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	ΔO_x	Odd oxygen loss[§]
O_x	$O + O_3 \rightarrow 2\times O_2$	−2	$Ox_{-Loss} = 2\times R_{O+O3} + R_{O1D+H2O}$
	$O(1D) + H_2O \rightarrow 2\times OH$	−1	
HO_x	$HO_2 + O \rightarrow OH + O_2$	−2[†]	$HOx_{-Loss} = 2\times(R_{HO2+O} + R_{HO2+O3})$
	$HO_2 + O_3 \rightarrow OH + 2\times O_2$	−2[†]	
NO_x	$NO_2 + O \rightarrow NO + O_2$	−2	$NOx_{-Loss} = 2\times(R_{NO2+O} + J_{NO3})$
	$NO_3 + h\nu \rightarrow NO + O_2$	−2	
Halog	$ClO + O \rightarrow Cl + O_2$	−2	$ClOx_{-Loss} = 2\times(R_{ClO+O} + J_{CL2O2} + R_{ClO+ClO}{}^{a} + R_{ClO+ClO}{}^{b} + R_{ClO+HO2})$
	$Cl_2O_2 + h\nu \rightarrow 2\times Cl + O_2$	−2	
	$ClO + ClO \rightarrow Cl_2 + O_2$	−2	
	$ClO + ClO \rightarrow Cl + OClO$	−2	
	$ClO + HO_2 \rightarrow HOCl + O_2$	−2[£]	
	$BrO + O \rightarrow Br + O_2$	−2	$BrOx_{-Loss} = 2\times(R_{BrO+O} + R_{BrO+BrO} + R_{BrO+HO2})$
	$BrO + BrO \rightarrow 2\times Br + O_2$	−2	
	$BrO + HO_2 \rightarrow HOBr + O_2$	−2[£]	
	$BrO + ClO \rightarrow Br + Cl + O_2$	−2	$ClOxBrOx_{-Loss} = 2\times(R_{BrO+ClO}{}^{b} + R_{BrO+ClO}{}^{c})$
	$BrO + ClO \rightarrow BrCl + O_2$	−2	

$O_x = O(3P) + O(1D) + O_3 + NO_2 + 2\times NO_3 + HNO_3 + HO_2NO_2 + 2\times N_2O_5 + ClO + 2\times Cl_2O_2 + 2\times OClO + 2\times CLONO_2 + BrO + 2\times BrONO_2$

§R_{A+B} is the reaction rate for reaction A+B→products and J_C is the photodissociation rate constant (i.e. photolysis × concentration) for C+$h\nu$→products. Units are molec.cm^{-3}s^{-1}.

†HO_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.

£Reactions $XO + HO_2 \rightarrow HOX + O_2$, 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 + HO2 reaction are the rate limiting step, their loss rates have been multiplied by two.

