**Supplementary Information**

**Supplementary methods**

**Measurement site and instrumentation**

All the measurements were done at the Mace Head atmospheric research station on the west coast of Ireland (53°19’ N, 9°54’W) in August - October 2013. Mace Head is known for the strong tidal changes and presence of iodine emitting macroalgae beds consisting of e.g. kelps such as different *Laminaria* species and other brown algae such as *Ascophyllum nodosum* and *Fucus vesiculosus*. Mace Head represents of typical North Atlantic rocky shores in terms of the macroalgae exposure times.

Instrumentation at the station contained both ion and neutral cluster detecting devices and multiple particle counters. The smallest particles or clusters in the 1.5–3 nm range were detected with two particle size magnifiers (PSM, Airmodus A11, ref. 35). The PSM utilizes supersaturated diethylene glycol vapor to grow even the smallest particles or clusters to a detectable sizes for the condensation particle counter (CPC, Airmodus A20). During this campaign one PSM was set to scan continuously from 1.5 to 3 nm and the other one was set to a constant cut off size of 1.5 nm (based on calibration by negatively charged ammonium sulphate particles). Due to extremely intense new particle formation events, the sample had to be diluted by a factor of up to 50 for the PSM so that the CPC optical counter was able to count the particles accurately. A Neutral cluster and Air Ion Spectrometer (NAIS) was used for measuring total concentration and size distributions of clusters and particles between 2.5 and 40 nm.

Naturally-charged ions were detected with an atmospheric pressure interface-time-of-flight (API-TOF) mass spectrometer (Tofwerk A.G., ref. 36) that was run in the negative polarity mode detecting negatively charged ions. The API-TOF inlet flow was set to a constant ~7.5 liters min⁻¹, from which a 0.8 liters min⁻¹ sample was then introduced to the mass spectrometer through an orifice and two ion guiding quadrupoles. The ions were detected in the high vacuum of the TOF and separated according to their time-of-flights and reported as mass-to-charge (m/z) ratios.

The elemental composition of neutral molecules and clusters was analyzed with a CI-API-TOF (chemical ionization-API-TOF) that was equipped with a nitrate ion (NO₃⁻) based chemical ionization inlet prior to the API-TOF. The original design of the inlet that minimized wall losses of the sample is described in ref. 37 and the CI-API-TOF used here for acidic cluster detection is described in details in refs 38&9.

The CI-API-TOF was run in the negative ion mode and the signals detected are either negatively-charged analyte ions (e.g. IO₃⁻) or analyte ion clustered with the charger ion (e.g. HIO₃·NO₃⁻). NO₃⁻ was produced by ionizing HNO₃ containing sheath gas with a soft X-ray source (Hamamatsu). Reagent ions were then introduced into the sample flow that travels in the center of the inlet with a flow rate of ~10 liters min⁻¹. The ion–molecule/cluster interaction time was ~200 ms. The reported signals were normalized with the sum of the charger ions and for concentration multiplied with calibration factor of $C_{HHO3} = 9.8 \cdot 10^8$ molecules cm⁻³. The calibration of the CI-API-TOF was conducted with sulfuric acid that has been found to be ionized at the collision frequency with the reagent ion, NO₃⁻. The calibration with sulphuric acid yielded $C_{H2SO4} = 1.3 \cdot 10^9$ molecules cm⁻³. $C_{HHO3}$ was obtained by applying the transmission correction since the ion transmission through the API-TOF mass spectrometer is mass dependent. The mass-dependent transmission was experimentally determined before the campaign. Corrections for different ion – dipole interactions between NO₃⁻ – H₂SO₄ and NO₃⁻ – HIO₃ or differences in collision diameter between HIO₃ and H₂SO₄ were not applied.

If the detected iodine clusters are not charged as efficiently as sulfuric acid, it could lead to underestimating the concentration of iodine containing clusters. However, the proton affinity of IO₃⁻ is considerably lower than that of NO₃⁻ and therefore collision limited ionization should be a valid approach. Uncertainties in
reported concentrations of sulphuric acid and iodic acid have estimated to be at least +100/-50%. A collision-
limited ionization cannot necessarily be assumed in case of containing iodous acid (HIO₂) or hypoiodous
acid (HIO). Therefore, concentrations reported represent their lower-limit estimates.

All the mass spectrometric data was analyzed with TofTools software.

**Particle growth rate calculations**

Particle growth rates were calculated using the method that has previously been applied to coastal particle
formation events. For each new particle formation event (Figure S1), we determined the average diameter
of the mode $D_p$. Then we determined the time that an air parcel arriving at the station had travelled
after passing over the coastline, i.e. the growth time of particles ($t_{gr}$). For this we used the local wind direction and
wind speed measured at the station, and assumed that an air parcel travelled to the station at a constant speed
following a straight line from the coastline. We excluded from the analysis the cases for which the air had
likely passed over the coastline more than once. By assuming that all the particles were formed at the
coastline with the initial diameter $D_{p,0} = 1$ nm, we obtained the growth rate of particles from:

$$GR = \frac{D_p - D_{p,0}}{t_{gr}}.$$  \hspace{1cm} (1)

By using this method, we were able to determine the growth rate for three new particle formation events
occurring on 12, 19 and 20 September (Table S1). The average particle growth rates for these events were
390 nm/h, 66 nm/h and 167 nm/h, respectively. Such growth rates suggest that the average concentration of
condensable vapours were in the range from a few $10^8$ to a few $10^9$ molecules cm$^{-3}$ in line with earlier
estimates. Such growth rates are also consistent with the observed of HIO₃ concentrations.

