

Molecular-scale evidence of aerosol particle formation via sequential addition of HIO₃

Mikko Sipilä¹, Nina Sarnela¹, Tuija Jokinen¹, Henning Henschel¹, Heikki Junninen¹, Jenni Kontkanen¹, Stefanie Richters², Juha Kangasluoma¹, Alessandro Franchin¹, Otso Peräkylä¹, Matti P. Rissanen¹, Mikael Ehn¹, Hanna Vehkamäki¹, Theo Kurten³, Torsten Berndt², Tuukka Petäjä¹, Douglas Worsnop^{1,4,5,6}, Darius Ceburnis⁷, Veli-Matti Kerminen¹, Markku Kulmala¹ & Colin O'Dowd⁷

Homogeneous nucleation and subsequent cluster growth leads to the formation of new aerosol particles in the atmosphere¹. The nucleation of sulfuric acid and organic vapours is thought to be responsible for the formation of new particles over continents^{1,2}, whereas iodine oxide vapours have been implicated in particle formation over coastal regions^{3–7}. The molecular clustering pathways that are involved in atmospheric particle formation have been elucidated in controlled laboratory studies of chemically simple systems^{2,8–10}, but direct molecular-level observations of nucleation in atmospheric field conditions that involve sulfuric acid, organic or iodine oxide vapours have yet to be reported¹¹. Here we present field data from Mace Head, Ireland, and supporting data from northern Greenland and Queen Maud Land, Antarctica, that enable us to identify the molecular steps involved in new particle formation in an iodine-rich, coastal atmospheric environment. We find that the formation and initial growth process is almost exclusively driven by iodine oxoacids and iodine oxide vapours, with average oxygen-to-iodine ratios of 2.4 found in the clusters. On the basis of this high ratio, together with the high concentrations of iodic acid (HIO₃) observed, we suggest that cluster formation primarily proceeds by sequential addition of HIO₃, followed by intracluster restructuring to I₂O₅ and recycling of water either in the atmosphere or on dehydration. Our study provides ambient atmospheric molecular-level observations of nucleation, supporting the previously suggested role of iodine-containing species in the formation of new aerosol particles^{3–7,12–18}, and identifies the key nucleating compound.

The question of how new clusters and particles form in the atmosphere has so far remained unanswered, owing to the lack of a measurement technique that is sufficiently sensitive to detect or identify the chemical composition of nucleating clusters, given that most new atmospheric particle formation events occur at modest intensities. An exception, in terms of nucleation burst intensity, is the formation of new particles in coastal regions, where exceptionally high formation and growth rates—relative to any other environment—have been observed^{3,7}. The observed rapid formation and growth in coastal air requires extraordinarily high production rates of particle precursors. Biogenic emissions of iodine vapours, mainly I₂ (refs 14, 15, 19), from marine algae have been implicated in the production of iodine atoms by photolysis reactions. Iodine atoms would then rapidly undergo a chain of reactions initiated by ozone to form IO radicals^{3,12,20,21}, OIO (refs 3, 21, 22), HIO (refs 3, 12), HIO₃ (ref. 23), I₂O_{2–4} (ref. 3) and I₂O₅ (ref. 16)—all potential precursors of new particles. Particle production from iodine-containing vapours that are not yet identified has also been experimentally demonstrated^{3,12,13}. Laboratory experiments starting with I₂ and ozone suggested that particles formed in dry conditions are composed of I₂O₅ (refs 16, 17).

To identify the molecular steps involved in the formation of new particles in an iodine-rich environment, a field campaign was performed at the Mace Head coastal station on the west coast of Ireland in August–October 2013. A suite of novel instrumentation (in particular, a nitrate ion-based chemical ionization atmospheric pressure interface flight (CI-API-TOF) mass spectrometer, which is capable of resolving the chemical composition of freshly formed electrically neutral clusters⁹) was applied to collect the data (see Supplementary Information).

