Responses to comments (author responses in red)

Short comment (R. Saunders):

The reported detection of iodine in Arctic nanoparticles is an exciting one. As the authors suggest, a number of possible sources could be responsible - the ice-algal one is a strong candidate as in Antarctic ice. I would like to bring to the authors' attention a couple of recent reports (see below) of algal release from melting Arctic ice in the previous year's summer (2012). In particular, the Assmy paper shows images of brown-coloured 'algal-aggregates' observed in/collected from ice/ice-water (Fig. 2) and reports elevated iodide concentrations from these features (2-3 times that in surface water) (Figure S1). Were no observations made of discolouration in melting ice on the author's own cruise?

Assmy, P., et al. (2013): Floating ice-algal aggregates below melting Arctic sea ice. PLOS, 8(10), e76599, 1-13.

Boetius, A., et al. (2013): Export of algal biomass from the melting Arctic sea ice. Science, 339(6126), 1430-1432.

We thank R. Saunders for pointing this work out. While we were aware of the potential for changes in iodine speciation associated with algal-aggregates, high levels of algal aggregate material comparable to those reported by Assmy et al., (2013) were not observed from the ship. We note that the observations of Assmy et al. (2013) and Boetius et al. (2013) were made further north and in denser ice coverage than our cruise ventured. Given that the iodine during the strongest events was probably produced upwind of the ship, the lack of aggregate material in the vicinity of the ship does not preclude these playing a role, so this has been added as a speculative possibility to the discussion alongside the other possible biogenic iodine sources.

Anonymous Referee #1

Allan et al. present an interesting, important and well-written study of new particle formation in the Arctic which they argue is related to iodine. As the authors point out iodine mediated particle nucleation has been know about for some time, but the majority of work has been on particle production in coastal regions where macro-algae release iodine at low tide. The authors present new measurements which show that there may be another source of iodine particle precursors possibly related to diatoms in sea ice. They correctly acknowledge that more work is needed and provide a compelling case for this future work. I recommend this paper for publication in ACP once the authors have addressed the following points to the editor's satisfaction:

1. The authors have written a concise article focused on a specific point, but I think more figures could be included in the main text which are currently included in the supporting information. Specifically, I think the hygroscopicity data in S1.4 should be included in the main paper since this data is central to the conclusion that this aerosol is consistent with particles being composed of an iodine oxide. Also consider bringing S1.1 and 1.2 into the main paper.

As suggested, these figures have been moved into the main document.

2. The fact that the growth factor was relatively small for this aerosol is used in the conclusions and elsewhere to make the case that the aerosol are consistent with being composed of a large fraction of iodine oxide. However, this topic is only addressed briefly in the paper on p28957 ln18-20. It is argued that the low growth factor of the aerosol is consistent with iodine oxide, I2O5. It is also stated that the growth factors ': : :are consistent with a dense by low-hygroscopicity substance such as iodine oxide (I2O5: : :'. The authors need to expand the discussion here. I2O5 is a wellknown highly hygroscopic material (hygrosopic in the traditional sense – affinity for water). I understand that it is used in chemical synthesis as an agent to remove water vapour because it is so hygroscopic. But, it appears that I2O5 has some unusual properties for a hygroscopic material. Despite having a very high solubility and a great affinity for water, its growth factor (at 90% RH) has been shown to be small (1.3) (Murray et al. Atmos. Chem. Phys., 12, 8575–8587, 2012; http://www.atmos-chemphys. net/12/8575/2012/acp-12-8575-2012.pdf). In this article the mass growth factor was measured and is consistent with the growth factor measured in systems where iodine oxide aerosol were generated from gas phase precursors. Hence, I agree with the interpretation by Allan et al. that the low growth factor is consisnet with I2O5, but more discussion is needed and also suitable references included.

The reviewer is correct in pointing out that using the term 'hygroscopic' synonymously with 'having a low growth factor' is incorrect in this instance. This has been fixed in the revised version. However, as also pointed out, we are consistent with the laboratory iodine oxide data whichever way, and thus the conclusion still stands.

Anonymous referee #2

General comments: The manuscript describes observations of iodine in the Artic, measured by aerosol mass spectrometer (AMS), and associated with Arctic new particle formation (NPF) events. While NPF has been observed in the Arctic previously, this is the first time iodine has been observed in the growing particles by the AMS method. The topic is certainly interesting and significantly extends previous observations made in coastal areas and lower latitudes that have identified Iodine as an important component in coastal nucleation events. The iodine observed may or may not have similar origins as found in lower latitudes and also this issue is briefly touched in the paper. The manuscript presents qualitative results stemming from current and previous observations and does not try to quantify the issue – in part due to the lack of suitable instrumentation to investigate the composition of the smallest particles. However, these observations, as they are, are significant and supply new information of iodine species in the Arctic and their potential relation to Arctic NPF events. The manuscript is well written and reports an important addition to our knowledge on sources and availability of nucleating precursors on the pristine Arctic areas, which many of the common precursors of atmospheric particle formation are absent. The measurements seem to be carefully performed and the methods used have been previously validated.

Specific comments:

Have the authors considered photolysis of iodocarbons as a source of the observed iodine? Can this be excluded? In addition, it is said that halocarbons were measured from air and water but no iodocarbon data are presented (only CH2Br2). Why is this so? This data could potentially strengthen the presented results.

No significant fluxes or concentrations of iodocarbons were detected on this cruise. These data are now included in the supplement, which has also necessitated the inclusion of two new co-authors (S. J. Andrews and S. C. Hackenberg). While it has been shown that iodocarbons can act as a source of nucleating IO in the laboatory (e.g. Jimenez et al., 2003), as discussed in the paper, they have shown to be insignificant compared to molecular iodine in other environments.

Iodine emissions have been quite conclusively shown to lead to NPF, but often the halogen chemistries are coupled to each other. Was bromine or its oxidation products sought from the AMS spectra? Same (or similar) algae that produce iodinated species are known to produce even bigger amounts of bromine species.

There was no evidence of bromine compounds being present in the AMS data. Also, in contrast to iodine, bromine does not form stable oxides in the particle phase. This is pointed out in the revised version.

The time period of the case-study highlighted in Figure S1.2 shows a very large portion of organic matter. Is it, or can it be excluded that some larger (and/or heavier) halogenated organic compounds contribute directly to the phenomena, or is it necessarily I2 and its further oxidation products? I suggest this should be discussed in more length in the text.

As already discussed in the manuscript, the organics present include misattributed sea salt, MSA and OOA. Given that the AMS destroys much chemical information through its vaporisation and ionisation processes, it is impossible to rule out the possibility that the OOA fraction contains halogenated organics. However, one might expect ions such as Br^+ to be present, which they are not. Furthermore, OOA is usually associated with heavily functionalised, higher molecular weight species than what would be expected from the gas-phase oxidation of biogenic halocarbons.

in Page 28956, Line 15 it is said that: "The I+ signal was not represented in any of the factors derived, only manifested in the residual data, which implies that the particulate iodine had a source that was distinct from the processes controlling the formation of particulate organic matter". Maybe it would be worth to mention here about the size limitation of AMS, and on the timescales the particulate matter has needed to grow to be detectable by the AMS. In addition, I would like to see a sentence about the PMF analysis in the main text describing how the different sources are decided based on the data and the PMF analysis.

The sentence regarding PMF is added as suggested. The size limitation is explained in the paragraph above and further explained in the revised version.

I would suggest adding a Figure showing some of the basic meteorological parameters during the case study. I guess these were also routinely measured during the campaign? For example, temperature and humidity could be useful. Even better if solar UV flux measurements are available (as comments above show), or, even just the indication of 'cloudy or sunny' would make the estimation of the importance of photolytic processes easier. Iodine species are known to be especially photochemically active and the study was performed during the Arctic summer, when the sun never sets. Thus it would help to know about these parameters.

Temperature, humidity and total incident radiation added to the figure.

Figure 2. The 127 Th signal seems to have a time lag with respect to observed NPF event. If iodine is the initiating compound, then how come its observation has a time lag? Comments?

The AMS does not detect iodine until significant amounts of mass reside in particle greater than 30 nm. This will not occur until significant amounts of growth have occurred after the initial nucleation. This is reiterated in the revised version.

Page 28950, Line 8: What is a persistent event in this context? Suggest adding an explanation. (cf. Page 28952, Line 21: "a particularly strong and persistent case study..")?

By persistent, we mean that the phenomenon was evident in the data for a protracted period. This is clarified in the revised version.

Page 2891, Lines 22-24: This sentence is hard to understand. Suggest rewriting it.

Revised as suggested.

Page 28952, Line 1: I would add few words explaining the concept of "organic biogel".

This is explained in the revised version as aggregations of biological macromolecules.

Page 28955, Line 14: Suggest giving a short description already here on what is meant by "ice diatom" (this is explained later in page 28958). For people familiar with the topic, this is trivial, but for interested non-specialized reader, especially the word diatom can be confusing.