**Table S1.** Mean diameter of the mode, growth time and growth rate for three new particle formation events
during the campaign.

| Date (dd/mm) | $D_p$ (nm) | Growth time (s) | Average growth rate (nm/h) |
|-------------|------------|-----------------|---------------------------|
| 12/9        | 4.2        | 29.8            | 390                       |
| 19/9        | 3.7        | 147.3           | 66                        |
| 20/9        | 3.2        | 47.5            | 167                       |

The total concentration of clusters, and thus, the total formation rate of clusters was very high (of the order of
$10^4$ cm$^{-3}$ s$^{-1}$), whereas the formation rate of ion clusters could not exceed the natural ion production rate of a
few cm$^{-3}$ s$^{-1}$ in maximum. Therefore, neutral processes dominated the new particle formation process in this
location, as shown previously.

**Further theoretical considerations**

**Cluster formation pattern**

Our observations invariably suggest, in line with studies of Saunders and Plane (2005, ref. 16), that the
chemical composition of even the smallest particles and initial clusters is close to that of I₂O₃. The detected
iodine oxide clusters contain either zero or one hydrogen atom. From the atomic compositions of clusters
observed in the CI-API-TOF spectra, a general pattern of compositions can be derived. Almost all clusters
can be described as composed of $(I_2O_3)_h(HIO_3)_h:IO_3^-$, with a small number of oxygen atoms missing
(commonly 0–4). With increasing cluster size there is a slight trend towards larger numbers of missing
oxygen atoms as compared to this basic formula. Although this does not provide any information on the
exact molecular mechanism of the cluster growth process, it implies a general growth pattern that proceeds by addition of iodic acid (HIO₃) units, followed by a condensation step after every second iodic acid addition:

\[
Q + \text{HIO}_3 \rightarrow Q \cdot \text{HIO}_3 \quad (1)
\]

\[
Q \cdot \text{HIO}_3 + \text{HIO}_3 \rightarrow Q \cdot (\text{HIO}_3)_2 \quad (2)
\]

\[
Q \cdot (\text{HIO}_3)_2 \rightarrow Q \cdot \text{I}_2\text{O}_5 + \text{H}_2\text{O} \quad (3)
\]

where \(Q\) is an arbitrary starting cluster. Loss of one proton (upon ionization) from the clusters formed in step (1) or (2) yields the exact composition of clusters, with zero or one hydrogen atom, respectively, observed in the CI-API-TOF spectra. Although the cluster formed in step (3) can not immediately be ionised by deprotonation, it is likely to be hydrated under atmospheric conditions, and a potentially bound water molecule might be able to lose a proton, leading to the same composition as direct deprotonation of the cluster formed in step (2). Potentially, this could lead to a reversal of the condensation step (3), yielding not only the same atomic, but also molecular composition, as direct deprotonation of the cluster formed in step (2). Any additional (non-deprotonated) water molecules potentially bound to any of the clusters would very likely evaporate from the cluster in the high vacuum of the mass spectrometer.

The small, but with size increasing, number of missing oxygen atoms compared to the basic formula can, within this scheme, be easily explained by lower oxidised iodine oxoacids (iodous/hypoiodous acid, HIO₂/HIO) having a small chance to be added instead of iodic acid units at each step, while otherwise following the scheme. However, it should be noted that, for reasons detailed below, the number of oxygen atoms missing compared to the basic formula is likely underestimated by the CI-API-TOF measurements.

**Comparison of proton affinities of nitrate and iodine based ions**

For the proton affinity calculation, molecular structures were optimized using a PBE₀⁴₀-⁴₂ functional with a aug-cc-pVQZ basis set⁴³-⁴⁴ on all atoms (aug-cc-pVQZ-PP on iodine) and an ECP28MDF effective core potential⁴⁵ for iodine. Optimized geometries were confirmed by frequency calculations yielding no imaginary frequency. All geometry optimizations and frequency calculations were performed using the Gaussian program package⁴⁶. Single point energy calculations on CCSD(T)(ref. 47)/aug-cc-pV5Z (refs. 40-41) level with an ECP28MDF pseudopotential (and correspondingly aug-cc-pV5Z-PP basis set) for iodine⁴⁵ were performed on the obtained molecular geometries using the Turbomole program package⁴⁸. Basis sets were obtained from the EMSL Basis Set Library⁴⁹-⁵⁰. The calculated values reproduce the trends found in experimental gas phase acidity well, although they are generally offset by approximately 10 kcal/mol.

Results indicate that both iodide (I⁻) and iodate (IO₃⁻) have a lower proton affinity than nitrate, meaning that these could be easily formed from their corresponding acids with nitrate ions, and collision limit ionization can be assumed. Assuming that the simultaneously formed nitric acid molecule is only weakly bound to the the iodine-based ion (or the cluster containing it), this can explain why nitrate ions are found in only very few of the clusters observed in the CI-API-TOF spectra.

