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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Size and composition measurements of background aerosol and newparticle growth in a Finnish forest during QUEST 2 using an Aerodyne Aerosol Mass Spectrometer" *by* J. D. Allan et al.

J. D. Allan et al.

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8758, Line 4: remove "the" before "each" Authors' response: Corrected.

Line 4-5: "and can be of either" does not fit (grammatically) with the earlier clause of the sentence. Consider revising to "which can be" or "and these can be". Authors' response: Corrected.

Line 18: "size" is ambiguous here. Consider revising to "mobility diameter". Authors' response: Corrected.

Line 20: Consider revising “compositional nature” to simply “composition”. Authors’ response: Corrected.

Line 25: A comment here on the lower size limit and required mass for ultrafine particle (low pressure) impactors would seem appropriate here... Authors’ response: The following has been inserted on line 21: “It is possible to collect particles as small as 10 nm with suitable low-pressure impactors, although concentrators must be used to collect large enough samples, even when working in a polluted environment (Geller et al., 2002).” The following statement about the length of time needed is also qualified by adding that the amount of material needed is dependent on the analytical technique that is to be applied.

8759, Line 5: Please confirm where a binary mechanism is actually proposed in the Kulmala 2004a reference. I don’t believe any statement is made regarding the mechanism of nucleation other than the belief that it is decoupled from growth. Authors’ response: Kulmala et al. (2000) should have been cited in the previous sentence. This has been corrected.

Line 7: check tense agreement of “occurs”. Authors’ response: Corrected.

Line 22: Consider revising “different to urban” to “differ from that in” Authors’ response: Corrected.

8759: The top paragraph on this page, which is an introduction to the site and the study, seems out of place from the other two paragraphs which provide background information on similar studies. Consider changing the order such that the top paragraph is the last one in the section, placing the other two background paragraphs more appropriately with the background material on offline (impactor-based) techniques. Authors’ response: Revised as suggested.

8760, Line 23: consider changing “aerosol particles” to simply “particles”. Authors’ response: Revised as suggested.

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8761, Line 5: Consider deleting the word “derived”. Authors’ response: Revised as suggested.

Line 9: For this sentence (which continues a point made by the sentence that precedes it), it is not clear how molecular decomposition on the vaporizer is an exception to the bias towards low molecular weight peaks caused by the temperature of the vaporizer. If I understand this correctly these two sentences seem to be making the same point. If so consider combining into one. Authors’ response: There are two effects caused by the vaporiser; firstly, the molecules may decompose on the surface of the heater, causing the vaporised species to be chemically different from their parents. The second is that the vaporised molecules will possess a greater internal energy than they would if they had been subject to more conventional gas-phase analysis (e.g. GC), which results in the molecules obtaining a systematically greater energy after 70 eV electron impaction. While both effects cause the peak locations to be shifted to lower m/z’s, it is important to distinguish between them because the former effect can cause extra peaks to appear (e.g. 44) due to the chemical transformations that can take place, whereas the latter only changes the bias of existing peaks. A more explicit explanation has been added to the text.

Line 13: is “ensemble” necessary when this is inherent in the meaning of the word “aerosol”? Authors’ response: In a way, yes. This word is used (within the AMS community) to distinguish the data produced from those of other aerosol analytical procedures, as the AMS does not use any separation (other than size) or selective ionisation and even includes part of the gas phase, which is in contrast with other techniques.

Line 18: Regarding the point made on the power of size-resolved composition in this sentence and the one that follows the authors state a “direct linkage” and “assignment” of particle sizes determined by the AMS to those obtained through other means, but as I understand it the vacuum diameter derived from the AMS requires knowledge of particle density in order to make correspondences with the mobility or aerodynamic diameter. Please discuss in the text (or just clarify my misunderstanding!). Authors’

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response: See response to reviewer #1.

Line 28: Here I assume “size” refers to “diameter”? Authors’ response: Yes. This has been corrected.

8762, Line 6: I suggest changing the first of 3 “it was” appearances in this paragraph with “the instrument” or something similar. The use of passive voice is especially apparent in this paragraph. Authors’ response: Revised as suggested.