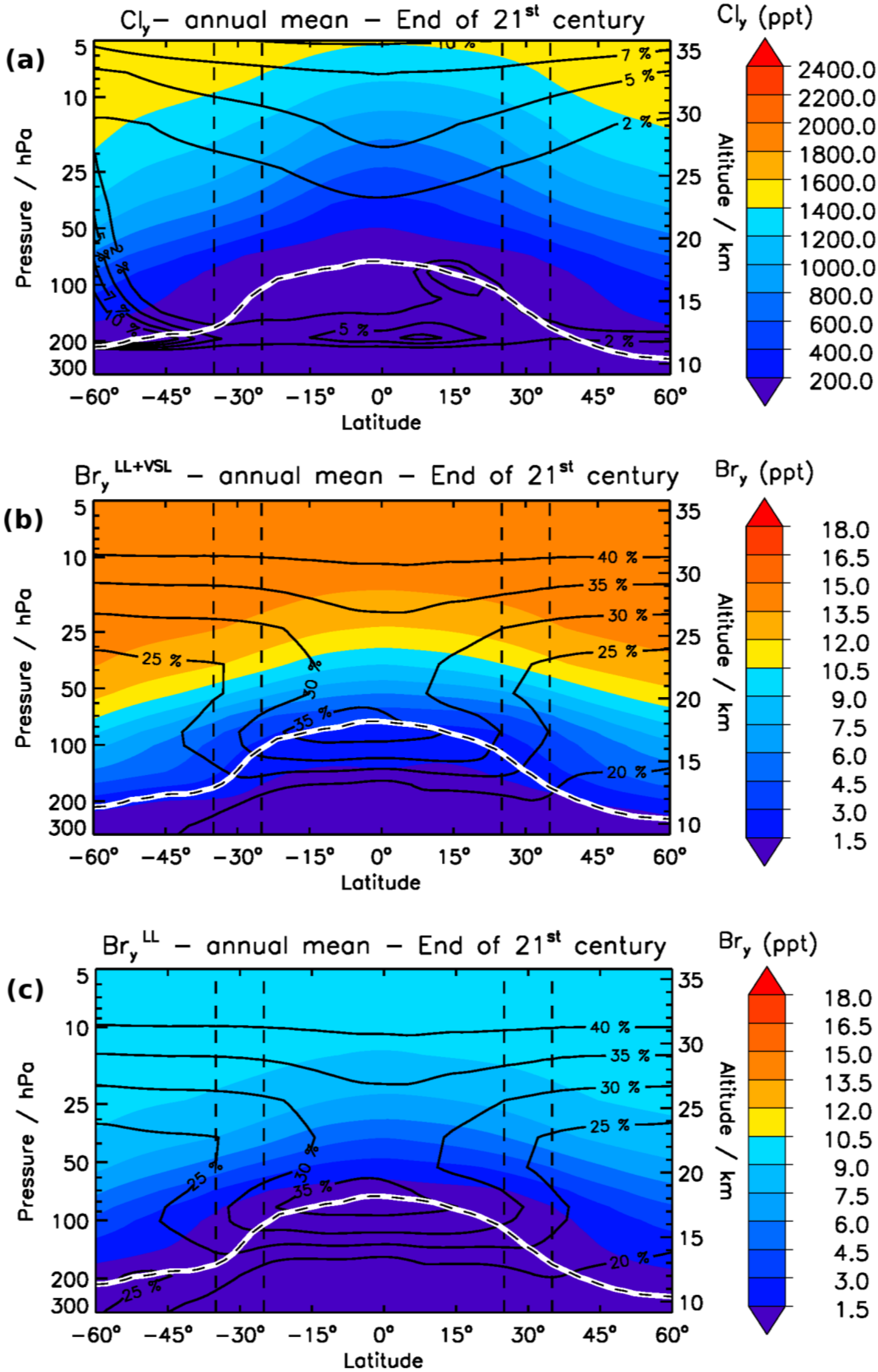

Figure S1: As Fig. 2 but for the end of the 21st century period.