Simultaneously, the data could suggest that clusters containing iodic acid (HIO₃) are over-proportionally detected by the CI-API-TOF as compared to clusters containing iodous acid (HIO₂) or hypoiiodous acid (HIO), as the latter are much less likely to be deprotonated by nitrate ions. While this, due to the remaining cluster's influence on the proton affinity, is not necessarily true for all cluster compositions containing iodous, or hypoiiodous acid, it might lead to an overestimation of the average oxygen content of clusters from CI-API-TOF results, due to a more effective detection of clusters with high oxygen content.
Table 2: Proton Affinities calculated at CCSD(T)/aug-cc-pV5Z//PBE0/aug-cc-pVQZ level of theory, at \( T = 298.15 \text{ K and } p = 1 \text{ atm.} \) Experimental values in parentheses.

| Reaction                  | \( \Delta E \) [kcal/mol] | \( \Delta G^0 \) [kcal/mol] |
|---------------------------|---------------------------|------------------------------|
| \( \text{H}^+ + \text{I}^{-} \rightarrow \text{HI} \)    | -321.21                   | -319.93 (-309.28±0.06 \[51]\) |
| \( \text{H}^+ + \text{IO}^{-} \rightarrow \text{HIO} \)  | -361.36                   | -355.39 (-347.3±2.1 \[52]\)   |
| \( \text{H}^+ + \text{IO}_2^{-} \rightarrow \text{HIO}_2 \) | -345.27                   | -338.14                       |
| \( \text{H}^+ + \text{IO}_3^{-} \rightarrow \text{HIO}_3 \) | -326.16                   | -320.82                       |
| \( \text{H}^+ + \text{NO}_3^{-} \rightarrow \text{HNO}_3 \) | -331.65                   | -330.73 (-317.80±0.20 \[53]\) |

**Laboratory experiments**

We performed two series of laboratory experiments.

The first series of experiments were conducted in a flow tube with a length of 200 cm and an inner diameter of 15 cm at a temperature of 295 ± 2 K and 1 bar pressure of purified air. The total flow was set to 13.5 L min\(^{-1}\) (STP) leading to a bulk residence time of about 160 seconds. Ozone was produced by passing 1 L min\(^{-1}\) air through an ozone generator (UVP OG-2). Pure iodine was stored in a flask maintained at 248 K, carried along with 20 cm\(^3\) min\(^{-1}\) (STP) air, and diluted immediately with the ozone containing main air stream just before the entrance of the flow tube. Laboratory lights served as the light source. The initial concentrations were (unit: molecules cm\(^{-3}\)): \([\text{I}_2]\) = 7.2 \(\cdot\) 10\(^{10}\) (upper limit, calculated from equilibrium vapour pressure of I\(_2\) \[51\]) \([\text{O}_3]\) = 1.5 \(\cdot\) 10\(^{12}\).

These laboratory experiments were conducted at elevated concentrations of HIO\(_3\), and thus the contribution from ion induced clustering inside the CI-source cannot be completely excluded at concentrations approaching 10\(^9\) molecules cm\(^{-3}\). Ion induced clustering may increase the collision rate between the charged cluster and HIO\(_3\) molecules. Ion clusters may, theoretically, also be more stable than their corresponding neutral counterparts. Therefore, no definite conclusions regarding the dynamics of neutral cluster formation can be drawn. However, the data unambiguously point toward the critical role of HIO\(_3\) in cluster formation and provide evidence supporting the proposed reaction scheme. Starting from HIO\(_3\) (or IO\(_3\)\(^-\) in case the artificial charge plays a role), addition of HIO\(_3\) and recycling of water explain the presence of next two clusters HIO\(_3\)·HIO\(_3\) and I\(_2\)O\(_5\)·HIO\(_3\) (or HIO\(_3\)·IO\(_3\)\(^-\) and I\(_2\)O\(_5\)·IO\(_3\)\(^-\)) in the recorded mass spectra (Figure S4). It should be emphasized that HIO\(_3\)·HIO\(_3\) and I\(_2\)O\(_5\)·HIO\(_3\) are detected as HIO\(_3\)·IO\(_3\)\(^-\) and I\(_2\)O\(_5\)·IO\(_3\)\(^-\) since they lose a proton upon ionization and therefore the data alone will not provide an answer if the cluster was originally neutral or formed on top of IO\(_3\)\(^-\)· ion. Also, unlike in field conditions where cluster concentrations were approximately linearly dependent on [HIO\(_3\)], in this experiment both neutral and ion-induced process should yield similar relation between cluster concentration and [HIO\(_3\)]. The data demonstrates the expected dependency nicely (Figure S5).

The second series of experiments were conducted in order to rule out any artificial mechanisms producing HIO\(_3\) in the ion source and to probe the mechanism in more detail. These experiments were performed in a flow tube with a length of 1 m and inner diameter of 5 cm. We used a standard fluorescent lamp to initiate the photolysis, ozone generator, and a gas wash bottle filled with purified water to provide water vapour. After reacting in the flow tube, the sample was mixed with a small stream of nitrogen passing through a radioactive Am-241 ion source. In some of the experiments, we varied the ion concentration by varying the flow through the ion source. In a few experiments we added nitric acid to provide a source for nitrate ions,
and in a few experiments we activated the system walls for nitric acid by adding a small stream of ammonia vapour to the gas flow through the ion source. Results of these experiments are discussed below.

The above experiments (Figure S5) were performed without actively adding water vapour to the system. The presence of HIO₃ indicates that if its formation requires water, the reaction should be reasonably rapid as the only sources of water vapour were the system walls and synthetic air used as carrier gas. In order to probe the formation of HIO₃, we performed an experiment where we started from “dry” conditions (RH < 1%) and increased the humidity up to few percent (Figure S6). We found that the IO₃⁻ signal increased with an increasing humidity and that the increase was even more pronounced for the HIO₃·IO₃⁻ signal. Indeed, the HIO₃·IO₃⁻ signal here did not any more follow the quadratic dependency on IO₃⁻, as observed in experiments where I₂, O₃ or light intensity was used to change the reaction conditions, but instead depended on IO₃⁻ to the power of 3.1. At the same time, the I₂O₅·NO₃⁻ signal decreased slightly. This decrease, together with the “too” strong power dependency shows that the restructuring reaction of HIO₃·HIO₃ to form I₂O₅ and H₂O slowed down. This is expected because bulk I₂O₅ is known to be relatively hygroscopic. Therefore, there is most likely a humidity-dependent balance between iodic acid dimer and iodine pentoxide in the atmosphere.

