Marine Aerosol – Cloud Interactions*, *MaCloud Inc. 2.1
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- **Introduction and motivation**

The general aim of the MaCloud Inc. (Marine Aerosol –Cloud Interactions) was to build on recent advances in marine aerosol formation processes. In addition to coastal iodine-driven nucleation and growth events, it has been established that open ocean particle production and growth is frequent over the NE Atlantic and appears to be driven by organics. We aimed to better characterize these coastal and open ocean events. Recently, aerosol mass spectrometry has revealed unique marine aerosol organic characteristics with effective cloud nucleating properties despite low hygroscopic growth factors. We also looked into the role of halogens as well as organic ions in the burst-like new particle events at Mace Head.

- **Scientific objectives**

(1) To source apportion marine aerosol
(2) Quantify formation and evolution characteristics
(3) Quantify hygroscopic and Cloud Condensation Nuclei (CCN) properties
(4) Quantify marine aerosol impacts on cloud microphysics.

The purpose of the winter campaign in 2010 is to quantify sea-salt production and it will characterise the low biological activity period on aerosol-cloud interactions. This will be followed up by a 2011 summer campaign to quantify primary/secondary and organic/biological impact on cloud microphysics within a high biological activity period.

- **Reason for choosing station**

Coastal new particle formation is a frequent phenomenon (O'Dowd and Hoffmann, 2005) that has a strong connection to coastal tides, air mass origin and solar radiation. In addition to coastal iodine-driven nucleation and growth events, it has been recently established that open ocean particle production and growth is common over the NE Atlantic. We also observe sulphuric acid production with a distinctive diurnal cycle, but the involvement to the new particle formation bursts is much less than in continental air masses. The unique location of Mace Head station with strong costal tides makes it possible to study the two different nucleation pathways.

- **Method and experimental set-up**

Our contribution to project "MaCLOUD Inc." was to quantify atmospheric ion population in both in terms of the chemical composition and their physical character. A special focus was put to bursts of freshly nucleated particles in the coastal environment of Mace Head. We measured with an Atmospheric Pressure interface- time-of-flight mass spectrometer (APi-TOF, Junninen et al. 2010, Ehn et al. 2010), which can probe the chemical composition of naturally charged ions in the atmosphere.

We also provided a detailed physical characterization of the ion population with a long term (6 months) commitment using an Air Ion Spectrometer (AIS, Mirme et al. 2007) for size segregated ion concentration.
Furthermore we deployed a Particle Size Magnifier (PSM, Vanhanen et al. 2010), which reveals the concentration of both charged and neutral particles in sub-3 nm particle size. These instruments provided data in the sub-3 nm particle size, which is the size where the gas-to-particle conversation occurs (Kulmala et al. 2007).

- **Preliminary results and conclusions**

Preliminary data indicates that during the campaign the ion composition during the new particle formation bursts (Fig. 1) was dominated by iodine, iodic acid and their clusters. We also observed sulphuric acid production with a clear correlation with solar radiation. The involvement of sulphuric acid to the new particle formation bursts was much less than in continental air masses. Negative ions such as bromine, bromate, perchlorate and their clusters were often present as well as multiple positively charged organic ions. Example of the identified negative ions is presented in figure 2 and time series of the most abundant negative ions in figure 3. The process of assimilating the ion composition of the marine aerosol with the coastal tides, temperature and radiation is still ongoing.

A more detailed data analysis is currently underway and the results presented in this short report need to be considered as a preliminary effort only. However, already the vast amount of data that we gathered during the MaCLOUD experiment will definitely improve our understanding about the marine and coastal aerosol particles and ions and their role in the atmosphere.