New particle formation associated with the low tide and the subsequent exposure of seabed macroalgae to ambient air was observed almost every day throughout the campaign (Supplementary Fig. 1). An example of a new particle formation event is shown in Fig. 1. Soon after noon when the low tide occurred, a strong burst (Fig. 1a) of new particles was detected with the total concentration of particles larger than 1.5 nm in size exceeding 10⁶ cm⁻³. Clusters of 1.5–3 nm in diameter reached concentrations of the order of 10⁵ cm⁻³ (Supplementary Fig. 2).

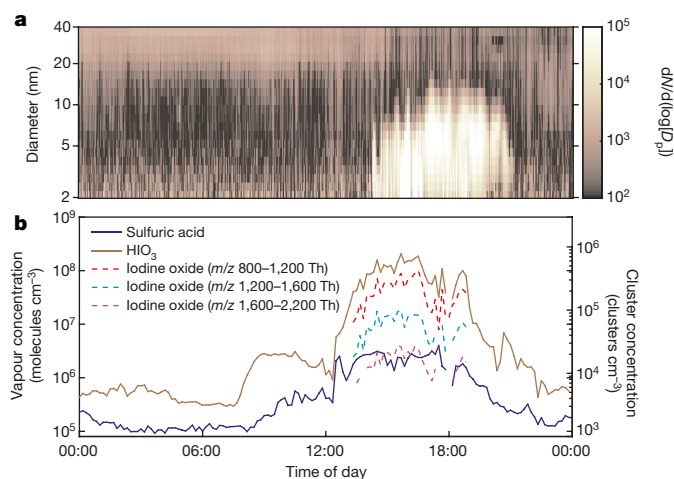


Figure 1 | A typical particle formation event recorded at Mace Head. **a**, The event is initiated approximately two hours after noon at low tide owing to iodine emissions from marine algae. Particles then grow rapidly to sizes of 2–10 nm (N is the particle number concentration and D_p is the particle diameter). When the tide gets high again approximately 6 h after the event began, particle production stops. **b**, The event is associated with a slight increase in the concentration of sulfuric acid, which is typically thought to be the key player in atmospheric nucleation. However, a much more prominent increase in HIO₃ (with a peak concentration of greater than 10⁸ cm⁻³) is observed. Together with HIO₃, iodine oxide clusters with mass/charge (m/z) ratios that exceed 2,000 Th (1 Th = 1 Da/e) are observed. The solid lines represent vapours (measured on the left-hand y axis) and the dashed lines represent clusters (measured on the right-hand y axis).

¹Department of Physics, University of Helsinki, Helsinki, Finland. ²Leibniz-Institute for Tropospheric Research (TROPOS), Leipzig, Germany. ³Department of Chemistry, University of Helsinki, Helsinki, Finland. ⁴Department of Applied Physics, University of Eastern Finland, Kuopio, Finland. ⁵Aerodyne Research Inc., Billerica, Massachusetts 01821, USA. ⁶Finnish Meteorological Institute, Helsinki, Finland. ⁷School of Physics and Centre for Climate & Air Pollution Studies, Ryan Institute, National University of Ireland Galway, University Road, Galway, Ireland.

Because of the short distance between the emission source and the measurement site the particles rarely grew larger than 10–20 nm. However, previous studies have demonstrated that these particles reach comparable sizes to cloud condensation nuclei in a few hours²⁴.

Preceding the new particle production event, a strong increase in the HIO₃ signal was seen (Fig. 1b) with concentrations reaching 10⁸ molecules cm⁻³ during the course of the event. The presence of HIO₃ was unexpected as there have been no reported observations in ambient air. At the same time, neutral iodine oxide clusters of up to approximately 2,200 atomic mass units were detected, confirming that iodine oxides (including HIO₃) were almost solely responsible for new particle formation.

