ISAFME

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Introduction and motivation

Nucleation and subsequent growth of new atmospheric aerosol particles form a major source of cloud condensation nuclei globally (Merikanto et al., 2011). Despite significant efforts, no nucleation or growth mechanism has been solved on molecular level in any atmospheric environment. Strong nucleation bursts have been regularly observed in many coastal areas and the particle formation has suggested to be related to halogen, specifically iodine, emissions of marine algae (e.g. O'Dowd et al., 2002; Huang et al., 2010). These vapors are emitted during low tide when the algae beds become in contact with ambient air. Iodine vapors can then be oxidized in the atmosphere to form iodine oxides, which might undergo homogeneous nucleation.

However, the coastal nucleation process – like any other atmospheric nucleation process – has not been resolved at a molecular level. Neither has been shown, that iodine containing species drive the nucleation and initial growth, or are other species, such as sulfuric acid triggering new particle production.

Scientific objectives

Main scientific objective was to resolve the molecular steps of nucleation of new particles in the coastal environment.

First secondary objective was resolving the existence, chemical compositions, and dynamics of highly oxidized, extremely low volatile organic compounds (ELVOC) in marine, coastal and continental air of Ireland. The existence and formation pathway of these ELVOC was recently discovered by Ehn et al., (2014) in boreal forest environment, where ELVOC form mainly form oxidation of monoterpenes and subsequent auto-oxidation of reaction products. Ehn et al. (2014) used the exactly the similar suite of instrumentation as we here, and therefore the campaign offered the great opportunity for second observation of ELVOC related chemistry and physics on the planet.

Second secondary objective was to get further insight on non-OH oxidation process of SO2 observed in Mace Head recently (Berresheim et al., 2014).

Reason for choosing station

Mace Head station is located next to marine algae beds of Atlantic coast. Because the hypothesized iodine oxide nucleation occurs in vicinity of such algae beds when exposed to ambient air during low tide, Mace Head station was a natural choice for the study. Nucleation in Mace Head is also

very intense and therefore resolving the molecular steps of nucleation is easier than in locations where nucleation rates are low or moderate.

Method and experimental set-up

Setup we used at Mace Head station comprised following instruments

- Chemical Ionization – Atmospheric Pressure interface – Time of Flight Mass Spectrometer (CI-API-TOF, Jokinen et al., 2012)
  CI-APi-TOF was our primary tool. CI-APi-TOF detects neutral molecules and clusters from less than 100 up to over 2000 atomic mass units in mass. CI-APi-TOF's mass resolution is such good that it enables identification of atomic composition of detected clusters. With CI-APi-TOF nucleation process has been solved in laboratory facilities (unpublished), but before this work, nowhere in the atmosphere.
- Atmospheric Pressure interface – Time of Flight Mass Spectrometer (API-TOF, Junninen et al., 2010)
  APi-TOF is similar to CI-APi-TOF, but does not contain the chemical ionization source used for charging the neutral clusters. APi-TOF thereby detects naturally charged molecules and clusters and measures their composition. APi-TOF data can be used to support observations made by CI-APi-TOF and to resolve the molecular steps of potential ion induced nucleation.
- Particle size magnifier (PSM, Vanhanen et al., 2011).
  PSM measures particle size distribution between ~1.5 and 4 nm. PSM is used for measuring the concentrations of newly formed clusters. During campaign two units were deployed.
- Neutral cluster and Air Ion Spectrometer (NAIS, Asmi et al., 2008).
  NAIS measures neutral particle size distribution between ~2 and 40 nm and natural ion size distribution from 0.5 to 40 nm. NAIS is used for measuring the concentrations and size distributions of newly formed neutral and charged clusters and particles.

Supporting data used from Mace Head station included particle size distribution data recorded by DMPS, meteorological data, and sulphuric acid concentration data measured by a Chemical ionization mass spectrometer (CI-MS). Data related to particle dynamics was and will further be analyzed by methods described in Kulmala et al. (2012). TOF mass spectrometer data was and will further be analyzed by TofTools software (Junninen et al., 2010).

Preliminary results and conclusions

Preliminary results suggest the following:

(1) The molecular steps of nucleation can be resolved from the recorded data. Atomic compositions of both neutral and charged clusters were measured up to over 2000 atomic mass units during several coastal nucleation events.

(2) Also ELVOCs were discovered, at least from continental air masses. ELVOC are more diverse and more concentrated than ELVOC in boreal forest environment (Ehn et al., 2014). These continental ELVOC might have strong impact on secondary cloud condensation nuclei production in the region.

(3) Sulphuric acid production was observed in virtual absence of OH radical. This observation supports the findings of Berresheim et al. (2014) that yet unknown oxidant(s) are present in the region.

Outcome and future studies

Outcomes of the measurement campaign will comprise at least 3 publications. Publication related to result (1) is under preparation for Nature with the expected submission in Aug-Sep 2014. Publications related to results (2) and (3) will be prepared as well with expected submission by the end of 2014. Near future studies will comprise laboratory experiments aiming to replicate the field observations.

References

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