

Secondary Organic Contribution to Particles Formed on the Ice Melted Arctic Ocean

Petri Vaattovaara, Zoran D. Ristovski, Martin Graus, Marcus Müller, Eija Asmi, Luca Di Liberto, Staffan Sjögren, Douglas Orsini, Caroline Leck, Ari Laaksonen

Abstract—Due to climate warming and consequently due to ice and snow melting of the Arctic Ocean, the highly biologically active ocean surface area has been expanding quickly making possible longer marine biota growth seasons during polar summers. That increase the probability of the remote marine environment secondary contribution, especially secondary organic contribution, to the particle production and particle growth events and particle properties, consequently effecting on the open ocean, pack ice and ground based regions radiation budget and thus on the feedbacks between arctic biota, particles, clouds, and climate.

Keywords—Arctic Ocean, ice melting, nucleation, secondary organics, clouds, climate.

I. INTRODUCTION

NEWLY-FORMED nanometer-sized particles have been observed at coastal and remote marine environments worldwide (see references within [1]). Such nanoparticles can grow into larger sizes [2], being able to scatter incoming radiation and contribute to direct and indirect (via clouds) cooling effects to the Earth's radiation budget [3]. Marine coastal nucleation events are frequently observed and the size and composition of newly-formed particles has been intensively studied especially at Mace Head in Irish coast [4]. Observation of nucleation events in open oceans are much more rare (e.g., [5]) and the composition of observed particles is still unknown. A common feature of the coastal and open water nucleation events is that they have occurred on highly biologically active waters [6].

It is important to note that the surface of these biologically active open waters has expanded especially in the Arctic Ocean region during the last decades due to climate warming and consequent ice melting [7]. Arctic Ocean open waters have been reported to contribute to new particle production (e.g., [8]) during the nightless polar summer season. More generally, the solar radiation is known to play an important role in the presence of nucleation mode sized particles in the Arctic Ocean region [9]. However, the formation, composition and growth of those newly-formed particles should be better understood in order to better understand also the effects of ice melting Arctic Ocean on the connections between Arctic biota, clouds and climate.

Petri Vaattovaara is with Department of Applied Physics, University of Eastern Finland, Kuopio, Finland (phone: +358 44 578 4226; e-mail: petri.o.vaattovaara@gmail.com).

Zoran Ristovski is with ILAQH, Queensland University of Technology, Brisbane, Australia (e-mail: z.ristovski@qut.edu.au).

We carried out this Arctic Ocean open water study of nucleation mode and Aitken mode sized particles growth and organic fraction as a part International Polar Year (IPY) 2007-2009 related "Arctic Summer Cloud Ocean Study (ASCOS)" project on the board of Swedish Icebreaker Oden during solar radiation intensive and the biologically active polar summer time in August 2008. The chosen measurement route and time opened up a good opportunity to study the processes of ultrafine particles ($d < 100\text{nm}$) on the Arctic Ocean conditions expected to dominate also in the near Arctic future.

II. METHODS

A. The Measurement Location

Measurements were carried out on the ice melted part of Greenland Sea, covering a highly biologically active surface region (about $78^\circ\text{N} - 79^\circ\text{N}$ and $9^\circ\text{E} - 5^\circ\text{E}$, to the west from the Spitzbergen) close the ice edge, during the nightless polar summer time period (3rd August 3 p.m. – 4th August 12 a.m.). The air was drawn for sampling of atmospheric aerosol and trace gases from about 25 meters above the sea surface into the measurement containers fixed on the 4th deck of Oden. The inlet system extended at an angle of 45° to about 3 meter above the roof of the containers. In order to avoid the emissions from the ships diesel motors the ship was moving continuously heading against the wind direction. The wind speed onboard was about 2 m/s that is generally typical for polar summers. Typically, the ice coverage, the ice thickness and the antropogenic transportation from continents to the ice melting Arctic Ocean are in minima whereas photosynthetically important solar radiation effect on the marine biota is high during this time of polar summer.

