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Atmospheric
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Discussions

Interactive comment on “Hygroscopic properties of different aerosol types over the Atlantic and Indian Oceans” *by* A. Maßling et al.

Anonymous Referee #1

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GENERAL COMMENTS

First, I would like to apologize for being rather late sending in this referee report. It is certainly not due to a lack of interest in the paper.

The paper describes measurements of aerosol particle hygroscopic properties in marine environments, in truly background air masses as well as those influenced by anthropogenic (continental) pollution. More data of this kind are definitely needed for reasons clearly stated in the paper. This paper constitutes an important contribution to this database. The paper is well written, albeit a bit lengthy, and it definitely qualifies for publication in Atmos. Chem. Phys.

The data could have been used further. Aerosol processing time scales might have been studied by plotting the growth factors or soluble volume fractions as function of travel time over the ocean away from major sources. Also the time scales for removal of nearly hydrophobic and less-hygroscopic particles could have been studied in this way. Primary particle sea spray production might have been related to wind speed, either local wind speed or along the trajectory. Considering the high soluble volume fractions (even $>$1), many of the observed aged aerosol particles probably originate from sea spray.

There are too many figures showing the temporal variation of growth factors. In fact, it seems that every single data point has been plotted. Is this really necessary? The tables that are included, expressing the data classified according to air mass origin, are sufficient in my opinion.

SPECIFIC COMMENTS

Abstract

The abstract is a bit too long. Hygroscopic growth factor is not defined. What relative humidities (both dry and wet) does it refer to? It would be more useful to mention typical soluble volume fractions and their range for some selected air masses than to just state that these were calculated.

1 Introduction

Page 137 - line 21. Aerosol radiative forcing has same magnitude as the greenhouse gases, but of opposite sign!!

2 Field studies

Page 140 - line 8. If the classification of the 13 air masses reaching the ship was identical to that used by Bates et al. (2001), then this should be stated clearly, since it will facilitate for the readers when comparing data.

3 Chemical and physical measurements

Page 141 - line 10. Some additional details about the OC/EC thermo-desorption technique (temperatures, pyrolysis correction etc.) would be useful. The OC/EC detection limits might also be mentioned here.

Page 142 - line 15. Capacitive RH sensors tend to drift. A dew point hygrometer is a more reliable reference for measurements of RH.

Page 143 - line 2. An error of 2.5% in the sheath air volume flow rate corresponds to a much larger error in the aerosol flow, unless the excess air flow is adjusted correspondingly.

Page 143 - line 6. HTDMA size calibration. Latex spheres were passed through the two DMAs, and a correction factor was applied to achieve the same diameter in both DMAs. Was the high voltage calibrated? Why not slightly change the dimensions of one of the two DMAs instead to achieve unity growth factors? Aerosol flows were obviously monitored continuously, probably by measuring the small pressure drop over a flow restriction. This means that the pressures inside the DMAs are slightly lower than ambient. Was the volume flow rate in the DMAs set at the pressure prevailing inside the DMAs, or against ambient (higher) pressure? If the latter is true, then one might expect a slight shift in size calibration.

4 Results and Discussion

Page 146 - line 21. The statement that the Atlantic Ocean aerosol particles were sulphuric acid seems a bit exaggerated, considering the high fraction of residual ions in Figure 2. It would be informative if an ion balance was presented. Then it might be possible to estimate the equivalent molar concentration of H+ ions (in the diluted solution going into the IC). This concentration should be similar to that of sulphate if sulphuric acid is a major compound. There are nevertheless other cations present (sodium, calcium, magnesium, potassium mentioned), which makes it difficult to say that the aerosol particles consist of sulphuric acid.

