

## ***Interactive comment on “Long-term chemical characterization of tropical and marine aerosols at the CVAO: field studies (2007 to 2011)” by K. W. Fomba et al.***

**K. W. Fomba et al.**

herrmann@tropos.de

Received and published: 30 May 2014

Answer to the interactive comment of Sergio Rodriguez: At first, the authors wish to thank you for intensive reading of our manuscript and the helpful comments and suggestions. Now I will answer more detailed to your comments: An important difference exists between IzaníCa and the CVAO – the distance to the coastline and to the next possible anthropogenic sources of pollutants is not comparable. The distance to the source regions in Africa or Europe is much longer at the CVAO than is the case at IzaníCa. The precision of calculated backward trajectories does not allow identifying sources in the same way as for IzaníCa. The ensemble plots also portray

C2974

the uncertainty of the backward trajectories. Most of the dust events were connected to air masses crossing not only Mauritania but also Western Sahara, Morocco and Algeria. An exact localization of dust origin will be a separate study. Some of the dust events, connected to the more southern parts of the Sahara, show lower nss-sulphate concentrations than those connected to more northern dust origin. Free sulfuric acid formed from anthropogenic and biogenic precursors may react with CaCO<sub>3</sub> which is an important compound in the Saharan dust. The water soluble calcium is not CaCO<sub>3</sub> but CaSO<sub>4</sub> or Ca(NO<sub>3</sub>)<sub>2</sub> and possibly salts of organic acids which are formed in the atmosphere during the transport. 1) SULPHATE Authors said (section 3.3.3): -The highest sulfate concentrations were strongly connected to Saharan dust events but not all dust events were responsible for the elevated sulfate concentrations. The same behavior is observed in Izaña free troposphere site (<http://www.atmos-chemphys.net/11/6663/2011/acp-11-6663-2011.pdf>). Have authors done any other analysis about the origin of sulphate during dust events?

The collection time differs between 24 and 72 hours, especially for the longer sampling periods the variability of air mass origin is wide. During the events connected to the southern Sahara the time over the ocean is typically much shorter than during events with air mass origin in the northern parts of the Sahara. Since the variability of sulfate in dust is high, we're looking for further possible sources. During days with low Ca content and elevated nss-sulfate content secondary sulfate is the most likely explanation. Anhydrite and gypsum are negligible in these cases. The production of sulfuric acid from marine DMS emissions is another source of sulfates.

2) By using ammonium data, nss-sulphate may be split into two components: Ammonium-sulphate (a-sulphate) + none-ammonium-sulphate (na-sulphate) Inzaña, by using MCAR based backtrajectories analysis, we found that (above link): -a-sulphate was strongly linked to transport from regions with important industrial emissions in Morocco, Algeria and Tunisia. -na-sulphate was highly influenced by transport of some gypsum / anhydrite minerals from regions where dry lakes were abundant (in

C2975

parts of Algeria and Tunisia), although anthropogenic na-sulphate may also contribute. This discussion is not included in this paper (although authors cited potential influence of anthropogenic SO<sub>2</sub> emissions in North Africa, without any other specification). Authors have already calculated back-trajectories and they have ammonium data as well. To do a similar analysis with the data collected in CVAO may contribute to identify other source regions of the pollutants mixed with dust; for example regions located southern than the Canary Islands for which Izaña is not sensitive (e.g. Mauritania). This could be included in this paper, or be subject of a further publication.

Ammonium sulfate is another possibility as a secondary product beside the natural origin from DMS oxidation. Unfortunately we have only a small number of MSA data which have not been published in this study. In these samples we found a proportion of MSA to nss-SO<sub>4</sub>, which is close to the natural proportion from the DMS decomposition. Detailed studies on the source apportionment of sulfate will be subject to a further publication. Therein, we intend to perform similar investigations on size resolved particles to better understand in which form the sulfate and other major aerosol ionic components are available. We are aware similar analysis could be done on bulk measurements as well but we plan to do these in detailed with the size resolved measurements. 3) AMMONIUM AND NITRATE Authors said (section 3.3.5): - Ammonium and nitrate showed no correlation amongst each other. Apparently, these ions had different major sources During dust events at Izaña it is observed (above link) that: -ammonium is present as a-sulphate mostly in the PM<sub>2.5</sub> fraction, whereas nitrate is mostly present in the coarse fraction (2.5-10 microns) as a none-ammonium salt. -both ammonium and nitrate are linked to transport from regions with important industrial emissions in Morocco, Algeria and Tunisia. Probably, the lack of correlation between ammonium and nitrate is not a matter of source region, but probably to a question of thermodynamic stability of ammoniumnitrate.

The situation is much more complicate in the case of ammonium and nitrate. The thermal stability of NH<sub>4</sub>NO<sub>3</sub> is one of the problems for interpretation of data. Under

C2976

typical temperatures of 23 to 25°C ammonium nitrate is decomposed into ammonia and nitric acid. The observed maximum of ammonium does not correspond with the annual nitrate concentration course. The low ammonium concentrations are found in nearly all types of samples, independently of the air mass origin – with an exception for air masses reaching the CVAO from Europe (about two times higher than in other air mass types, cf. Table 5). We know that nitrates are found only in coarse mode particles, typically as NaNO<sub>3</sub> after the reaction of nitric acid with sodium chloride. Ammonium we have measured in size segregated measurements only in submicron particles but this discussion will be further addressed in a further publication about size-segregated collected PM. The observed levels of nitrate and nss-sulphate are relatively high, so your hint to anthropogenically released PM from NW Africa is one possibility as an explanation.

4) CALCIUM In this paper, Ca is presented as soluble (Ca<sup>+2</sup>). Unpublished data we have produced at Izaña shows that 64% of Ca (total elemental calcium) is as Ca<sup>+2</sup>, as average during dust events. Section 3.3.6, authors said: A strong correlation between nss-calcium and total calcium (with r<sup>2</sup> = 0.98) during dust events 10 confirmed that the Saharan dust was the main source of nss calcium in these samples What do authors mean with total calcium?, total elemental calcium (Ca) or total soluble Ca (Ca<sup>+2</sup> = nss-Ca<sup>+2</sup> + ss-Ca<sup>+2</sup>)? Total soluble Ca is meant in the whole manuscript because we used IC without an acidic treatment of the samples. As already said above, in Izaña Ca is linked to transport of evaporites dust minerals (CaCO<sub>3</sub>, gypsum and anhydrite) from dry lakes of North Africa. In an earlier publication (Müller et al., 2010) about a short measurement campaign in May/June 2007 we found from TXRF measurements and IC analyses that Ca is found mainly as soluble Ca. Only about 6% of the measured Ca was insoluble. However, the number of analyses was small and the dust events during this measurement period were few. For further thoughts about solubility see comments above.

5) SUGGESTION Because of the strong impact of dust events on the chemical com-

C2977

position of PM10, I think that it would be interesting that mean concentrations of each compound be also presented during none dust events and during dust events; e.g. included in Table 2.

The mean values and standard deviations of the PM10 constitution for the main categories including the dust periods and the other non-dust types of PM are given in Table 5.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C2974/2014/acpd-14-C2974-2014-supplement.pdf>

---

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 3917, 2014.