Merete Bilde

Aerosols, chemistry and clouds

It was a great pleasure to participate in the Bunsen-Tagung 2025 (Physical Chemistry of the Climate and the Atmosphere) in Leipzig. At the conference I discussed aerosols, chemistry and clouds with a focus on aerosols formed from wave breaking processes.

Aerosol particles are produced and emitted to the atmosphere from many different processes including combustion, volcanic activity and wave breaking. Their size spans orders of magnitude from few nano-meters to several micro-meters [1]. Aerosol particles can also be formed in situ in the atmosphere via formation of molecular clusters which evolve into aerosol particles via condensational growth processes. The chemical composition of aerosol particles is complex and changes with time along their atmospheric path: aerosol particles exchange molecules with the surrounding atmosphere and they are affected by oxidants such as ozone and exposure to UV light. Thus, during their atmospheric lifetime, aerosol properties including size, chemical composition, phase state and surface structure can change, and we refer to such processes as atmospheric ageing.

Aerosol particles play a crucial role in the climate system of Earth: their interaction with solar radiation results in absorption or scattering of light thereby affecting the radiative balance [2]. Aerosol particles are also important for the formation and the properties of clouds including brightness, lifetime and precipitation. Currently, there are significant limitations in our scientific understanding of aerosol-cloud interactions as for example pointed out by the Intergovernmental Panel on Climate Change [2].

One of the major sources of aerosol particles to the atmosphere is sea spray aerosol [3] formed from bubble bursting processes at the sea surface. Sea water contains several inorganic ions [4] with the most prominent being Na^+, Cl^-, Mg^{2+}, SO_4^{2-}, Ca^{2+} and K^+. Seawater also contains biological material and a multitude of organic molecules, including proteins, lipids and sugars. Several of these accumulate in the thin film at the surface separating ocean and atmosphere [5]. This film is referred to as the sea surface microlayer. Inorganic salts as well as organic and biological material may be transferred to the atmosphere as sea spray aerosol via wave breaking processes and influence cloud formation and properties [6-8].

Prof. PhD. Merete Bilde
Director, Center for Chemistry of Clouds
Department of Chemistry Aarhus University
Langelandsgade 140, DK-8000 Aarhus
bilde@chem.au.dk

DOI-Nr.: 10.26125/tctc-m779

I here present some of our work on sea spray aerosols and point to two interesting aspects of sea spray aerosol formation and properties: First, the ability of some of the inorganic salts in seawater to bind water as hydrates and how this may affect the way we describe volatility and water uptake of sea spray aerosol. Second, formation of aerosols from bubble bursting processes and the effect of water composition and temperature on the particle production.

Chemically bound water in dried sea spray aerosol

In laboratory experiments targeting volatility of sea spray aerosol particles [9] we found, consistent with other studies [10], that dry aerosol particles generated from artificial sea salt or real seawater shrunk significantly upon heating in contrast to particles consisting of NaCl only. Via a series of targeted experiments addressing one salt after the other we could explain such observations by the presence of hydrate forming salts (e.g. $MgCl_2$ and $CaCl_2$), implying that chemically bound water can make up a significant volume fraction of dried sea spray aerosol particles.

As shown by other groups (Zieger et al.) [11] such chemically bound water likely also explains reduced water uptake of sea salt aerosol compared to NaCl at subsaturated conditions, and since NaCl has often been used as a proxy for sea spray aerosol water uptake, this has implications for the prediction of aerosol-radiation interactions.

In the troposphere, cloud droplets form under supersaturated conditions of water vapor when suitable aerosol particles provide surfaces for the water to condense on. Such aerosol particles are referred to as cloud condensation nuclei. The size, phase state and chemical composition of aerosol particles influence their ability to act as cloud condensation nuclei. Hydrate forming salts likely contribute to explaining our observations from several years ago [12] that dried sea salt aerosol and NaCl aerosol behaves differently when it comes to their ability to form cloud droplets: particles consisting of artificial sea salt need a slightly higher supersaturation of water vapor to activate into cloud droplets than particles of the same size consisting of NaCl only. Further work provided hydrate correction factors for $MgCl_2$ and $CaCl_2$ for use in predictions of water uptake of sea spray aerosol [13].

Interestingly, additional hydrate forming salts may form when sea spray aerosol age in the atmosphere. In the work of Rosati et al. [14] experiments were designed for the AURA atmospheric simulation chamber in Aarhus to elucidate atmospheric ageing of sea spray aerosol. Sea spray aerosol generated from artificial sea salt or NaCl was exposed to UV light and ozone under humid conditions, and the experiments suggest that reactions in sea salt droplets, likely at the surface, may lead to further formation of salts that can form hydrates upon drying, warranting further investigation.