The term is replaced with 'microalgal' here for the sake of brevity. Later in the manuscript, the following is added: "these are prominent members of microalgal blooms occurring at the receding ice edge, and also in communities growing within the ice itself"

Page 28955, Line 23: To me the presented Figures show quite banana type events.

The following behaviours noted in these events distinguish these from the 'banana' events noted at Hyytialla and other sites: 1) There are breaks in the growth observed (e.g. 25 Jul 00:00) 2) The apparent growth around 26 Jul 20:00 is exponential rather than linear in diameter space 3) The growth apparently reverses at 26 Jul 00:30 and 27 Jul 09:00. These are pointed out in the revised text.

What is meant by saying (Line 25): "result from diurnal modulation of boundary layer dynamics and photochemistry, which is missing under the continuous insolation of the Arctic summer."? If the meteorological situation is so different, maybe an explanation is required to explain why the observed events look so similar.

The text is rephrased as follows for brevity: "...the previously reported behaviours result from the diurnal modulation of boundary layer dynamics and photochemistry caused by the local day-night cycle in conjunction with a stable source footprint. This is not the case here, due to continuous insolation and reduced dynamics of the marine boundary layer, combined with a varying source footprint (due to the movement of the ship and varying wind direction). Therefore, analogies with the temporal behaviour at other locations cannot necessarily be drawn." This statement is intended

not to specifically contrast the two cases, but to explain why the apparent growth around 26 Jul 20:00 cannot be assumed to be indicative of in situ growth, as is done at other sites.

Page 28958, Line 24: "There are also sources of atmospheric iodine in the form of iodocarbons, but we do not consider these likely to be responsible for the observations, as it has been shown that these have a much lower NPF potential compared to I2 (McFiggans et al., 2004)." This relates to comment presented already above: Iodine baring hydrocarbons are very photolabile and thus some information on available radiation would be useful to estimate the importance of photochemistry of the iodocarbon species.

See response to point above. Note that McFiggans (2004) reference took account of the photolysis yields of iodocarbons relative to iodine and found them to be orders of magnitude different.

Figure 1 The Figure size should be increased to enable better readability.

The size of this figure is dictated by how the online PDF was generated, which we had little control over. We envisaged this occupying the full width of the final 'printer friendly' version and will naturally ensure that it is clear when the proofs are generated.

Figure 1b Include arrows to indicate wind direction for the trajectories.

We feel that the wind direction, i.e. towards the ship, is unambiguous and arrows would only serve to provide additional clutter. Note that it is not standard practice to use such arrows when plotting back trajectories, such as those generated by the commonly-used NOAA READY online HYSPLIT service.

Figure S2.2. More details on the mass-axis would benefit the reader. At the moment it's not possible to read the masses of the observed peaks.

These have been made clearer in the revised version.

Many of the supplemental figures are not mentioned in the text.

The S1.x figures are referred to in the main article and all of the S2.x figures are referred to within section S2. The latter are included to document the process performed to generate the PMF outputs and take the form of standard diagnostic outputs from the PET toolkit. They do not have a direct bearing on the text, but are still important to document in the interests of full disclosure and replicability. This is standard practice in PMF papers.

Technical corrections:

Page 28951, Line 15: Should it be "atmosphere"?

Corrected

Page 28957, Line 9: Should it be "Aitken"?

Corrected

Figure 3 is apparently mislabelled as Figure 4 (mentioned in Page 28957, Line 1).

Supporting Figure S1.4 caption: case study time period is not found on the reported Figure S1.3.

Removed reference to S1.3, as the case study period is specified anyway.

Add spaces between supplemental references to enable "better browsing".

Corrected

Revised article (changes underlined)

Iodine observed in new particle formation events in the Arctic atmosphere during ACCACIA

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Abstract

Accurately accounting for new particle formation (NPF) is crucial to our ability to predict aerosol number concentrations in many environments and thus cloud properties, which is in turn vital in simulating radiative transfer and climate. Here we present an analysis of NPF events observed in the Greenland Sea during the summertime as part of the Aerosol-Cloud Coupling And Climate Interactions in the Arctic (ACCACIA) project. While NPF events have been reported in the Arctic before, we were able, for the first time, to detect iodine in the growing particles using an Aerosol Mass Spectrometer (AMS) during a persistent event in the region of the coastal sea ice near Greenland. Given the potency of iodine as a nucleation precursor, the results imply that iodine was responsible for the initial NPF, a phenomenon that has been reported at lower latitudes and associated with molecular iodine emissions from coastal macroalgae. The initial source of iodine in this instance is not clear, but it was associated with air originating approximately 1 day previously over melting coastal sea ice. These results show that atmospheric models must consider iodine as a source of new particles in addition to established precursors such as sulphur compounds.

Introduction

In the Arctic, clouds are the dominant factor in the control of the incoming and outgoing energy balance at the Earth's surface and, here and throughout the troposphere, the largest single source of uncertainty in climate predictions. Understanding processes governing atmospheric aerosol concentrations is critically important to improved prediction of clouds and thus weather and climate (Boucher et al., 2013). The optical thickness and lifetime of clouds can be strongly influenced by the population of aerosol particles available to act as cloud condensation nuclei (CCN) (Haywood and Boucher, 2000). Particle concentrations in the summertime Arctic are typically very low (of the order of 10^2 cm^{-3}) and therefore cloud properties in this region are highly sensitive to the mechanisms by which new particles are formed and are grown to viable CCN sizes (roughly 50-100 nm, depending on the cloud conditions) (Merikanto et al., 2009). Understanding these processes is crucial to our predictive capability of climate in the Arctic, as clouds can have a strong warming or cooling effect, depending on a variety of conditions (Hodson et al., 2013).

New particle formation (NPF) can dramatically increase aerosol number concentrations in the atmosphere (Kulmala et al., 2004; Spracklen et al., 2006), alongside direct emissions of particles (e.g. through combustion, sea spray, dust suspension etc.), contributing up to half of the global CCN burden (Merikanto et al., 2009; Yu and Luo, 2009). NPF generally occurs through the rapid photochemical production of low vapour pressure secondary material such that stable molecular clusters are able to grow to viable sizes (nm) (Kulmala et al., 2013; Kulmala et al., 2000). As they grow, the freshly nucleated particles act as sinks for the secondary condensable material, potentially shutting off the nucleation process. NPF has been observed in a variety of different environments across the world. The role of sulphuric acid (produced in the atmosphereic from the gas phase oxidation of marine biogenic dimethyl sulphide or SO_2 from fossil fuel burning or volcanoes) and organic matter (chiefly from terrestrial biogenic sources) has been extensively studied (e.g. Laaksonen et al., 2008; Zhang et al., 2004a; Riccobono et al., 2014) and it has also been shown that ammonia and amines have very important roles in promoting NPF through ternary processes (Kirkby et al., 2011; Almeida et al., 2013; Berndt et al., 2014).

Because of the generally low CCN number concentrations present, the Arctic CCN populationatmosphere is highly sensitive to NPF. This in turns means that predictions of CCN are highly sensitive to and thus the processes responsible for NPF, which are currently highly uncertain in this environment (Lee et al., 2012). NPF has previously been observed during Arctic ship-based measurements and given the lack of significant biogenic or anthropogenic sources of organic precursors, most efforts to model these observations have only invoked NPF from the oxidation of sulphur species (Korhonen et al., 2008). An alternative hypothesis is that rather than nucleation, the initial source of the new particles is the fission of organic biogels (aggregations of biological macromolecules) in primary particles (Karl et al., 2013; Karl et al., 2012).

In coastal environments at lower latitudes, frequent daytime NPF events have been observed associated with gaseous iodine at low tide. This suggests that in these environments, iodine is the dominant source of nanoparticles, which have been observed to grow to larger sizes able to scatter radiation and contribute to CCN (McFiggans et al., 2004; McFiggans et al., 2010; O'Dowd et al., 2002; Whitehead et al., 2009; Yoon et al., 2006; Lehtipalo et al., 2010). Gaseous I_2 is produced in abundance by macroalgae species (*Laminaria digitata*, *Fucus vesiculosus* and *Ascophyllum nodosum* have been identified as being responsible for NPF) in response to being exposed to the atmosphere (Küpper et al., 2008; Huang et al., 2013) and is rapidly photooxidised to iodine monoxide (IO) and higher iodine oxides, which polymerise to forming particles (Saiz-Lopez et al., 2012; Saunders et al., 2010). To date, iodine-initiated NPF has most commonly been observed in seaweed-rich coastal areas but the theoretical potential exists in low background aerosol conditions with associated high iodine fluxes (Mahajan et al., 2010). Atkinson et al. (2012) attributed NPF events observed in the Weddell Sea in Antarctica to iodine emissions from sea ice, although no data on aerosol composition was presented.

Here we present data on NPF events recorded aboard the RRS James Clark Ross in the Greenland Sea during the summer ACCACIA cruise. Through the analysis of a particularly strong and persistent case study, we show evidence for the role of iodine in NPF events in this region.

