

Interactive comment on “Single particle analysis of the accumulation mode aerosol over the northeast Amazonian tropical rain forest, Surinam, South America” by R. Krejci et al.

R. Krejci et al.

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Authors reply to comments from Anonymous referee #1

We thank referee for comments and suggestions and below present our answers. First the original comment from reviewer is presented in *Italic*, followed by author's reaction.

Overall comments

Unfortunately the analysis presented here is limited to chemical elements with $Z > 11$ and solely to non-volatile particles $> 0.2 \mu\text{m}$. A large portion of the aerosol probably consists of compounds containing carbon, hydrogen, nitrogen and oxygen (organics,

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soot, ammonium nitrate?). Additionally, Krejci et al., 2003, shows that by far the most particles encountered during their measurements were smaller than $0.2\ \mu\text{m}$. Therefore the vast majority of atmospheric particles cannot be accessed with the presented technique.

Yes, reviewer is correct, but not entirely. Soot particles can be identified by their specific morphology. Organic aerosol particles cannot be detected directly, but indirectly as described in the paper, under assumption that pure ammonium nitrate particles do not represent significant fraction of the aerosol population in the accumulation mode. As far as we are aware, there is no study available from Amazonia or elsewhere from similar environment suggesting such a possibility.

Taking into account aerosol number density, the particles $>0.2\ \mu\text{m}$ represent only small fraction of total number, as shown in the paper. But if volume/mass is taken into account, the analyzed particles represent much larger fraction. Therefore the results can still be of interest for community using bulk or size segregated aerosol composition data.

A point that should be discussed in detail is, why no pure sulfate or sulphuric acid particles were detected, and why the fraction of sulfur containing particles is so small. Are these particles too volatile to be analysed? Especially in the free troposphere a large fraction of the particles should be sulfate particles (e.g. Sheridan et al., GRL, 1994; Murphy et al., Science, 1998; Curtius et al., JGR, 2001; Papaspiropoulos et al., JGR, 2002, etc). The results presented in the manuscript should be discussed in the light of these findings. Krejci et al., 2003, themselves model the evolution of free tropospheric aerosol including uptake of H_2SO_4 as the only condensing gas-phase species!

When the first results of data analysis shown almost no sulfate particles present, our interpretation was along the point made by reviewer. But consequent analysis and results obtained with the same technique and analytical procedure during the INDOEX

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99 experiment shown that volatility is not a reason why we did not observe sulfate or sulfuric acid particles over Amazonia. Our results can be supported by several arguments:

1. If the sulfate and sulfuric will be too volatile to be detected with this techniques than we would not observe for example mineral dust particles and sea salt particles with high S content (groups “aged mineral dust” and “aged sea salt”)
2. Assuming that volatility of sulfate or sulfuric acid is a significant problem means that tens of previous studies reporting S-rich or sulfate particles using SEM-EDX method are principally wrong, which was not proven. Moreover, there are other non-destructive instrumental analytical techniques, e.g. Proton Induced X-Ray Emission (PIXE) where samples are analyzed using very similar analytical procedure at very high vacuum. And PIXE is well known technique to analyze S content in atmospheric aerosol.
3. During INDOEX 99 experiment we used the same equipment, same airplane and same analytical technique to perform single particle analysis (results are not published yet). Samples collected during ferry flights from Europe to Maldives and back contained up to 50% particles classified as S-rich (Fig. 1). Based on the characteristic morphology of the sulfuric acid and sulfate aerosol particles majority of them was represented by sulfate aerosol in different stage of neutralization (Fig. 2).
4. Reviewer recalls several earlier studies reporting sulfate aerosol in the different parts of free troposphere. However, neither of them reports results from Amazonia or similar part of tropics. Sheridan, GRL, 1994 presented results from northern mid-latitudes and Curtius, JGR, 2001 from subtropics. Papaspiropoulos, JGR, 2002 (as well as Martinsson, GRL, 2001) shown results from the CARIBIC project, where data from mid-latitudes to tropics were collected during flights between Europe and Maldives. Observations from the CARIBIC projects agree well

