

Interactive comment on “Observations of I₂ at a remote marine site” by M. J. Lawler et al.

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Author Responses to Referees

Response to Referee #2

page 25924, line 8: modification

corrected

At some point in the description of the Carpenter et al. (2013) study (probably in the paragraph beginning line 7 on page 25924), it should be pointed out that THAMO was used in that paper to model IO at Cape Verde successfully, so the good fit shown in Fig 6 (lower right panel) is not surprising. What is novel in the present paper is the very nice fit to the I₂ in Fig 6 (lower left panel).

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Revised the first sentence in the paragraph to:

“In the HOI simulation, sea-air fluxes of both HOI and I₂ were prescribed after Carpenter et al. (2013), without modification or optimization. Carpenter et al. (2013) showed that THAMO simulations using these fluxes showed good agreement with IO observations at CVAO (Fig. 6), but I₂ observations were not available in that study.”

Response to Referee # 1

The authors state, correctly in my view, that the open ocean plankton may emit I₂, although the emission rate is unknown. Could this be an explanation for some of the model-measurement discrepancies, without invoking the O₃ + I- chemistry? Can the contribution of plankton emissions in the open ocean be ruled out? The authors should comment on this, as they draw the conclusions of their study.

There could be another mechanism that results in significant fluxes of inorganic I to the atmosphere. For it to be released as I₂, regardless of the mechanism, requires a strange (and strong!) diel cycle. It seems possible that organisms could also release (or cause the release from seawater of) HOI and I₂ in similar ratios to that of the O₃ mechanism. It's certainly not impossible, but the evidence so far points to an important role for the O₃ reaction, with little data to support or refute a planktonic source. We added this sentence to the end of the first paragraph of the Discussion: Ix Sources and Halogen Cycling section:

“Similarly, a direct biological source of I₂ is not precluded by the observations, but it would also require very strong diurnal variability. The seawater ozonolysis source of HOI appears to be sufficient to explain most of the flux of inorganic I to the atmosphere at this site and is clearly the more straightforward explanation.”

I think a more detailed “review” of the various mechanisms proposed over the past few years to explain the release of iodine from the sea-surface should be added on p. 25913. Some these mechanism propose the release of organoiodide compounds,

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as well as I₂, and the implications of this for the conclusions of this study should be discussed.

Modified the end of this paragraph as follows:

"Organiodide compounds such as CH₂I₂ and CHClI₂ are also emitted from the sea surface. These gases are formed in seawater as a result of the interaction of HOI and/or I₂ with dissolved organic matter, likely as a result of ozonolysis (Martino et al., 2009). These compounds are rapidly photolyzed, in some cases releasing I atoms on timescales of minutes in the daytime marine boundary layer (Martino et al., 2005). The most abundant and longest-lived organiodide compound, methyl iodide, has a photolysis lifetime of several days. The global I release attributed to organiodides is on the order of 0.4-1 Tg I yr⁻¹, with CH₃I dominating (Jones et al., 2010, and references therein). A detailed review of marine iodine gas production mechanisms is found in Saiz-Lopez et al. (2012)."

Regarding the macroalgal emissions, the authors state that they collected some samples near the site, but no I₂ emissions were observed from them. Were the authors able to identify the algae species? Were they different from those collected at other sites, such as Mace Head or Roscoff? This could explain why they did not emit I₂, maybe.

Added this text:

"No enhancement in I₂ levels was observed for any of the specimens tested (species unknown). Large brown kelp (*Laminaria*) were not observed at the site. These are the dominant iodine emitters at well-studied North Atlantic coastal sites (McFiggans et al. 2004, Saiz-Lopez et al. 2004, Jones et al. 2009)."

How do the fluxes assumed in the FLAT and PHOTO model simulations to match the observations compare to those assumed by other studies (eg, Jones et al., 2010, Mahajan et al., 2010, Carpenter et al., 2013, Grossman et al., 2013)? Maybe the fluxes

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from other studies could be added to figure 7 for easy comparison?

We added descriptions of fluxes from other studies as follows:

"Jones et al. 2010 found that a constant I₂ flux of at least 170 nmol m⁻² d⁻¹ would be required to achieve observed IO levels."

"For comparison, Mahajan et al. (2010) used a time-varying flux which peaked at 818 nmol m⁻² d⁻¹ and was zero at night to fit the same IO observations."

"In the HOI simulation, sea-air fluxes of both HOI and I₂ were prescribed without modification or optimization after Carpenter et al. (2013), where daytime fluxes were roughly 10 nmol I₂ m⁻² d⁻¹ and 100 nmol HOI m⁻² d⁻¹."

