Authors' response to the review by R. Von Glasow

The authors would first like to thank Roland Von Glasow for his thoughtful review and helpful comments on our paper. We address his comments here and provide information on how we have integrated these recommendations into the final version of our paper.

Parella et al present very interesting results of the inclusion of bromine chemistry in two global CTMs with a strong focus on results from GEOS-CHEM. The manuscript is well written and shows very interesting results of the impact of bromine chemistry on global ozone and OH concentrations as well as mercury cycling. The impact of bromine chemistry on mercury concentrations is discussed as well and runs without anthropogenic emissions are included in the discussion. I suggest publishing the manuscript after minor modifications have been made.

Specific comments

With a study like this there will always be some shortcomings and most of them are discussed in the manuscript but I think that a few need a bit more thorough discussion.

(i) Polar bromine explosion: It is surprising that p-TOMCAT requires the inclusion of a polar source to reproduce the satellite columns but GEOS-CHEM doesn't. This indicates that the required simplified inclusion of bromine chemistry in global models still has quite significant uncertainties. Some of these might also be "hidden" by the presentation of large scale averages. Please discuss this more.

This has been addressed in the text by (1) clarifying how both models capture the polar springtime maximum in the satellite and (2) stressing that the processes underlying bromine explosions are highly uncertain and that our models contain representations of polar chemistry that are likely oversimplified.

The 4th paragraph in Section 4 of the paper now reads as (with new text highlighted in red):

> A major feature in the BrO observations of (Theys et al., 2011) is the strong Arctic

spring maximum. This is reproduced by both GEOS-Chem and p-TOMCAT but for different reasons. In GEOS-Chem it is due mainly to fast HBr+HOBr recycling (R30) (γ_{HOBr} = 0.2 in GEOS-Chem compared to γ_{HOBr} = 0.02 in p-TOMCAT for aqueous aerosol), with no springtime emissions of Br_y from sea ice. The spring shift in GEOS-Chem (relative to the winter maximum at northern mid-latitudes) is due to the need for some insolation to drive HOBr production. p-TOMCAT simulates a spring maximum with slower HBr+HOBr recycling by including a blowing-snow source for Br_y (Yang et al., 2008, 2010). The Arctic column amounts in GEOS-Chem are dominated by the free troposphere, while those in p-TOMCAT have a large boundary layer contribution. In-situ observations of BrO during the ARCTAS aircraft campaign over Alaska in April 2008 found significant mixing ratios in the free troposphere, with a mean of ~2 pmol/mol (Salawitch et al., 2010). In comparison, GEOS-Chem simulates a 9-17 LT mean of 1.3 pmol/mol BrO for the Arctic free troposphere in April. Both models likely oversimplify photochemistry in polar spring, as local emissions of Br_y and the extent of heterogeneous recycling remain poorly constrained (Simpson et al., 2007).

(ii) Release of bromine from sea salt: The use of the assumption that 50 % of bromide gets released is a simplification of a rather complicated multiphase reaction cycle which should probably be acknowledged more. Release of bromine form sea salt is acidity dependent and hence one would expect latitudinal differences and also differences in modern versus pre-industrial conditions. Details of this will require a much more thorough examination which is beyond the scope of this paper but these shortcomings should be acknowledged and this caveat discussed when the pre-industrial runs are presented. Arguably anthropogenic emissions have increased the fraction of bromine

depletion from sea salt which cannot be captured with the "50% release" assumption so the bromine chemistry in pre-industrial times might have been different from what is presented here.

We address these comments in two ways: (1) We stress that our sea salt bromine emission scheme is a simplified parameterization for the underlying multiphase chemistry that releases Br– from the aqueous phase; (2) We acknowledge that changes in particle acidity between preindustrial and present may introduce error in our preindustrial sea salt bromine emissions. The 1st point is clarified in paragraph 1 of Section 2.1 in our paper. The 2nd point is clarified in paragraph 1 of Section 6.

