Interactive comment on "A method for sizing submicrometer particles in air collected on formvar films and imaged by scanning electron microscopy" by E. Hamacher-Barth et al.

Anonymous Referee #2
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The manuscript "A method for sizing submicrometer particles in air collected on formvar films and imaged by scanning electron microscope" by Hamacher-Barth et al. presents a quantitative offline characterization of size and morphology of ambient aerosol particles using scanning electron microscopy. Standard aerosol particles have been used to evaluate the reliability of the method. Further, two aerosol samples from an Artic ship campaign were systematically analyzed and SEM-results are compared against online techniques. The study is well written and easy to follow. It deals with the microscopic investigation of aerosol microstructure (e.g. morphology, mixing state, surface properties), which is an important topic with regard to aerosol properties and their impacts on atmospheric cycling. In general, I think the study is appropriate for AMT and should be published after some minor revisions as listed below.

- p. 5402 / l. 22 to p. 5403 / l. 6: This is a well written and short introduction. Please add some references for the crucial statements (e.g. CCN, optical properties, multiphase processes).

This has been done, see chap. 1. The following references were added:

Influence of aerosols on global climate:

IPCC: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor M., and Miller, H. L. (eds.)), Cambridge University Press, Cambridge, New York, 2007.

Direct aerosol effect:

Haywood, J. M. and Boucher, O.: Estimates of the direct and indirect radiative forcing due to tropospheric aerosols: A review, Rev. Geophys., 38, 513-543, 2000.

Andreae, M. O. and Crutzen, P. J.: Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry, Science, 276 (1997) 1052-1058.

Indirect aerosol effect:

Twomey, S. A.: The Nuclei of Natural Cloud Formation. Part II: The Supersaturation in Natural Clouds and the Variation of Cloud Droplet Concentrations, Geofys. Pure Appl., 43, 227–242, 1959.

Baker, M. B.: Cloud microphysics and climate, Science, 276, 1072-1078, 2007.

Lohmann, U. and Feichter, J.: Global indirect aerosol effect, Atmos. Chem. Phys. 5, 715-737, 2005.

CCN:

Charlson, R. J., Schwartz, S. E., Hales, J. M., Cess, R. D., Coakley Jr**,** J. A., Hansen, J. E. and Hofman, D. J.: Climate forcing by anthropogenic aerosol, Science, 255:5043, 423-430, 1992.

- p. 5405 / l. 3-5: Do you expect a loss of volatile compounds from the aerosols particles in

the SEM? Do you think that harsh high-vacuum conditions in the SEM could change particle composition and morphology? Could this potential artifact be taken into account in the analysis? Please add a statement.

See last paragraph of the chap. 1, Introduction. We added a statement on the SEM conditions:

"To maximize the surface information about the aerosol particles under investigation a relatively low accelerating voltage of 2 kV was applied and secondary electrons were detected. Electron miscroscopy generally has to tackle the conflict between sufficiently high spatial resolution which depends on the probe size determined by the accelerating voltage and on the other hand electron radiation damage due to the high electron energy of the probe (Terasaki et al., 2013). Therefore a stage bias was applied to reduce the impact electron energy onto the specimen (Michael, 2010). This reduced the volume that generated secondary electrons as well as radiation damage and charging problems (Terasaki et al., 2013)."

Michael, J. R., Joy, D. C., and Griffin, B. J.: Use of sample bias voltage for low-energy high-resolution imaging in the SEM, Microsc. Microanal., 16 (Suppl. 2), 614-615, doi: 10.1017/S1431927610055315, 2010.

Terasaki, O., Cho, HS, Cho, M., Jeong, HY, Asahina, S., Sakuda, Y., Suga, M., Kazumori, H., Kudo, M., Nokuo, T., Liu, Z., Stevens, S. M., Anderson, M. W., GaleanoNunez D. C., Schüth, F., Kjellman, T., Alfredsson, V., Ha, L., Che, S., Deng, H., Yaghi, O., Cho K. and Ryoo, R.: Novel structural characterisations of insulating and electron beam sensitive materials employing low voltage high resolution scanning electron microscopy, JEOL News 48:1, 21-31, 2013.