Another piece of evidence for I₂O₅ forming from restructuring of HIO₃·HIO₃ is shown in Figure S7, in which the observed I₂O₅·NO₃⁻ and HIO₃·IO₃⁻ signals followed each other very nicely. This would not be the case if I₂O₅ were formed by any other pathway, such as restructuring of I₂O₃ and I₂O₄. As will be discussed shortly, some of the restructuring reactions may still take place in regions of decreased water vapour concentration inside the API-TOF. However, formation of I₂O₅·NO₃⁻ inside the vacuum parts of the system is very unlikely. This is because it would require a nitrate ion to be adducted to HIO₃·HIO₃ before the entrance into the vacuum. We did not observe any HIO₃·HIO₃·NO₃⁻, indicating that I₂O₅ was formed in the atmospheric pressure parts of the system and, most probably, mainly in the atmosphere.

Consideration of other explanations for observed cluster spectra

Dehydration upon sample treatment.

As discussed above, the restructuring of the HIO₃-dimer to molecular gas phase I₂O₅ is humidity dependent. The same can possibly apply to iodic acid in clusters. The detected atomic composition with only one or two molecules of iodic acid in the clusters suggests that the rest of the acids had undergone a restructuring reaction. It is possible that restructuring takes partly place after the sample is exposed to decreased water vapour concentration after the pinhole of the mass spectrometer when the water concentration drops together with decreasing pressure. Water evaporation (or in some cases condensation in adiabatic expansion after pinhole at higher relative humidities) is generally an issue within the CI-MS community. If a water molecule evaporates, the cluster stability increases due to latent heat associated to evaporation, slowing down the further evaporation of water. However, there is no way to accurately assess the potential loss of water. We cannot thus exclude the possibility that clusters in the atmosphere are to some extent hydrated and would therefore contain more iodic acid than can be concluded from the measured mass spectra. This does not change our overall conclusions regarding the key role of HIO₃ in the cluster build up.

Oxidation by nitric acid

Another factor that might influence the clusters observed in the CI-API-TOF spectra is the oxidizing character of nitric acid/nitrate ions inside the instrument. In principle, this could lead to formation of additional particles due to the oxidation of gas phase iodine molecules (I₂) to iodic acid, which subsequently can condense to form I₂O₅. Although this process is known to take place in aqueous solution, it is unlikely to take place in the gas phase, as nitric acid molecules generally contribute no more than 1.5 oxygen atoms per molecule (forming nitric oxide (NO) and water) to an oxidation.
HNO₃ + 3 e⁻ → NO + 1.5 O²⁻ + 0.5 H₂O, while
I₂ + 2 O²⁻ + H₂O → HIO₃ + HI + 4 e⁻, alternatively
I₂ + 5 O²⁻ → I₂O₅ + 10 e⁻

For the oxidation of an iodine molecule to iodic acid, however, five oxygen atoms (and one water molecule) are necessary, thus requiring at least four nitric acid molecules/nitrate ions. This means that several reactive collisions with nitric acid/nitrate would be necessary. Therefore, this process of oxidation all the way from molecular iodine is unlikely to have a significant impact on the detected clusters. On the other hand, further oxidation of already present iodine oxoacids (iodous or hypoiodous acid) to form iodic acid can be expected to take place. This process would not affect the number of clusters or particles observed, but could by oxidation add a few oxygen atoms to clusters and thereby (similar to the effect discussed above) lead to an overestimation of the naturally occurring oxygen content of the clusters.

A possibility that needs to be ruled out is the oxidation of already oxidized iodine, such as OIO, to HIO₃ by its reaction with the nitrate ion used to ionize the sample. In order to rule out this possibility, we performed a series of laboratory tests.

First, we generated HIO₃ and clusters in the absence of added nitric acid to the ion source. The IO₃⁻ signal still appeared together with the clusters HIO₃•IO₃⁻, I₂O₅•NO₃⁻ (I₂O₅ detection bases on adducting with nitrate ion) and I₂O₃•IO₃⁻. Adding ammonia to the nitrogen flow through the ion source activated the surfaces preventing any nitric acid contaminant evaporation from the system wall. Upon adding ammonia, nitrate ion signals (NO₃⁻ and HNO₃•NO₃⁻) dropped by an order of magnitude (Figure S8). Meanwhile, the signal associated with IO₃⁻ showed only a slight decrease while the HIO₃•IO₃⁻ signal even increased. Obviously, adding ammonia to the system somehow affects the whole ionization process but altogether, the sum of the signals associated with iodic acid increased slightly with the added ammonia. This is an inevitable evidence on that NO₃⁻-related reactions in forming HIO₃ can be ruled out.

