

Interactive comment on “Changes in background aerosol composition in Finland during polluted and clean periods studied by TEM/EDX individual particle analysis” by J. V. Niemi et al.

J. V. Niemi et al.

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AUTHORS COMMENTS TO THE REFEREES

We thank the referees for their constructive reviews and suggestions. All three referees suggested similar changes for particle classification and we will first respond to that subject. Then we will respond to the other comments of each referee individually.

RESPONSE TO PARTICLE CLASSIFICATION

The referees suggested that groups 3 to 6 (3 = soot/sulphate mixture, 4 = carbon/sulphate mixture with dark inclusion(s), 5 = ammonium sulphates with/without carbon and dark inclusion(s) and 6 = K-rich particles with S and/or C) could be combined

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into one group, because the boundaries between those groups are obscure and because section 3.3.3 (“Beam-sensitive S-, C- and/or K-rich particles with/without dark inclusions”) feels confusing and hard to follow. Furthermore, referees #1 and #2 pointed out that it is not clear (based on TEM/EDX results) in which chemical forms ammonium and sulphate containing salts are (e.g. $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)\text{HSO}_4$, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$). It is common inaccuracy in many TEM/EDX and SEM/EDX works to name these particles as ammonium sulphate, as referee #2 mentioned, and we agree that. Based on above-mentioned referee comments, we combined the particle groups 3-6 as one large particle group which was named as “(ammonium)sulphates and their mixture with C, K, and/or inclusions”. We rewrote section 3.3.3 almost completely.

More detailed classification of particles in “(ammonium)sulphates and their mixture with C, K, and/or inclusions” group is challenging and partly artificial because the variations in elemental ratios of S, C and K were continuums and because the size and morphology of soot inclusions and other non-recognizable beam-resistant inclusions varied strongly. However, we felt important to highlight some essential, interesting and (quite) clear characteristics of this largest particle group in PM1 samples. Therefore, we decided to divide these particles into three different subgroups in section 3.3.3. The new subgroups are a) (ammonium)sulphates mixed with recognizable soot, b) (ammonium)sulphates mixed with carbon and c) (ammonium)sulphates without detectable carbon. Although there are no sharp boundaries between those subgroups (more like continuums in reality), they show with simple and clear way some basic characteristics and differences in mixing states of particles.

All referees suggested that it would be clear to separate “sea salt particles and other Na-rich particles” into two different groups already in Table 4; 1) sea salt and 2) porous Na-S-K-O-containing particles. This change was made.

RESPONSE TO REFEREE #1

REFEREE: Abstract, line 15: “samples contained elevated proportions of silicates (22-

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33%, also fly ash particles).” This is a little confusing. Is the fly ash lumped in with silicates? This sentence should be modified to make it clearer what the authors are suggesting.

RESPONSE: Both silicates and metal oxides/hydroxides with spherical morphology are named as fly ash particles. We removed “also fly ash particles” text from the abstract to keep it as short and clear as possible. In “Summary and Conclusions”, fly ash particles are mentioned and explained.

REFEREE: Page 6759, line 14. Should PM1 be replaced with PM1.6?

RESPONSE: All PM1.6 results were replaced with PM1 results. See comments to referee #3.

REFEREE: Page 6769, line 1: “as fractional recrystallization of sea salt particles or marine organisms.” I do not understand the fractional recrystallization of sea salt particles. If it is a sea salt particle it should contain Na and be grouped with the Sea-Salt particles? Are the authors suggesting that a sea-salt particle can break into a Na-component and Ca-component when it crystallizes? Is there any evidence in the literature for this? Please explain and expand.

RESPONSE: We added discussion on fractional recrystallization of sea salt particles into the beginning of the second paragraph in section 3.3.6 (Sea salt and porous Na-rich particles): “When water evaporates from seawater droplets, different compounds crystallize separately according to their solubility products (Borchert, 1965; Zayani et al, 1999). After evaporation, sea salt particles may form aggregates of loosely attached crystals that can shatter and produce pure crystals and crystal mixtures (Parungo et al, 1986). Thus, fractional recrystallization may change elemental ratios of sea salt particles in atmosphere and/or during aerosol sampling (Parungo et al, 1986; Ro et al., 2001; Niemi et al, 2005b). However, the porous morphology of Na-S-K-O-rich particles strongly suggests that they were not fractional recrystallization products of sea salt.”

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REFEREE: Page 6774: line 3: “silicates and metal hydroxides/oxides with spherical morphology (fly ash),” Are the authors indicating that some of the silicates have spherical (fly ash) morphology and some of the metal hydroxides/oxides have spherical (fly ash) morphology? Please modify this sentence to make this point more clear. Table 3: for the metal oxides/hydroxides, the morphology is irregular angular or circular particles. Should this be “circular fly ash particles” to make this description more consistent with the rest of the document? What subgroup does fly ash belong?

RESPONSE: These changes were made. Both silicates and metal oxides/hydroxides with spherical morphology are named as fly ash particles. Their abundance in silicate and metal oxides/hydroxides groups are shown in Table 4 (in parentheses).

RESPONSE TO REFEREE #2

REFEREE: Some generic name like “NH₄/SO₄ salts” would be more appropriate for these particles.

RESPONSE: This change was made, and we selected to use “(ammonium)sulphates” expression (see section 3.3.3).

REFEREE: Finally, findings of the mixed soot/sulfate particles presented in this paper are very consistent with those reported recently by Johnson et al (Atmos. Chem. Phys., 5, 3033-3043, 2005) in their study of aerosols collected in Mexico city. Comparison with that study might be an excellent point for additional discussion.

RESPONSE: This interesting article was added with a short text to section 3.3.3.

RESPONSE TO REFEREE #3

REFEREE: Abstract: I suggest the authors to insert a sentence mentioning how they determined the polluted, clean, and intermediate samples (mass concentrations of particulate matter and backward air mass trajectories) either in the 3rd or 12th line in p.6754.

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RESPONSE: The determination of different sampling periods was added: “ \ddot{E} during pollution episode ($PM_{1 \sim 16} \mu g m^{-3}$, backward air mass trajectories from south-east), intermediate period ($PM_{1 \sim 5} \mu g m^{-3}$, backtrajectories from north-east) and clean period ($PM_{1 \sim 2} \mu g m^{-3}$, backtrajectories from north-west/north).”

REFEREE: Materials and methods: p.6758, l.26; “ \ddot{Y} and these results were used to calculate $PM_{1.6}$ mass concentrations \ddot{Y} ” I wonder why the authors use $PM_{1.6}$ concentration as indicator of pollution rather than $PM_{2.5}$. $PM_{1.6}$ does not fit the size ranges for TEM ($PM_{0.2-1.0}$, $1.0-3.3$, $3.3-11$) and VI ($PM_{1.3}$ and $1.3-10$) samples either. A brief explanation for the reason would be helpful for readers.

RESPONSE: We decided to show $PM_{1.6}$ concentrations because the mass concentrations results for larger particle sizes (larger cut-off sizes of impactor) were quite inaccurate. However, we decided to replace all $PM_{1.6}$ concentrations with PM_1 concentrations to reduce the number of different size limits presented in this new revised paper. Now PM_1 mass concentration results are more comparable with $PM_{0.2-1}$ samples for TEM/EDX analysis.

REFEREE: p.6773, l.7;”No clear difference was observed in the proportions of biological particles and C-rich fragments related to source regions of the air masses.” Is it possible that these particles resulted from contamination during handling of the samples?

RESPONSE: The contamination is very unlikely. We don't find any plausible reason or source for contamination.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 6753, 2006.

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