Paragraph 1 of Section 2.1 now reads as (new text highlighted in red):

> Tropospheric Br_y is produced in the model by debromination of sea salt aerosol (SSA), photolysis of $CHBr_3$, and oxidation of $CHBr_3$, CH_2Br_2, and CH_3Br by OH (Table 1). SSA observations indicate typically a 50% loss of bromide (Br^-) relative to seawater composition, implying release to the atmosphere as Br_y (R. Sander et al., 2003). This release may take place by a set of complicated multiphase reactions producing Br_2, BrCl, or HOBr (Vogt et al., 1996; R. Sander et al., 1999, 2003), all of which rapidly photolyze to release BrO_x radicals. Our simplified treatment of SSA debromination follows the Yang et al. (2005) observation-based parameterization of Br^- depletion factors relative to seawater for particles in the 1-10 μm diameter range. These depletion factors are applied to the size-dependent SSA source function in GEOS-Chem (Alexander et al., 2005). Uncertainties in modeled debromination are introduced by the parameterization of bromide depletion (R. Sander et al., 2003) as well as the factor of 4 uncertainty in sea salt aerosol sources (Lewis and Schwartz, 2004). The resulting Br_y is released as Br_2 uniformly

> through the depth of the marine boundary layer (MBL) diagnosed from the GEOS-5 meteorological data. Though SSA debromination is the largest source of tropospheric Br_y in GEOS-Chem, removal by deposition in the MBL is fast. We find that this source contributes 48% of Br_y in the global free troposphere, the rest originating from bromocarbons.

Paragraph 1 of Section 6 now reads as (new text highlighted in red):

> A long-standing problem in global modeling of tropospheric ozone has been the inability of models to reproduce the very low ozone concentrations measured in surface air worldwide at the turn of the 20th century (Y. Wang and Jacob, 1998; Mickley et al., 2001; Shindell et al., 2003; Lamarque et al., 2005; Horowitz, 2006). Calibration of these older measurements is controversial (Marenco et al., 1994) but the Montsouris (Paris) measurements are considered reliable (Volz and Kley, 1988). To examine the potential for bromine chemistry to address this discrepancy we conducted a GEOS-Chem sensitivity simulation for the pre-industrial atmosphere removing all anthropogenic sources (including NO_x from fertilizer use), and reducing methane from 1700 nmol/mol to 700 nmol/mol. We decreased biomass burning to 10% of its present value (Y. Wang and Jacob, 1998), though this has little impact on our results. Bromine sources were held to present-day estimates, except for CH_3Br and the stratospheric boundary condition. We used 5 pmol/mol $CHBr_3$ in surface air worldwide based on ice core records (Saltzman et al., 2004). Concentrations of stratospheric Br_y species were scaled from a total of 22 pmol/mol to 12 pmol/mol Br_y (Liang et al., 2010; Montzka et al., 2011). Sea salt debromination rates may have increased between the

> preindustrial and present-day due to enhanced particle acidity from anthropogenic emissions (R. Sander et al., 2003) but this effect is not considered here.

(iii) Heterogeneous/multiphase reactions: This paper showed again that the multiphase cycling of bromine is key to maintain realistic (as compared to satellite columns) BrO mixing ratios but it should be acknowledged that the lumped treatment of R29 and R30 is a great simplification and that these reactions are in fact not occurring as listed but involve multiple steps.

It is not clear what is meant by “multiple steps”. We have acknowledged that our treatment is oversimplified and highlight the following reasons in the text:

1. Limited information on how the kinetics of (R29) and (R30) change with aerosol composition;
2. Our HBr+HOBr reaction assumes that the non-limiting gas is at equilibrium with the aerosol phase.

