

Interactive comment on “Modelling molecular iodine emissions in a coastal marine environment: the link to new particle formation” by A. Saiz-Lopez et al.

A. Saiz-Lopez et al.

Received and published: 7 January 2006

We would like to thank the referees and Susanne Pechtl for their comments and suggestions, which have now been addressed and included in the final version of this paper.

Response to the referees:

Referee #1 (Roland von Glasow)

Specific comments:

p 5406/5407: This part has been re-worded to point out that most studies agree in the

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

relatively slow rate constant for the IO + DMS reaction.

p 5407, 2nd paragraph: A more appropriate reference to the iodine enrichment in particles has been included.

p 5407, line 17: The citation to Jimenez et al., has been amended and the work of Burkholder et al., (2004) included as a reference

p 5407, last paragraph: The sensitivity of the instrument and, therefore, the time resolution of the instrument does not allow measurements at the timescales at which photochemistry of the molecule occurs. Hence it might be reasonable to think of peak values larger than those reported here, because they are not captured at the time resolution of the DOAS.

p 5407, line 29: Garland and Curtis (1981) has been introduced as reference for a possible open ocean source of iodine.

Section 2, Model description: It has now been pointed out that none of the species are constrained in the model but are initialized and/or held constant at typical mixing ratios. The list of reactions and rate constants used in the model is that of McFiggans et al., 2000 with updates on recent data about the IO/OIO kinetics as reflected in Section 2. Initially, the model runs do not assume recycling of iodine from particles. However, sensitivity studies have been carried out including iodine recycling on aerosols via uptake of HOI and IONO₂. The first order rate of uptake is calculated with $\gamma = 1$ for both species giving a lifetime with respect to uptake in the range of 15-20 minutes, comparable to that in McFiggans et al., 2000. The assumption being that the rate limiting step in the recycle process is the uptake of both species and that once they are taken up they will be released as IBr and ICl. Based on this, the introduction of recycling in the model has no effect, as expected, in the model runs where we aim to see the evolution of gaseous iodine species from the emission point and after 5 minutes (figure 7). Likewise, the effect is null for the attempt to replicate the particle bursts on a low tide event with a transport time of 1 minute from the shore (Figures 8 and 10) to

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

the measurements point. These two effects are obviously assuming freshly generated sea salt aerosols, where no halogen processing is occurring at time zero. However, when running the model for 1 hour with iodine recycling, under the abovementioned assumption, the total number of ultrafine (diameter 3-10 nm) particles) is now 3 times greater. It is, without processing of HOI and IONO₂ N is 110 cm⁻³, assuming iodine processing and subsequent release of IBr and ICl the total number is about 300 cm⁻³, which still makes a contribution to the typical range of 100-500 cm⁻³ in clean coastal environment. Of course, in this scenario the role of the I₂O₂ dimer as condensable unit is crucial since any little IO formed as a consequence of IBr and ICl photolysis, when there is no I₂ around, will react with itself and contribute to the particle formation in the model. For instance, when the model is run without I₂O₂, the particle formation is less sensitive to iodine recycling in aerosols. These results have been included in the discussion section.

p. 5409, line 26: In this model the I₂O₂ molecule is considered to be a condensable unit and parameterized as a particle of smallest size in the nucleation code.

p.5411, line 8: This point has been amended and the NO₂ and NO₃ mixing ratios are typical for Mace Head under maritime air mass conditions.

p. 5411, line 12: In addition to O₃ entrainment, the model allows an air parcel, initially containing the iodine species, to evolve within an internal boundary layer depth given by the simple linear parameterization based on in-situ micro-meteorological measurements. The model is therefore a box model with dilution parameterized as rate of entrainment from the background air.

p. 5411, line 20-25: A reference for the micro-meteorological measurements has been included (Norton et al., 2005).

p. 5416, line 10 and p5417, line 4-6: The corresponding change from “O₃ depletion rate” to “Rate of O₃ depletion resulting from iodine-mediated photochemistry” has been made.

p.5417, line 18/19: the reference to the period of BCCRDS measurements has been rephrased in the text.

p.5418, line 20 and p. 5419, line26: the word “profile” has been substituted by “evolution with time”.