Methods

As part of the Aerosol-Cloud Coupling And Climate Interactions in the Arctic (ACCACIA) project, intensive measurements of aerosol composition and properties were made aboard the RRS *James Clark Ross*, an ice-hardened research vessel. The cruise (JR288) consisted of a number of traverses in and out of the sea ice margin in the region of Greenland and Svalbard during July and August 2013 (see Fig. 1).

The University of Manchester instrumentation was located in an instrumented sea container on the foredeck of the *James Clark Ross*, sampling air through a 5 metre stack via a 3.5 μm cut cyclone, as has been performed during previous measurement campaigns (Allan et al., 2009). No attempt to correct for size-dependent particle losses has been made for this work, as it will not affect the qualitative results presented here. No in-line drier was used, as the relative humidity (RH) in the container was maintained low due to the temperature differential. A number of instruments sub-sampled from the main inlet manifold.

A Differential Mobility Particle Sizer (DMPS) system was used to measure size-resolved particle number concentrations. This was built at the University of Manchester (Williams et al., 2007) using dual 'Vienna' design Differential Mobility Analysers (DMAs) (Winklmayr et al., 1991) of different lengths (to cover different particle size ranges) with stepping voltages, selecting negatively-charged particles. TSI (Shoreview, MN, USA) model 3010 and 3025a Condensation Particle Counters (CPCs) were used to count the particles and the Wiedensohler (1988) charging parameterisation used to invert the data. The sheath air system uses a recirculating system dried to a low (<20% RH) humidity using a membrane drier linked to a dry compressed air system. Total number concentrations were provided by a TSI model 3776 CPC.

An Aerodyne (Billerica, MA, USA) Aerosol Mass Spectrometer (AMS) of the High Resolution Time-of-Flight (HR-TOF) design (Canagaratna et al., 2007) was also used to measure particle composition. Calibrations were performed using monodisperse ammonium nitrate for mass and NIST-certified Polystyrene Latex (PSL) Spheres (Thermo Scientific) for size. The data was collected in 'V' and 'W' mass spectral modes, which have $m/\Delta m$ resolutions of 2100 and 4300 at m/z=200 respectively (DeCarlo et al., 2006), although only 'V' mode data is presented here due because of the low signal-to-noise ratio of the 'W' mode data.

A Droplet Measurement Technologies (Boulder, CO, USA) Single Particle Soot Photometer (SP2) was used to measure black carbon. This was a version 'D' instrument, calibrated using monodisperse Aquadag, scaled by a factor of 0.75 as recommended by Laborde et al. (2012)

Sub-saturated particle growth factors were measured using a Hygroscopicity Tandem Differential Mobility Analyser (HTDMA). This was the second Manchester-built instrument (Whitehead et al., 2014), conforming to EUSAAR specifications (Duplissy et al., 2009). This uses two Brechtel Manufacturing Inc. (Hayward, CA, USA) DMAs housed in temperature-controlled boxes and linked in series. The first had dry sheath air (<20% RH) while the sheath air in the second was maintained at 90% RH, using a membrane humidification system on a feedback loop with an Edgetech (Marlborough, MA, USA) dew point monitor. The particles were counted using a TSI model 3782 water-based CPC. Sizes were calibrated with PSL spheres and humidity was validated through the comparison of the measured deliquescence humidities of ammonium sulphate and sodium chloride with modelled values (Topping et al., 2005). Data were inverted using the method of Gysel et al. (2009).

Halocarbons were quantified in air and seawater using two Agilent 6850 gas chromatographs (GC) with 5975C mass selective detectors (MSDs) coupled to commercial thermal desorption units (TD, Markes Unity2-CIA8) in a system described by Andrews et al. (2014). One instrument was dedicated to air analysis and the other to water, and both instruments were calibrated daily for halocarbons using NOAA gas standard SX-3570 (Jones et al., 2011). Instrument drift was corrected for during (air analyses) or after (water analyses) each sample using atmospheric carbon tetrachloride as an internal standard. Underway seawater samples were collected from the pumped non-toxic seawater supply of the ship using a semi-automated purge and trap system (Andrews et al., 2014)plumbed directly into the underway supply. The sample lines and valves were flushed with underway water before each sample. 20 mL water samples was pumped into the purge vessel (2 minute sampling time) and purged with 1 L of zero-grade nitrogen gas. Purge efficiencies were 100 + 2% for bromocarbons and 90 + 10% for iodocarbons. All water samples were passed through an in-line pre-combusted grade GF/F filter. A bake-out program was also run between each pair of air and water samples. The duration of each sampling cycle (air-water-bake) was 65 minutes.

Halocarbons were quantified in air and seawater using an Agilent 6850 gas chromatograph (GC) with 5975C MSD coupled to a commercial thermal desorption unit (TD, Markes Unity2-CIA8) (Andrews et al., 2014).

Back trajectory analysis was performed using HYSPLIT 4 (Draxler and Hess, 1998), employing GDAS reanalysis wind fields (NOAA Air Resources Laboratory, Boulder, CO, USA). Back trajectories were started at 20 m above mean sea level and run using modelled vertical velocities.

Results

During the measurements, a number of events were noted in the DMPS data whereby a large number of small particles contributed dramatically to the ambient population. Contributions from combustion sources (e.g. ship plumes) were eliminated by the lack of black carbon (BC) detectable by the SP2. The data were also filtered according to short-lived spikes seen with the CPC that could be associated with other sources from within the ship. The DMPS occasionally showed 'open' distributions, whereby the peak existed at or below the lower size limit of the instrument (3 nm), providing evidence for NPF (Fig. S1.12). Time periods where a significant portion of the detected particles were smaller than 10 nm are identified on Fig. 1a, on an overlay of the cruise track and sea ice concentration data using the polar stereographic product from the Special Sensor Microwave Imager/Sounder (SSMIS) instrument on the Defense Meteorological Satellite Program (DMSP) F17 platform (Cavalieri et al., 2013).

These periods all occurred in proximity to coastal locations around Iceland, Greenland and Svalbard and the influence of terrestrial air is seen in the lowering of the RH in Fig 2, which is otherwise close to saturation. The most significant and persistent of these events occurred between the 25th and 27th of July, when the ship was close to the sea ice margin off the coast of northeastern Greenland and the air had previously travelled over the breaking sea ice off Greenland. (Fig. 1b). Markers for ice diatommicroalgal activity in the form of CH_2Br_2 were also observed to be elevated during this period (Fig 1c). During this period, the nonrefractory aerosol composition was mainly organic, with only around 0.1 µg m^{-3} of sulphate present (Fig. 1.23).

The candidate NPF events were also associated with elevated number concentrations, with transitions over periods of hours (Figs. 2 and ~~S1.1~~4), indicating that the new particles last long enough to grow to the larger sizes that can contribute to CCN. It is likely that the transitions in the size distributions resulted from changes to the source footprint in relation to the position of the ship rather than in situ growth of the observed new particles. While the growth events reported here may seem to resemble the ~~the~~ characteristic 'banana' ~~growth~~ events observed at coastal sites and other locations (Kulmala et al., 2004; Ehn et al., 2010; Yli-Juuti et al., 2011), they differ in the following behaviour: 1) There are breaks in the growth observed (e.g. 25 Jul 00:00) 2) The apparent growth around 26 Jul 20:00 is exponential rather than linear in diameter space 3) The growth apparently reverses at 26 Jul 00:30 and 27 Jul 09:00. It is worth noting that ~~the characteristic 'banana' growth events observed at coastal sites and other locations (Kulmala et al., 2004; Ehn et al., 2010; Yli-Juuti et al., 2011)~~ the previously reported behaviours result from the diurnal modulation of boundary layer dynamics and photochemistry caused by the local day-night cycle in conjunction with a stable source footprint. This is not the case here, due to continuous insolation and reduced dynamics of the marine boundary layer, combined with a varying source footprint (due to the movement of the ship and varying wind direction). Therefore, analogies with the temporal behaviour at other locations cannot necessarily be drawn. ~~, result from diurnal modulation of boundary layer dynamics and photochemistry, which is missing under the continuous insolation of the Arctic summer.~~

Aerosol Mass Spectrometer (AMS) data during the 25-27th July showed a signal at m/z=127 during the periods when larger particles were present (Fig. ~~3~~4), which is identified as I$^+$ ions by its precise mass/charge ratio of 126.90 (Fig. S1.~~3~~1) (Wang et al., 2012). I$^+$ has previously been reported as the largest peak in photochemically-produced iodine oxide AMS mass spectra in the laboratory (McFiggans et al., 2004; Jimenez et al., 2003), but this is the first time that it has been reported in ambient particles. In previous coastal studies, owing to the proximity to the initial source of iodine, particles did not grow to sizes large enough (around 30 nm) to be transmitted by the AMS aerodynamic lens inlet (Liu et al., 2007; Zhang et al., 2004b; Zhang et al., 2004a). In this study, the particles grew to sufficient sizes, however it should be noted that the AMS is still not able to observe iodine during the periods where the particles were smaller than this, so does not see iodine during the very early stages of growth.

