainland China into the marine site. See the supporting information.

7. Page 7, line 6, re-phrase the sentence “we feel that” .

**Response:** We deleted this paragraph for the discussion of levoglucosan hydrolysis.

8. Page 6, lines 3-5, why is levoglucosan lower than “other primary WSOCs” in coarse mode?

**Response:** The related explanation has been presented in the following phrase rather than here to avoid a repetition. See page 7, line 154-157, 161-164

9. Page 6, lines 13-16, is the formation mechanism of levoglucosan the finding of this paper? Should cite literature if not.

**Response:** Suggestion taken, a reference was cited. See page 7, line 157.

11. Page 7, first paragraph, what are the sampling conditions? Are the conditions the same as the conditions in the papers you cite? What is the RH and acidity of sampled aerosol?

**Response:** In the current work we do not have enough evidence demonstrating the hydrolysis of levoglucosan in the atmosphere. So, this paragraph was deleted as mentioned above.

12. Page 7, lines 18-19, need citations.

**Response:** Suggestion taken, see page 8, line 174-175.

16. Page 8, line 13, is there evidence of long-range transport?

**Response:** Yes, we have the evidence. An example of trajectories of air mass long-range transported from inland China to the marine site can be found in the supporting information section.

18. Page 9, line 25, is “development of inverse layer” observed? How is “development of inverse layer” related to coagulation?

**Response:** We deleted this phrase and revised the related discussion, see section 3.3, page 11, line 238-252.

Technical corrections:

1. Page 2, line 19: “however” is not necessary. 2. Page 6, line 1, delete “to be”. 3. Page 6, line 3, change “on the fine mode” to “in the fine mode”. 4. Page 7, line 20, delete “somewhat”. 5. Page 7, line 28, delete “thus”. 6. Page 8, lines 4-5, grammar mistake “Such a molecular compositions”. 7. Page 8, line 21, delete “in the smoke particles”. 8. Page 10, line 4, typo “levoglucosn”.

**Response:** Suggestion taken, see those corresponding corrections in (1) page 2, line 51; (2) page 6, line 142; (3) page 6, line 144; (4) page 8, line 175-176, also, in page 6, line 129-132; (5) page 8, line 178; (6) page 8, line 183; (7) page 9, line 197-198; and (8) page 12, line 258.

## Anonymous Referee #2

### **General comments**

The manuscript is based on a total of 14 sets of size-segregated samples, 6 sets collected in an urban location in China, 3 sets on the mountaintop of Mt. Tai, and 5 sets in a remote marine location. The samples at different locations were collected on different days and in different seasons. The work focuses on the size distribution characteristics and relative abundance of sugar compounds (include levoglucosan) and dicarboxylic acids. While levoglucosan and the sugar compounds are mainly derived from primary emission sources, the dicarboxylic compounds are of mainly secondary origin. The site contrast offers an opportunity to compare size distribution characteristics of the same class compounds in different atmospheric environments and to explore source information of the measured WSOC species. However, wording of a few major findings presented in the abstract and in the summary/conclusion sections could be misleading. A more serious problem is lack of rigor in data interpretation. Specific comments are given below.

**Response:** We thank the reviewer's comments and revised some discussions on the data. After revisions, we believe that the data interpretation in current format is much better than its ACPD version, and paper quality is good. See the detailed response below.

### **Specific comments**

1. The description of size distribution characteristics for the secondary WSOCs is not accurate. The authors state that ". . . all the secondary WSOCs, except for benzoic acid and azelaic acids, showed a unimodal size distribution with a peak at 0.7-1.1 $\mu$ m" (Lines 15-16 in abstract). The size distribution of succinic acid in Figure 5 clearly shows a dominant coarse mode in the marine samples and a minor but nevertheless noticeable coarse mode in both the urban and the mountaintop samples.