Furthermore we discussed the SEM conditions and evaporative losses in chap. 5.1.1:

"Volatile organic compounds typically evaporate under the electron beam (Gelencsér, 2004). Pósfai et al. (1998) discuss the evaporation of volatile compounds from ammonium sulfate aerosol particles at an accelerating voltage of 200 kV. They observed a decrease of the particle diameter by 20(±5) % due to evaporative losses which could be recognized on the formvar-coated Cu TEM grids by a dark halo around the particles that marked the area where the evaporation occurred. In contrast to the study of Pósfai et al. (1998) the conditions in our study were very mild with an accelerating voltage of 2 kV and the applied Gentle Beam mode. The purpose was to minimize the risk of evaporative losses and damaging of the aerosol particles through the electron beam. No signs of evaporation in form of halo-like shadows around the aerosol particles were observed during this study."

Gelenscér, A.: Carbonaceous Aerosol, Springer, Dordrecht, The Netherlands, p. 167, 2004.

Pósfai, M., Xu, H., Anderson, J. R., and Buseck, P. R.: Wet and dry sizes of atmospheric particles: An AFM-TEM study, Geophys. Res. Lett., 25(11), 1998, 1907-1910.

- p. 5408 / l. 21: The focus of the ASCOS campaign was the link between marine microbiological life and aerosol properties. Did the SEM analysis provide any evidence for a microbiological aerosol source?

  The link between marine biology and atmospheric aerosol particles was not focus of this article. However, Orellana et al. (2011) found strong evidences that marine gels from biogenic sources in the surface water dominate the cloud condensation number population in the high Arctic during the summer season.

  Orellana, M. V., Matrai, P. A., Leck, C., Rauschenberg, C. D., Lee, A. M., and Coz, E.: Marine microgels as a source of cloud condensation nuclei in the high Arctic, PNAS, 108(33), 13612-13617, 2011.

- p. 5409 / l. 3-26: Did you dry the air stream before sampling? If yes, how? What was the ambient RH and what was the RH behind the dryer?

The aerosol samples were drawn into the aerosol inlet at an ambient relative humidity of 100 % and temperatures of about 0° C (Tjernström et al, 2012). Directly after the inlet tube passed the container roof the air was distributed to the TDMPS and the electrostatical precipitator for sampling onto the TEM grids with a short stainless steel tube of 1 m length. The temperature in the container was kept at 20° C which resulted in a RH of 20% when the sampling onto the TEM grid occurred. These relative dry conditions are commonly chosen for sampling of aerosol particles and were the same for the TDMPS instrument and the electrostatic precipitator. Both instruments were placed closely together along the inlet to ensure that sampling conditions and lossees were the same for both instruments.
Volatile organic compounds on the particle surface as well as weakly bound water molecules (see discussion below) are propably lost during the sampling procedure and require other measurement techniques to capture them. In the Arctic the concentration of volatile organic compounds in the atmosphere is generally lower than at lower latitudes (Bates et al., 1987) and thus the losses due to evaporation during our measurements can be considered to be very small.

Tjernström, M., Birch, C. E., Brooks, I. M., Shupe, M. D., Persson, P. O. G., Sedlar, J., Mauritsen, T., Leck, C., Paatero, J., Szczodrak, M., and Wheeler, C. R.: Meteorological conditions in the central Arctic summer during the Arctic Summer Cloud Ocean Study (ASCOS), Atmos. Chem. Phys., 12:15, 6863-6889, doi: 10.5194/acp-12-6863-2012, 2012.

Bates, T. S., Cline, J. D., Gammon, R. H., and Kelly-Hansen, S. R.: Regional and seasonal variations in the flux of oceanic dimethylsulfide to the atmosphere, J. Geophys. Res., 92:C3, 2930-2938, 1987.