To investigate whether the I$^+$ signal could be associated with processes governing the formation of organic aerosols (Fig. ~~S1.2~~3.), Positive Matrix Factorisation (PMF) was performed on the data (Paatero and Tapper, 1994; Ulbrich et al., 2009). This assigns the organic mass to different 'factors' according to the temporal behaviour of the mass spectral matrix and is detailed in section 2 of the supplementary material. Once shipping emissions and misattributed sea salt are excluded, this analysis found that the organic matter detected by the AMS could be attributed to methyl sulphonic acid (MSA) (Phinney et al., 2006; Decesari et al., 2011) and highly-oxygenated organic material (McFiggans et al., 2005; Jimenez et al., 2009). The I$^+$ signal was not represented in any of the factors derived, only manifested in the residual data, which implies that the particulate iodine had a source that was distinct from the processes controlling the formation of particulate organic matter (be they primary or secondary). A further implication of the MSA observation is that this compound was at least partly responsible for the reported sulphate concentrations, as this also produces SO$^+$ and SO$_2^+$ ions in the mass spectrum (Zorn et al., 2008). Therefore, the actual non-seasalt sulphate concentration is likely to be lower than what is reported, but the quantitative fraction of MSA is

difficult to estimate, as the fragmentation behaviour is highly variable and not calibrated during this study. Further details are presented in section S2 of the supplementary material.

Discussion

To link the I^+ signals detected by the AMS to the particles seen by the DMPS, the size-resolved data from the two instruments were quantitatively compared through the fitting of lognormal distributions. Shown in Fig. 4 5 are the DMPS volume-weighted size distributions from the period of peak I^+ concentrations (26 July 22:50-23:45 UTC), together with the AMS Particle Time-of-Flight size-resolved data for I^+, organics and sulphate. The AMS data was of a low signal-to-noise ratio, due to the short averaging time and low signal levels (Allan et al., 2003), however the fits converged consistently using a standard Levenberg-Marquardt algorithm, with the peak centres, widths and heights allowed to vary freely. The DMPS distribution is bimodal, with the Aitken mode related to the I^+ peak in the AMS data and the accumulation mode related to the sulphate and organic modes. The ratio of the fitted Aitken mode diameters yields a particle effective density of 1.77 ± 0.23 g cm^{-3}, which is typical of an inorganic aerosol (Cross et al., 2007). Given that this quantity is a product of the material density and the Jayne shape factor (DeCarlo et al., 2004; Jayne et al., 2000), this may be an underestimate of the material density if the particles are nonspherical, as has been suggested by electron microscopy of laboratory-generated particles (McFiggans et al., 2004).

The shift in composition of these particles is also reflected in the HTDMA data, which shows that during this period, the growth factor of 50 nm dry particles at 90 % RH is 1.34, whereas for the rest of the cruise, values were always greater than 1.5 (Fig. S1.4 6). The low growth factor and the density estimate are consistent with a dense but low-hygroscopicity substance such as iodine oxide making up a significant portion of the particulate volume; (I$_2$O$_5$ has a material density of 5 g cm^{-3} and laboratory studies have shown iodine oxide particles to exhibit low growth factors) making up a significant portion of the particulate volume (Jimenez et al., 2003; McFiggans et al., 2004; Murray et al., 2012). This is different to what would be expected of organic matter, which tends to be of a low density and low hygroscopicity growth factor, and inorganic salts and sulphuric acid, which are high density and high hygroscopicity growth factor (Cross et al., 2007; Gysel et al., 2007).

While the data discussed above provides strong evidence for the presence of iodine in the particles during these events, it does not prove that iodine was responsible for the initial NPF, which will have occurred upwind prior to measurement. However, given the rapidity of the iodine oxidation process and the very low volatility of the products (McFiggans et al., 2010; Whitehead et al., 2009; Lehtipalo et al., 2010), it is reasonable to assume that the presence of iodine-based secondary particulate matter implies that iodine-initiated NPF was also occurring. It is also worth noting that sulphate concentrations were low during the main case study, so this NPF event did not occur during a period of particularly strong sulphuric acid production.

In situ sea-air fluxes and atmospheric mixing ratios of iodocarbons (CH$_3$I, CH$_2$I$_2$ and CH$_2$ICl) measured during the NPF event were very low (< 2 nmol m^{-2} d^{-1} and $\approx$ 0.5 pptv for CH$_3$I; < 1 nmol m^{-2} d^{-1} and < 0.02 pptv for both CH$_2$I$_2$ and CH$_2$ICl, see Fig. S1.2). Although these compounds are found in sea-ice (Atkinson et al., 2012; Granfors et al., 2014) and have been shown to cause NPF in the laboratory (Jimenez et al., 2003), the iodocarbon emissions and atmospheric concentrations found in this and earlier studies are insufficient to sustain the very high local concentrations of IO required for iodine

nucleation (McFiggans et al., 2004), suggesting the gaseous precursor may have been an inorganic form of iodine such as I2.

The initial source of the iodine responsible for these events is not known. Macroalgae have been identified as a molecularnan iodine source in midlatitude coastal studies (Küpper et al., 2008; Huang et al., 2013) and macroalgae beds containing kelps and wracks also occur on the northeast coast of Greenland (Borum et al., 2002), albeit with a different species composition. Elevated CH_2Br_2 levels would be consistent with a macroalgal source (e.g. Laturnus, 1996). However, the biomass density of the north-east Greenland kelp beds may be considerably less than found at temperate locations such as Galway Bay (Werner and Kraan, 2004), and ice scouring may reduce macroalgal density in shallower waters where the algae are more likely to be exposed to the atmosphere (Wiencke and Amsler, 2012; Borum et al., 2002).

Microalgal aggregates released from melting sea-ice have also been proposed as a source (Assmy et al., 2013; Boetius et al., 2013), although these were not observed from the ship during this work (we note previous observations were made at higher latitudes). However, given that the initial source of the iodine was upwind, this does not rule this out as a possibility.

A source of inorganic iodine from the marginal sea-ice zoneice sheets themselves is plausible, and would be consistent with the findings of Atkinson et al. (2012). Microalgae, particularly diatoms, may be considered as a potential source of iodine in this region. Diatoms are prominent members of microalgal blooms occurring at the receding ice edge, and also in communities growing within the ice itself. Ice diatoms have previously been shown to be a potential direct source of HOI and I_2 to the Arctic atmosphere (Hill and Manley, 2009). The presence of elevated levels of CH_2Br_2 in air compared to levels in seawater during the iodine particle event (Fig 1c) is consistent with this suggestion, as polar diatoms are known to be a strong source of bromocarbons (Sturges et al., 1992; Sturges et al., 1993). NA potential biogenic source are microalgae such as ice diatoms, which have previously been shown to be a potential source of HOI and I_2 to the Arctic atmosphere (Hill and Manley, 2009). The presence of elevated levels of CH_2Br_2 in air compared to levels in seawater during the iodine particle event (Fig 1c) is also consistent with this suggestion, as polar diatoms are known to be a strong source of bromocarbons (Sturges et al., 1992; Sturges et al., 1993). Diatoms are prominent members of microalgal blooms occurring at the receding ice edge, and also in communities growing within the ice itself. (Atkinson et al., 2012; Granfors et al., 2014)(McFiggans et al., 2004)A potential biogenic source are microalgae such as iIce diatoms, which have also previously been shown to be a potential direct source of HOI and I_2 to the Arctic atmosphere (Hill and Manley, 2009). Note that it is not expected that the observed bromocarbons directly participate in the NPF; the molecules are too small to form low volatility organic oxidation products and bromine, unlike iodine, does not form a series of stable condensed-phase oxides. Furthermore, there was no trace of any bromine-containing signal in the AMS data.

I_2 and HOI may also be formed by the abiotic oxidation of iodide, either by gaseous ozone on the sea surface (Carpenter et al., 2013), or within sea-ice brine channels followed by emissions from the quasi-liquid layer on the surface of the sea-ice (Saiz-Lopez et al., 2015). High levels of iodide associated with biological activity in the sea ice region have sometimes been observed (Chance et al., 2010). More recently, mMicroalgal aggregates released from melting sea-ice have also been proposed as an iodide source (Assmy et al., 2013; Boetius et al., 2013)., Aalthough such

aggregates~~these~~ were not observed from the ship during this work, given that the initial source of the iodine was upwind, the possibility this was an iodine source is not ruled out. (Indeed, we note previous observations of elevated iodide associated with microalgal aggregates were made at higher latitudes than the ship position during the NPF event). ~~However, given that the initial source of the iodine was upwind, this does not rule this out as a possibility.~~

~~Alternative abiotic~~An additional suggestion~~abiotic suggestions~~ for the source of iodine is~~are~~ chemical production from the ice surface itself, promoted by the freezing of sea salt in the presence of nitrite ions (O'Driscoll et al., 2006)~~ or high levels of iodide sometimes associated with the sea ice region (Chance et al., 2010) and oxidation to I₂ and HOI, either by gaseous ozone on the sea surface (Carpenter et al., 2013), or within sea-ice brine channels followed by emissions from the quasi-liquid layer on the surface of the sea-ice (Saiz-Lopez et al., 2015). There are also sources of atmospheric iodine in the form of iodocarbons, but we do not consider these likely to be responsible for the observations, as it has been shown that these have a much lower NPF potential compared to I₂ (McFiggans et al., 2004).~~ It should be noted that no NPF events were recorded near the ice margin to the northeast of Svalbard during the latter stages of the cruise, so it may be that th~~is~~e phenomenon observed here is restricted to coastal areas or certain stages of the ice melt process.