Second, we basically reproduced the experiment depicted in Figure S5. This experiment was performed in elevated concentrations of precursors to suppress the relative importance of nitrate or any other ion chemistry in production of our HIO₃ and cluster signals. In case of the HIO₃•IO₃⁻ signal, a quadratic dependency on IO₃⁻ signal was expected (Figure S9). The observed slope of 2.3 between these signals is close to the expected one, suggesting that HIO₃•IO₃⁻ was formed upon the collision of two HIO₃ molecules, and that the formed dimer was ionized via the deprotonation of one of the acids. However, this experiment alone does not yet exclude the possibility that the observed IO₃⁻ signal (x-axis) was formed via the OIO + NO₃⁻ reaction.

However, the neutral HIO₃ observed in a cluster with IO₃⁻ cannot be formed to such a high extent via reaction with NO₃⁻ that there could be such predominant signals of HIO₃ in a cluster with IO₃⁻. It would be kinetically impossible since the concentration of nitrate ions in the system is far less than 10⁶ ions cm⁻³.

The observed I₂O₅ signal (I₂O₅ clustered with nitrate ion) followed the behaviour of HIO₃•IO₃⁻ close exactly. This observation would support the idea that the formation of I₂O₅ proceeds via the restructuring of a HIO₃-dimer.

The slope of 3.7 (expected 3) in case of I₂O₅•IO₃⁻ and the slope of 6.1 (expected 5) in case of (I₂O₅)₂•IO₃⁻ agree, to a reasonably extend, with the theory involving HIO₃ clustering. And with these larger clusters it becomes more and more unlikely that the molecular species observed in these clusters were produced via any reaction involving ions.

Additional information that can be extracted from these data is that if I₂O₅ + I₂O₃ → I₂O₅ reaction (ref 28) explained I₂O₅ concentrations, one would expect a dependency of I₂O₅ to the power of 4 of the IO₃⁻ signal, not to the power of 2. Our theory can explain also the observations reported in refs. 16&17, assuming minute
water background (RH << 1%) in their experimental system. See discussion regarding pure iodine oxides in next chapter.

Third, an experiment to obtain independent piece of evidence against any formation mechanism involving nitrate ions (or any ions) was conducted by varying the ion concentration in the ion-molecule interaction tube (Figure S10). All the signals, including those accompanying a neutral HIO$_3$, showed a very closely linear dependency on the ion concentration. If neutral HIO$_3$ was formed in a reaction involving an ion, one would expect a clear quadratic dependency of HIO$_3$•IO$_3^-$ on the IO$_3^-$ signal.

We finally considered a hypothetical possibility that I$_2$O$_5$ (observed as adduct with NO$_3^-$ or with IO$_3^-$) would form purely from I and O$_3$ via some unknown mechanism, and that HIO$_3$ would result from the hydration of I$_2$O$_5$ resulting in formation of a hydrated HIO$_3$ dimer. This dimer would then partly, upon ionization, result in the formation of a HIO$_3$ molecule and IO$_3^-$, which we would detect by the MS and incorrectly interpret to be formed in a straightforward gas phase reaction. In order to exclude this possibility, we conducted an experiment where we changed the concentration of I$_2$ and thus I in the system. The I$_2$O$_5$ signal (Figure S11; green) showed a clear quadratic behavior with respect to IO$_3^-$ (so did also HIO$_3$•IO$_3^-$, blue). If IO$_3^-$ was formed via I$_2$O$_5$ or any other I$_2$O$_y$ compound, a linear dependency would be expected. The quadratic dependency shows that the formation of IO$_3^-$ requires only one I atom, while the I$_2$O$_5$ production needs two I atoms. Thus, this observation strongly supports our proposed mechanism that I$_2$O$_5$ is formed via a dimerization of HIO$_3$ followed by restructuring and loss of water, rather than the other way around.

**Pure iodine oxides**

Our findings are in apparent conflict with some previously published investigations. This is natural since HIO$_3$ was not observed or suggested to have a role in cluster formation before, either was cluster chemical composition never measured before. But let us slightly reflect our findings with the previous research.

A study by Gomez Martin et al. (2013, ref. 54) explored the formation of I$_2$O$_3$ and I$_2$O$_4$ in a flow system involving I$_2$ and O$_3$, where these higher iodine oxides were measured by a Photoionization (PI) – Time-of-Flight mass spectrometer. HIO$_3$ was not observed, and nor was I$_2$O$_5$. This observation is in apparent conflict with our results, as also we used I$_2$ and O$_3$. However, it is possible that the photoionization method can be insensitive toward HIO$_3$. At least, HIO$_3^+$ should be reasonably unstable. Acids readily donate their protons, but PI is based on photoelectric effect. On the other hand, our chemical ionization technique may be less sensitive toward I$_2$O$_3$ and I$_2$O$_4$. As discussed, we do not exclude the presence and role of I$_2$O$_y$ compounds in clusters and cluster growth, even though with our methods we were unable to detect them from the gas phase. Furthermore, the study by Gomez Martin et al. (2013, ref. 54) was performed in a decreased pressure with a relatively short residence time. In decreased pressure collisions with any background water molecules decrease as well, and thus, it is possible that due the lack of water residuals, no HIO$_3$ and thus I$_2$O$_5$ were formed.