B. Instruments

In this study, the measurement systems used to characterize the newly-formed particles consisted of the UFO-TDMA (ultrafine organic tandem differential mobility analyzer [10]), measuring the 10-50 nm (in mobility diameter) particles, the VH-TDMA (volatile and hygroscopicity tandem differential mobility analyzer [11]), measuring particles with 16nm mobility diameter and H-TDMA (hygroscopicity tandem differential mobility analyzer) measuring the Aitken mode sized particles. A HR PTR-ToFMS (high resolution proton transfer reaction time of flight mass spectrometer [12]) was used to measure the gaseous particle precursors as well as to check for anthropogenic traces in the air masses. The particle size distribution from 3-800nm (in mobility diameter) was measured by a twin DMPS (differential mobility particles

sizer). The particles relative vertical concentration was followed using LIDAR (light detection and ranging). The marine origin of the air masses were followed using 96 hours HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model ([13] and [14]) backward trajectories and marine biological activity using Sea-WiFs (Sea viewing Wide Field-of-view Sensor) and MODIS (Moderate Resolution Imaging Spectroradiometer) Aqua and Terra satellite data (NASA/Goddard Space Flight Center and ORBIMAGE).

III. RESULTS AND DISCUSSION

The nucleation mode sized particles included to a particle mode from 10nm to 40nm, were observed starting around 3 p.m. (see Fig. 1 for particle size distribution) on the Greenland Sea, at about 78° N and 9° E, when local wind and ship direction were western and air mass arrived from East Greenland Sea. The VH-TDMA data reveal the hygroscopicity of 16 nm particles with the GF about 1.3-1.35 in the start of event. The particle concentration increased from below 100 up to 1500 #/cm³.

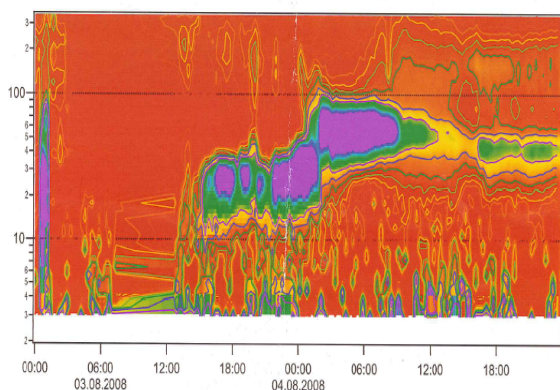


Fig. 1 Particle size distributions measured on the Greenland Sea during 3.8-4.8.2008 ultrafine particle event

Potential reasons for the observed biogenic nucleation mode sized particles close to sea level could be related to free troposphere transport (e.g., [15]), cloud induced nucleation [16] and marine biota (e.g., [6] and [17]). LIDAR polarized aerosol backscattering data reveal that the particles did not arrived downwards at the moment of observation of nucleation mode sized particles. When the local wind direction and ship turned to more northern direction after 6 p.m. and the lowest air masses still travelled from East Greenland Sea, a new 15-40nm particles mode was observed and particle concentration increased from about 500 up to 3500 #/cm³ until midnight during particles growth with the mode median growth rate (GR) 1.6 nm/h. After midnight the local wind direction and ship turned to north-westerly direction and new particles arrived upwards from few hundred meters (LIDAR data) and particle concentration was about 2000 particles cm⁻³. Since that, the particles size was 30-100nm and thus the upper end of these Aitken mode sized particles being potentially cloud condensation nuclei (CCN). The hygroscopicity of 72nm (in

mobility diameter) Aitken mode sized particles was measured by HTDMA, the growth factor (GF) around 1.4 at 90% RH (relative humidity, corrected to 90%) supporting the CCN potential of the particles. The GR of the mode median was about 1.2 nm/h after midnight.

The lowest 100m air masses were travelled several days from the biologically active East Greenland coast and the island of Jan Mayen directions close the biologically active coastal regions and ice edges with blankton blooms. The observation day was more or less cloudy. However, the Sun was able to shine through the cloud cover about at the moment of the first nucleation mode sized particles observation. The results of the UFO-TDMA and VH-TDMA show that the 15-30nm particles consisted of at least 20-50 volume percent organics (see Fig. 2) during the first few hours, the nucleation mode sized particles were observed. Since 6 p.m. until midnight, the organic volume fraction (OVF; for OVF calculation method, see[6]) of the UFO-TDMA measured 15-30nm particles increased to a minimum estimate of about 55-65% (Fig. 3). After midnight, an organic volume fraction estimate of the UFO-TDMA measurements was about 55-60 % for 50nm particles until 3 a.m. of August 4 (Fig. 4) when the upper end of Aitken mode particles reached 100nm in size. After 3 a.m. air mass changed again, now arriving from western direction, and the OVF of 50nm particles consequently dropped down to 25 % until 6 a.m., meanwhile particle number concentration dropped from 2000 to 500 #/cm³.

