

## ***Interactive comment on “Investigation of coastal sea-fog formation using the WIBS (Wideband Integrated Bioaerosol Sensor) technique” by Shane M. Daly et al.***

### **Anonymous Referee #1**

Received and published: 27 September 2018

### **General comments**

Daly et al present a very interesting study of particle formation in a coastal environment. Using a wideband integrated bioaerosol sensor (WIBS), a scanning mobility particle sizer (SMPS) and laser scattering visibility observations, they found evidence linking molecular iodine release and particle formation with sea-fog formation. The paper addresses a relevant scientific question within the scope of ACP, presents a novel concept and reaches substantial conclusions. I recommend publication after some minor changes.

### **Specific comments**

C1

While the timeline link between molecular iodine release at low tide, iodine oxide formation (in daytime) and particle formation is well established (references cited in the paper itself), the study links these two with the formation of coastal mist for the first time. I would then recommend a slightly more nuanced statement about the novelty of this 3-step time-line in the abstract and conclusions. What is certainly new and exciting about the study is the field observation of I<sub>2</sub> adsorbed onto water droplets. This appears to be a previously unknown stabilizing transport mechanism for the dispersal of I<sub>2</sub> in the marine environment. This finding is supported by targeted laboratory experiments demonstrating that the non-biological WIBS signals observed in the field are in fact consistent with the adsorption of I<sub>2</sub> on the surface of nebulized pure water droplets.

The absence of fluorescence for nebulized seawater in the presence of iodine vapour may well be explained by the formation of trihalide ions as the authors suggest. It would be interesting to know, though, whether the saline solutions prepared for the lab experiments have similar iodide and chloride concentrations to those expected in sea spray, and whether more diluted concentrations would have resulted in increased signal in the FL1 channel. Also, whether changing the residence time of the nebulized sea salt solution in the chamber could have shown some evidence of the kinetics of the removal of the adsorbed I<sub>2</sub> molecules at the surface. In any case, the characterisation of the sea salt solution should be included in section 2.3. I would like to see also some information about the pressure, temperature, flow rate, and residence time conditions in the aerosol dispersion chamber.

The absence of fluorescence when only iodine vapor is admitted in the laboratory chamber is very interesting, but I don't find very convincing the argument given by the authors to explain this point. The WIBS-4 instrument is optimized for particle detection, but in its configuration (<http://www.dropletmeasurement.com/wideband-integrated-bioaerosol-sensor-wibs-neo>) I don't find any obstacle for the detection of gas-phase fluorescence (perhaps the authors could comment more on that to make it

C2

clearer). I<sub>2</sub> molecular iodine presents a strong absorption feature in the 170–210 nm spectral range (the Cordes bands, D-X system), with peak absorption cross section of  $2\text{E}-17\text{ cm}^2\text{ molecule}^{-1}$  at 188 nm (Myer and Samson, 1970; Roxlo and Mandl, 1980). After absorption of VUV and middle UV photons, fluorescence from the D ion-pair state back to the ground state exhibits an ordinary bound to bound spectrum together with a bound to free diffuse quantum interference spectrum (the McLennan bands) (Tellinghuisen, 1974; Exton and Balla, 2004). Concurrently, a significant fraction of the initial D state population is collisionally transferred to the D' state at increasing buffer gas pressure, resulting in fluorescence in the D'-A' band at 340 nm. Since the transition probability of the D-X system at 280 nm is small (absorption cross section of  $6\text{E}-19\text{ cm}^2\text{ molecule}^{-1}$  (Saiz-Lopez et al., 2004)), this may explain why I<sub>2</sub> is not observed in the gas phase. On the other hand, complexation with water may red-shift the absorption spectrum. E.g. the peak of the I<sub>2</sub> VUV band shifts to 203 nm in aqueous solution (Kireev and Shnyrev 2015). This would be a plausible explanation as to why 280nm-pumped fluorescence in the 310 - 400 nm range can be observed when I<sub>2</sub> is complexed with water and not in the absence of water droplets. In feel that some spectroscopic discussion in this sense is pertinent.

Section 2.3 mentions that fluorescence spectra of the solutions were investigated using a Shimadzu RF-6000, but the results of these investigations are not reported. I also find that the solution absorption data is presented in a rather schematic way and that it would be more informative to show absorbance spectra (perhaps in the supplementary material) to demonstrate how efficient is the absorption of the two WIBS wavelengths.

The suggested link between I<sub>2</sub>.(H<sub>2</sub>O)<sub>x</sub> and HIO<sub>3</sub> is a problematic one. Sipila et al. 2016 did observe HIO<sub>3</sub> and molecular cluster formation in their laboratory experiments, but in the presence of water vapor (no nebulized water droplets). Daly et al. do not report WIBS measurements of a mixture of water and iodine vapor, but it is known that I<sub>2</sub> and H<sub>2</sub>O form a weakly bound complex (Galvez et al. 2013), and under atmospheric conditions only a residual amount of I<sub>2</sub> would be complexed with H<sub>2</sub>O. The presence

C3

of I<sub>2</sub>.(H<sub>2</sub>O)<sub>x</sub> in the laboratory experiments of Sipila et al. is therefore unlikely. Furthermore, HIO<sub>3</sub> increase was observed by Sipila et al. in the field at daytime, well after noon, while Daly et al show that I<sub>2</sub>(H<sub>2</sub>O)<sub>x</sub> is a night time reservoir which disappear quickly after sunrise.

#### **Minor comments**

Page 6, line 20: 0.5-20 m. do you mean micron?

Page 11, lines 2 and 3: it looks like all these size ranges should be microns rather than meters.

All figures. In general, the legends and axis labels are too small and difficult to read, especially in multi-panel figures.

Figure 9: some of the tidal height data is missing: the 6:00AM and 18:00 tidal values are not shown (as opposed to figure 1 in the supplementary information).

---

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-673>, 2018.

C4