The study by Burkholder et al. (2004, ref. 55), on the other hand, investigates IOP formation from CH$_2$I$_2$ photolysis and subsequent reaction of I with ozone. They performed a modeling study assuming OIO homogeneous nucleation. From our data we cannot exclude the presence of OIO or I$_2$O$_4$, which would be represent the first steps of OIO nucleation. Still, our observed O:I ratios are far higher than what would be expected from pure OIO nucleation. As stated in ref. 55 (and references therein), average OIO concentrations in Mace Head are unlikely high enough to explain the observed particle formation rates, and therefore “hot spots” of CH$_2$I$_2$ emissions were suggested. Based on our data, iodine oxides other than HIO$_3$ are needed to explain the observed spectrum and the variation in level of oxygenation while HIO$_3$ plays the key role. These compounds can either include smaller iodine oxyacids or, maybe more likely, iodine oxides, such as I$_2$O$_4$.
One apparent issue is that there is no known pathway of gas phase HIO$_3$ formation that could readily explain our observations. Reaction of OIO with OH is known to lead to HIO$_3$ formation$^{56}$ but it is kinetically implausible that HIO$_3$ would form to such a high extent from OH reactions in the atmosphere (even though this reaction pathway cannot be fully excluded), or in the flow tube conditions where there should not be a known source for producing OH. Our data unambiguously shows that HIO$_3$ forms in the gas phase in presence of I$_2$, light, ozone and water vapour. Iodine chemistry in general is highly complex and though the detailed chemical steps remain to be resolved, we believe that our work and our observations on HIO$_3$ and cluster chemical composition will serve as a starting point for fundamental experimental and theoretical work probing the iodine oxide, and iodine oxyacid chemistry in high detail.

Laboratory experiments of Saunders and Plane (2005, ref. 16) on particle formation starting from I$_2$ and ozone suggested that particles formed in “dry” conditions are composed of I$_2$O$_5$. They speculated that I$_2$O$_5$ forms in the oxidation of I$_2$O$_4$ by O$_3$. Later studies revealed$^{17}$, however, that O$_3$ is not needed in the particle formation process if O atoms are available to react with I$_2$, thereby demonstrating that ozonolysis is not a necessary step in the formation of I$_2$O$_5$. Combined, this would suggest that new particle formation may thus proceed via oligomerization/polymerization of I$_2$O and I$_2$O$_3$ which could then restructure in particle phase to form I$_2$O$_3$ and I$_2$, with I$_2$ being recycled back to gas phase$^{26}$. Since our detection technique is most likely not as sensitive toward iodine oxides other than iodine oxoacids, the presence of I$_2$O$_3$ and I$_2$O$_4$ cannot be excluded. Neither can their restructuring reaction to form I$_2$O$_5$. However, such a reaction would be in contradiction with our observed dependency of I$_2$O$_3$ on single iodine species (IO$_x$) (Figures S5 & S9). If I$_2$O$_3$ or I$_2$O$_4$ were needed in the formation of I$_2$O$_5$, one would expect I$_2$O$_3$ to show a dependency of the power of four on single iodine species. This, as discussed above, was not the case. Furthermore, if particles were formed according to that scheme, we would not expect to see the systematic variation in hydrogen number between zero and one (in chemically ionized clusters) depending on number of iodine atoms. On the other hand, oligomerization/polymerization reaction of I$_2$O and I$_2$O$_3$ cannot be completely excluded, since it could be hypothesized that the pure iodine oxide clusters formed in the reaction and containing an even number of I would then attach either one or two molecules of iodine oxoacid thereby enabling ionization. Such mechanism would result in the similar variation of hydrogen number as observed in the field.

Reaction scheme based on the polymerization of I$_2$O$_3$ and I$_2$O$_4$ also does not include molecular iodic acid and, unlike the mechanism proposed in this work, would not provide answer to question about the fate of iodic acid, present at significant concentrations. However, as stated above, our detection system may be sensitive only toward clusters containing an acid and therefore any parallel pathway not including addition of acid and restructuring in clusters cannot be fully ruled out.

Despite apparent disagreement with some previous studies, our study can be considered to be also is in line with the work by Saunders and Plane (2005, ref. 16) and Saunders et al. (2010, ref. 17). These studies started with I$_2$ photolysis and subsequent reaction of I with ozone exactly like us. They concluded that the formed particles had a composition of I$_2$O$_5$ with an observed O:I ratio of 2.45, close perfectly in line with our observations and theory. Assuming Saunders and Plane had any H$_2$O residuals in their system (similar to ours), our mechanism could readily describe their findings.

In our field data, O:I ratio varied between 2.2 and 2.6. Therefore, our observation allows many mechanisms to work in parallel, or together, with I$_2$O$_5$ in the particles formed upon dehydration and restructuring of HIO$_3$–dimer. To conclude, even though the key mechanism of cluster formation is iodic acid addition, our work does not exclude pure iodine oxides to have a certain role in particle formation, and therefore, our work does not invalidate the previous research on the topic.

**Ion induced clustering inside the ion source**
Critical range for ion induced clustering inside the CI-source starts when precursor concentration exceeds some $5 \cdot 10^8$ molecules cm$^{-3}$. Ion-induced nucleation may become an issue if clusters formed via neutral pathway would be significantly more unstable than those stabilized by presence of charge. This is the case e.g. with sulphuric acid self-nucleation or sulphuric acid – water binary nucleation (see e.g. Petäjä et al., 2011). Our highest concentrations never exceeded few $10^8$ molecules cm$^{-3}$ and therefore small contribution from ion induced processes to signals can with reasonably high confidence be ruled out. However, we rely on the collision-limited ionization of HIO$_3$ in derivation of concentration to from measured signals. If this assumption would not be justified, the iodic acid concentration would be underestimated. In that case, conclusions regarding ion induced clustering should be revisited. Nevertheless, as shown below, the proton affinity of IO$_3^-$ (ionized iodic acid) is clearly lower than that of NO$_3^-$ ion used to deprotonate iodic acid. This fact strongly suggest that collision limited ionization efficiency is a good assumption.

