

Atmospheric science

Marine aerosols and iodine emissions

Arising from: C. O'Dowd *et al.* *Nature* **417**, 632–636 (2002)

O'Dowd *et al.*¹ describe the formation of marine aerosols from biogenic iodine and the growth of these aerosols into cloud-condensation nuclei (CCN). Based on chamber and modelling results, the authors suggest that biogenic organic iodine compounds emitted from macroalgae may be responsible for coastal particle bursts and that production of these compounds in the open ocean could increase CCN there too. It has since been shown that coastal particles are more likely to be produced from the photooxidation of molecular iodine². Moreover, I contend that open-ocean particle production and cloud enhancement do not result from emissions of organic iodine at atmospheric levels. For iodine particles to affect cloud properties over the remote ocean, an additional source of iodine is necessary as organic precursors cannot be responsible.

O'Dowd *et al.* propose that, in the presence of ozone, photolysis of atmospheric iodocarbons emitted from marine algae is a viable mechanism for the coastal production of new particles. This follows directly from observations relating aerosol formation and macroalgal iodocarbon emissions³ to the tidal cycle. However, particles formed by a variety of methods² have the same composition as those formed in the chamber study of O'Dowd *et al.*¹. The methods tested include exposing various *Laminaria* species to ambient and higher levels of ozone; mixing ozonized air with ozone-free air that has been passed over macroalgae; or exposing molecular iodine vapour (I₂) to ozone². The *Laminaria* macroalgae species are among those responsible for coastal iodine emissions.

Iodine-atom fluxes from an inorganic source, such as gaseous iodine⁴, have been shown to dominate² those from the organic compound diiodomethane (CH₂I₂; the most photolabile iodocarbon in the coastal environment and the one used by O'Dowd *et al.* in their chamber). Iodine-atom flux from atmospheric I₂ greatly exceeds that derived from the lowest CH₂I₂ concentrations used in the chamber experiments of O'Dowd *et al.*, which were more than an order of magnitude higher than atmospheric levels. Coastal iodine-containing particles are therefore much more likely to be formed from I₂ than from CH₂I₂.

Particle bursts have been measured at Mace Head in Galway, Ireland, alongside iodocarbon fluxes. The phenomena are characterized by extremely high concentrations and production rates of 3-nm-diameter particles⁵. Some have deduced⁶ that the precursor vapour sources are biologically rich tidal regions, tens to hundreds of metres from the

measuring location (or tens of 'transit seconds'). On these timescales, average atmospheric CH₂I₂ concentrations, which are two orders of magnitude lower than those in the smog chamber¹, would not be able to form the observed 10⁴ to 10⁶ particles cm⁻³. And yet for the laboratory mechanism to work in the coastal atmosphere, nucleation and growth characteristics must behave in the same way.

O'Dowd *et al.* used a model to demonstrate nanometre-scale sulphate-cluster stabilization by condensation of condensable iodine vapours (CIVs) and a consequent increase in CCN number. Their concentrations of CIVs are consistent with unrepresentatively low source estimates from a model⁷ that is aimed at explaining open-ocean iodine monoxide observations⁸. By assuming that CH₂I₂ is the coastal atmospheric iodine source, the model successfully replicates coastal observations⁷. However, coastal iodine-atom production from I₂ that is associated with an iodine monoxide mixing ratio of a few parts per trillion is about 5 × 10⁷ cm⁻³ s⁻¹, and not 1 × 10⁴ cm⁻³ s⁻¹ as calculated from CH₂I₂.

Assuming a common chemical mechanism, the open-ocean iodine-atom production that is required to explain the observed remote marine iodine monoxide must be much higher than that proposed by O'Dowd *et al.* To achieve this rate, however, a further remote marine-atmospheric iodine source must be found (abiotic production⁹, for example), as the original flux estimate is consistent with the observed open-ocean organic iodine. At increased concentrations, iodine oxides may nucleate in the absence of pre-existing clusters^{1,2}, a mechanism that could explain the coastal phenomenon and possibly play a part in the open ocean. There is little evidence to support sulphate nucleation in the marine boundary layer following dimethylsulphide oxidation, hence the existence of pre-existing sulphate clusters should not be relied upon to explain marine-iodine enhancement of CCN. The identity of CIVs and their role in aerosol and CCN formation are unclear, as are their production rates as a function of an enhanced iodine-atom source. Taken together, all this calls for an improved understanding of the key species and processes involved in aerosol nucleation and growth in the marine boundary layer.