Page 148 - line 2. The values below detection limit for OC and EC should not be given in Table 1. The standard deviation given in Table 1 obviously does not include errors due to variability in the blank. When presented in this way, they give an erroneous impression that the values are valid and representative of the clean air masses. The casual reader of Table 1 has to find Page 148 - line 2 to realise that the values are below detection limits. Please correct the table. You might consider propagating the blank variation into the error estimate. The means should then in some cases be smaller than the absolute errors. State detection limits clearly in the Table.

Page 148 - line 10. Change this sentence to read "...mass concentrations of EC above the detection limit were observed only for continentally influenced air masses." Otherwise, the meaning of the word "significant" is difficult to assess.

Page 148 - line 25. Can you give some more details on just how well EC and PSAP light absorption data correlated, or refer to other papers. This correlation is not obvious from Table 1.

Page 149 - line 5 and Table 1. The PSAP value for period 8 is below the stated detection limit. Please exclude.

Page 149 - line 23, page 150 - line 11. The growth factors are rather high, also in comparison with the references given. As mentioned, they seem to indicate that some sodium ions are mixed with the ammonium bisulphate to increase growth factors. Should this be interpreted as sea salt particles being internally mixed with sulphate? If so, were the original particles formed from sea spray? Coagulation is probably a week process in marine environments, since concentrations are low. If some particles were formed from sea spray and others from, for instance, homogeneous nucleation of water vapour - sulphuric acid - ammonia, then one might expect to see two groups of hygroscopic particles. The sea spray particles would then have slightly higher growth factors than the sulphate particles. Is the H-TDMA sensitive enough to see this separation of particle according to their formation process even in an aged marine aerosol?

Page 151 - line 13, page 151 - line 21. First, nearly hydrophobic particles are defined as those having growth factors < 1.2. Then during INDOEX Period 9, the nearly hydrophobic particles have growth factors as high as 1.3. Is the limit 1.2 not definite? Does it vary with particle dry size to account for the Kelvin effect? Or is it simply to allow for three groups of particles simultaneously, where the smallest growth factor is denoted nearly hydrophobic?

Page 156 - line 10, page 160, line 19. A pure ammonium sulphate particle would deliquesce at RH=80%, thus providing a growth behaviour similar to that observed for the less-hygroscopic particles in Figure 11. Inorganic salts can not be ruled out completely. It is likely that organics play a role here, but difficult to prove. My guess would be that the less-hygroscopic particles consist of a large fraction of organic compounds that are slightly hygroscopic, mixed with ammonium sulphate salts. The sharp increase in growth factors might then be explained by the limited solubility of the organics, combined with the deliquescence behaviour of ammonium sulphate. However, when studying organic-inorganic mixtures in our aerosol laboratory, we do not observe this jump.

Page 156 - line 21. It is often quite informative to calculate the soluble volume fractions also for lower RH, and for air masses where ammonium and sulphate ions are not dominant. These values give an impression of the solubility of the water-soluble compounds, and are useful for calculations of CCN concentrations as function of water vapour supersaturation.

Page 157 - line 6. To me, it doesn't seem reasonable that condensable species increase solubility beyond that of ammonium bisulphate. What possible species would that be? The most likely gases to condense in a remote marine environment are ammonia, sulphuric acid (or sulphur dioxide), and possibly nitric acid. These wouldn't increase the solubility beyond that of ammonium bisulphate. Ions that might do this include sodium, chloride and potassium, but they are more likely to be part of the original primary particle than being the result of atmospheric aerosol processing. Internally mixed sea salt would explain the soluble volume fractions larger than unity.

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Interactive Discussion

Discussion Paper

It is not entirely clear to me what compound was used as model substance when calculating soluble volume fractions (from section 3.6). Is it ammonium bisulphate, ammonium sulphate, or variable ammonium-sulphate ratios based on the ionic composition? If modellers are to use the solubility data for CCN calculations, they need to know the model substance in order to be able to extrapolate to supersaturation. For that reason, it would be better to calculate soluble volume fractions using a fixed ammonium-sulphate ratio, and state clearly which ratio was used.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 135, 2003.