p.5418, line 7: The denuder tube measurements were made on September 2003, whereas the NAMBLEX campaign took place in 2002. However, the misleading word “campaign” has been deleted in the description of the denuder measurements of I2.

p.5418, line 17: New particle formation events were observed on most days with more or less intensity depending on conditions such as wind direction. However, on some days the low water period was not correlated with high solar irradiance. A tidal height curve has been superimposed onto Figure 5.

p. 5420, line 7: When the model is initialized with in-situ concentrations as stated in the paper and run for conditions shown in Figure 7, at the beginning the loss due to iodine chemistry ($I + O_3$) is 0.12 % s⁻¹ and decreases as the iodine is disappearing. This has now been added in the text.

p. 5420/5421, discussion of correlation of I2 with particle peaks: The typo on p. 5421, line 2 has been corrected. The possibility that the tide can be higher and still allow nucleation if it is arriving from certain sectors (i.e. the kelp beds extend further up the shore), this has been included in the text. Note that the high tide was still fairly low (see figure) and that it was a day of highly variable local meteorology, in particular in terms of wind direction.

p.5421, discussion of timescale for particle growth: According to our model the time required for particle to grow to sizes bigger than 4 nm is over 1 minute. This has been now included in this discussion section.

p. 5422, line 5: The internal boundary layer depth is derived from vertical mixing measurements at the site and the subsequent evolution of the boundary layer is assumed

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

to be linear based on these meteorological observations. However, we do not have measurements of how the vertical mixing developed 14 km inland, so we work on the abovementioned assumption.

p. 5422, line 16-22: The statement that iodine particles are “fully mixed vertically up to 1 km” has been changed in the text to make clear that this is how the model was set up.

p. 5422, line 16-22: In the model an upper limit to the first order loss rate of new particles due to intermodal coagulation is approximated as the first order loss rate of monomer units. Intermodal coagulation represents the integral of the coagulation kernel convolved with the number distribution for larger (measured) aerosol. The value we have chosen represents an upper limit to the loss rate since, as the freshly nucleated particles grow, their coagulation loss rate to the larger particles will only decrease below that for the monomer units. The reason for this treatment is that we use measured large mode aerosol for constraint, and the nucleation and growth description for the small aerosol does not interact with the measured aerosol. The coagulation to pre-existing aerosol does not greatly affect the result.

p. 5423, line 8-9: The contribution to CCN has now been changed in the text to “significant contribution to viable CN”.

Figures:

Fig 3: the suggested change has been made

Fig. 3, 6, 10: further explanation for $\Delta(t)$ has been included in caption for Fig 3, 6 and 10.

Fig 4: the denuder measurements were made in September 2003.

Fig 7: “O₃ depletion” has been changed to “O₃ mixing ratio”

Fig 9 and 10: the color code of the DMPS refers to $dN/d\log D_p$

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Fig. 11: the caption of this figure has been rephrased to make it clearer.

References:

Burkholder et al.: has been corrected

Typos:

Mössinger has been corrected

Ladstätter-Weißenmayer has been corrected

von Glasow has also been amended

Referee # 2

General comments:

The assumption made in this model that I₂O₂ participates as a condensable unit in the iodine particle nucleation is key for the reproduction of the particle formation at short timescales (e.g. about 1 minute). The sensitivity study carried out without including I₂O₂ in the particle nucleation shows a significant reduction in the particle formation at this timescale. Therefore, the results are sensitive to this assumption, showing that more work is needed to clarify the roles of I₂O₂, I₂O₃ and I₂O₄ in new particle formation.

Specific comments:

p. 5409, line 19: The particle nucleation treatment in this model is based on the assumption that once the gas phase iodine oxides species (I₂O₂, I₂O₃ and I₂O₄) are formed they completely undergo the formation of small particles. Evaporation is not expected to occur, and so is not treated in the model. This assumption is based on laboratory studies of iodine oxide particle growth kinetics (Saunders and Plane, 2005), which show that the growth of these particles through coagulation and condensation proceeds at the collision frequency, in accord with the model scheme employed for this

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

study. The material density of the small particles used here is 4 g cm^{-3} taken from Daehlie and Kjekshus, 1964.