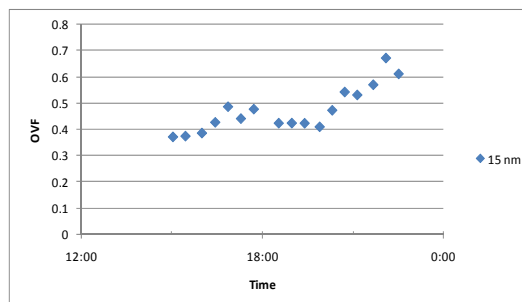


Fig. 2 OVF estimated for 15 nm particles based on the UFO-TDMA measurements 3.8.2008 on the open water Arctic Ocean

In addition to the organic fraction, the growth of the observed particles can be related to the presence of DMS (Dimethyl Sulfide) and its elevated levels from 50 ppt (3 p.m. on August 3th) up to 130 ppt (5 a.m. on August 4th). When the air mass turned to ice covered region after midnight, DMS concentration dropped down, being about 1-2 ppt. Those support the important role that marine biota played in the origin of the precursor gases. Potential candidates for the precursors of the secondary organic contribution could be atmospherically very reactive phytoplankton biosynthesis products such as isoprene ([18]), monoterpenes ([19]), chlorobenzenes ([20]), and their derivatives and organic derivatives of DMS.

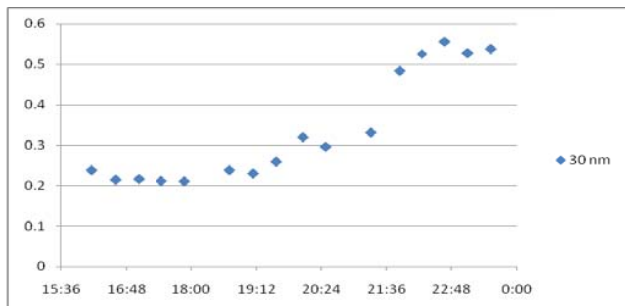


Fig. 3 OVF estimated for 30 nm particles based on the UFO-TDMA measurements 3.8.2008 on the open water Arctic Ocean

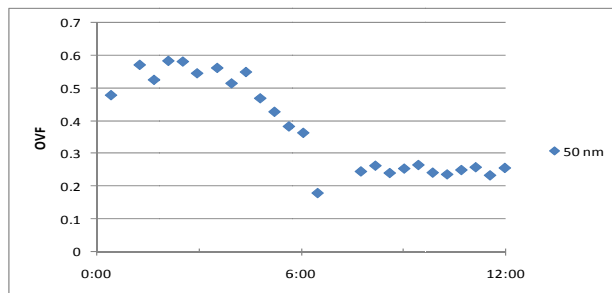


Fig. 4 OVF estimated for 50 nm particles based on the UFO-TDMA measurements 4.8.2008 on the open water Arctic Ocean

A growth (even though disturbed by local wind direction and ship direction change) in particle size distribution as a function of time indicates that the particles production was a large area phenomena, further supporting also the role of biologically active sea surface as an origin for the observed particles. The observations also support the importance of biologically active marine areas for secondary organic contribution to the properties of atmospheric particles.