**Response:** We think that the reviewer may have a misunderstanding on our discussions on the size distribution. Unimodal means a size distribution pattern presenting one peak only, which can be a fine mode, or a coarse mode, or a mixed fine and coarse mode with one peak in anywhere of the whole particle size range. In contrast, bimodal means a size distribution pattern presenting two peaks within a certain size range, which can be fine mode, coarse mode, or whole particle size range. Therefore, a compound that is described as a unimodal size distribution does not mean that it should be either fine mode or coarse mode, instead, just means that size distribution of this compound only has one maximum or peak within a certain size range. Similarly, if a compound that is described as a bimodal or multiple mode distribution means that concentration of this compound within a certain size range has two or more peaks. Such a word of unimodal has also been used to describe the molecular composition pattern, which means that for a series of compounds studied, only one compound has the maximum, and concentrations of its neighborhoods gradually decrease.

Such a description format on aerosol size distribution using the word of unimodal has broadly been used by many scientists in the field of atmospheric science. For example, in the study on size distribution of diacids by Kerminenn et al (J. Aerosol Sci. Vol. 31, No. 3, pp. 349-362, 2000), the authors state in page 358, the sixth paragraph that "Contrary to oxalate, the size distribution of malonate was usually unimodal with a supermicron mode peaking between 1 and 3  $\mu$ m". From the Figure 1 below, we can see a significant fraction of malonate in fine particles, but the concentration had one peak in the whole particle range with a dominant peak in the coarse mode. Salma et al., (2002) also used such a method to describe the unimodal size distribution of elements in atmospheric aerosols, in the paper abstract they stated that "Typical coarse-mode elements, i.e., Na, Mg, Al, Si, P, Ca, Ti, Fe, Ga, Sr, Zr, Mo and Ba, exhibited unimodal size distributions at all four urban locations studied.". From Table 1 in the paper page 344 (a copy of the table shown below), it is clear that these elements are abundant in fine fraction. Because size distributions of these elements only had one peak in the whole size range, and are thus described as a unimodal pattern. Many other papers using the same descriptions can be found (Blendo et al., 1998; Hays et al., 2005; Hays et al., 2003; Karanasiou et al., 2007). We have also described the aerosol size distribution using the same format in previous studies on the aerosol size distributions (Wang et al., 2009a; Wang et al., 2009b)

Therefore, we think that the reviewer misunderstood our description on the size distribution. Because succinic did presented a minor peak in the coarse range at the urban site during spring (Figure 5a), we revised the related discussion (See page 9, line 203-208). Moreover, to make our statement clear to readers, we modified some sentences, see the abstract and the summary sections.

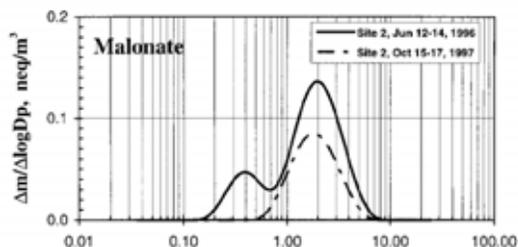


Figure 1. A copy from Kerminen et al J. Aerosol Sci. Vol. 31, No. 3, pp. 349-362, 2000

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I. Salma et al. / Aerosol Science 33 (2002) 339–356

Table 1

Mean atmospheric concentrations and standard deviations in  $\text{ng}/\text{m}^3$  STP of some selected elements and PM as measured in the coarse and fine size fraction of the SFU samples collected at the KFKI campus, Lágymányos campus, Széna Square and within the Castle District Tunnel

Element	Fraction	KFKI campus	Lágymányos campus	Széna Square	Castle District Tunnel
Na	coarse	125 ± 49	236 ± 35	293 ± 83	3078 ± 95
	fine	66 ± 43	100 ± 29	56 ± 21	76 ± 6
Mg	coarse	92 ± 39	257 ± 19	310 ± 91	6600 ± 278
	fine	26 ± 8	56 ± 7	33 ± 9	215 ± 29
Al	coarse	171 ± 19	680 ± 134	788 ± 120	15000 ± 300
	fine	37 ± 4	153 ± 17	69 ± 6	410 ± 9
Si	coarse	459 ± 40	1780 ± 301	2586 ± 507	45600 ± 912
	fine	104 ± 15	224 ± 35	285 ± 69	1419 ± 56

