

Comments on Cao et al. manuscript titled 'Numerical Analysis of the role of snowpack in the ozone depletion events during the Arctic spring'

Comments in general:

This manuscript by Cao et al., certainly attempts to prove snowpack acting as a major source of reactive bromine during the ozone depletion events, by using a box model. A large number of model sensitivity experiments has been performed, with great effort made on model results interpretation. Some model experiments are very interesting/indicative, for example the one shown in Figure 7 (with snow depth set to 5cm). However, I found the manuscript contains many faults, particularly in the model setup regarding to snowpack chemistry (see below for detail). Since some are fatal making their conclusions unconvincing, therefore I reject the current manuscript publishing in ACP.

Fatal problem 1:

According to the table 4 in the manuscript, the initial ozone concentration for interstitial air of snowpack was set to 40 ppbv (from surface down to 35 cm below). This simple assumption triggers all the problems and makes 'standard scenario' results and conclusions unbelievable. As we know, to keep 'bromine explosion mechanism' going on (through $\text{HOBr}(\text{g}) + \text{Br}^-$ reaction on surface of snow grain to produce Br_2), a certain level of ozone is needed (even only a few ppbv of ozone). If ozone concentration in the interstitial air is zero, the net release of bromine from snowpack will stop as reflected in the experiment shown in Figure 7. Since the vertical mixing of species within the snowpack is getting more difficulty when getting deeper, the initialized amount of ozone at a deeper layer will not be consumed completely by reacting with atomic bromine (no other physical removing mechanism applied in the model). Then the non-zero ozone at a certain depth will serve as a driving or seeding source for the 'bromine explosion', even above boundary layer (BL) ozone is already completely depleted. This is the a fatal problem in the whole bromine chemistry of this study. How to photochemically maintain an ozone level of e.g. 30-40 ppbv in snowpack where photons are pretty low? How to physically keep interstitial air ozone unaffected by above surface ozone where the ozone is zero for >10 days (as shown in Figure 2)?

Though the 'standard scenario' result is questionable, the figure 7 result is very interesting and worthy further investigation. Here I suggest two experiments for Cao et al. to test: (1) initialising ozone concentration to zero within the snowpack; (2) same as (1) but allowing vertical mixing of ozone between BL and interstitial air (same as treating with HOBr).

Fatal problem2:

It is very strange to me that author and co-authors applied a VOLUME fraction of liquid-like layer (LLL) (=0.2%) to the total liquid layer surface of snowpack in estimating the heterogeneous reaction rate of HOBr and HBr. In section 2.1.2 (line 22 of page 11), it reads: 'As a result, the term of $A_{\text{LLL},i}/V$ can be written as $(0.002XA_{\text{L},i})/V$ ', where $A_{\text{L},i}$ is total surface area provided by the snowpack (see lines 31-32 of page 6). What is the physical base of doing that conversion? By doing this, it means only 0.2% of the total liquid layer surface area is involved in the heterogeneous reaction (with 99.8% liquid surface area untouched by gaseous molecules?). The heterogeneous reaction rate seems being underestimated by about 500 times. This is another fatal problem of this study. May be I missed something here, but unlikely.

Minor comments:

The discussions shown in figure 3 and figures 8-10 are all based on model day 3 result. But Figure 2 shows modelled ozone and Br_2 fields are never reaching a steady state during the whole 14 days integration. Thus, the conclusions made based this specific day are not robust.

Equation 1 misses subscripts of i, j and t for factors.