Conclusions

Herein we show observations of new particle formation (NPF) over the Greenland Sea in summer. A ~~persistent~~ long-lasting event, associated with air originating over the breaking sea ice off Greenland, featured NPF and particles growing to sizes in excess of 50 nm. During this period, iodine was unambiguously detected by an Aerodyne Aerosol Mass Spectrometer. Furthermore, ~~and~~ measurements of hygroscopicity and effective density were consistent with iodine oxide comprising a significant portion of the particulate volume. This strongly implies that iodine had a role in the initial NPF events, which is a phenomenon previously associated with coastal locations at lower latitudes (Huang et al., 2013; McFiggans et al., 2010; McFiggans et al., 2004). The initial source of the iodine in this case is unlikely to be the macroalgae identified during previous studies, but could be speculatively related to other macroalgae species or microalgae associated with the sea ice, which would be consistent with the findings of Atkinson et al. (2012) based on measurements in Antarctica.

These results show that correct prediction of Arctic aerosol number concentrations requires knowledge of iodine processes in new particle nucleation and growth. Our observations suggest that the source of iodine is related to processes associated with coastal sea ice, so this could represent a potentially significant source of particles during periods of ice loss and thus a potential climate feedback mechanism. As yet we have insufficient data to predict how widespread these processes are, but if this phenomenon is limited to coastal areas, it would not explain the events above 80 °N studied by Karl et al. (2012). More work is required to identify the initial source of the iodine and the exact mechanisms for iodine NPF at a molecular level (Kulmala et al., 2013).

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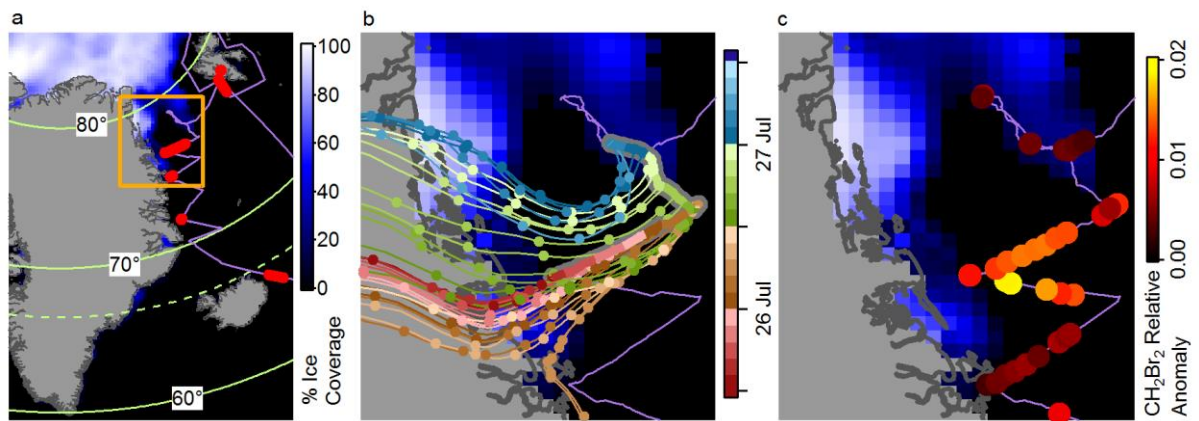
Revised figures