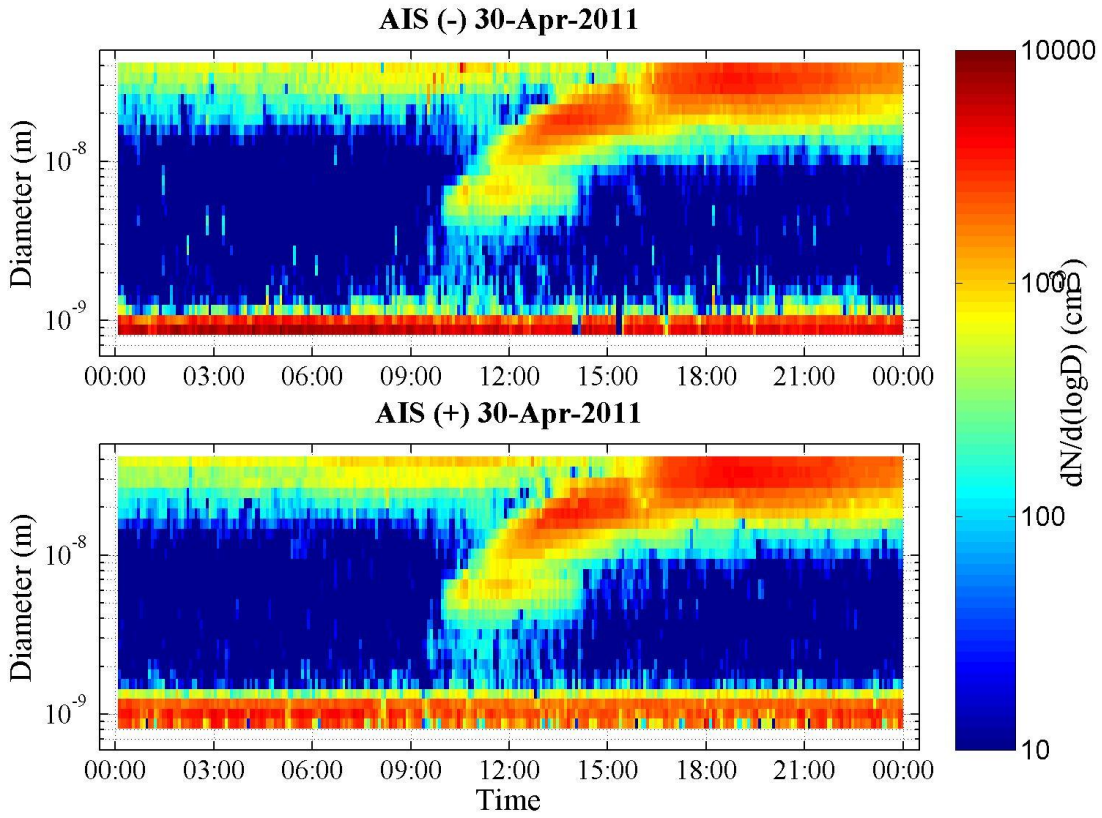

Figure 1. Number size distribution of ambient ions measured with AIS at Mace Head on 30th April 2011 showing Class I type new particle formation event.

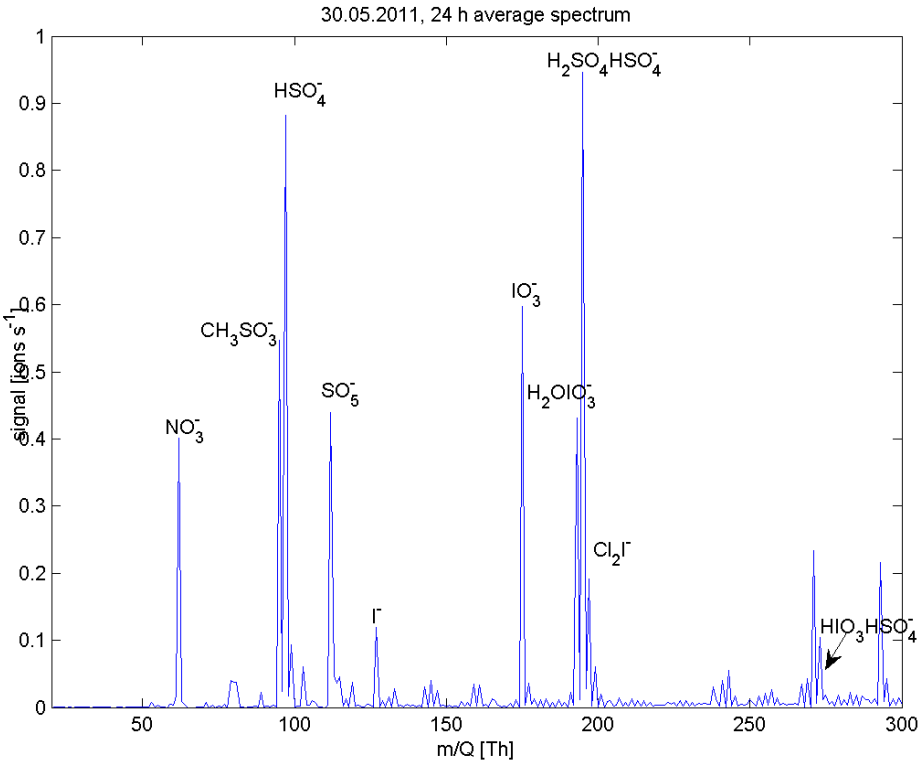

Figure 2. Negative ion spectrum measured with the APi-TOF at noon 30th May 2011 showing iodine containing ion clusters and sulphuric acid and its clusters.