The chemically ionized cluster distribution, which represents clusters that were originally neutral clusters gaining charge on chemical ionization (see Supplementary Information), is shown in Fig. 2. The depicted mass defects (that is, the total deviation of the molecule/cluster mass from the integer mass defined as the sum of neutrons and protons in the atomic nuclei of the molecules) emphasize the high iodine and oxygen contents of the measured clusters, because oxygen has a moderate and iodine a strong negative mass defect. Although sulfuric acid, methyl sulfonic acid and highly oxidized multifunctional organic vapours²⁵ were detected, neutral clusters were composed almost exclusively of iodine and oxygen and, to a very small extent, hydrogen. Chemically ionized clusters contained either no (an odd number of iodine) or one hydrogen atoms (an even number of iodine), suggesting one (odd iodine) or two (even iodine) hydrogen atoms in their original neutral form. Minute quantities of sulfuric acid, as well as nitrogen, in the form of ammonia or nitric acid, were detected in clusters, but pure iodine oxide clusters clearly dominated over the other compounds.

The average O:I ratio was generally 2.4, but varied between 2.2 and 2.6 for a fixed number of iodine atoms. This shows that simple condensation of OIO (ref. 12), I₂O₃ (ref. 17) or I₂O₄ (ref. 17) alone, or any combination of compounds with O:I of two or below, is not sufficient to explain the observed cluster formation. However, compounds such as I₂O₅ (ref. 16, 17, 26) or HIO₃ (ref. 23) should be major contributors to cluster production. Signals attributable to I₂O₅ were low, suggesting that I₂O₅ condensation alone cannot explain the observed cluster growth. However, the relatively high concentrations of HIO₃ point towards its important role in the build-up of clusters.

The concentration of HIO₃ during the events reached 10⁸ molecules cm⁻³ and should have been considerably higher in the immediate vicinity of algae beds. These concentrations would be sufficient to explain the observed cluster growth rates (see Supplementary Table 1). Further evidence of the role of HIO₃ comes from the observed cluster concentrations (Fig. 3), which have an almost linear dependence on the concentration of HIO₃. Near-linear dependencies of cluster and vapour concentrations can in general be caused by arbitrary combinations of clustering mechanisms and sinks. In this particular case, the formation rates are so high that the sinks are likely to play a negligible role. Thus, the linear dependence indicates that the clusters grow by sequential HIO₃ additions, which are much faster than the competing evaporation or fragmentation processes. The critical role of HIO₃ was also seen in a series of supplementary laboratory experiments (Supplementary Figs 4–11). No chemical mechanism for producing HIO₃ from primary molecular iodine emissions has been determined; however, the formation of clusters can, to a large extent, be explained by the uptake of HIO₃ and the subsequent reaction of two HIO₃ molecules in the cluster, resulting in the formation of I₂O₅ + H₂O, whereupon H₂O evaporates from the cluster (Fig. 2). Such a mechanism also perfectly explains the hydrogen content in the detected (chemically ionized) clusters being either one (even I) or zero (odd I). It should be noted that the sampled clusters are exposed to decreased water vapour concentrations after entering the vacuum of the mass spectrometer, so further restructuring of HIO₃ to I₂O₅ can take place on dehydration. It may be that corresponding clusters in the atmosphere are more hydrated and contain more HIO₃ than could be directly inferred from the mass spectra. The general mechanism of sequential HIO₃ addition outlined