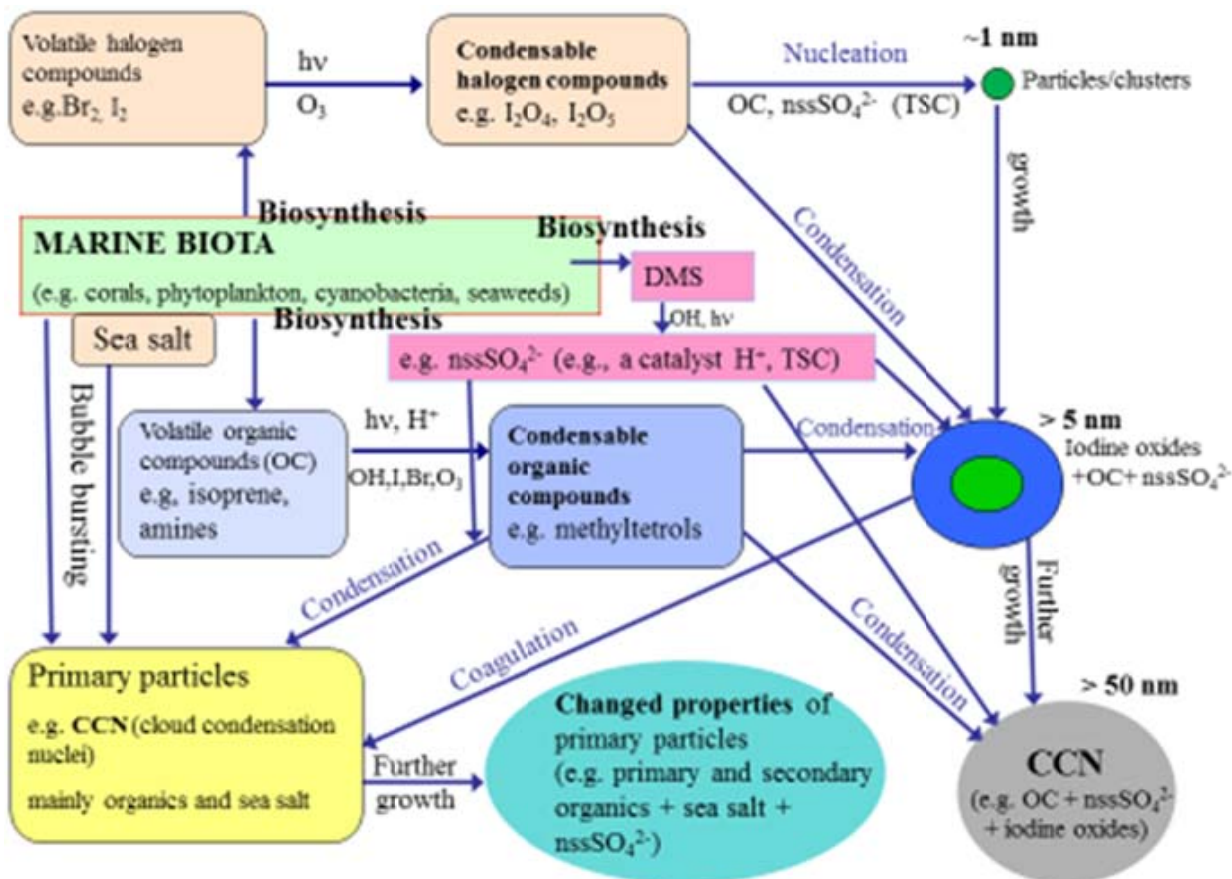


Fig. 5 A schematic of potential biogenic nucleation, Aitken and accumulation mode particle formation, growth, and composition during daylight hours at Arctic Ocean close to ice edge

IV. CONCLUSIONS

Due to climate warming and consequently due to ice and snow melting of the Arctic Ocean, the highly biologically active ocean surface area has been expanding quickly making possible longer marine biota growth seasons during polar summers. This increase the probability of the remote marine environment secondary contribution, especially secondary organics contribution, to particle production and particle growth events and particle properties consequently effecting on the open ocean, pack ice and ground based regions radiation budget and thus on the feedbacks between arctic biota, particles, clouds, and climate.

ACKNOWLEDGMENTS

The authors thank for the help and facilities provided by the ASCOS (Arctic Summer Cloud Ocean Study) team and Swedish Secretariat for Polar Research through an agreement with the Swedish Maritime Administration and the crew of the icebreaker Oden. We are grateful for the financial support from the Finnish Cultural Foundation through Lapland Regional Fund, the Academy of Finland through the Center of Excellence, EU-project DAMOCLES (Developing Arctic Modeling and Observing Capabilities for Long-term Environmental Studies), Swedish Research Council and the Knut and Alice Wallenberg Foundation. PV wish to thank Emil Aaltonen foundation for the visiting grant for this work. The authors also gratefully acknowledge Sea-WiFs and MODIS Aqua and Terra (NASA/Goddard Space Flight Center and ORBIMAGE) for satellite data and the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and READY web site (<http://www.arl.noaa.gov/ready.html>) used in this study.