Figure 1: a) Cruise track (purple), ice coverage and locations of NPF events (red), defined by the presence of a mode of particles smaller than 10 nm not attributable to combustion or ship emissions (parts of the cruise outside of the area depicted did not show evidence of NPF). b) HYSPLIT back trajectories from cruise track corresponding to the 25-27 July case study. Markers are at 6-hourly intervals. c) Ratio of atmospheric concentrations of CH_2Br_2 (a product of ice diatom activity) to its saturation levels in seawater.
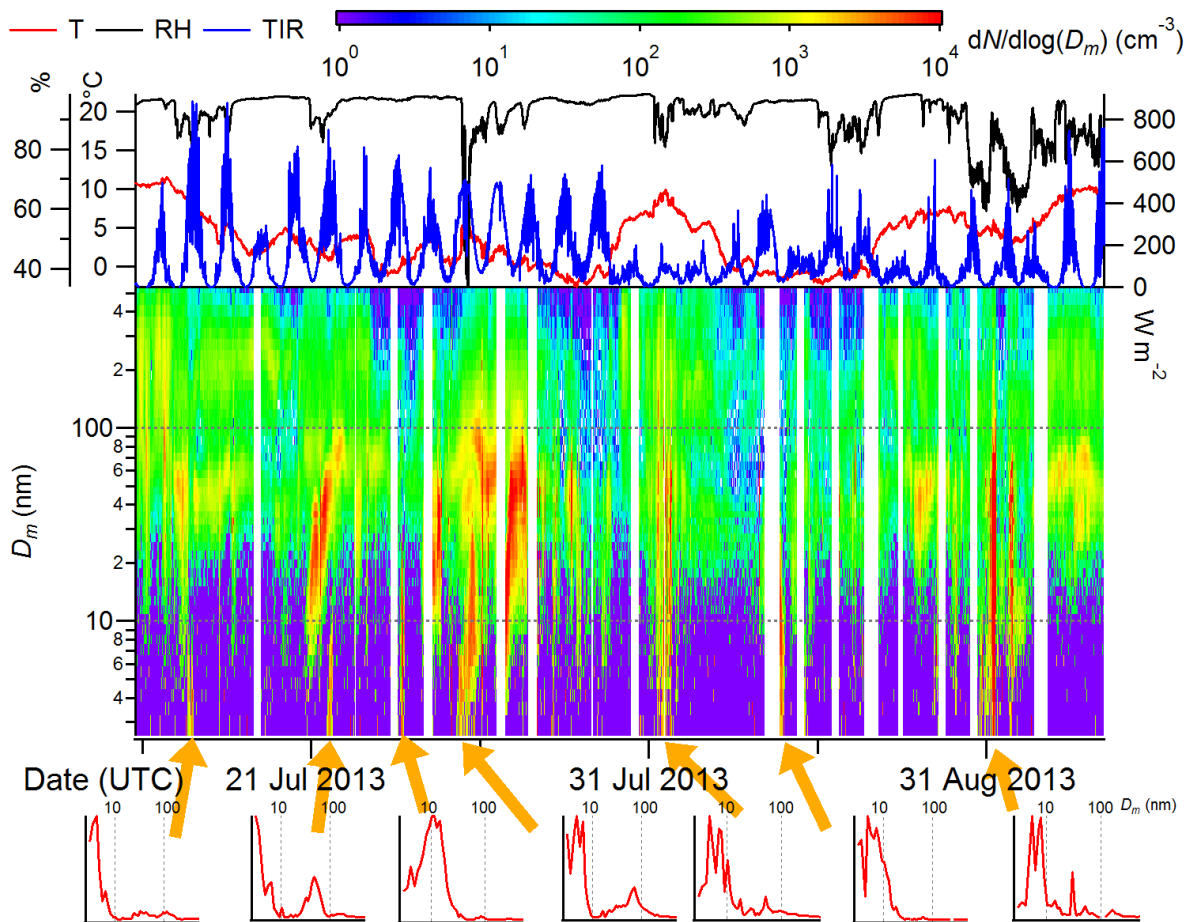
Figure 2: Temperature (T), relative humidity (RH) and total incident radiation (TIR) during the cruise, with DMPS size-resolved number concentration plotted data against electrical mobility diameter (D_m). White areas on the plot denote instrument downtime or when it was otherwise not sampling ambient air. Distributions from the seven candidate events in Fig. 1 are shown below to illustrate the shapes of the distributions during these events. Axis labels have been omitted for clarity, but are the same as the plot above, i.e. dN/dlog(D_m) (cm^{-3}) vs D_m (nm).
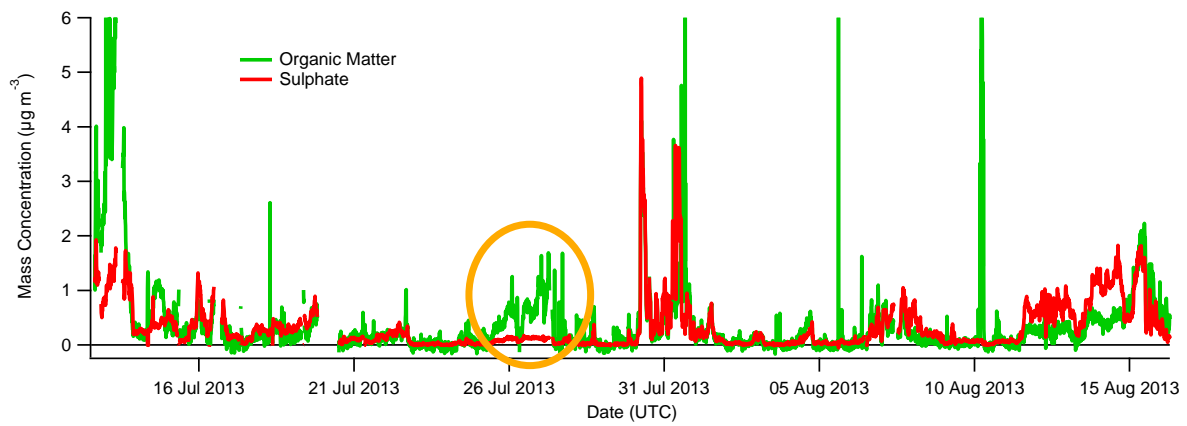
Figure 3: AMS-derived organic and sulphate mass concentrations, as calculated using the standard fragmentation tables (see section S2). Other commonly-reported species (nitrate and ammonium) were below detection limit outside of areas in close proximity to ports in the UK or Svalbard and thus considered irrelevant. The period of the main case study is highlighted in orange.
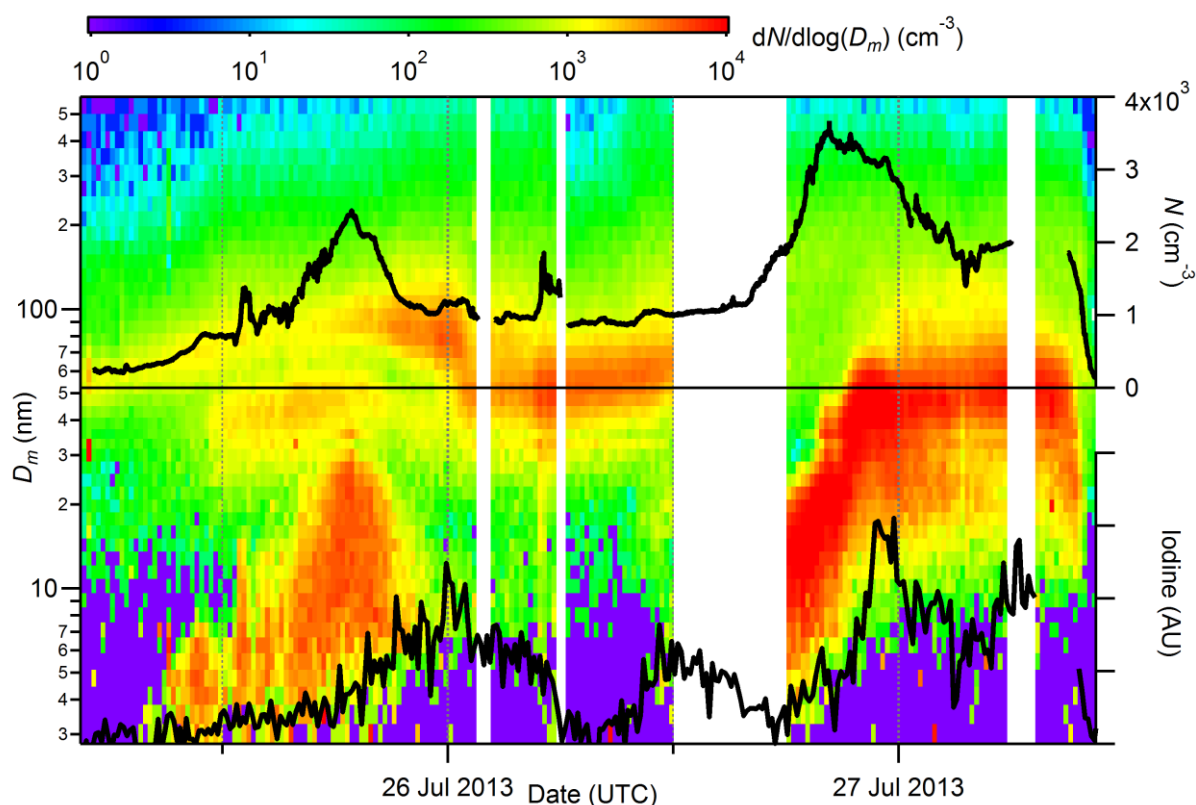
Figure 4: Size-resolved number concentrations (dN/dlog(D_m)) from a differential mobility particle sizer (DMPS) as a function of electrical mobility diameter (D_m), total number concentrations (N) from a condensation particle counter (CPC) and uncalibrated iodine ion concentrations from an Aerosol Mass Spectrometer (AMS) based on the signal at m/z=127 (I$^+$) during the main case study. White areas in the DMPS data show periods of ship influence or when the instrument was not sampling ambient air.
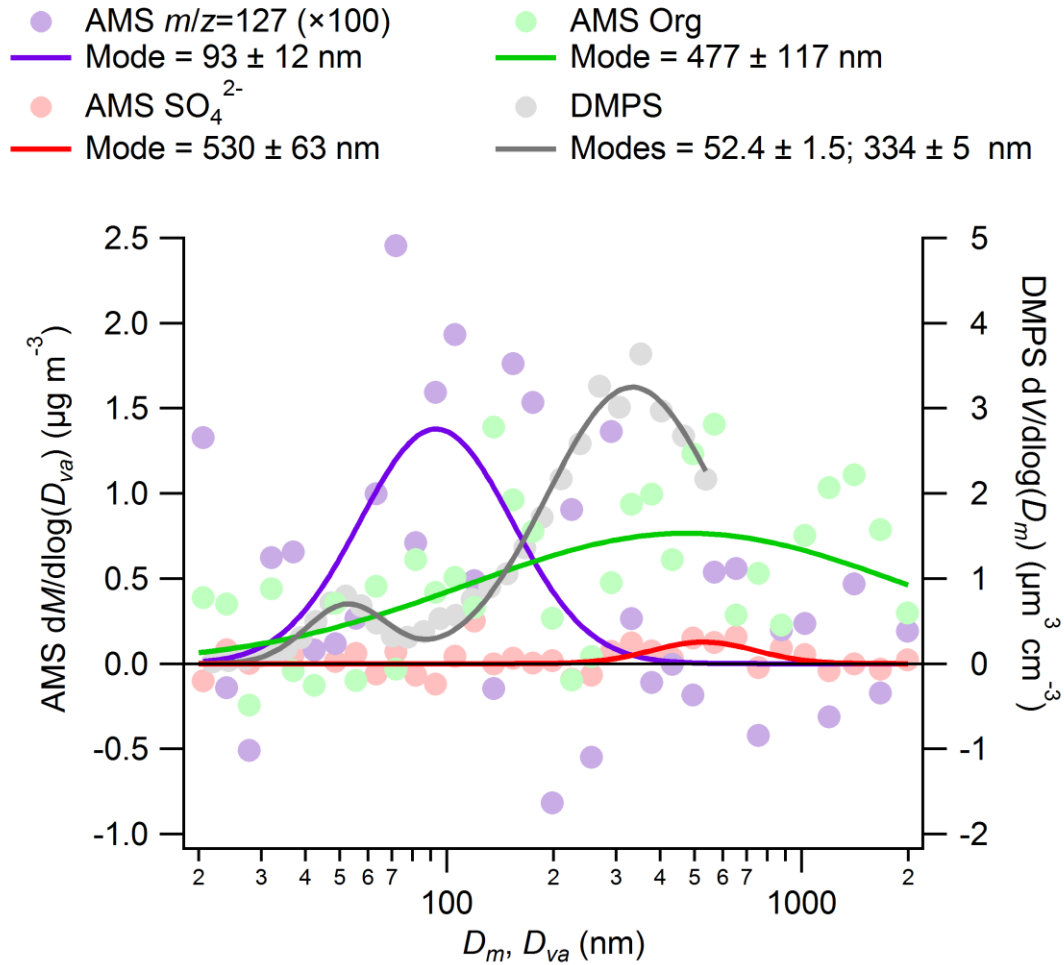
Figure 5: Size-resolved data from the DMPS and AMS, against electrical mobility and vacuum aerodynamic diameters respectively, during the period of highest iodine loading (26 July 22:50-23:45 UTC) with lognormal nonlinear least squares fits and associated standard errors, comparing DMPS volume with AMS mass at m/z=127, corresponding to I^+, and sulphate and organic matter. The low signal-to-noise ratios of the AMS data are due to the low concentrations and short averaging time. Note that the widths of the AMS distributions should not be directly compared against the DMPS, as the AMS distributions are subject to broadening introduced by the chopper wheel and variations in particle density.
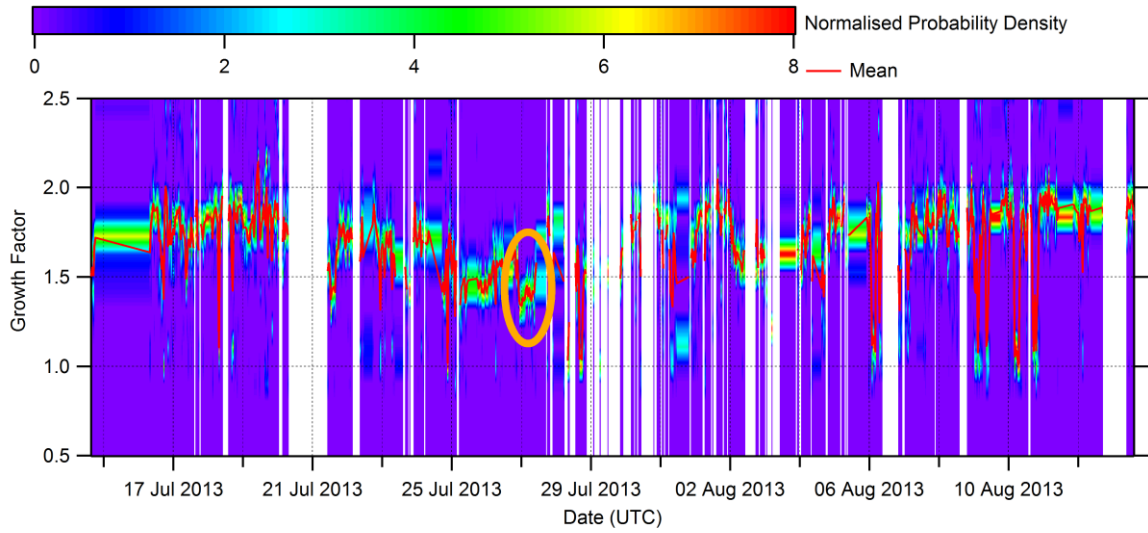
Figure 6: HTDMA-derived growth factor probability distribution functions for 50 nm dry particles at 90 % relative humidity, with associated mean growth factors. The low growth factors associated with the case study time period (26 July 22:50-23:45) are highlighted.