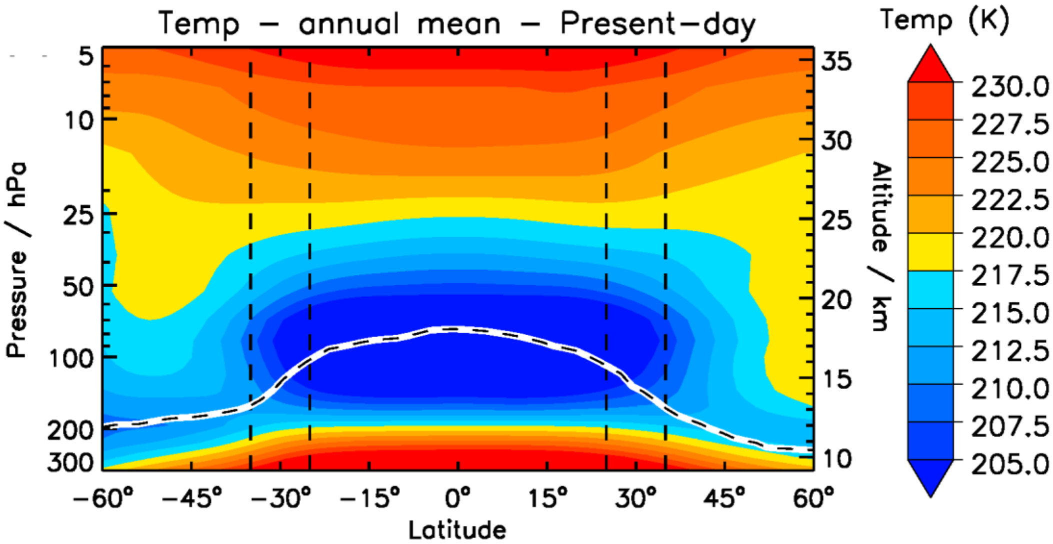

Figure S2: Annual zonal mean Temperature (K) for the present-day period. The lower solid white line indicates the location of the tropopause (chemical definition of 150 ppb ozone level from run^{LL} experiments).

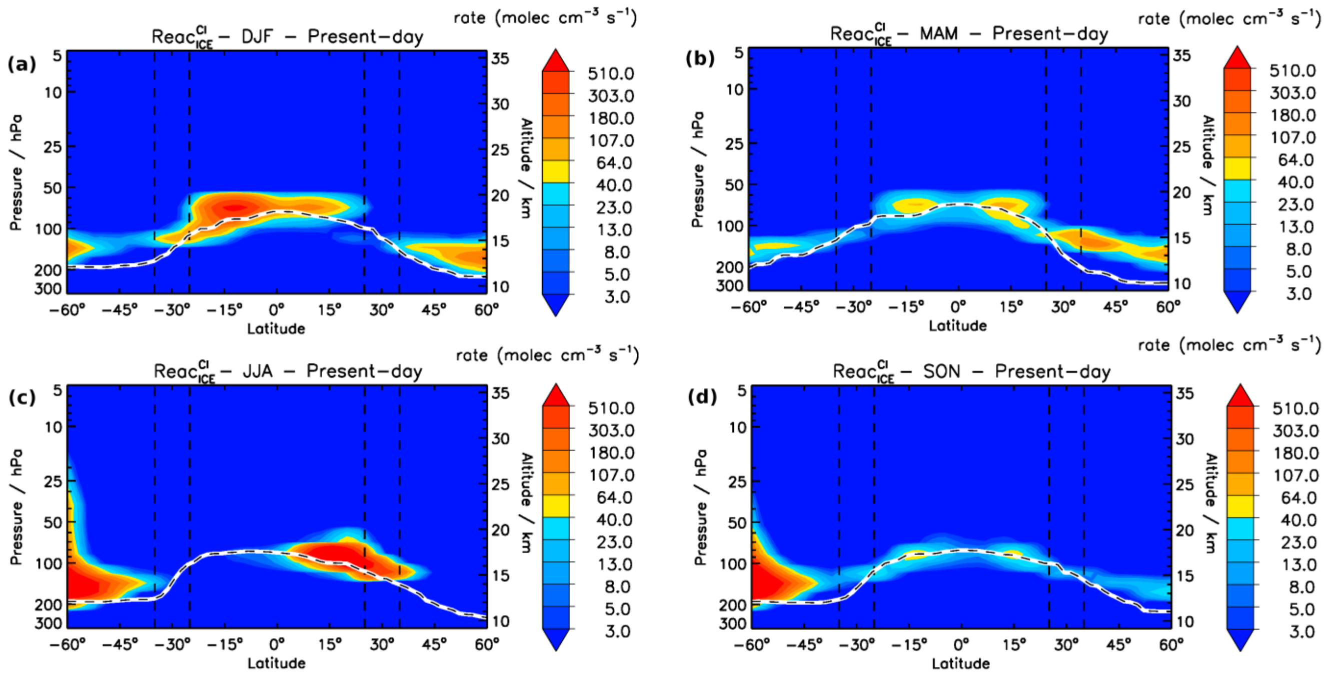

Figure S3: Seasonal zonal mean distribution of the heterogeneous reactivation of $ClONO_2$ (Het2,4) and HOCl (Het5) on ice-crystal during the present-day period. The reactions have been specified in table S1 with the label Het and the corresponding number.