with results of our single particle analysis shown on Fig. 1. The samples collected in tropics (# 5–9) show lower fraction of S-containing particles compared to mid-latitude samples (rest of the samples). Sampling altitude was similar in both studies. In both cases it was performed on board of jet plane at typical cruising altitudes around 9–12 km. Last paper mentioned by reviewer (Murphy et al, Science, 1998) reports single particle analysis performed by different method, mass spectrometry. The size detection limit of the mass spectrometer was set to the same level as our SEM analysis ($0.2 \mu\text{m}$). Here I use explicitly Fig. 3 from this paper, which actually supports our observations. Two vertical profiles, one at mid-latitudes and one in tropics, show decrease sulfate particle ions fraction by factor 3 – 5 in the upper tropical troposphere and on the other hand increase of organic ions fraction by the same magnitude. It was reported already earlier, that high content of organics in the aerosol can be a good indicator of the air masses originated over Amazonia (Talbot, JGR, 1988). Similar conclusion pointing to dominance of organic matter in the aerosol over Amazonia was presented in several studies later on (e.g. Artaxo et al, JGR, 2002; Maenhaut, NIMB, 2002; Echalar, JGR, 1998; Zhou, JGR, 2001). Rain forest ecosystem is well known to be deficient in sulfur (Andreae, JGR, 1990) and major source of sulfur is the import with trade winds from above the ocean. Organic aerosol is known to be less hygroscopic compared to sulfate and therefore has a higher chance to stay as interstitial aerosol and be transported through convective clouds to free troposphere. This will result in enrichment of organic aerosol in the free troposphere.

In previous paper (Krejci et al, JGR, 2003) we used H_2SO_4 as only condensable specie in a simple model of the aerosol growth via condensation and coagulation in the free troposphere. We are aware of the fact that it can be seen as contradiction to the finding we present in this paper. However, the model was mainly used to show that new aerosol particles have very short lifetime in the atmosphere and that they have to be produced almost on semi-continuous basis to be able to explain persistently high

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number densities observed over large regions of tropical free troposphere. It is still assumed that new particle formation in the free troposphere happens through binary ($\text{H}_2\text{SO}_4\text{-H}_2\text{O}$) or ternary ($\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$) nucleation. About role of organic gaseous precursors in new particle formation is known very little and there are almost no good thermodynamic available data to be used. Therefore we used sulfuric acid as the only condensable specie and as the rapid sink of the newly formed particles is coagulation, the result will be most likely similar if organics will be used instead of sulfuric acid, but at this point it is of course only speculation.

The largest fraction of analysed particles fall into the “not-determined” category. Arguments are presented that these particles are mostly of organic origin. Although this conclusion is likely to be correct (at least if there are really no sulfates), it should be stated in the text (especially in the abstract and in the conclusions) that the largest fraction of particles was not-determined particles that are possibly organic particles.

Including the “not determined” and organic aerosols in both, abstract and conclusions will always require also explanation of the relations between these two definitions. This on our opinion does not belong there as it needs quite some space to give proper link in between both terms and therefore the link between both groups is given inside the results and experimental parts of the paper.

The calculation of absolute concentrations for an aerosol category, as well as statements like 90% are organic cannot be made from the presented analysis, because it is not known which fraction of the atmospheric particles volatilises in the vacuum environment. Such statements would only be correct if formulated as “90% of the non-volatile particles $>0.2\ \mu\text{m}$ are likely to be organics”. Statements like “4–10 cm^{-3} are sea salt particles” cannot be made at all. Therefore the ms should be rephrased or cut accordingly throughout.

The fact that certain material can volatilize in high vacuum is well known drawback of the analysis when SEM, TEM and also PIXE techniques are used. On page 539 (lines

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18–21) we described this possibility in a similar way as it is done in majority of the other publications presenting results of the single particle analysis using above mentioned techniques. Similar presentation of the percentage fractions, the way it is done in this paper, is used almost in all other papers dealing with this subject. Therefore it is used here as well.

Concerning the attempt to derive some estimates of the absolute number densities of certain types of particles, on our opinion one can apply the same approach as to presentation of abundance of particle groups in percents as the absolute concentrations are derived from the abundances of particle groups obtained from SEM analysis. The uncertainty here is probably larger as the size distribution was measured with different technique (Optical Particle Counter), but on our opinion it still presents useful information. Moreover, being aware of the possible errors, we used this approach only when the differences were very large to highlight the contrast between aerosol composition in different air masses.