I am trying to image what the water content of the sampled aerosol particle may have been when they were deposited on the substrate. Given that the aerosol particles in the marine environment had certain water content, how may this have changed their morphological appearance after residual water has evaporated from particle on the sampling substrate? Please state.

Inorganic particles like NaCl are expected to recrystallize at a RH of 20% which allows the observation of their crystallinic structure under the electron microscope (for an example see Bigg and Leck, 2001).
Marine gels are highly hydrated, they contain up to 99% water. But the water molecules are mainly bound within the polymer gel structure and do not evaporate at dry ambient conditions. Only a relatively small number of molecules that is located on the surface of the marine gel particles can evaporate. But the evaporation of these surface bound water molecules does not affect the structure of the aerosol particles (Leck and Bigg, 2005).

Bigg, E. K. and Leck, C.: Properties of the aerosol over the central Arctic Ocean, J. Geophys. Res., 106:D23, 32101-32109.

Leck, C. and Bigg, E. K.: Source and evolution of the marine aerosol – A new perspective, Geophys. Res. Lett. 32, L19803, doi: 10.1029/2005GL023651, 2005.

In general, I wonder what the influence of sampling on the particle morphology, mixing state etc. may have been. The standard PSL cell can be treated as spheres and the diameter can be easily retrieved. But how do ambient particles behave during sampling?

We discuss the effect of sampling in detail in chap. 5.1 (see discussion below). Following the observations of Freedman et al. (2010) we can assume that the particles sampled on the formvar-coated Cu TEM grid mainly remain their size and morphology.

What is their diameter to height ratio on the substrate?

This was not the focus of this article. Nevertheless, to determine the diameter to height ratio of a particle the sample has to be shaded with a thin layer of e.g. platinum. This produces a shadow of every individual aerosol under the electron microscope which can be used to

determine the height of a particle. Our samples are not shaded to avoid any biase in size determination of the particles this would cause.

How is the polarity of the substrate influencing their shape (compare Freedman et al., 2010)? Please discuss more explicitly how these uncertainties are taken into account.

The size and shape of a particle that impacted onto a surface is dependent on the polarity of the substrate and the solubility of the particle. In our study a polar substrate (formvar-coated Cu TEM grid) was used. The aerosol particles can be assumed to be insoluble. According to Freedman et al. (2010) the impaction of an insoluble particle on a polar substrate leave the particle size and shape unchanged compared to its initial state.

We added the discussion below to chapter 5.1:

"Freedman et al. (2010) discuss changes in aerosol particle shape and size after impaction onto a substrate. Two critical factors are pointed out, the hydrophilic properties of the aerosol particle outer layer and the polarity of the sampling substrate. Facchini et al. (2008) found that artificial aerosol particles generated by bubble bursting and ambient aerosol particles collected over the North Atlantic contain organic carbon that is to a large extent (94 ± 4 %) water insoluble in the submicron range. The main part of the water insoluble organic fraction is attributed to marine gels which exist in a dynamic equilibrium between small macromolecules and large aggregates (Verdugo et al., 2004). Assumed that the organic fraction of the samples collected during the present study contain an equally high amount of water insoluble organic carbon as in Facchini et al. (2008) the aerosol particles can be characterized as mainly hydrophobic.
The sampling substrate on the other hand, the formvar-coated Cu TEM grid, is hydrophilic and thus polar due to the chemical nature of the formvar film (Rocha et al., 2005). The impaction of an insoluble organic particle onto the polar formvar film leaves left the particle compact and retained its shape (Freedman et al., 2010). An impacting particle with a higher solubility splattered upon impaction onto the hydrophilic substrate and formed a high number of satellite particles. The more soluble the organic substance was the smaller and more numerous the satellite particles were. Based on these former studies it can be assumed that most of the particles imaged in the present study retained their initial morphology and size due to the specific physic-chemical interaction between sampling substrate and aerosol particle."