Evidence against ion induced cluster formation inside the ion source can be obtained also from the laboratory experiment depicted in Figures S4 & S5 (see discussion in previous chapter). In case of short residence time from vapour formation to cluster detection the process is in rapid dynamic change and very strong power dependencies for cluster concentration vs. [HIO$_3$] would be expected. In contrast to that, cluster concentrations observed during the field study show close linear dependency thereby ruling out the possibility for any artefact related to ion induced nucleation. Laboratory experiments were performed at HIO$_3$ concentration of $10^8 – 10^9$ molecules cm$^{-3}$, relevant for field study. However, in laboratory, the clusters never grew even close to sizes observed in field. Together with the observed slopes, this evidences that ion induced clustering does not significantly interfere with our field observations.

There is further evidence suggesting that ion induced effects do not play a significant role. If the ion induced cluster production inside the CI-system was so fast that it would result in the production of clusters in excess of 2000 Da in mass within a 0.2 second effective residence time in the ion source, such processes would, in the ambient time scales of several tens of seconds or minutes (from the emission area to the sampling site), grow the naturally charged clusters outside the measurement range of a API-TOF instrument (Figure S3). Naturally produced ions – which API-TOF is used to detect – are produced at a rate of approximately 2 ion pairs per second mostly due to cosmic radiation. Since the cluster ion concentration is in the range of few hundreds the loss term should be of the order of $10^{-2}$ s$^{-1}$ and the corresponding life time of the order of at least several tens of seconds. This is roughly hundred times longer than the residence time in the CI-API-TOF ion source. We still can detect the ambient ion cluster distribution with API-TOF demonstrating that the reaction time of 200 milliseconds is far from sufficient to significantly affect the detected signals via ion induced growth.

**Iodic acid and cluster formation at Arctic**

We performed a field experiment at Station Nord / Villum Research station in northern Greenland (81°43’N, 17°47’W) in February – August 2015. Station is located next to sea, which was throughout the campaign covered by ice, though during the summer ice shattered and also open waters were observed. The station was equipped with essentially a similar set of equipment as Mace Head. During springtime, after the sunrise in late February, we started to see iodic acid in elevated concentrations often associated with new particle formation events observed by Air Ion Spectrometer (AIS).

Figure S12 shows an example of such an event recorded on 31 March. Figure S13 depicts the mass spectrum recorded at the same time. Cluster formation here can be explained virtually purely with iodic acid clustering mechanism. However, since the signals were generally much lower than during highly intense particle formation periods in Mace Head, we cannot exclude the role of other iodous compounds in the cluster production. Their concentrations might just be too low to exceed the detection threshold.
In order to provide further evidence that HIO$_3$ is not formed in any reaction involving NO$_3^-$, we analysed the data measured by a low-pressure acetate CI-APi-TOF. The acetate CI is not optimized for detecting low vapour pressure sticky compounds as our nitrate CI, yet we detected IO$_3^-$ signals simultaneously in both instruments. The signals showed also a reasonable correlation with each other (Figure S14; the instruments were located in the same building but sample inlets pointing to different directions). Even if NO$_3^-$ were formed IO$_3^-$ by the mechanism, acetate ion could do this (see next paragraph). This observation, though not made at the Mace Head site, shows that the method of chemical ionization does not explain the formation of IO$_3^-$ or HIO$_3$.

In order to demonstrate that the acetate ion cannot oxidize OIO, we computed the reaction energy for the proposed reaction OIO + NO$_3^-$ $\rightarrow$ IO$_3^-$ + NO$_2$ using the qualitatively reliable wB97xd/6-311+G(2df,2p) level of theory (with LANL2DZ pseudopotentials for the core electrons of iodide). We obtained a value of +2.9 kcal/mol (i.e. a slightly endothermic reaction). Computing energies for reactions where covalent bonds to iodide are broken and formed is highly challenging, as issues such as spin-orbit coupling would need to be treated for accurate results (i.e. with likely error margins smaller than several kcal/mol). Thus, based on this calculation, we cannot rule out that the proposed reaction could indeed be exothermic, as suggested by the reviewer (though we note that since it requires breaking a N-O bond, it might still have a significant kinetic barrier). However, the corresponding reaction with acetate; CH$_3$COO$^-$ + IO$_2$ $\rightarrow$ CH$_3$CO + IO$_3^-$ is endothermal by 37.4 kcal/mol at the same level of theory. This is certainly much larger than the error sources in the calculation, demonstrating that IO$_3^-$ cannot be formed from IO$_2$ in an acetate-based CIMS. Thus, observations of IO$_3^-$ with acetate-based CIMS proves that the origin of IO$_3^-$ cannot be ionic oxidation of IO$_2$ inside the instrument.

**Iodic acid at Antarctica**

We also performed a field study at the Abua research station, Queen Maud Land, Antarctica (73°03′S, 13°25′W) in November 2014 – February 2015. As shown in previous studies, the Antarctic Ocean, especially the Weddell Sea region is biologically very active, and new particle formation is regular. NPF is thought to be connected to DMS emissions, but some studies have indicated that iodine compounds would play a role in NPF. Our measurement site was far away from immediate vicinity of Arctic Ocean / Weddell Sea. The shortest distance to the sea (which was mostly covered by ice) is 130 km, but air masses rarely travelled the shortest route from the sea but rather entered the continent ca. 300 km North-East from our site. Despite the distance from the potential iodine emission areas, we recorded iodic acid concentrations well above the limit-of-detection (Figure S15). Observation suggests that Weddell Sea or Antarctic Ocean is a strong source of molecular iodine that is converted to iodic acid in gas phase reactions at the emission area or during the transportation to our site. Because of the extensive time between the emission and detection it is likely that most of iodic acid would have condensed on particles, which naturally would greatly suppress its concentration.

