Supplementary online material

Seasonal impact of biogenic VSL bromine on the evolution of mid-latitude lowermost stratospheric ozone during the 21st century

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Table S1. Heterogeneous reactions on ice-crystals and sulphate aerosols involving halogens in CAM-Chem.

| Reactions | Comments |
|-----------|----------|
| **Ice-crystal** | |
| Het1 | $N_2O_2 + H_2O \rightarrow 2HNO_3$ |
| Het2 | $ClONO_2 + H_2O \rightarrow HOCl + HNO_3$ |
| Het3 | $BrONO_2 + H_2O \rightarrow HOBr + HNO_3$ |
| Het4 | $ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$ |
| Het5 | $HOCl + HCl \rightarrow Cl_2 + H_2O$ |
| Het6 | $HOBr + HCl \rightarrow BrCl + H_2O$ |
| **Sulfate aerosol reactions** | |
| Het7 | $N_2O_2 + H_2O \rightarrow 2HNO_3$ |
| Het8 | $ClONO_2 + H_2O \rightarrow HOCl + HNO_3$ |
| Het9 | $BrONO_2 + H_2O \rightarrow HOBr + HNO_3$ |
| Het10 | $ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$ |
| Het11 | $HOCl + HCl \rightarrow Cl_2 + H_2O$ |
| Het12 | $HOBr + HCl \rightarrow BrCl + H_2O$ |

* As in Table A4 from Auxiliary Material in Kinnison et al. (2007).

For a complete list of heterogeneous reactions implemented in CAM-Chem see Table 4 in the Supplementary Material of Ordoñez et al. (2012).
Table S2. Odd oxygen (Ox) loss rates reactions grouped by family cycles

| Family | Reaction                              | \(\Delta O_x\) | Odd oxygen loss$^\dagger$                      |
|--------|---------------------------------------|----------------|-----------------------------------------------|
| Ox     | \(O + O_3 \rightarrow 2\times O_2\)  | -2             | \(\text{Ox}^-\text{Loss} = 2\times R_{O+O_3} + R_{OID+H_2O}\) |
|        | \(O(1D) + H_2O \rightarrow 2\times OH\) | -1             |                                               |
| HOx    | \(HO_2 + O \rightarrow OH + O_2\)   | -2$^f$         | \(\text{HOx}^-\text{Loss} = 2\times (R_{HO_2+O} + R_{HO_2+O_3})\) |
|        | \(HO_2 + O_3 \rightarrow OH + 2\times O_2\) | -2$^f$         |                                               |
| NOx    | \(NO_2 + O \rightarrow NO + O_2\)   | -2             | \(\text{NOx}^-\text{Loss} = 2\times (R_{NO_2+O} + J_{NO_3})\) |
|        | \(NO_3 + h\nu \rightarrow NO + O_2\) | -2             |                                               |
| Halog  | \(ClO + O \rightarrow Cl + O_2\)    | -2             | \(\text{ClOx}^-\text{Loss} = 2\times (R_{ClO+O} + J_{Cl_2O_2} + R_{ClO+ClO^a} + R_{ClO+ClO^b} + R_{ClO+H_2O})\) |
|        | \(Cl_2O_2 + h\nu \rightarrow 2\times Cl + O_2\) | -2             |                                               |
|        | \(ClO + ClO \rightarrow Cl_2 + O_2\) | -2             |                                               |
|        | \(ClO + ClO \rightarrow Cl + OCIO\)  | -2             |                                               |
|        | \(ClO + HO_2 \rightarrow HOCl + O_2\) | -2$^e$         |                                               |
|        | \(BrO + O \rightarrow Br + O_2\)    | -2             | \(\text{BrOx}^-\text{Loss} = 2\times (R_{BrO+O} + R_{BrO+BrO} + R_{BrO+H_2O})\) |
|        | \(BrO + BrO \rightarrow 2\times Br + O_2\) | -2             |                                               |
|        | \(BrO + HO_2 \rightarrow HOBr + O_2\) | -2$^e$         |                                               |
|        | \(BrO + ClO \rightarrow Br + Cl + O_2\) | -2             | \(\text{ClOBrOx}^-\text{Loss} = 2\times (R_{BrO+ClO^b} + R_{BrO+ClO^c})\) |
|        | \(BrO + ClO \rightarrow BrCl + O_2\)  | -2             |                                               |

\(O_x = O(3P) + O(1D) + O_3 + NO_2 + 2\times NO_3 + HNO_3 + HO_2NO_2 + 2\times N_2O_5 + ClO + 2\times Cl_2O_2 + 2\times OCIO + 2\times CLONO_2 + BrO + 2\times BrONO_2\)
$R_{A+B}$ is the reaction rate for reaction $A+B\rightarrow$products and $J_C$ is the photodissociation rate constant (i.e. photolysis $\times$ concentration) for $C+hv\rightarrow$products. Units are molec.cm$^{-3}$s$^{-1}$.

1HO$_x$ loss cycles represent a net change $2O_3\rightarrow 3O_2$ ($\Delta O_x = -2$) due to reactions $OH + O \rightarrow H + O_2$ and $OH + O_3 \rightarrow HO_2 + O_2$. As $O_x$ reactions with OH are faster than with HO$_2$, only the rate determining steps (RDS) have been considered multiplied by two.

4Reactions $XO + HO_2 \rightarrow HOX + O_2$, with $X = Cl$ or Br, have been computed for each family with $\Delta O_x = -2$ because the photolysis of HOX produces an additional $O_x$ loss by the OH radical (i.e. $OH + O_3 \rightarrow HO_2 + O_2$). As these $XO + HO_2$ reaction are the rate limiting step, their loss rates have been multiplied by two.
Figure S1: As Fig. 2 but for the end of the 21st century period.
Figure S2: Annual zonal mean Temperature (K) for the present-day period. The lower solid white line indicates the location of the tropopause (chemical definition of 150 ppb ozone level from run$^{14}$ experiments).
Figure S3: Seasonal zonal mean distribution of the heterogeneous reactivation of ClONO$_2$ (Het2,4) and HOCl (Het5) on ice-crystal during the present-day period. The reactions have been specified in table S1 with the label Het and the corresponding number.
Figure S4: Annual zonal mean distribution of the heterogeneous reactivation of BrONO₂ (Het9) and HOBr (Het12) on sulphate aerosols for the run⁺LL+VSL (a) and run⁺LL (b) experiments during the present-day period. The reactions have been specified in table S1 with the label Het and the corresponding number.
Figure S5: Zonal mean distributions of the seasonal $\Delta O_3(z)$ trends (% dec$^{-1}$) over the century. The masked regions in the left panels indicate where of seasonal relative $\Delta O_3(z)$ between the present-day and the end of the 21st century periods are statistically significant at the 95% confidence interval using a two-tailed Student’s $t$ test.
Figure S6: As Fig. 8 but for the lowermost stratosphere (120 hPa) at northern hemisphere mid-latitudes (NH-ML).
Figure S7: As Fig. 8 but for the lower stratosphere (50 hPa) at tropics.
Figure S8: As Fig. 9 but for the lowermost stratosphere (120 hPa) at northern hemisphere mid-latitudes (NH-ML).
Figure S9: As Fig. 9 but for the lower stratosphere (50 hPa) at tropics.

References

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