Revised supplement

J.D. Allan et al., "Iodine observed in new particle formation and growth events in the Arctic atmosphere": Supplementary information
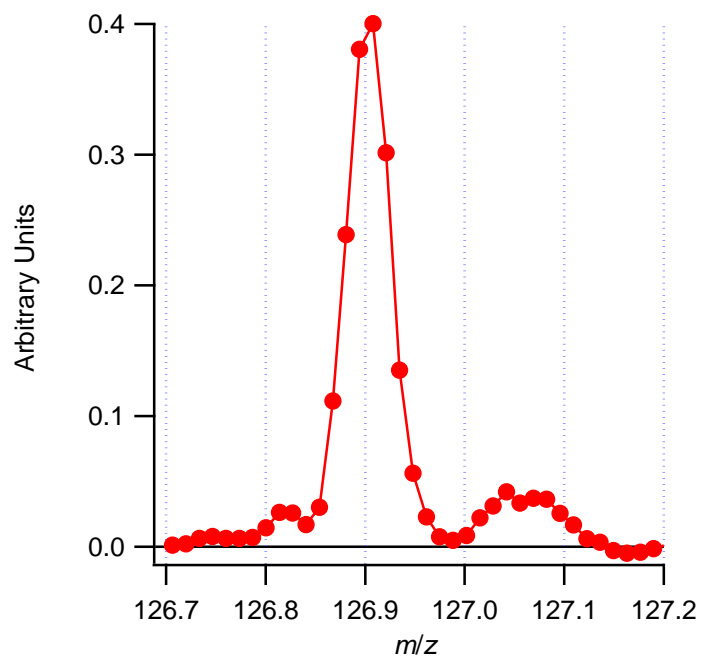
Section S1: additional figures

Figure S1.1: Detail of the AMS 'V' mode peak at m/z=127 during the high-iodine event, showing a peak at 126.90, consistent with I^+. The second peak could be a combination of $C_{10}H_7^+$ (127.05), $C_6O_3H_7^+$ (127.04) and $C_7O_2H_{11}^+$ (127.08).
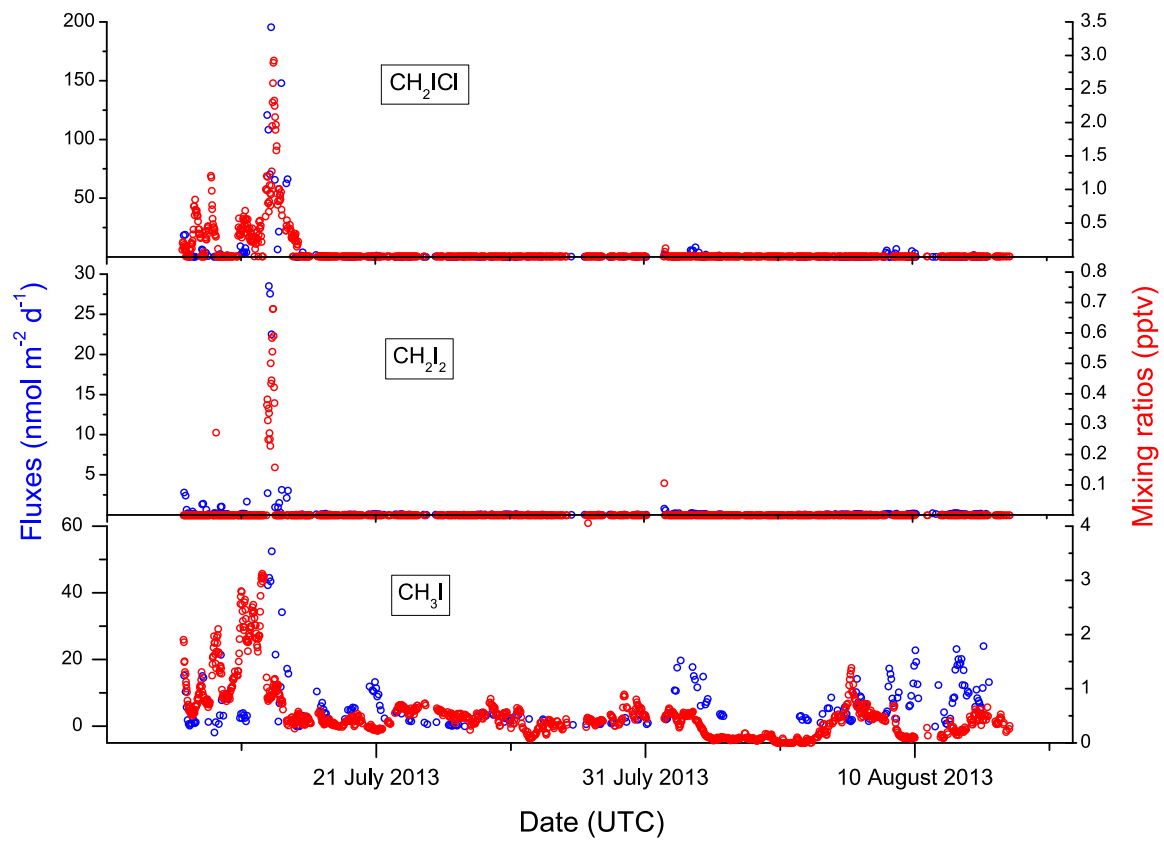
Figure S1.2: Fluxes and concentrations of iodocarbons measured during this study.

Section 2: AMS Data Processing

Data were processed using SQUIRREL V1.5E, with the default fragmentation tables (Allan et al., 2004; Aiken et al., 2008), adjusted to remove gas phase interferences at m/z=16 (O^+) and 44 (CO_2^+). Positive Matrix Factorisation (PMF) (Paatero and Tapper, 1994) was performed using PMF2 V4.2 in robust mode and the PET V2.06 toolkit (Ulbrich et al., 2009). The Unit Mass Resolution (UMR) data were used for this, as the High Resolution (HR) data was not reliable at the high m/z values of interest here. The data pretreatment steps recommended by Ulbrich et al. (2009) were followed, using the error model of Allan et al. (2003).

PMF converged successfully for a large number of factors, however the 5-factor solution was deemed the most physically meaningful. The results of this factorisation are shown in figures S2.1 and S2.2. Rotational ambiguity was explored using the FPEAK parameter (Paatero et al., 2002), however nonzero values either yielded unphysical results or failed to converge. While larger numbers of factors (up to 8) converged successfully, these showed evidence of factor 'splitting' and 'mixing' (Ulbrich et al., 2009; Allan et al., 2010), meaning the results were probably not physically meaningful. Regardless, no factor was found that explained the signal at m/z=127.