According to reviewer comment the paragraph dealing with this issue in the experimental part of the paper (from p. 539) is moved to the beginning of the result part and changed to:

An unavoidable limitation of the SEM-EDX technique is that volatile material will evaporate in high vacuum inside of the SEM chamber. This may cause some particles to shrink or deform, or even disappear completely. Particles potentially affected by this problem have not been treated in any specific way as part of the analysis. Therefore the abundances of certain groups presented later in the paper should be seen as upper limit assuming that certain particles could volatilise in high vacuum present during analysis. The same view should be applied whenever the absolute number density of the specific group of particles is estimated using results of the single particle analysis and independent aerosol size distribution measurements.

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Technical comments

p. 3, l. 7, "Artaxo et al., 1998, reported results from a..." (omit brackets),

changed

p. 5, "near-isokinetic inlet", please explain, for which altitudes and velocities is the sampling isokinetic, in how far is it anisokinetic at other altitudes?

The inlet was design for Cessna Citation airplane using theoretical calculation, but it was not tested in wind tunnel. Therefore we prefer to use term "near-isokinetic". One of the possibilities can be to check data from OPC inside the cabin, which use the air sampled through this inlet, with wing mounted probes measuring in-situ. The direct comparison between cabin-mounted OPC and wing-mounted instruments was not made during the LBA-CLAIRE. The wing-mounted probes were not used. However, identical OPC and inlet was deployed during ACE-2 experiment onboard of the same aircraft and comparison between our OPC and FSSP showed good agreement (de Reus et al., JGR, 2000)

p. 6, l. 11, ...along the way that introduce uncertainties...

changed

p. 6, l. 15, "live time" please explain; also, life time?

Dead time of the X-ray detector should be correct term

p. 7, l. 8, "...convective systems then transported..."

changed

p. 14, l. 3 in Section 5: "...particles larger than 1 μm represented less than 1% of the aerosol..."

changed

p. 16, l. 4 "...marine conditions than typical..."

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changed

p. 17, l. 8, "...from the source region, requires a more..."

changed

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 533, 2004.

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4, S4061–S4070, 2004

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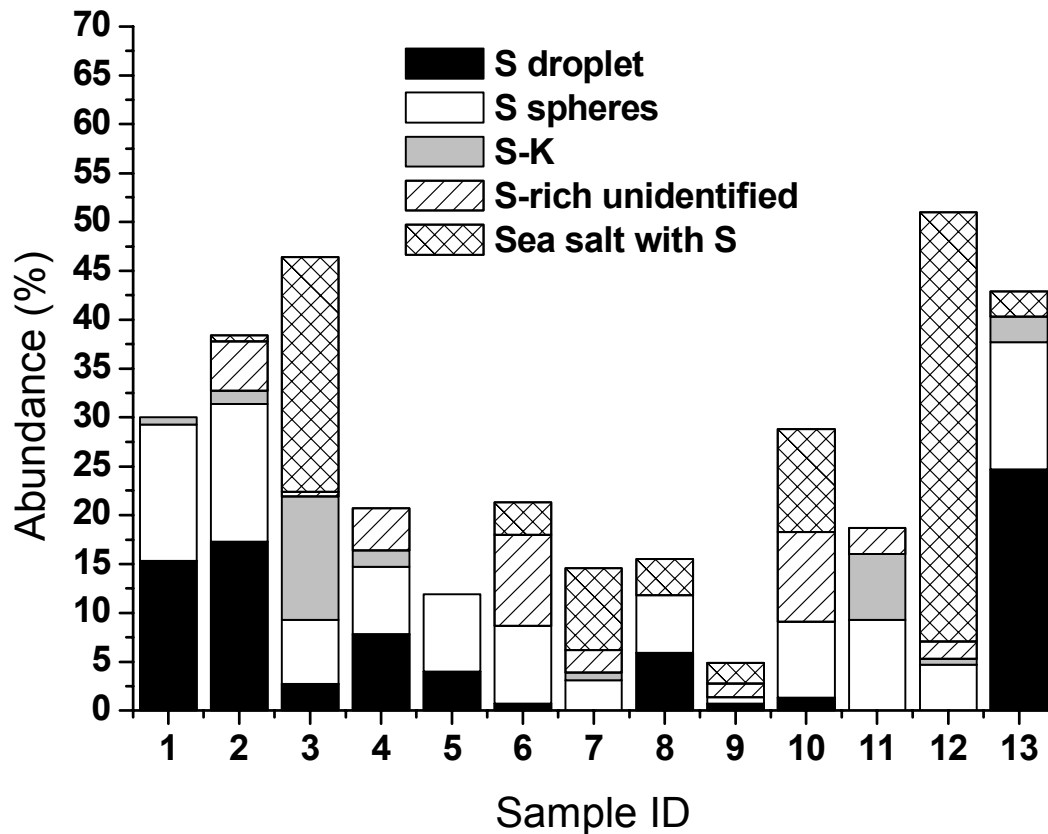