The 1st point is clarified in the first paragraph of Section 2.2 (page 9673, l. 4-23) (new text highlighted in red):

> Table 2 lists…
>
> $$k = \left(\frac{a}{D} + \frac{4}{v\gamma} \right)^{-1} A \qquad (1)$$
>
> Here D is the molecular diffusion coefficient in air, v is the mean molecular speed of the gas, and A is the aerosol surface area concentration per unit volume of air (cm^2/cm^3) (Schwartz, 1986; Jacob, 2000). GEOS-Chem simulates explicitly the mass concentrations of different aerosol types, and we integrate k over the prescribed relative humidity-dependent size distributions as described by Martin et al. (2002). Reactive uptake probabilities for both (R29) and (R30) are based on existing laboratory evidence (Table 2d) but with limited information on the sensitivity to temperature and aerosol composition. For $BrNO_3$ hydrolysis (R29)

> on liquid cloud droplets, the cloud surface area concentration A is calculated from GEOS-5 liquid water content data, assuming effective droplet radii of 10 μm and 6 μm for marine and continental clouds respectively (Park et al., 2004; Fu et al., 2008). For HBr+HOBr (R30) on ice cloud surfaces, we use $A = 2\text{x}10^{-4} I^{0.9}$ cm^2/cm^3 (Lawrence and Crutzen, 1998) applied to the local ice water content I (cm^3/cm^3) from the GEOS-5 data.

We also note that the 1st point is stressed in the final 3 sentences of paragraph 2 in our Conclusions (page 9687, l. 7-12). We left this in the text as it was presented previously.

> … Laboratory studies provide ample evidence for the HOBr+HBr reaction but offer limited quantitative information to constrain models. The reactive uptake probability approach used here (γ=0.2 for sulfate and sea-salt aerosols, γ=0.1 for ice crystals) is probably too simplistic. There is a need to better characterize this reaction over a range of aerosol types and temperatures relevant to the troposphere.

We highlight the 2nd point in the last sentence of paragraph 2, Section 2.2 (page 9674, l. 12) (new text highlighted in red):

> … Based on this ensemble of evidence and the recommendation of S. Sander et al. (2010), we assume that (R30) proceeds with γ = 0.2 for sulfate and sea salt aerosol (presumed aqueous) and γ = 0.1 for ice surfaces, where γ is applied to the locally limiting reactant. This simplified approach assumes that the non-limiting gas is at equilibrium with the aerosol phase.

(iv) Comparison with data: Only satellite observations are considered for comparisons, which is to some extent understandable for a global model study. Nevertheless, the long-term data from Cape Verde (Read et al., Nature, 2008; Mahajan et al., ACP, 2010, see their supplement) provide quite good coverage over 8 months and show large variability. This data set is not even mentioned in the current manuscript which should be improved. How does GEOS-CHEM fare in the tropical North Atlantic?

This comparison is currently being prepared for publication by D. Stone, M. J. Evans et al. We acknowledge this and cite their paper now in the first paragraph of Section 3.

p. 9675, l. 15 – 17 (new text highlighted in red):

> Figure 3 shows the global annual mean budget and cycling of tropospheric Bry in our simulation. The BrO mxing ratio is 0.32 pmol mol−1, which implies a daytime mean of 0.64 pmol mol−1 since nighttime concentrations are near zero. This is at the low end of the oft-cited (but poorly constrained) 0.5 – 2 pmol mol−1 range in the observations; more detailed comparison with satellite observations will be presented in Sect. 4, and comparison against ground-based BrO observations taken at Cape Verde will be presented by Stone et al. (in prep.). The global mean Bry mixing ratio is 3.2 pmol mol−1, with HBr and HOBr as the principal reservoirs accounting respectively for 34% and 28% of total Bry. Bry has a lifetime of 7 days against deposition, with HBr accounting for 55% of that sink and HOBr for 40%. Chemical lifetimes are short relative to deposition; that of HBr (the longest-lived reservoir) is only 6 hours. Thus the BrOx radical concentrations are effectively maintained by chemical recycling from non-radical reservoirs.