Figure 2, A copy of Table 1 from Salma et al, Aerosol Science, 33, 2002, 339-356

### **Specific comments**

2. Related to the previous comment, there are more examples in which the authors describe the size distributions of a species to be unimodal while data in Table 2 show significant presences of the species in both fine and coarse mode. For example, the authors reported that phthalic acid showed a unimodal size distribution in samples at all three sites (page 17475). However, the phthalic data in fine and coarse modes (using  $2.1\mu\text{m}$  as the cut point) show that there were comparable abundances in the fine and coarse modes (e.g.,  $102\text{ ng}/\text{m}^3$  in the fine mode vs.  $47\text{ ng}/\text{m}^3$  in the coarse mode in the urban winter samples).

**Response:** Our statement is correct. The reviewer misunderstood it (See the our explanation above). To more accurately and clearly describe the size distributions of the aromatic acids, we modified the related discussion. See page 10, line 220-236.

### **Specific comments**

3. The authors reported a larger geometric mean diameter (GMD) of the WSOCs in the fine mode in the winter samples than in the spring samples at the urban site. They attributed this to an enhanced coagulation effect under the development of an inversion layer (Lines 16-19, abstract). However, they did not present an analysis to support this speculation. While it is possible that coagulation plays a role, it is also possible that this might be caused by more condensation of secondarily-formed species due to more abundant precursors in the winter. A more quantitative analysis is needed to ascertain the relative importance of condensation vs. coagulation before such a speculation can be included in the abstract or the summary section.

**Response:** We agree with the reviewer that the larger GMD values of the WSOCs in the fine mode in the inwter samples were also possibly caused by more condensation of secondarily-formed species due to more abundant precursors in the winter, in addition to an enhanced coagulation due to higher concentration of particles in winter. In the current stage, we do not have the data to quantitatively analyze the relative importance of condensation vs.

coagulation. Instead, we presented a qualitative analysis. See the revised explanation in the abstract, line 47-51, and page 11, line 244-252.

#### **Specific comments**

4. In the abstract and summary sections, the authors state that “levoglucosan is the most abundant WSOCs in the urban and mountain atmosphere”. This statement is misleading. Oxalic acid/oxalate is typically more abundant than levoglucosan. Oxalic acid is not among list of the analytes that can be reliably quantified using the method employed here by the authors (presumably due to low recovery as a result of the TMS derivative of oxalic acid being relatively too volatile). A more accurate description is: “levoglucosan is the most abundant compound among the quantified WSOCs in the urban and mountain atmosphere”. Similarly, the statement in the summary section “. . . WSOCs in the marine air are dominated by malic and succinic acids” is misleading for the same reason. The range of dicarboxylic acids and aromatic acids quantified by the analytical method should be clearly described in the sample analysis section. I note this information was given in section 3.2. It is more suitable to place it in the experimental section, where readers expect to find such information.

**Response:** We agree with the reviewer that the previous version of the statements on levoglucosan and related compounds were misleading, and have revised the related sentences, see page 2, lines 35 and 38, page 12, line 269-271. The information on the range of dicarboxylic and aromatic acids determined by the analytical method has been moved into the experimental section, see page 6, line 128-132.

#### **Specific comments**

5. Page 17474, line 1: It should be “Among the measured secondary WSOCs in the urban and mountain top air, . . .”.  
Line 7: it should be “However, the composition of the measured secondary WSOCs is different. . .”