**Supplementary References**

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Supplementary Figures
**Figure S1.** Particle size distribution measured with the NAIS. Data depicts three weeks of the measurement campaign (5 September – 29 September). A new particle formation event was observed almost every day. The event starting late 09/08 and continuing through 09/09 is associated with continental air mass and is not explained by iodine emissions. NAIS was not operating between 14th-18th Sept.

**Figure S2.** Cluster and particle concentrations recorded using different instruments. Besides CI-API-TOF, small sub-3nm clusters were observed also by a Particle Size Magnifier (PSM). PSM detects clusters in the size range of approximately from 1-1.5 nm to 2.5 nm in diameter and thus the results are not exactly comparable to clusters detected by CI-API-TOF. Assuming the density of that of I2O5 (4.98 g cm⁻³) the above depicted mass range corresponds to diameter range of 0.8 – 1.1 nm.
Figure S3. Mass defect plot from naturally charged clusters. Naturally charged ion clusters show the same behavior with the difference that more sulphur is detected in the nucleating iodine oxide clusters. Reason is most likely that iodine acid and other iodine oxides can condense on bisulphate ions formed before the air mass passes the emission zone. Another difference is that number of different chemical cluster compositions that can be extracted from the spectra is lower than in case of neutral clusters but the signals, in general, are much lower and many of the cluster ions probably just do not exceed the detection threshold. The general picture, however, with iodine oxides dominating the signals, is very similar to that of neutral clusters. Since the cluster formation at the site is fully dominated by neutral process, any ion induced pathway is of marginal importance.
Figure S4. Mass defect plot from laboratory experiment. Laboratory study provide support for the proposed mechanism. Due to short residence time clusters do not grow to large sizes, but the HIO$_3$ addition and water recycling explain also the laboratory data.

Figure S5. Dependence of cluster concentration on iodic acid in laboratory experiment. In contrast to field observations, due to very short residence time the clustering process is in dynamic range, and instead of linear or close linear correlation between cluster concentration and [HIO$_3$] a power dependence was
observed. Slope is approximately 2 (2.0) in case of ionized product of HIO₃·HIO₃ as would be expected if HIO₃·HIO₃ is produced from collision of two HIO₃ molecules. Formation of I₂O₅·HIO₃ requires three collisions. If the 1ˢᵗ step proceeds on collision limit a slope of approximately 3 (or slightly less due to [HIO₃]-dependent loss term, i.e. addition of one more HIO₃ to cluster) would be expected. Observed slope is 2.8 in line with the proposed reaction scheme.

**Figure S6.** Humidity dependence of iodic acid (observed as IO₃⁻), iodic acid dimer (HIO₃·IO₃⁻) and iodine pentoxide (I₂O₅·NO₃⁻).

**Figure S7.** Iodic acid dimer and iodine pentoxide show nice correlation at Mace Head suggesting restructuring of iodic acid dimer as a source of observed molecular iodine pentoxide.
Figure S8. Eliminating nitrate ions (NO$_3^-$, HNO$_3$• NO$_3^-$, and (HNO$_3$)$_2$• NO$_3^-$) from the system resulted only a slight decrease in IO$_3^-$ while some iodic acid associated clusters, such as HIO$_3$• IO$_3^-$, show increase. Observation excludes the role of NO$_3^-$ in formation of HIO$_3$.

Figure S9. Dependence of cluster signal on iodic acid in second series of laboratory experiments. See text for discussion.
Figure S10. Altering the ion concentration in the ion – molecule interaction tube resulted in linear response of all studied clusters, including HIO$_3$$^-$•IO$_3^-$ demonstrating that ions do not have an effect of iodic acid formation.

Figure S11. Quadratic dependency of I$_2$O$_5$ on signal associated to iodic acid (IO$_3^-$) shows that IO$_3^-$ is not produced by hydration of I$_2$O$_5$ (formed via some hypothetical gas phase mechanism not involving HIO$_3$) and subsequent formation and fragmentation of iodic acid dimer because in that case, a linear dependency would be expected. These data strongly suggests I$_2$O$_5$ is rather formed from restructuring of iodic acid dimer, formed via collisions of two iodic acid molecules.
Figure S12. New particle formation event observed with an Air Ion Spectrometer (upper panel) and concentrations of iodic acid and sulphuric acid measured with a CI-API-TOF on 31st March, 2015 at Station Nord / Villum Research station, Northern Greenland. Iodic acid concentration is significant and far higher than that of sulphuric acid.
Figure S13. Mass defect plot recorded on 31st March 2015 at Station Nord / Villum Research station, Northern Greenland demonstrates the iodic acid cluster formation and provides evidence for the potential role of the proposed mechanism to have a role in new particle formation at arctic areas.
Figure S14. Iodic acid measured simultaneously with the low pressure acetate and the atmospheric pressure nitrate ion CI-API-TOFs at Station Nord / Villum Research station, Northern Greenland. Observation of iodic acid also in the acetate ion chemistry based system provide further evidence that iodic acid is not connected to the presence of nitrate ions.

Figure S15. Iodic acid concentration measured at the Aboa research station, Queen Maud Land, Antarctica.