Bubble mediated aerosol formation

In another line of laboratory experiments, we probed temperature dependent formation of aerosol particles from bubbles generated in a setup designed to minimize bubble interactions. We found a striking link between the effect of temperature on aerosol particle production and the presence of specific inorganic ions, particularly divalent cations in the water [15] which may have implications beyond sea spray aerosol studies. For other experiments we used a sea spray simulation chamber (AEGOR) to target bubble mediated aerosol formation from bubble plumes where entrainment of air into real or artificial seawater was simulated using a plunging jet or a diffuser. In this laboratory system we observe a non-linear dependence of aerosol production on temperature in the range –2 – 35 °C for the plunging jet and that the presence of phytoplankton biomass can influence bubble mediated aerosol production [16]. The picture is however complex, and contrasting observations of temperature trends from different laboratory systems and air entrainment methods [17] highlight the need for further studies and mechanistic insight into the processes involved.

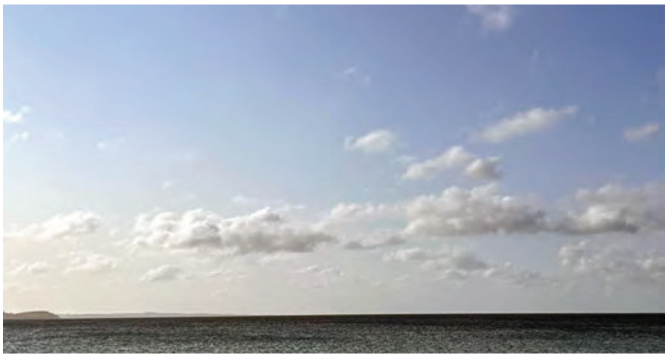
In conclusion, the formation and properties of sea spray aerosol presents a multitude of important, challenging and interesting questions for the physical chemist to investigate. In our ongoing and future work in this direction, we hope to further elucidate properties of fresh and aged sea spray aerosol including the ability to act as seeds for cloud formation.

Center for Chemistry of Clouds

Center for Chemistry of Clouds (C3) at Aarhus University was established in 2023 with funding from the Danish National Research Foundation. C3 aims to contribute molecular level understanding of the processes leading to clouds. Within the center, we apply and pursue development of and synergy between a variety of methods from the fields of physical, analytic, atmospheric and theoretical chemistry.

CleanCloud

CleanCloud is a Horizon Europe Cluster 5 project (started in 2024) investigating how aerosol cloud interactions will evolve in a post-fossil world where natural aerosols such as sea spray aerosol are expected to play a larger role.



Clouds, Bay of Aarhus, Denmark.

Acknowledgements

I thank current and former members of my research group and collaborators at Aarhus University and elsewhere who contributed to our work on sea spray aerosol referenced herein: Berit B. Rasmussen, Quynh T. Nguyen, Kasper Kristensen, Lærke Sloth Nielsen, Stephanie M. King, Andrew C. Butcher, Thomas Rosenørn, Esther Coz, Kirsten I. Kling, Gerrit de Leeuw, E. Douglas Nielsson, Bernadette Rosati, Andreas Paul, Emil M. Iversen, Andreas Massling, Sigurd Christiansen, Anders Dinesen, Pontus Roldin, Matthew E. Salter, and Elena Gorokhova.

References

[1] Seinfeld, J. H. and Pandis, S. N., *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. 2nd ed.; Wiley and Sons Inc.: 2016.

[2] Masson-Delmotte, V., P. Zhai, A. Pirani, S. L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M. I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J. B.; R. Matthews, T. K. M., T. Waterfield, O. Yelekçi, R. Yu and B. Zhou, *IPCC, 2021: Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change.*; Cambridge University Press, 2021

[3] Andreae, M. O.; Rosenfeld, D., Aerosol–cloud–precipitation interactions. Part 1. The nature and sources of cloud-active aerosols. *Earth-Science Reviews* 2008**, 89**, (1), 13–41.

[4] Millero, F. J., The physical chemistry of seawater. *Annual Review of Earth and Planetary Sciences, Vol.* **2***, p.* 101 1974**,** *2*, 101.

[5] Cunliffe, M.; Engel, A.; Frka, S.; Gašparović, B.; Guitart, C.; Murrell, J. C.; Salter, M.; Stolle, C.; Upstill-Goddard, R.; Wurl, O., Sea surface microlayers: A unified physicochemical and biological perspective of the air–ocean interface. *Progress in Oceanography* 2013**, 109**, 104–116.