My major concern with the paper is about the daytime I₂ concentrations. The authors conclude in section 4.3 that these are likely artifacts. The reasoning is well explained and convincing, but I think that the way in which the data are presented in the abstract, on p. 25918-25919 and in figures 2, 3, 4 gives the reader the false impression that these concentrations might be real. I suggest the authors rephrase the abstract and the text on those pages and modify the figures to make it clearer that the daytime data are likely spurious. It is also confusing that the discussion of the model results (section 5 and figure 6) apparently attempts to explain the I₂ daytime observations. If they are indeed artifacts I don't think the lack of agreement with the model is an issue and therefore both the FLAT and the PHOTO models can be said to explain the measurements rather well (considering the variability in IO showed in the Mahajan et al, 2010 paper). If, instead, the authors believe they may be real then they should be more explicit about it and revise the text in section 4.3.

We appreciate the reviewer's concern about the daytime measurements. We spent a long time considering what they mean and how to represent them and are glad to get some feedback. We suspect that the cycle and absolute levels of I₂ measured during the day may be dominated by the artifact, but it's really impossible to say that

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a significant fraction of what was measured was not I₂. For this reason we don't fully discount the daytime I₂ data. We do hope it is useful to show these data, in part for the reason that at some point, someone will find out what causes the artifact and will have something to compare to.

In the abstract, we changed the text about the midday maximum from "at least partly due to a measurement artifact" to "probably caused by a measurement artifact". In the 2007 and 2009 Results sections, we now refer the reader to the discussion about the artifact: "See Section 4.3 regarding a daytime artifact." In Fig. 4, we now point out the covariance of the daytime blank and sample.

We rearranged the "positive artifact" subsection for clarity.

In figures 2 and 3, we modified the caption as follows:

"Open circles are daytime points which likely include a measurement artifact and should be considered upper limits."

The authors make an assumption that there are no atmospheric losses during the night (p. 25920): this assumption requires a justification. The authors should also explain why they think I₂ emissions are high during the first part of the night and negligible during the second part of the night (as stated on p. 25920).

We added the statement:

"The main loss of I₂ overnight is expected to be via NO₃ reaction, but DOAS observations have indicated that NO₃ mixing ratios are extremely low at this site (Mahajan et al. 2010)."

We removed the statement that the nighttime profile suggests a reduction in the latter half of the night- from the model runs it's clear that even a constant emission source can result in this profile, due to mixing. We now point this out in the modeling section.

SPECIFIC COMMENTS

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p. 25916: have the data been filtered for possible influences from the diesel generator?

All data presented are from onshore wind periods. As stated, in 2009 there was NO_x evidence for an influence by the generator, but the iodine observations were similar for the two years.

p. 25916: did you notice any significant difference wrt design, position and length of the inlet in the two studies?

The physical differences between the inlets are described in Section 2.3 and Figure 1. Sensitivity was slightly lower with the longer inlet, but the background signal was very low so this translated to only a small increase in the detection limit (which is reported in sections 3.1 and 3.2). The main difference we observed was the apparent effect on the blanks, as described in Section 4.3.

p. 25919, l. 11: it seems to me that in 2009 the concentrations were higher.

We changed the wording from "very similar" to 2007 to "slightly higher" than 2007.

p. 25920, l. 11: is 1000 m a reasonable assumption at Cape Verde?

The boundary layer height is quite variable. Added this text to the "Setting and ancillary observations" section:

"The planetary boundary layer at the site ranges from about 300 to 1500 m with no clear seasonal or diel pattern (Carpenter et al. 2011)." *—fig. 4: can you show also the 2009 campaign?*

We have now included a figure with these data from the 2009 campaign. *—fig. 6: a comment on the different shapes of calculated IO seems warranted.*

Added this text to the section about the FLAT model case:

"The modeled IO diel profile in this and the other cases shows prominent peaks around sunrise and sunset. These are an artifact resulting from the problem of treating highly

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photolyzable species in a model with discrete time steps.”

And this text to the section about the PHOTO case:

”The strong midday flux results in much higher midday IO levels.”

TECHNICAL CORRECTIONS

p. 25913, l. 14: check the syntax of this sentence. l. 15: add a reference

Changed ”20x” to ”20 times” to make syntax clearer. This was just a simple upscaling calculation we performed- nothing to reference. Added a ”therefore” to imply we inferred this ourselves.

p. 25914: subscript Ix and IOx Done.

p. 25915: I think Jones et al., used a 1D model

Right, corrected this.

p. 25924, l. 8: correct ”modification”

Corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 25911, 2013.