Figure 1: Abundance of S-rich particles in the individual samples.

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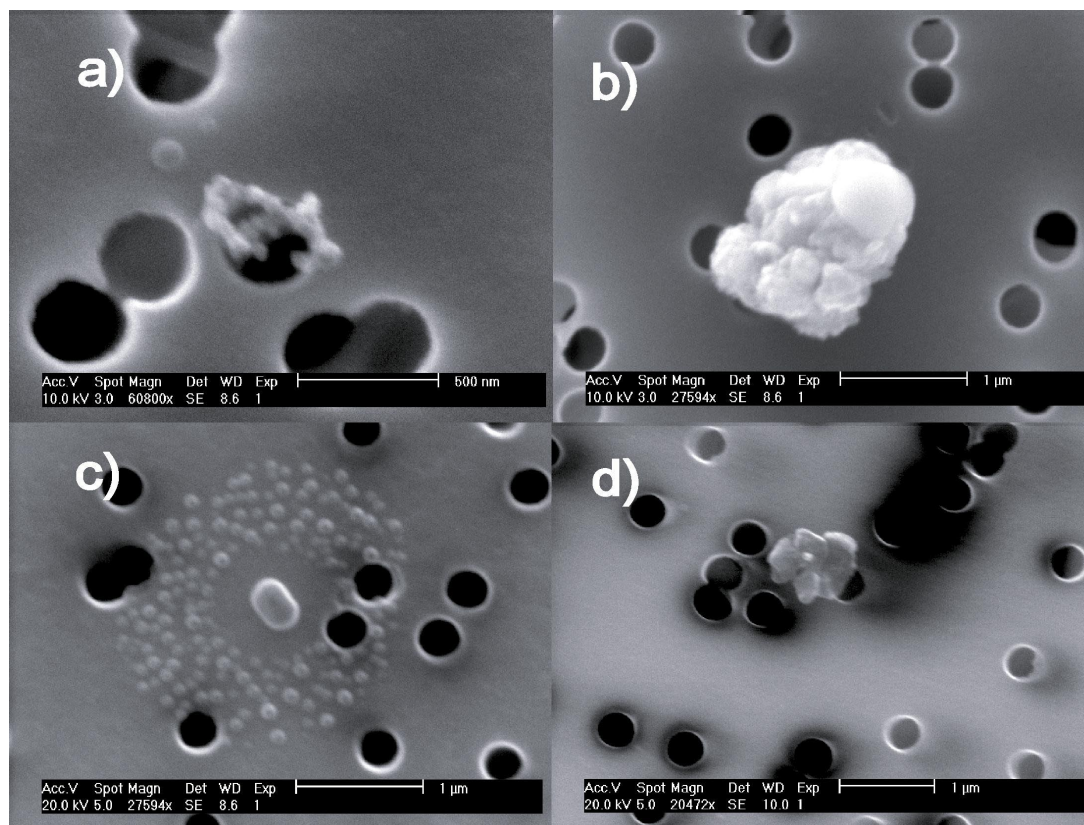


Figure 2: Secondary electron images of the particles observed in the upper troposphere: (a) soot agglomerate with the S-sphere on the left hand side; (b) Al-silicate particle; (c) Sulfate drop; (d) low-Z particle (most probably organics), which was classified as bio-debris.

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