Freedman, M. A., Baustian, K. J., Wise, M. E. and Tolbert, M. A.: Characterizing the Morphology of Organic Aerosols at Ambient Temperature and Pressure, Anal. Chem., 82, 7965-7972, 10.1021/ac101437w, 2010.

Facchini, M. C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E. D., de Leeuw, G., Martino, M., Woeltjen, J., and O'Dowd, C. D.: Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates, Geophys. Res. Lett., 35(17), L17814-17819, 2008.

Verdugo, P., Alldredge, A. L., Azam, F., Kirchman, D. L., Passow, U., and Santschi, P. H.: The oceanic gel phase: a bridge in the DOM-POM continuum, Mar. Chem., 92(1-4), 67-85, 2004.

Rocha, S., Krastev, R., Thünemann, A. F., Pereira, M. C., Möhwald, H., and Bezesinski, G.: Adsorption of amyloid ß-peptide at polymer surfaces: a neutron reflectivity study, ChemPhysChem. 6, 2527-2534, doi: 10.1002/cpc.200500158, 2005.

p. 5415 / l. 1-10: The figure numbers are mixed up here (Fig. 8, Fig. 13, Fig. 14, . . .).

Sorry for the mistake - the figures are in the right order now.

p. 5416 / l. 1-28: Three morphologically different aerosol particle types are characterized here.

Do you have any EDX-data to check if morphological differences correspond with chemical differences?

EDX analysis will be subject of a subsequent article which is in preparation.

p. 5416 / 1-4: You state that the observed particles were not "necessarily spherical but can show a very irregular shape and surface". If I understand correctly, you use the appearance of the particles on the sampling surface to infer their morphology in airborne state. Again, how does sampling change their morphology and surface?

See discussion in chap. 5.1 and remarks above.

The gel particles (GP) appeared as a "film-like structure" – how is the equivalent spherical diameter retrieved in such cases?

The particle equivalent diameter is the diameter of a circle with the same projected area than the particle that is characterized. From the SEM images the projected area of a particle can be deduced by calculating the number of pixels that comprise the surface of a article . From this value the Dpa value can be calculated according to Eq.(1).

The "film-like structures" are treated in the same way as the other particles by counting the numbers of pixels that comprise them.

In the manuscript the description of particle size is somewhat misleading and is modified for a better understanding (see chap. 2.3.2).

How can the volume of the particles be calculated without information about the height of the impacted particle?

The volume of the particles cannot be calculated from the two-dimensional SEM images without shading the aerosol particles on the substrate with a metal film; see also remarks above.

p. 5419 / l. 7: How exactly does information about elongation and circularity "improve the understanding" of the aerosol population?

Aerosol particles change their chemical composition and morphology when they are transported in the atmosphere. These changes can be due to condensation of vapours onto the aerosol surface or in cloud transformation processes. These processes can alter the morphology of the aerosol particles which results in a change of their morphological parameters. The morphological parameters thus can be used to obtain information about the transport history of the aerosol particles.

We discuss this topic in detail in chap. 5.2:

"...For two types of aerosol particles (SP, GP) investigated in this study we observe a transition from stronger elongated and branched to more closed structures in course of increased DOI. The lower value in elongation for SP in Sample B could point towards a process that changes the particle shape to a rounder structure and is favored through a longer residence time in the atmosphere. The observed differences in circularity, however indicate changes of the particles towards a higher surface area (expressed by an increased value for CP and a lower circularity) for GP and SP due to a higher DOI in Sample B. The surface of the particles did change towards a rougher contour, e.g. by condensation of vapours on the particle surface. Whether these morphological changes lead to changes in hygroscopicity and the incorporation of matter with surface-active properties, as it has been described for soot by Lehmann et al. (2006) and Coz and Leck (2011) has to be investigated in subsequent studies"