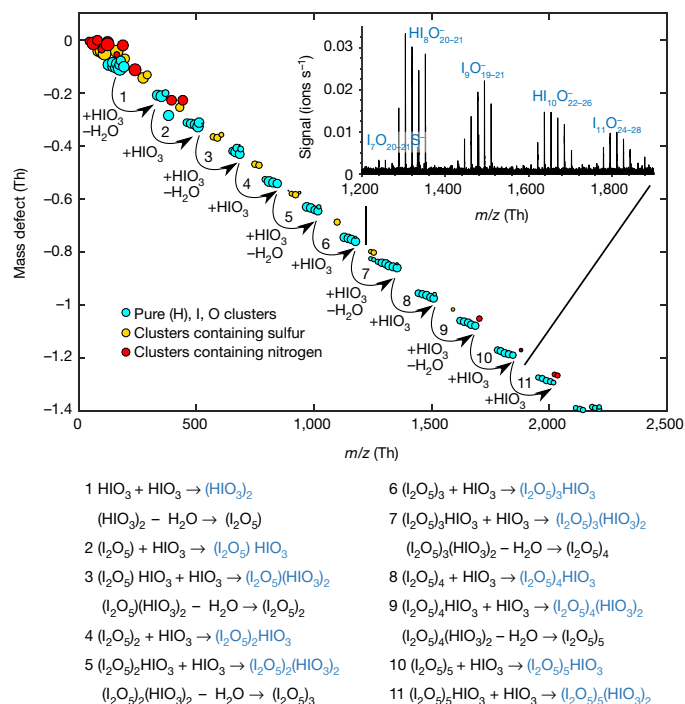


Figure 2 | Plot of mass defect versus cluster mass depicting the abundance and atomic composition of nucleating neutral clusters during the event. The distribution of the clusters is dominated by iodine oxides. The mechanism that explains the cluster formation starting from HIO₃ and proceeding through further additions of HIO₃ is shown below the plot. A neutral cluster loses one H atom on chemical ionization and some of the restructuring reactions can take place only on detection; in the atmosphere, the depicted clusters may thus be more hydrated (that is, some of the I₂O₅ could be in the form of two HIO₃ molecules). The area of the dots is proportional to the observed signal. Inset, a portion of the recorded raw mass spectrum.

above, however, remains unaffected, even when further dehydration takes place during the sampling.

The average O:I ratio of 2.4 suggests that besides the major role of HIO₃, other iodine oxoacids—iodous acid (HIO₂) or hypoiodous acid (HIO)—could act in the same way as HIO₃. That would explain the variation in the oxygenation of the observed clusters. Both acids were detected during the event, but with much lower intensities than that of HIO₃ with the lower limit of the concentrations estimated to be 2 × 10⁶ molecules cm⁻³ and 1 × 10⁶ molecules cm⁻³ for HIO₂ and HIO, respectively, during the peak concentration period. It is more likely that non-hydrogen-containing compounds with two iodine atoms (I₂O₂₋₅) have been condensed on clusters rather than these small iodine oxoacids. The condensation of IO or OIO should have been less pronounced because H atoms were detected in only every second group of the clusters separated by I₂O₅. The addition of IO or OIO to a cluster, formed according to our proposed scheme, would result in hydrogen-containing peaks in the cluster spectrum for odd numbers of I. The overall mechanism should therefore be a mixture of the straightforward addition of HIO₃ accompanied by restructuring and water recycling and a less pronounced addition of HIO, HIO₂ and/or I₂O₂₋₅ compounds. Fig. 2 depicts the process starting from an HIO₃ molecule and proceeding purely via the addition of HIO₃ accompanied with the loss of water. However, a parallel process that involves only non-acidic I₂O₂₋₅ cannot be fully excluded. In the mass range of 1,000–2,000 Da, 65% to 73% of the total cluster mass can be explained by HIO₃ and I₂O₅, whereas a minimum of 27% (if only I₂O₃ is co-condensing) or a maximum of 35% (if only I₂O₄ is co-condensing) of this mass is explained by less-oxygenated compounds.

In addition to the campaign at Mace Head, we used a CI-API-TOF mass spectrometer for two field campaigns at high-latitude sites that

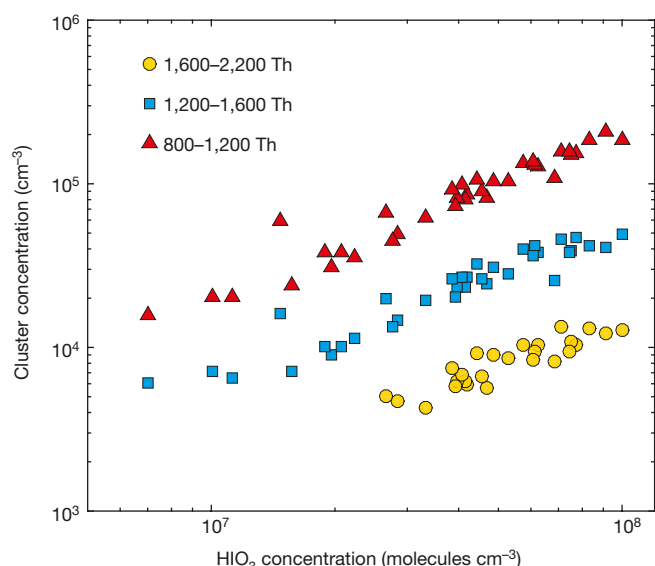


Figure 3 | Cluster concentration versus HIO₃ concentration. Cluster concentrations depend almost linearly on the HIO₃ concentration, as demonstrated by the slopes of the data series being close to unity in a logarithmic space. This linear dependency suggests that the main clustering mechanism is the addition of HIO₃.