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O'Dowd *et al.* reply — McFiggans¹ raises some interesting, but partly speculative, issues about the possibility of additional condensable-iodine-vapour (CIV) precursors being involved in marine aerosol formation from biogenic iodine emissions, and about the relative roles of iodine oxide and sulphuric acid in the marine new-particle formation process.

We linked biogenic iodine compounds that were released by marine biota to particle formation through the formation of iodine oxides and focused on diiodomethane (CH₂I₂) as an iodine oxide precursor². As a result of new experiments, McFiggans now adds a further candidate to the list of aerosol precursors — molecular iodine (I₂). Like the iodocarbons, I₂ is rapidly photolysed during the daytime to yield highly reactive iodine atoms, which start the chain of gas-phase reactions that finally lead to the higher iodine oxides. This inclusion of another, previously unrecognized, iodine source reinforces our central hypothesis that biogenic iodine emissions have a potentially significant effect on global radiative forcing.

We agree that molecular iodine is a previously unidentified and important candidate that contributes to this process when macroalgae and tidal effects are considered: during the BIOFLUX campaign³, we measured I₂ and new particles at Mace Head in Galway, Ireland, at nearby biological hot-spots where nucleation intensity is even higher than at Mace Head, and in chambers containing different *Fucus* species. We found that there was a significant release of I₂ from macroalgae under natural conditions. During these experiments, the presence of I₂ was correlated with algal biomass, and the production of new particles was linearly correlated with I₂ concentrations; ambient concentrations of I₂ were of the order of 20–200 parts per trillion and so I₂ concentrations are higher than those previously reported for CH₂I₂ (about 1 part per trillion).

However, quantitative information on the source strength of I₂ is not available, nor is an understanding of the biological or chemical mechanism of its release. It is unknown which CIV source dominates over the open ocean, where different algal species are found and different sea–air transfer processes for iodine gases prevail. We highlighted² the fact that, based on the available information, there is a significant missing source or sources

of iodine over global oceans — hence the generic term CIV that we used is still valid.

McFiggans *et al.*⁴ link enhanced molecular iodine emissions to the significant concentration of inorganic iodine species in tidal waters as the water level subsides. This process is first linked to macroalgae as a source of precursors and second, and more particularly, to the concentrating effects of inorganic iodine species driven by tides that will not apply over the open ocean. Nevertheless, the suggestion that an additional source of iodine over the open ocean needs to be identified warrants further investigation.

The issue of nucleation of iodine oxides or thermodynamically stable sulphate clusters (TSCs) is still an open question. Detailed modelling studies⁵ of TSC nucleation in the marine boundary layer predict that TSC nucleation can easily occur under ambient conditions, but that these nuclei are rapidly scavenged by the existing aerosol before they can grow into aerosol particles or CCN. The addition of CIVs to the condensation process increases the survival probability of TSCs as they grow.

The suggestion that iodine concentrations could be greater than previously anticipated supports our predictions. But, given current understanding of the complex iodine-vapour system, it is not yet possible to determine whether CIV nucleation dominates over TSC nucleation. Whether or not CIVs nucleate and require sulphuric acid to grow nuclei into new aerosol particles, or vice versa, or whether a combination of both species participates in the nucleation and growth processes requires a deeper knowledge of gas-phase iodine processes and the role of iodine oxides in nucleation.

In conclusion, our original hypothesis remains valid but there is still an urgent need to understand more fully the production of iodine vapour, gas-phase interactions and particle production over the open ocean, as highlighted by McFiggans¹.

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