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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Glass formation and unusual hygroscopic growth of iodic acid solution droplets with relevance for iodine oxide particles in the coastal marine boundary layer" *by* B. J. Murray et al.

Anonymous Referee #2

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This manuscript presents some interesting laboratory studies of iodic acid solution droplets. The experimental methodology appears appropriate and the experiments carried out carefully enough in most cases.

However, contrary to the title, and many of the statements throughout the manuscript, I see much less relevance to the atmosphere than the authors. The problem lies in the fact that, although iodine oxides may provide the initial stable clusters, even in the very strong source regions with high emission fluxes of molecular iodine, particles of any significant size (beyond a few nm diameter) will contain negligible amounts of

iodine oxides. The properties of particles of a few tens of nanometres or greater will be largely unaffected by those of the components making up the initially stable cluster. This is because of the abundance of material in even the clean marine atmosphere which, although not as involatile as the iodine oxide vapours that act as nucleants, can readily grow particles once the Kelvin term reduces exponentially above a few nanometres. The condensable iodine oxide vapours may be as high as a few ppb within a few centimetres or a metre or so of the emission source, but are too reactive or condensable to persist more widely. This gives the nucleated clusters a few seconds to grow in the very high concentrations in the coastal hotspots. Even in the most rapidly growing coastal particle events, growth rates are order of magnitude too slow for them to have occurred predominantly by condensation of iodine oxide vapours. Air would need to move slowly within a few metres of seaweed for tens of km along the coast to give the growth rates of tens of nm/hour would be needed for the particles to contain a significant fraction of iodine oxides. Air becomes mixed vertically and horizontally in the boundary layer far too rapidly for this behaviour. This behaviour is recognised in the paper (page 7881, "Under suitable conditions these particles may grow, through the condensation of OTHER condensable vapours (MakelaÌĹ et al., 2002; Saunders et al., 2010), to sufficiently large sizes that they can serve as cloud condensation nuclei (McFiggans et al., 2010)" so one could be forgiven for thinking that the atmospheric relevance has been mischievously rather than mistakenly exaggerated.

Example statements relating to the concern above: p7881, line 10: "There has been some debate in the literature over the most likely composition of iodine oxide particles with insoluble I2O4 and the soluble I2O5 being identified as the most likely candidates". The debate has been over the stoichiometric composition of the initially formed clusters, not molecular identification of iodine-containing particles. Is it likely that the stable tetroxide or pentoxide are the actual molecules comprising bulk particles in the atmosphere, when they are likely to be the products of the condensation of many various oxides and there will likely be water and many other components present?

p7881, line 13: "Ultrafine particles sampled during low tide particle “bursts” at Mace Head in Ireland were reported to have a characteristic hygroscopic (diameter) growth factor (based on electrical mobility diameters, Dfinal/Dinitial) of less than 1.1 at an RH of 90% (VaÌĹkeva et al., 2002), ruling out sulfate or sea salt aerosol which are known to have much greater growth factors." Given that it is unlikely that the particles will have grown in situ from condensation of iodine oxides, the authors are invited to comment on the relevance of these measured growth factors of ambient particles.

p7881, line 13: The authors correctly state that "MaÌĹkelaÌĹ et al. (2002) showed that the ultrafine particles sampled at low- tide periods at the same coastal location contained iodine of biogenic origin". However Makela et al clearly stated that "it was not possible to quantitatively determine the iodine content in the particles", and the iodine oxide fraction and hygroscopicity of particles in the field is not necessarily related given the likely low fraction of iodine oxides.

Rather than trying to relate the current study to the atmospheric observations, it is more valid to build the study on lab studies as in the statement on p7881, line 21: "In general, a small growth factor indicates a weakly soluble material or an insoluble material internally mixed with a small amount of soluble material (Swietlicki et al., 2008; Vakeva et al., 2002). Since I_2O_5 is highly soluble (263.2 g per 100 g of water at 298 K, Kumar et al., 2010), Jimenez et al. (2003) concluded that I_2O_4 was the most likely composition of iodine oxide particles. However, elemental analysis of particles generated photochemically from I_2 in the presence of O_3 revealed a composition consistent with I_2O_5 (Saunders and Plane, 2005)". The lab studies of Jimenez are likely to relate to particles much richer in iodine oxides than atmospheric ufps. If the particles were made from I_2O_5, the hygroscopicity measured in such a study would indeed imply that there is an inconsistency with the assumption of particles made of a substance exhibiting high bulk solubility having high growth factor.

Another example of an imbalanced contextual basis for the paper starts on line 5, p 7882: The arguments relating iodine oxide ultrafine particles to the fashionable discussion of the amorphous phase state of ambient particulates is rather contrived. I understand that it is necessary to bridge the discussion between the earlier atmospheric discussion of coastal ufps to the later lab studies of HIO_3 behaviour. However, as stated earlier, the behaviour of a trace component is unlikely to determine the particle properties. This is particularly true of a property such as viscosity where even trace contaminants in a bulk liquid can act as a plasticiser. Perhaps the authors would like to give an example of the opposite (a trace component forcing increased viscosity) as a precedent for their contentions.

Notwithstanding the whole of my main criticism above, an entire industry has surrounded studies of the other major atmospheric nucleant, sulphuric acid. Granted, there is much more sulphate in ambient particulate material than iodine (because sulphur compounds are not only emitted in great abundance in thin strips along some coastline), but this fact should not preclude studies into the properties of iodine oxides as a minor aerosol component. I therefore suggest that the manuscript is suitable for publication when the authors have satisfactorily addressed my major criticism of context above (including those aspects of the study where particle properties could not possibly reflect those of iodine oxides), probably by simply focussing on the interesting laboratory experiments without exaggerated statements of relevance, and the following less serious concern.

Less serious concerns: The interpretation of the experimental results is sometimes erratic and possibly subjective: bottom 7888 - top p7889: it has been shown that iodine oxide particles are aspherical and hence the mobility will not be the same as that of a sphere. Restructuring under humidification would undoubtedly affect the recorded mobility. Similarly, restructuring by reducing viscosity enhancing flow would lead to a change in mobility indistinguishable by cause. Morphology and phase are only applicable to non-liquid particles so would require some probe other than phase state to distinguish the cause.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 7879, 2012.