[6] Cochran, R. E.; Ryder, O. S.; Grassian, V. H.; Prather, K. A., Sea Spray Aerosol: The Chemical Link between the Oceans, Atmosphere, and Climate. *Accounts of Chemical Research* 2017**, 50**, (3), 599–604.

[7] de Leeuw, G.; Andreas, E. L.; Anguelova, M. D.; Fairall, C. W.; Lewis, E. R.; O'Dowd, C.; Schulz, M.; Schwartz, S. E., Production flux of sea spray aerosol. *Reviews of Geophysics* 2011**, 49**, (2).

[8] Quinn, P. K.; Collins, D. B.; Grassian, V. H.; Prather, K. A.; Bates, T. S., Chemistry and Related Properties of Freshly Emitted Sea Spray Aerosol. *Chem Rev* 2015**, 115**, (10), 4383–4399.

[9] Rasmussen, B. B.; Nguyen, Q. T.; Kristensen, K.; Nielsen, L. S.; Bilde, M., What controls volatility of sea spray aerosol? Results from laboratory studies using artificial and real seawater samples. *J Aerosol Sci* 2017**, 107**, 134–141.

[10] Modini, R. L.; Harris, B.; Ristovski, Z. D., The organic fraction of bubble-generated, accumulation mode Sea Spray Aerosol (SSA). *Atmos. Chem. Phys.* 2010, **10**, (6), 2867–2877.

[11] Zieger, P.; Väisänen, O.; Corbin, J. C.; Partridge, D. G.; Bastelberger, S.; Mousavi-Fard, M.; Rosati, B.; Gysel, M.; Krieger, U. K.; Leck, C.; Nenes, A.; Riipinen, I.; Virtanen, A.; Salter, M. E., Revising the hygroscopicity of inorganic sea salt particles. *Nature Communications* 2017, **8**, (1), 15883.

[12] King, S. M.; Butcher, A. C.; Rosenoern, T.; Coz, E.; Lieke, K. I.; de Leeuw, G.; Nilsson, E. D.; Bilde, M., Investigating Primary Marine Aerosol Properties: CCN Activity of Sea Salt and Mixed Inorganic-Organic Particles. *Environmental Science & Technology* 2012, **46**, (19), 10405–10412.

[13] Rosati, B.; Paul, A.; Iversen, E. M.; Massling, A.; Bilde, M., Reconciling atmospheric water uptake by hydrate forming salts. *Environmental Science: Processes & Impacts* 2020, **22**, (8), 1759–1767.

[14] Rosati, B.; Christiansen, S.; Dinesen, A.; Roldin, P.; Massling, A.; Nilsson, E. D.; Bilde, M., The impact of atmospheric oxidation on hygroscopicity and cloud droplet activation of inorganic sea spray aerosol. *Scientific Reports* 2021, **11**, (1), 10008.

[15] Nielsen, L. S.; Bilde, M., Exploring controlling factors for sea spray aerosol production: temperature, inorganic ions and organic surfactants. *Tellus B: Chemical and Physical Meteorology* 2020.

[16] Christiansen, S.; Salter, M. E.; Gorokhova, E.; Nguyen, Q. T.; Bilde, M., Sea Spray Aerosol Formation: Laboratory Results on the Role of Air Entrainment, Water Temperature, and Phytoplankton Biomass. *Environmental Science & Technology* 2019, **53**, (22), 13107–13116.

[17] Forestieri, S.; Moore, K.; Martinez Borrero, R.; Wang, A.; Stokes, M.; Cappa, C., Temperature and Composition Dependence of Sea Spray Aerosol Production. *Geophysical Research Letters* 2018, **45**, (14), 7218–7225.

Prof. PhD. Merete Bilde

Merete Bilde is professor at the Department of Chemistry at Aarhus University, Denmark. She is leader of the Atmospheric Physical Chemistry research group, director of the DNRF Center of Excellence “Center for Chemistry of Clouds” at Aarhus University and member of The Royal Danish Academy of Science and Letters. Her group has built and operates state of the art laboratory facilities including the AURA atmospheric simulation chamber and the AEGOR sea spray simulation tank. Her research contributions encompass new insights into aerosol formation, aerosol-water interactions and fundamental thermodynamic properties of aerosol particles. Merete Bilde has contributed/contributes to national and international research consortia and collaborations: e.g. the Horizon Europe Cluster 5 project „Clean Cloud“ and the infrastructure consortium ACTRIS-DK.