8763, last paragraph: Fig. 1 seems to lend strong support to the notion that the particle beam indeed diverges significantly at low RH... Authors’ response: See responses to reviewer #1.

Line 10: please comment on the size range of the particles plotted here. Is this all ambient aerosol? If so, then perhaps the results plotted here are weighted by number concentration and may not be generally applied to a study that focuses on the chemical properties of ultrafine aerosol. Authors’ response: The graphs are normalised to 100 %, so number concentration is not a factor. Also, both are taken from periods where accumulation mode particles dominated the mass (the modal diameter was around 300-400 nm in each case) . These points have been added to the text.

8764, Line 19: consider changing “aerosol particles” to simply “particles”. Authors’ response: Revised as suggested.

Line 23: Here I believe you are referring to the mass concentrations and size of the background aerosol. Please clarify. Authors’ response: This is indeed the case. The text has been clarified to make this more explicit.

Figure 2: As in the text that refers to the figure, I am not sure if “arctic outbreak” means just the background aerosol during the days in which the wind blew from the north... Authors’ response: ‘Outbreak’ refers to the air mass origin. The text has been revised to make this more explicit and the use of this word has been removed to avoid future confusion. The overall composition is confirmed by the impactor analysis (see figure 5).

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The fact that the AMS result is so clearly sulphate-dominated is partly due to the high time resolution of the instrument, which allows periods without any local interferences to be selectively averaged.

Line 27: Similarly, I am not sure if the text and Fig. 3 refer to the composition of the background aerosol (i.e., the particles that existed prior to, and during, nucleation). Authors' response: Figure 3 shows the typical aerosol composition in a polluted airmass, which tended to result in non-nucleation days. This is made clearer in the text.

8765, Line 5: Forgive me for not having a good meteorological background, because (as in my comment above) when I hear the word "outbreak" I think about the sudden increase in particle number concentrations that characterize a new particle formation event. In this case I think the authors are again referring to air masses that originate from Europe. Please consider changing the terminology. Authors' response: See above.

Line 15: I don't understand this sentence. Is there a clause "Eˇ when the wind is blowing from the continent." missing at the end of this sentence? Authors' response: The impactor cassettes used for the samples were chosen based on wind sector and whether nucleation was taking place on a given day or not. However, as explained previously, the days when air originated from continental Europe tended to be non-nucleation days, especially during the AMS sampling period. This is made clearer in the text.

Line 25: this sentence of course begs the question: did back trajectories or other meteorological measurements support the idea that the emissions were relatively constant during nucleation and growth? Authors' response: Back trajectories were used to assess the suitability of event days to be used in AMS analysis, as explained in the text. While it would be interesting to know how constant the emissions and chemical production were over the air mass history, there is not currently enough known about the mechanisms responsible to make an easy estimate. Further investigation is a definite

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possibility but is outside of the scope of the paper.

8766, Line 13: In this paragraph, please identify the prevailing wind direction for each of the days plotted in Figs. 6 and 7. Authors' response: In the case of the 28th, the prevailing wind was from the northwest. On the 1st, it was from the north. The text has been revised as suggested.

Figure 6: As in the preceding comment, please note the prevailing wind direction in the caption if you think it's important... Authors' response: While the composition of the particles isn't particularly different, the total mass concentration in the lower particle diameters is greater during the latter stages of the growth event. What is important to note is the differences in how the organics are distributed as a function of particle diameter compared to the sulphate, which can be taken as a surrogate for the ambient accumulation mode. The significance is that in figure 6d, there is clearly extra organic matter in the lower sizes when compared to 6c, in addition to the material that has apparently condensed onto the accumulation mode. This explanation has been added to the text.

Figure 7: The chemical composition data suggest that this is an example of a northern air mass. Are the contours the same as those in the legends of Fig 6? Please state this in caption. Again there is not a clear correlation between the organic aerosol mass and the growth mode from the DMPS data, which is somewhat disappointing. Authors' response: Modified as requested. The DMPS data was originally intended as a point of reference for the stages of growth, not to illustrate a direct correlation. However, the volume distributions have been added, which show a better (although not perfect) relationship. See also responses to reviewer #1.

