Atmos. Chem. Phys. Discuss., 3, S1641–S1643, 2003
www.atmos-chem-phys.org/acpd/3/S1641/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "A box model study on photochemical interactions between VOCs and reactive halogen species in the marine boundary layer" *by* K. Toyota, et al.

R. von Glasow (Referee)

roland@fiji.ucsd.edu

Received and published: 1 October 2003

General comments

The work by Toyota et al is well thought-through study to show links between gaseous and particulate emissions from the oceans and their interactions in the atmosphere. It is a significant contribution to this field and I encourage to publish it after a few modifications.

Toyota et al estimated based on the available literature reactions of halogen compounds (chlorine and bromine) with organic compounds and studied the interaction of these groups of species with a box model of the marine boundary layer (MBL).

They found that halogens play only a minor role in the photochemical loss of alkenes and aldehyeds (shown for C_2H_2, C_3H_6, HCHO and CH_3CHO). On the other hand, the stable organic halogen products might tie up 10-20% or even more of the sum of inorganic halogens thereby reducing effects of halogens on O_3 destruction and DMS oxidation. Different emission rates for alkenes and acetaldehyde from the ocean lead to very different ratios of particulate to organic to inorganic bromine.

Specific comments

1) The description of the development of the chemical mechanism in chapter 3 is too detailed. This should be abbreviated and/or moved to a supplement. Could sections 3.2 and 3.3 be combined as "Alkene degradation"? Furthermore the description of the results in section 5 is quite lengthy, that should be shortened as well.

2) What about the production of organic halogen containing nitrates? In the text I found only PBrAN - are other nitrates not of importance due to low NO concentrations?

3) Previous work (e.g. Vogt et al, 1996, von Glasow et al 2000a) showed that the cycling of inorganic halogens on sulfate aerosol is very important due to the significantly higher acidity of these particles. Toyota et al only consider sea salt aerosol and might therefore underestimate the recycling of halogen species. Did you do model runs in which you included sulfate aerosols as well? This might change the organic - inorganic fractionation of halogens as well. It would especially reduce the fraction of bromine in HBr because that would be rapidly cycled in sulfate aerosols - this might change some of the conclusions of section 5.2 (p. 4582-4583).

4) Section 5.6, also at the end of the abstract: According to table 8 the contribution of Br- + PAA is only about 1% of the total halogen activation during day and about 10% during night (when the activation is about 10% of the daytime values) - why do you say that peroxyacetic acid is "one of the important agents" for triggering halogen release? Maybe you should rephrase that to : "unimportant during daytime and of minor importance during nighttime ".

ACPD

3, S1641–S1643, 2003

5) Toyota et al only used one prescribed size distribution of sea salt aerosol. Are there differences in the overall results for smaller windspeeds (i.e. less total bromine available) or higher windspeeds (i.e. more total bromine available)? Also: would the conclusion change if other "background" chemial conditions (O_3, NO_x, summer-winter) are used? A few more selected sensitivity runs that explore this would be helpful.

Technical comments

p. 4552 line 20: maybe you want to add the recent review by Sander et al, Inorganic bromine in the marine boundary layer: a critical review, ACP, 3, 1301-1336

p. 4556, line 9: hydration constant or Henry constant?

p. 4556, line 18/19: meaning unclear

p. 4560: check the stochiometry of oxygen in reaction 21

p. 4567, line 14: use complete citation for MCM

p. 4587, line 28: "more" instead of "less"?

p. 4596, line 5: drop "halogen" once

Tables:

Table 3 states that runs 1h and 1i are with [C_2H_2]=200pmol/mol what is the base value? Did you only change the initial mixing ratio or only the emission flux? Also: what are the initial mixing ratios for compounds other than those listed on p. 4578

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 4549, 2003.