Within the 5-factor solution, factor 1 is sea salt misattributed as organic matter, evidenced by the peaks at m/z=58 and 60 corresponding to $NaCl^+$. While the AMS is not optimised to study sea salt, it can be present in the mass spectra in marine environments (Ovadnevaite et al., 2012). The peaks at the high m/z are fragments of tungsten compounds containing various combinations of O, H and Cl atoms, caused by the corrosion of the vaporiser surface. Factors 2 and 3, which are designated aromatics (containing characteristic peaks at m/z=91 and 77) and hydrocarbon-like organic aerosol (containing aliphatic hydrocarbon series) respectively, can be associated with combustion sources (Canagaratna et al., 2004), specifically the ship's own stack emissions and sources around ports. Factor 4 is methyl sulphonic acid (MSA), evidenced by characteristic peaks such as m/z=79 (Phinney et al., 2006). Factor 5 has a characteristic peak at m/z=44 (CO_2^+), so is probably a highly oxygenated organic aerosol (McFiggans et al., 2005; Jimenez et al., 2009). While this factor does appear to show a degree of covariance with MSA, the exact chemical nature and source of this can only be speculated at.

In all of the convergent solutions up to 8 factors, no factor showed a significant contribution from m/z=127 (I^+). Upon inspection of the residuals, a clear signal can be seen associated with the 25-27 July case study. The residual diagnostic data from the 5-factor solution is presented in Figure S2.3. This implies that the I^+ signal is not covariant with any of the other factors identified using PMF. The reason it does not form the basis of its own factor is because it does not account for enough overall weighted variance compared to the other factors. While I_2O_5 is also known to produce other peaks (e.g. IO^+, IO_2^+), these are expected to be much smaller (McFiggans et al., 2004) and no signals were found in their residuals over the noise. Note that while no significant I^+ signal was found in association with the other candidate nucleation events, this does not mean that there was no iodine present; during these other events, not enough particulate mass existed above the sizes detectable by the AMS (>30 nm approx.) (Liu et al., 2007).
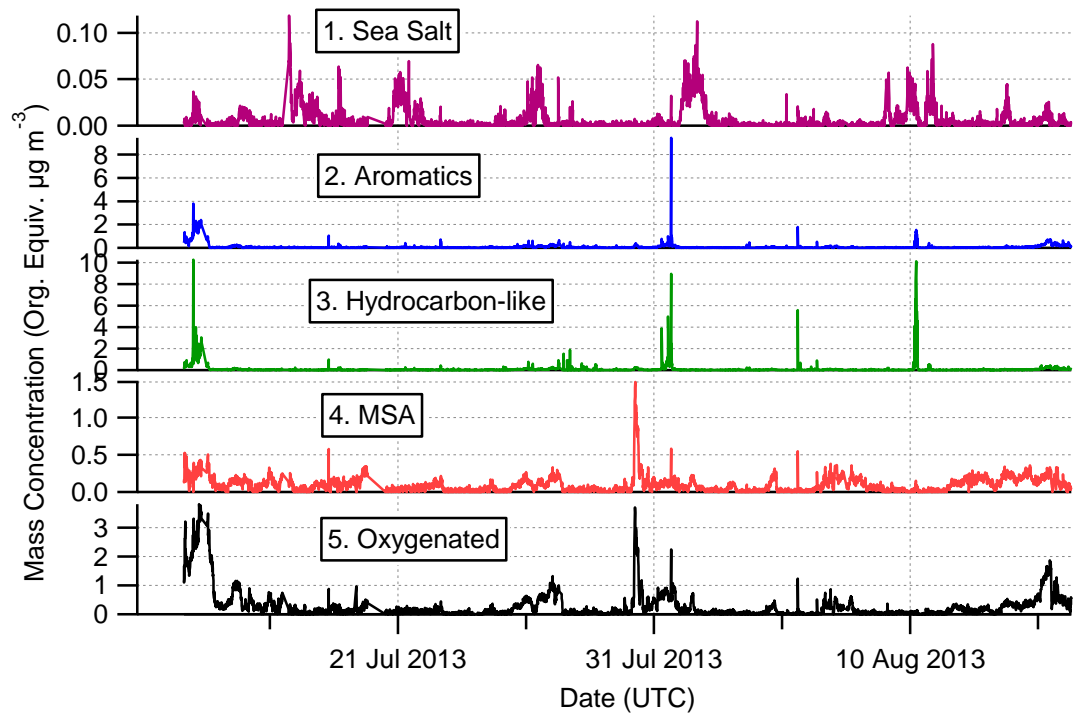
Section 2 figures

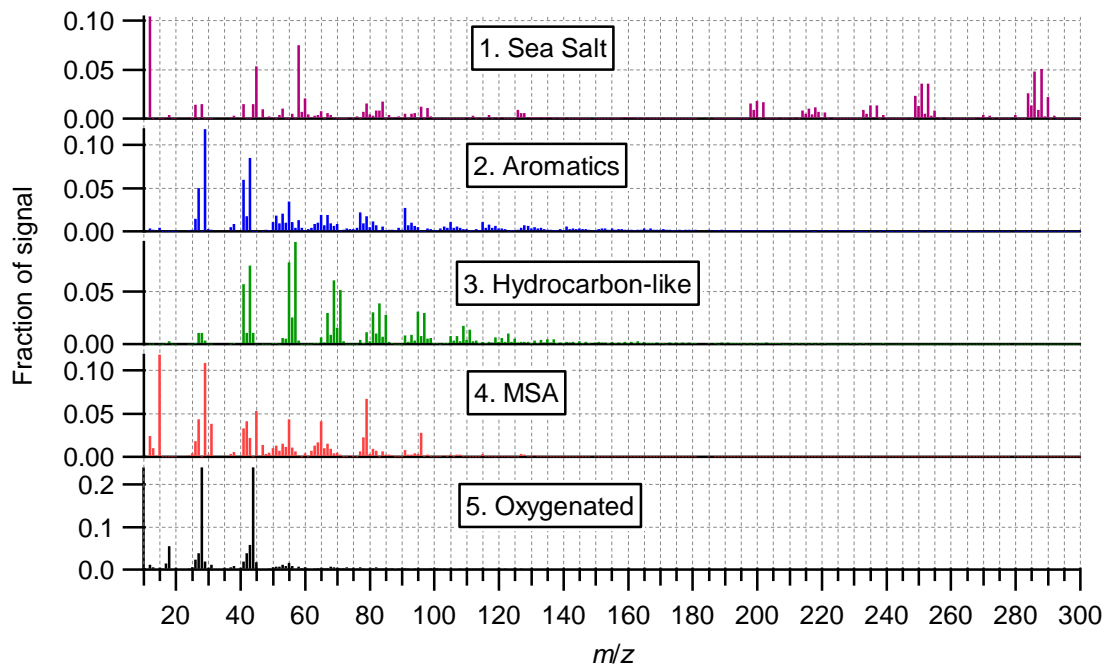Figure S2.1: Time series of derived factors from the 5-factor PMF solution.

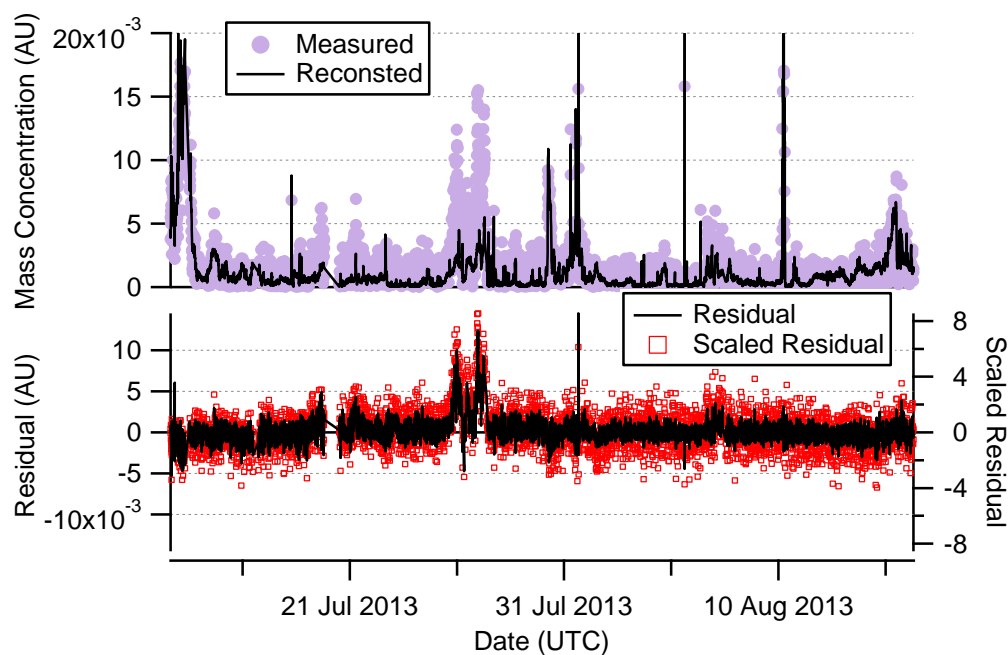Figure S2.2: Mass spectral profiles of the 5-factor PMF solution.

Figure S2.3: Residual diagnostics for m/z=127 (I$^+$) from PMF analysis. The scaled residual is scaled by the modelled error (i.e. the contribution of each datum to the Q statistic).

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