(v) GEOS-CHEM vs. GOME-2: GEOS-CHEM underestimates the satellite columns by about 30%. You wrote that this is within the error margin but it could also indicate that the sources of reactive bromine are stronger or lifetimes longer than assumed/calculated in the model. This is especially interesting in the light of the study by Hossaini et al (ACP, 2010) who presented detailed breakdown schemes for $CHBr_3$ *and* CH_2Br_2*. Their work suggested that the effective yield of bromine atoms is less than the maximum yield as assumed in this manuscript which would reduce the modelled bromine source.*

We have changed our wording in the 3rd paragraph of Section 4 (p. 9677, line 20 to the end of paragraph) to address that the simulated low-bias in BrO could reflect an underestimate in either emissions or heterogeneous recycling of Br_y (new text highlighted in red):

> The standard GEOS-Chem simulation underestimates the GOME-2 observations by 30% on a global mean basis, excluding the poles (40% including the air mass factor correction). This is marginally significant considering the observation error but might indicate a low bias in the simulated emissions or heterogeneous recycling of Br_y. The observations show a positive BrO gradient with increasing latitude that is well reproduced in GEOS-Chem contingent on the (R30) HBr+HOBr reaction.

We now cite Hossaini et al. (2010) on page 9671, following line 9. Their simulation results indicate that the assumption of direct production of Br from $CHBr_3$ and CH_2Br_2 photochemical loss is reasonable.

Technical Comments:

p. 9670, l. 22: These uncertainties should be discussed in more detail, here or in section 3, see above.

We highlight uncertainties in parameterizing sea salt debromination. We also note the factor of 4 uncertainty associated with state of the knowledge sea salt source function. These changes are made in the first paragraph of Section 2.1 (p. 9670), as shown above.

p. 9673, l. 24ff: See discussion above. Please add more discussion about the simplifications.

We now discuss the simplification used for HOBr+HBr, which assumes that the non-limiting gas is saturated at the aerosol surface. We also make note of the limited information available on the dependence of the reactive uptake coefficients on temperature and aerosol composition.

p. 9675, l. 14: When referring to mol mol−1 please use the correct term "mixing ratio" rather than "concentration". Please correct here and all other occurrences in the manuscript.

We have made this change.

p. 9677, l. 7: Why do you use an asymmetric time window around the satellite over pass time?
There is no reason. However, we ran sensitivities to the time window for model averaging, with one as large as 9AM – 5PM model means. This showed little difference from the results we present.

p. 9678, l. 16-26: Are these sensitivity studies specific for the tropics? If not, please consider moving to the related discussion on p. 9677, l. 20-25.
We took this recommendation as suggested.

p. 9680, l. 9-10: I can't read from figure 3 that HOBr sinks drive ozone loss, please explain.
We have clarified our explanation here. Also, we explain why the HOBr production and loss is the dominant Br-driven ozone loss mechanism globally instead of the BrO+BrO self-reaction, which is important in polar spring condition.

Page 9680, paragraph beginning with lines 9–16 (new text highlighted in red)

> A common step in all three mechanisms is the formation of HOBr. Loss of HOBr is either by photolysis or by reaction with HBr (Figure 3), and both of these sinks drive catalytic ozone loss (Mechanisms 1 and 3). Thus Br-catalyzed ozone loss is limited by the rate of HOBr production. This is in contrast to the polar springtime boundary layer, where the BrO+BrO self-reaction is the dominant catalytic ozone sink due to very high BrO concentrations. We see from Figure 3 that the self-reaction of BrO is 50 times slower than the reaction with HO_2 on the global scale. The BrO+HO_2 reaction (R14) accounts for 95% of global tropospheric HOBr production, while $BrNO_3$ hydrolysis accounts for the rest. Since 92% of HOBr is photolyzed, Mechanism 1 is responsible for about 90% of Br-catalyzed ozone loss. However, Mechanism 2 has the important secondary effect of providing a sink for

> NO_x and thus slowing down ozone production.

p. 9684, l. 4-5: It might be worth to highlight this result a bit more and add that this is an effect of about 20%.