are periodically exposed to marine air masses: Station Nord in northern Greenland during February–August 2015 and Aboa research station in Queen Maud Land, Antarctica, during November 2014–February 2015 (see Supplementary Information). In Greenland, we began to observe elevated concentrations of HIO₃ after sunrise in late February, often associated with new particle formation events. During such events, the HIO₃ concentrations tended to be much higher than that of sulfuric acid (Supplementary Fig. 12), and it seems that the cluster formation could be explained almost entirely by the HIO₃ clustering mechanism (Supplementary Fig. 13). In Antarctica, we measured gas-phase HIO₃ well above the instrumental limit of detection despite the distance of more than 100 km from the Antarctic coast (Supplementary Fig. 15). This observation suggests that the oceanic areas surrounding Antarctica may be strong sources of molecular iodine, which is then converted to HIO₃ in gas-phase reactions either at the emission area or during transportation to our measurement site.

Our measurements point towards prominent gas-phase production of HIO₃ associated with iodine emissions from different coastal areas, and show that this compound forms fast-growing molecular clusters. However, iodine is emitted not only in coastal areas, but also in the open ocean environment^{27,28}, as well as from Arctic and Antarctic sea ice^{29–33}. At present it remains uncertain whether the particle formation mechanism described here plays a role over the open ocean or whether it can make an important contribution to climate-relevant processes.

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- Kulmala, M. *et al.* Chemistry of atmospheric nucleation: on the recent advances on precursor characterization and atmospheric cluster composition in connection with atmospheric new particle formation. *Annu. Rev. Phys. Chem.* **65**, 21–37 (2014).
- Riccobono, F. *et al.* Oxidation products of biogenic emissions contribute to nucleation of atmospheric particles. *Science* **344**, 717–721 (2014).
- O'Dowd, C. D. *et al.* Marine aerosol formation from biogenic iodine emissions. *Nature* **417**, 632–636 (2002).
- Yoon, Y. J., O'Dowd, C. D., Jennings, S. G. & Lee, S. H. Statistical characteristics and predictability of particle formation events in Mace Head. *J. Geophys. Res.* **111**, D13204 (2006).
- O'Dowd, C. D. & de Leeuw, G. Marine aerosol production: a review of the current knowledge. *Phil. Trans. R. Soc. A* **365**, 1753–1774 (2007).
- McFiggans, G. *et al.* Iodine-mediated coastal particle formation: an overview of the Reactive Halogens in the Marine Boundary Layer (RHAMBLE) Roscoff coastal study. *Atmos. Chem. Phys.* **10**, 2975–2999 (2010).