An uptake loss for the different iodine species onto background aerosol was calculated based on aerosol measurements made during the campaign assuming γ as 1.

p. 5410, line 23: As has been pointed out in Section 4.2 the particle formation is sensitive to the rate of photodissociation of OIO, especially at shorter timescales. However, in this study this assumption is less sensitive since I₂O₂ is also considered a condensable unit and therefore the particle nucleation does not rely entirely on the participation of OIO.

p. 5411, lines 2-4: Please see response to Referee #1 on the Model description section.

p. 5411, line 9: The HO₂ mixing ratio is held constant during the model run time which for most of the case scenarios is about tens of seconds to minutes. The HO₂ value is taken to be representative of noon measurements of the radical during NAMBLEX.

p. 5413, section 3.3: The starch-iodine inclusion complex formation is very specific to molecular iodine and especially the size of the I₂ molecule. Therefore, the formation of similar inclusion complexes with other iodine compounds (e.g. IO, HOI) is not likely, although this possibility cannot completely be ruled out.

p. 5416, line 26: We estimated that a horizontal length of 160 m for the intertidal zone is covered with seaweeds under low tidal periods, particularly during spring tides. The “360 m” have been corrected by “320 m” in figure 3(b).

p.5418, line19: “particle mixing ratio” has been changed by “particle number density”.

p.5420, line 11: In one of the sensitivity studies we consider OIO to photodissociate to I + O₂ (Ashworth et al., 2002). Therefore, at high JOIO the formation of the IO dimer will be the dominant particle production channel and as we assume I₂O₂ as a condensable unit the rate of particle production at short timescales is larger for high JOIO.

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

p. 5421: For the results in Fig10a, the I2 emission will follow a Gaussian distribution resulting in different peak mixing ratios depending on the strength of the emission. In the x-axis the $\Delta(t)$ is in hours as opposed to Figs. 3b and 6 where it is in minutes. Further explanation on $\Delta(t)$ has been included in the caption of the different figures for clarity.

p. 5422, line 16: The figure of $2 \times 10^3 \text{ cm}^{-3}$ has been checked and seen to be incorrect. We thank the referees for pointing out this. The actual size-integrated particle number density after the model run under the conditions whose results are shown in Fig. 11 is 110 cm^{-3} .

p. 5424, line 33: this reference has been corrected

Figure 7: the right axis has been changed

Figure 9: the sunset time will be included in the caption.

Figure 5, 9 and 10b: reference to the color coded bar will be made in the caption for consistency with other figures.

Response to interactive comment by S. Pechtl:

p. 5409, line 12: We assume that the iodine condensing gases are non-volatile and every I₂O_x (x = 2, 3 and 4) formed is treated as a thermodynamically stable unit of the smallest size. Then, the used semi-implicit subroutine calculates the coagulation kernel for each possible collision pair, starting with the Brownian coagulation rate for the transition regime taken from Jacobson (1999, page 446, equation 16.28), after Fuchs (1964). This follows assuming that the convective Brownian diffusion enhancement (page 446, 16.30), turbulent inertia (page 447, 16.35), turbulent shear (page 447, 16.36) and gravitational collection (page 447, 16.32) do not contribute significantly at the size range in question (roughly 1 nm to 2-3 microns). The model also allows condensation of IO and OIO onto newly formed iodine particles. Condensation of H₂O, H₂SO₄ and organic vapors is not considered in this modeling study.

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

p. 5411, line 6-9: this point will be rephrased in the text to avoid confusion with “all iodine-containing species”.

p. 5416, line 1: In the box model runs we prescribe I2 mixing ratios so that the Gaussian distribution peak corresponds to measured mixing ratios either by DOAS or by in-situ techniques depending upon whether we test spatially distributed or hot-spot case scenarios. In the entraining box approach the model is initialized with a mixing ratio based on in-situ observations made during the same campaign by BBCRDS.

P 5416, lines 10-14: The initial conditions in the model are the same in Fig. 3b as in Fig. 6. Both show a similar trend of IO with respect to I2: the IO mixing ratio decays less rapidly than I2 because the rate of the IO self reaction (being its main sink) varies as $[IO]^2$.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 5405, 2005.

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)