**Response:** Suggestion taken. See page 8, line 179, and line 185.

#### **Specific comments**

6. p17475, lines 8-9: The authors state “. . .azelaic acid is much more abundant on coarse mode in the marine samples compared to the urban and mountain samples (Fig. 5d-f)”. While the separation between the fine and coarse modes in the urban spring samples (Fig. 5d) was less distinct than that in the marine samples (Fig. 5f), the abundance of the coarse mode relative to the fine mode in the urban spring samples (15 vs. 26 ng/m<sup>3</sup>) was similar to that in the marine sample (0.5 vs. 0.9 ng/m<sup>3</sup>) (Table 2). Therefore, the authors’ statement is not correct.

**Response:** We agree on the comment that the previous statement is not correct. Actually, azelaic acid showed a pronounced peak in the coarse range compare to that in the urban and mountain samples. We corrected the explanation. See page 10, line 217-219.

#### **Specific comments**

7. Work from Schauer and coworkers indicate that pathalic acid was likely a secondary product of vehicular emissions. It will be useful if the authors show the size distributions, along with that of benzoic acid in Figure 6.

**Response:** Suggestion taken. We added the size distribution figure for *o*-phthalic acid, and also updated the related discussion. See page 10, line 227-236.

#### **Specific comments**

8. Glucose has a more prominent fine mode than its coarse mode in the urban winter samples (Figure 2). Other sugars also have significant presence in the fine mode in the urban winter samples (Table 2). The authors attribute the fine-mode glucose to the hydrolysis of levoglucosan. The literature cited by the authors (Seinfeld and Pandis, 1998; Helle et al., 2007) could not support the authors’ argument as the conditions in the literature studies do not reflect typical tropospheric ambient conditions. In addition, such a hydrolysis mechanism could not explain the significant presence of fine-mode sugar alcohols (e.g., arabitol, mannitol, inositol, and glycerol).

**Response:** We agree with the reviewer that the conditions of acid-catalyzed hydrolysis of levoglucosan do not reflect the real situation in the atmosphere. Thus we deleted the paragraph, which explains the origins of fine mode of glucose and related sugar-alcohols by using the hydrolysis of levoglucosan, and gave a brief explanation by citing other literature. See page 8, line 169-171.

### **Specific comments**

9. Page 17472, line 7: levoglucosan was in the order of a few hundreds of ng/m<sup>3</sup> in the urban environment and in the order of a few ng/m<sup>3</sup>. Therefore, the concentration of levoglucosan in the urban atmosphere was two orders of magnitude higher than that in the marine atmosphere, not “three orders of magnitude”, as the authors have stated.

**Response:** We agree with the comment and corrected the mistake. See page 7, line 147.

### **Specific comments**

10. Table 3: The GMD for coarse-mode fructose and sucrose in the marine samples are larger than 14µm (14.2 and 14.7µm, respectively). How is this possible, considering the highest cut size provided by their sampler is 11.3µm?

**Response:** The first stage of the sampler gives the cutoff point 11.3 µm. We selected 20 µm as the maximum of particle size for the first stage, which means that particles in the first stage are of size in the range 11.3-20 µm, and then calculated GMD according to the method described by Hinds (1999)

### **Specific comments**

11. The authors attribute the larger GMAs of levoglucosan and the secondary WSOCs in the coarse mode in the marine air to enhanced hygroscopic growth of the marine particles related to higher humidity in the marine atmosphere. Again, there no analysis/ evidence presented to

**Response:** In the current stage we do not have direct evidence to demonstrate the enhanced hygroscopic growth of aerosols in the marine air. Instead, here we only gave a qualitative explanation. See page 12, line 258-265, and related statements in the abstract (page 2, line 51-54) and summary (page 13, line 283-285) sections.

### **Reference**

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Supporting Information

## **Size-Resolved Particulate Water-Soluble Organic Compounds in the Urban, Mountain and Marine Atmosphere**

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A summary of supporting information

Figure S1. Backward trajectories of long-range transport of air mass from inland China to the North Pacific during sampling period.