- Mahajan, A. S. *et al.* Concurrent observations of atomic iodine, molecular iodine and ultrafine particles in a coastal environment. *Atmos. Chem. Phys.* **11**, 2545–2555 (2011).
- Kirkby, J. *et al.* Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation. *Nature* **476**, 429–433 (2011).
- Kürten, A. *et al.* Neutral molecular cluster formation of sulfuric acid-dimethylamine observed in real time under atmospheric conditions. *Proc. Natl Acad. Sci. USA* **111**, 15019–15024 (2014).
- Kirkby, J. *et al.* Ion-induced nucleation of pure biogenic particles. *Nature* **533**, 521–526 (2016).
- Kulmala, M. *et al.* Direct observations of atmospheric aerosol nucleation. *Science* **339**, 943–946 (2013).
- Hoffman, T., O'Dowd, C. D. & Seinfeld, J. H. Iodine oxide homogeneous nucleation: an explanation for coastal new particle production. *Geophys. Res. Lett.* **28**, 1949–1952 (2001).
- Jimenez, J. L. *et al.* New particle formation from photooxidation of diiodomethane (CH₂I₂). *J. Geophys. Res.* **108**, 4318 (2003).
- McFiggans, G. *et al.* Direct evidence for coastal iodine particles from Laminaria macroalgae: linkage to emissions of molecular iodine. *Atmos. Chem. Phys.* **4**, 701–713 (2004).
- Saiz-Lopez, A. & Plane, J. M. C. Novel iodine chemistry in the marine boundary layer. *Geophys. Res. Lett.* **31**, L04112 (2004).
- Saunders, R. W. & Plane, J. M. C. Formation pathways and composition of iodine oxide ultra-fine particles. *Environ. Chem.* **2**, 299–303 (2005).
- Saunders, R. W. *et al.* Studies of the formation and growth of aerosol from molecular iodine precursor. *Z. Phys. Chem.* **224**, 1095–1117 (2010).
- Ehn, M. *et al.* Growth rates during coastal and marine new particle formation in western Ireland. *J. Geophys. Res.* **115**, D18218 (2010).
- Huang, R.-J. *et al.* *In situ* measurements of molecular iodine in the marine boundary layer: the link to macroalgae and the implications for O₃, IO, OIO and NO_x. *Atmos. Chem. Phys.* **10**, 4823–4833 (2010).
- Alicke, B., Hebestreit, K., Stutz, J. & Platt, U. Iodine oxide in the marine boundary layer. *Nature* **397**, 572–573 (1999).
- Atkinson, R. *et al.* Evaluated kinetic and photochemical data for atmospheric chemistry. Supplement VIII: halogen species evaluation for atmospheric chemistry. *J. Phys. Ref. Data* **29**, 167–266 (2000).
- Bloss, W. J., Rowley, D. M., Cox, R. A. & Jones, R. L. Kinetics and products of the IO self-reaction. *J. Phys. Chem. A* **105**, 7840–7854 (2001).
- Sunder, S. & Vikis, A. C. Raman spectra of iodine oxyacids produced by the gas-phase reaction of iodine with ozone in the presence of water vapour. *Can. J. Spectrosc.* **32**, 45–48 (1987).
- O'Dowd, C. D. On the spatial extent and evolution of coastal aerosol plumes. *J. Geophys. Res.* **107**, (2002).
- Ehn, M. *et al.* A large source of low-volatility secondary organic aerosol. *Nature* **506**, 476–479 (2014).
- Saiz-Lopez, A. *et al.* Atmospheric chemistry of iodine. *Chem. Rev.* **112**, 1773–1804 (2012).
- Mahajan, A. S. *et al.* Measurement and modelling of tropospheric reactive halogen species over the tropical Atlantic Ocean. *Atmos. Chem. Phys.* **10**, 4611–4624 (2010).
- Lawler, M. J., Mahajan, A. S., Saiz-Lopez, A. & Saltzman, E. S. Observations of I₂ at a remote marine site. *Atmos. Chem. Phys.* **14**, 2669–2678 (2014).
- Saiz-Lopez, A. *et al.* On the vertical distribution of boundary layer halogens over coastal Antarctica: implications for O₃, HO_x, NO_x and the Hg lifetime. *Atmos. Chem. Phys.* **8**, 887–900 (2008).
- Mahajan, A. S. *et al.* Evidence of reactive iodine chemistry in the Arctic boundary layer. *J. Geophys. Res.* **115**, D20303 (2010).
- Atkinson, H. M. *et al.* Iodine emissions from the sea ice of the Weddell Sea. *Atmos. Chem. Phys.* **12**, 11229–11244 (2012).
- Allan, J. *et al.* Iodine observed in new particle formation events in the Arctic atmosphere during ACCACIA. *Atmos. Chem. Phys.* **15**, 5599–5609 (2015).
- Roscoe, H. K. Particles and iodine compounds in coastal Antarctica. *J. Geophys. Res.* **120**, 7144–7156 (2015).

Supplementary Information is available in the online version of the paper.

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Author Information ToFTools for Matlab used for processing the mass spectrometer data is available upon request from the corresponding author. Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to M.S. (mikko.sipila@helsinki.fi).