REFERENCES

- [1] Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P.H., Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J. Aerosol Sci.*, 35, 143-176, 2004.
- [2] O'Dowd, C.D. Biogenic coastal aerosol production and its influence on aerosol radiative properties, *J. Geophys. Res.*, 106, 1545-1550.
- [3] Slingo, A. (1990). Sensitivity of the Earth's radiation budget to changes in low clouds. *Nature*, 343, 49-51, 2001.
- [4] O'Dowd, C.D. and de Leeuw, G., Marine aerosol production: a review of the current knowledge. *Phil. Trans. R. Soc. A*, 365, 1753-1774, 2007.
- [5] Katoshevski, D., Nenes, A., and Seinfeld, J.H., A study of Processes that Govern the Maintenance of Aerosols in the Marine Boundary Layer. *J. Aerosol Sci.*, 30, 503-532, 1999.
- [6] Vaattovaara, P., Huttunen, P.E., Yoon, Y.J., Joutsensaari, J., Lehtinen, K.E.J., O'Dowd, C.D., and Laaksonen, A., The composition of nucleation and Aitken modes particles during coastal nucleation events: evidence for marine secondary organic contribution. *Atmos. Chem. Phys.* 6, 4601-4616, 2006.
- [7] Arrigo, K., van Dijken, G., and Padi, S., Impact of a shrinking Arctic ice cover on marine primary production. *Geophys. Res. Lett.*, 35, L19603, 2008.
- [8] Wiedensohler, A., Covert, D.S., Swietlicki, E., Aalto, P., Heintzenberg, J., and Leck, C., Occurrence of an ultrafine particle mode less than 20 nm in diameter in the marine boundary layer during Arctic summer and autumn. *Tellus*, 48B, 213-222, 1996
- [9] Ström, J., Umegård, J., Torseth, K., Tunved, P., H.-C. Hansson, Holmén, K., Wismann, V., Herber, A., König-Langlo, G., One year of particle size distribution and aerosol chemical composition measurements at the Zeppelin Station, Svalbard, March 2000-March 2001. *Phys. Chem. Earth*, 28, 1181-1190, 2003
- [10] Vaattovaara, P., Räsänen, M., Kühn, T., Joutsensaari, J., Laaksonen, A., A method for detecting the presence of organic fraction in nucleation mode sized particles. *Atmos. Chem. Phys.*, 5, 3277-3287, 2005.
- [11] Johnson, G.R., Ristovski, Z.D., D'Anna, B., Morawska, L., Hygroscopic behavior of partially volatilized coastal marine aerosols using the volatilization and humidification tandem differential mobility analyzer technique. *J. Geophys. Res.*, 110, D20203, 2005.
- [12] Graus, M., Mueller, M., and Hansel, A.: High resolution PTR-TOF: quantification and formula confirmation of VOC in real time, *J. Am. Soc. Mass Spectr.*, 21, 1037-1044, 2010.
- [13] Draxler, R.R. and Rolph, G.D., HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory). Model access via NOAA ARL READY Website (<http://www.arl.noaa.gov/ready/hysplit4.html>), Silver Spring, MD: NOAA Air Resources Laboratory, 2003.
- [14] Rolph, G.D., Real-time Environmental Applications and Displays Ystem (READY) Website, Silver Spring, MD: NOAA Air Resources Laboratory, 2003.
- [15] Clarke, A.D. Atmospheric nuclei in the Pacific midtroposphere: Their nature, concentration, and evolution. *J. Geophys. Res.*, 98, 20633-20647, 1993.
- [16] Raes, F., and Van Dingenen. Simulations of condensation and cloud condensation nuclei from dimethyl sulphide in the natural marine boundary layer. *J. Geophys. Res.*, 97, 12901-12912, 1992.
- [17] Leck, C. and Bigg, K., Aerosol production over remote marine areas – A new route. *Geophys. Res. Lett.*, 23, 3577-3581, 1999.
- [18] Gantt, B., Meskhidze, N., Kamykovski, D., A new physically-based quantification of isoprene and primary organic aerosol emissions from the world's oceans. *Atmos. Chem. Phys. Discuss.*, 9, 2933-2965, 2009.
- [19] Yassaa, N., Peeken, I., Zöllner, E., Bluhm, K., Arnold, S., Sparclen, D., Williams, J., Evidence for marine production of monoterpenes. *Environ. Chem.*, 5, 391-401, 2008.
- [20] Colomb, A., Yassaa, N., Williams, J., Peeken, I., and Lochte, K., Screening volatile organic compounds (VOCs) emissions from five marine phytoplankton species by head space gas chromatography/mass spectrometry (HS-GC/MS). *J. Environ. Mon.*, 10, 325-330, 2008.