A thought about Figs. 6-7: Perhaps it makes more sense to plot the DMPS data in terms of dM/dlogDp (i.e., mass distribution, making some assumption of bulk particle density). If this is done then it may address my disappointment in not seeing a nice correlation between the AMS chemical data and the physical DMPS data. Authors'

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response: See above and responses to reviewer #1.

Line 21: It's not clear to me what particle size range corresponds to the spectrum plotted in Fig. 8. Is this an average of all particles sampled during the growth event? Of so, can the DMPS data be used to tell us how much of the data shown here can be related to the accumulation mode as compared to the Aitken mode? Authors' response: This is an average of an entire growth event but as stated in the text, this signature was fairly invariant of the period chosen and the dominant mode in the mass distribution. The text has been revised to make this clearer. The DMPS cannot be used to address this because sulphate in the accumulation mode tended to dominate the particle volume and subtracting this would prove problematic (see responses to previous comments).

Line 25: Just a point for clarification: the aliphatic sequence was observed in the smallest particles as well as the larger ones? By stating that the fingerprint was invariant, does that also mean that the relative abundances of the aliphatic peaks to the unsaturated and/or oxygenated peaks are invariant with particle size? Over what size ranges was this invariance observed? Authors' response: The organic spectrum was invariant in terms of the base peak and all the mass spectral features described previously, which included the aliphatic and oxygenated peaks. This was found to be invariant in all cases where a statistically significant mass spectrum could be derived, which translates to the organic mass mode ranging from approximately 80 to around 400 nm. This is made clearer in the revised text.

8768, Line 16: I very much enjoyed reading the insights of the authors presented in this section. Whereas I am not sure that the data show, unequivocally, that the particles that were involved in growth were organic... Authors' response: The section has been modified as follows: "The data from the AMS show that, as expected, the majority of the matter involved in the particle growth is organic in nature, within the measurement capabilities of the instrument. Limitations imposed by the low signal to noise ratios meant that only particle populations with mass modes with Dva values in the high tens of nm were observable, however signals at m/zs associated with organic species were

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always the first detected during growth events."

Line 20: I would argue that perhaps the observation that the chemical signature is the same... Authors' response: See the response to the comment before last. The statement has been qualified in the modified text by stating that it only applies within the measurement capabilities of the instrument. However, this is still an important statement to make, even from a mass-weighted perspective, as this has implications for the treatment of the data derived from bulk sampling.

8769, Line 9: When it's stated that the instrument's response is invariant as a function of carbon number, this would imply that the signal from a C20 is half that of a signal from a C10. Is this correct? If this is so, then why can't the AMS still obtain information on the carbon number? Is the signal too weak? Authors' response: See responses to reviewer #1.

8771, Line 4: The point made here regarding the AMS response to monocarboxylic acids brings to mind an important issue regarding the AMS... Authors' response: This is a valid point. Work has indeed been performed by multiple groups but regrettably, is still awaiting submission. Although not ideal, a reference to the forthcoming Silva et al. (in prep.) has been added in addition to the Alfarra PhD thesis reference, which should be submitted very soon. With reference to the reviewer's questions, it has been found that purely aliphatic organics do ionise slightly more easily than the oxidised fraction (by a factor of up to 33 %, based on laboratory studies). It has been found that the relative ionisation efficiencies of the different oxygenated types are fairly similar within the measurement uncertainties, so there should not be a bias towards any specific species in this work (this is mentioned in the revised text). However, without knowing the exact chemical composition of the atmospheric particles, it is difficult to apply detection efficiencies explicitly, so a single relative ionisation efficiency is used for all particulate organics (1.4). This subject has been mentioned in previous papers (specifically Alfarra et al., 2004 and Jimenez et al., 2003) and is the subject of the ongoing development of the analysis techniques.

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