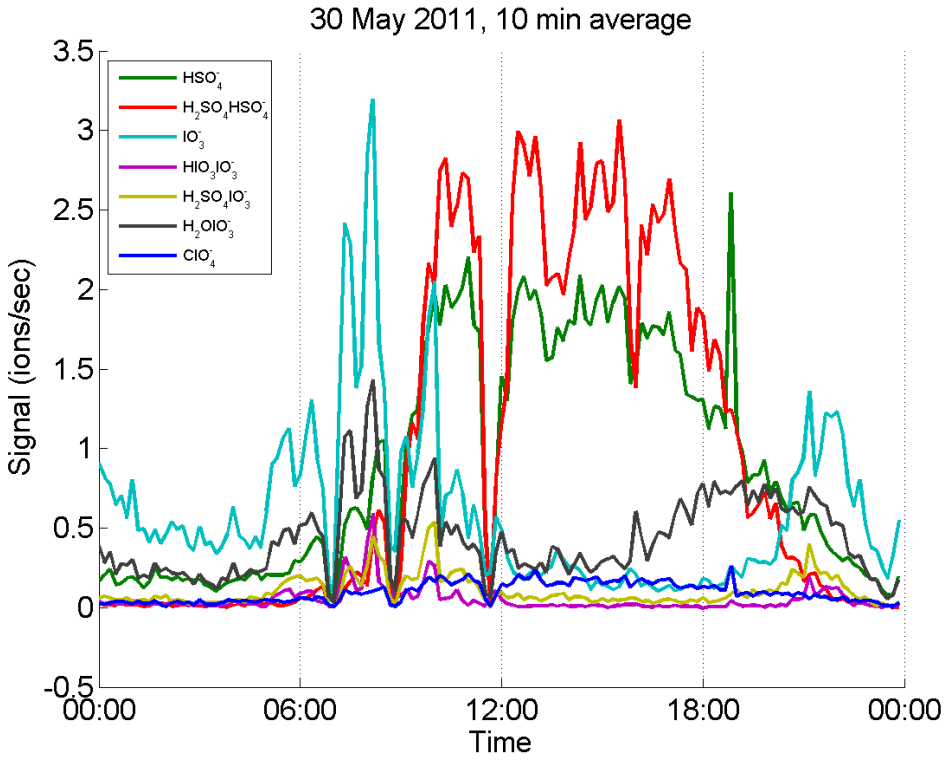

Figure 3. An exemplary time series of most abundant naturally charged negative ions in Mace Head, 30th May 2011.

- **Outcome and future studies**

Future studies will concentrate on better understanding the frequently observed coastal new particle formation. Preliminary results indicate iodine, bromine and sulphuric acid to dominate the chemical composition of the marine aerosol but more detailed analysis is yet required to further characterize positively charged organic ions and the effect of algae emission on nanocluster formation.

Due to a long period of ongoing measurements we are able to study seasonal variation and the influence of biological activity to ions and nanoclusters in Mace Head atmosphere. A vast amount of data gathered during MaCloud Inc campaigns will definitely improve our understanding about the marine and coastal aerosol particles and ions.

As a product of this TNA, the following conference abstract to was produced:

> Petäjä, T., Junninen, H., Äijälä, M., Franchin, A., Schobesberger, S., Manninen, H., Hirsikko, A., Vanhanen, J., Mikkilä, J., Lehtipalo, K., McGrath, J., Ceburnis, D., Berresheim, H.,Worsnop, D.R., Kulmala, M. and O'Dowd, C.D. (2011) Air ion chemical and physical characterization during MaCLOUD Inc at Mace Head, Proceedings of European Aerosol Conference, Manchester, UK, 4-9 September, 2011, Abstract 984.

Furthermore, the following manuscripts are currently under way;

1) Junninen H., Lönn G., Jokinen T., Schobesberger S., Äijälä M., Petäjä T., Kulmala M., Chemical compostion of ions in marine atmosphere, 2012
2) Pei X., Manninen H. E., Dal Maso M., Junninen H., Jokinen T., Schobesberger S., Äijälä M., Petäjä T., Kulmala M., Seasonal variation of ions and nanoclusters in Mace Head, 2012
3) Junninen H., Lönn G., Jokinen T., Schobesberger S., Äijälä M., Petäjä T., Kulmala M., Effect of algae emission on nanocluster formation, 2013

- References

Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostiainen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M. and Worsnop, D.R. (2010) API-ToFMS: a tool to analyze composition of ambient small ions. Atmos. Meas. Technol., 3, pp. 1039-1053.

Kulmala, M., Riipinen, I., Sipilä, M., Manninen, H.E., Petäjä, T., Junninen, H., Dal Maso, M., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R.M., Hanson, I., Leung, C., Lehtinen, K.E.J. and Kerminen, V.-M. (2007) Towards direct measurement of atmospheric nucleation Science, 318, 89-92, DOI: 10.1126/science.1144124.

Mirme, A., Tamm, E., Mordas, G., Vana, M., Uin, J., Mirme, S., Bernotas, T., Laakso, L., Hirsikko, A., and Kulmala, M. (2007) A wide range multi-channel Air Ion Spectrometer, Boreal Environ. Res., 12, 247–264.

O'Dowd C. D., Hoffmann T., Coastal New Particle Formation: A Review of the Current State-Of-The-Art, *Environ. Chem.* 2005, *2*, 245.

Vanhanen, J., Mikkilä, J., Lehtipalo, K., Sipilä, M., Manninen, H.E., Siivola, E., Petäjä, T. and Kulmala, M. (2011) Particle size magnifier for nano-CN Detection Aerosol Sci. Technol., 45, pp. 533-542.