We have now added the % change to help highlight the result and put it in better context.

p. 9685, eq (2): I couldn't quite follow the derivation of this expression, please explain.

This expression can be derived by assuming steady state for HgBr and solving for the lifetime [Hg(0)]/L(Hg(0)), where L is the loss rate. This was done by Holmes et al. (2006), and we followed his approach. We add a clarification that the derivation is from steady state. Holmes et al. (2006) is cited.

Page 9685, lines 5 – 9 (new text highlighted in red):

> The lifetime τ of Hg(0) against oxidation to Hg(II) by Reactions (R31)–(R33) can be expressed assuming HgBr steady state by (Holmes et al., 2006):
>
> $$\tau = \frac{k_{32} + k_{33,Br}[Br] + k_{33,OH}[OH]}{k_{31}[Br][M]\left(k_{33,Br}[Br] + k_{33,OH}[OH]\right)}, \quad (2)$$
>
> where we have assumed that X in Reaction (R33) can be either Br or OH, following Holmes et al. (2006, 2010).

p. 9685, l. 24 – p. 9686, l. 4: This is a very interesting result but please highlight the uncertainties with your "pre-industrial" runs somewhat as the bromine release from sea salt could be significantly different, see above.
We addressed these uncertainties in Sections 2.1 and 6 as shown and discussed above. Additionally, we have added a new paragraph at the end of Section 7 to highlight the sea salt debromination uncertainties as well as other caveats with heterogeneous chemistry and Hg(0) oxidation:

Page 9686, new paragraph between lines 21 and 22 (new text highlighted in red):

> Our work highlights a potentially important link between ozone trends and the lifetime of Hg(0) through partitioning of the Br_y family. Our result is contingent on Br playing a dominant role in Hg(0) oxidation. Changes in sea salt debromination between the preindustrial and present as well as our simplified treatment of heterogeneous bromine chemistry represent additional uncertainties that are potentially important in our Hg(0) lifetime estimates.

p. 9688, l. 6-9: Again, very interesting but please mention the uncertainties/caveats.

We have included this comment in our paper. Page 9688, lines 6 – 9 (new text highlighted in red):

> Because the effect of bromine chemistry on ozone is similar in the present-day and pre-industrial atmospheres, we find that the global radiative forcing from anthropogenic tropospheric ozone is negligibly affected. However, the impact on radiative forcing may be sensitive to changes in sea salt debromination and assumptions about heterogeneous chemistry that require further investigation.

p. 9697: The Saiz-Lopez paper is now in ACP

We have adjusted this in our paper.

p. 9697/8: JPL evaluation 17 was published in 2011, not in 2010

We have adjusted this in our paper.

p. 9711, caption: What do you mean by "all species are in steady state" On what time scales is this the case? Daily? Day vs night? Seasonally? Please explain.

By steady state we meant that the production rates balance the loss rates. We believe that our original wording gave the impression that we had imposed a steady-state assumption to make calculations in the figure; this is not the case. The reaction rates and budgets were calculated on-line from the model, during our full simulations. We have adjusted the text to clarify.

Page 9711, caption (removed text is crossed out):

> Figure 3. Global annual mean budget of tropospheric inorganic bromine (Br_y) in GEOS-Chem. The main reactions are indicated. Inventories are given as masses (Gg Br), with mixing ratios (pmol mol–1) in brackets. Rates are given in units of Gg Br s-1. Read 6.3(-5) as 6.3x10-5. ~~All species are in steady state;~~ HBr accounts for 55% of Bry loss by deposition~~, which closes the HBr budget~~. Sea-salt aerosol debromination is the dominant global source of Bry but is mainly confined to the marine boundary layer where Bry has a short lifetime against deposition. It accounts for 48% of the Bry source in the global free troposphere.