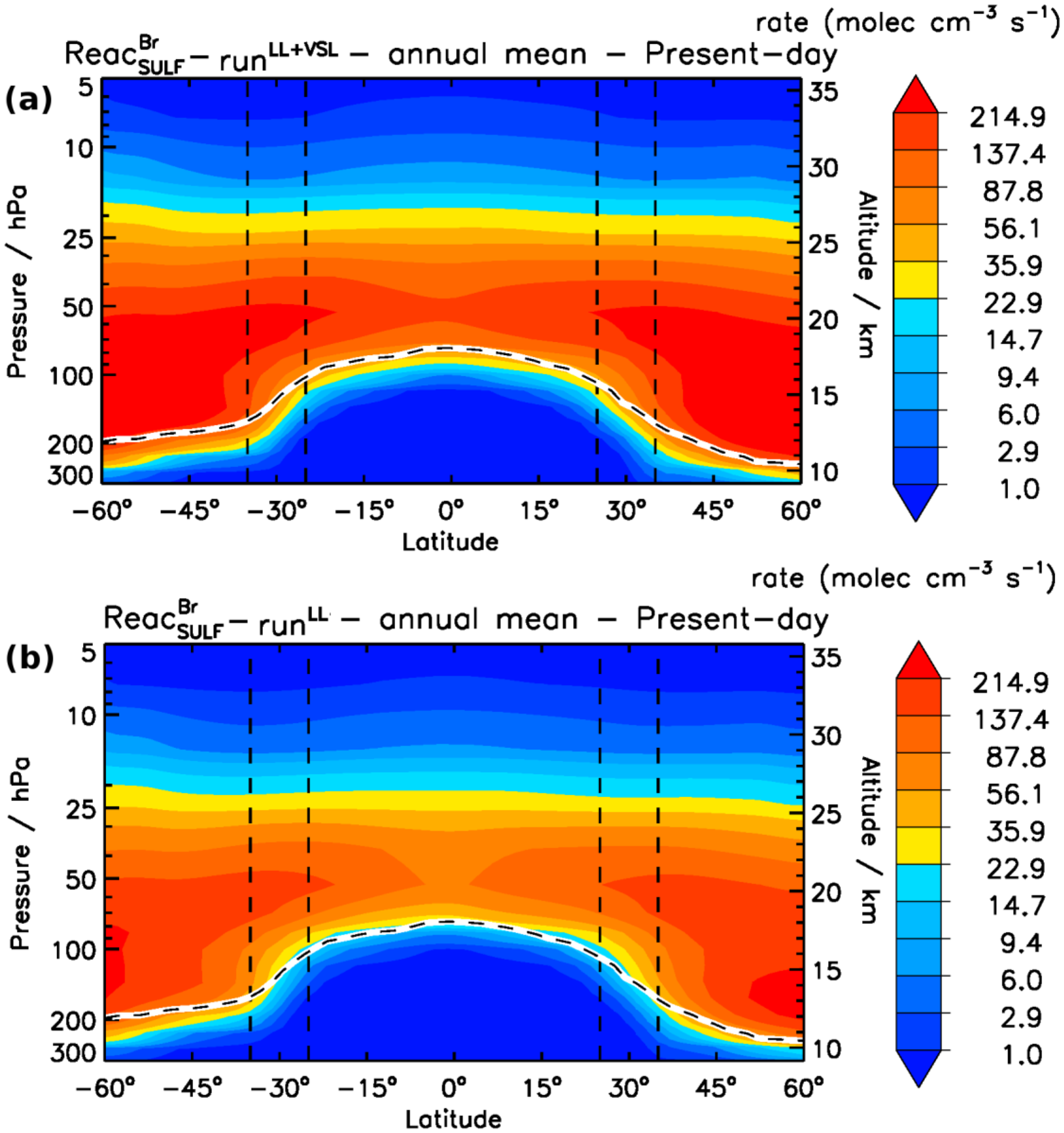

Figure S4: Annual zonal mean distribution of the heterogeneous reactivation of $BrONO_2$ (Het9) and HOBr (Het12) on sulphate aerosols for the run^{LL+VSL} (a) and run^{LL} (b) experiments during the present-day period. The reactions have been specified in table S1 with the label Het and the corresponding number.

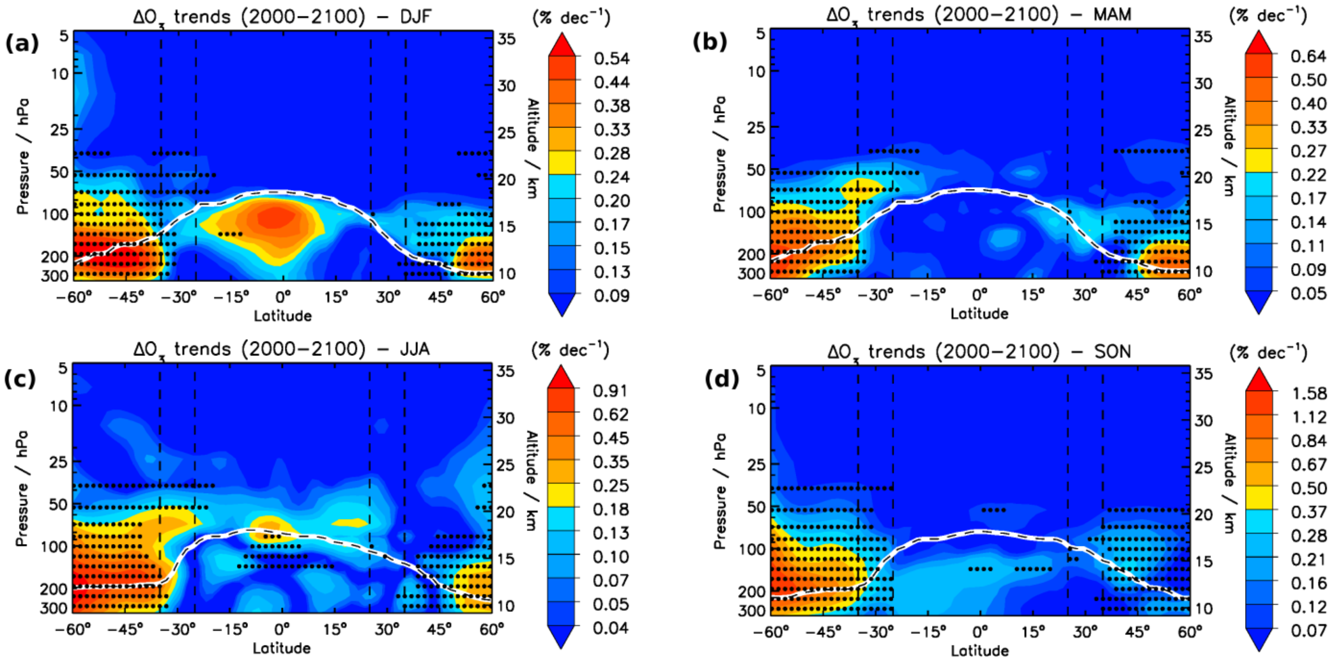

Figure S5: Zonal mean distributions of the seasonal $\Delta O_3(z)$ trends (% dec^{-1}) over the century. The masked regions in the left panels indicate where of seasonal relative $\Delta O_3(z)$ between the present-day and the end of the 21st century periods are statistically significant at the 95% confidence interval using a two-tailed Student's *t* test.

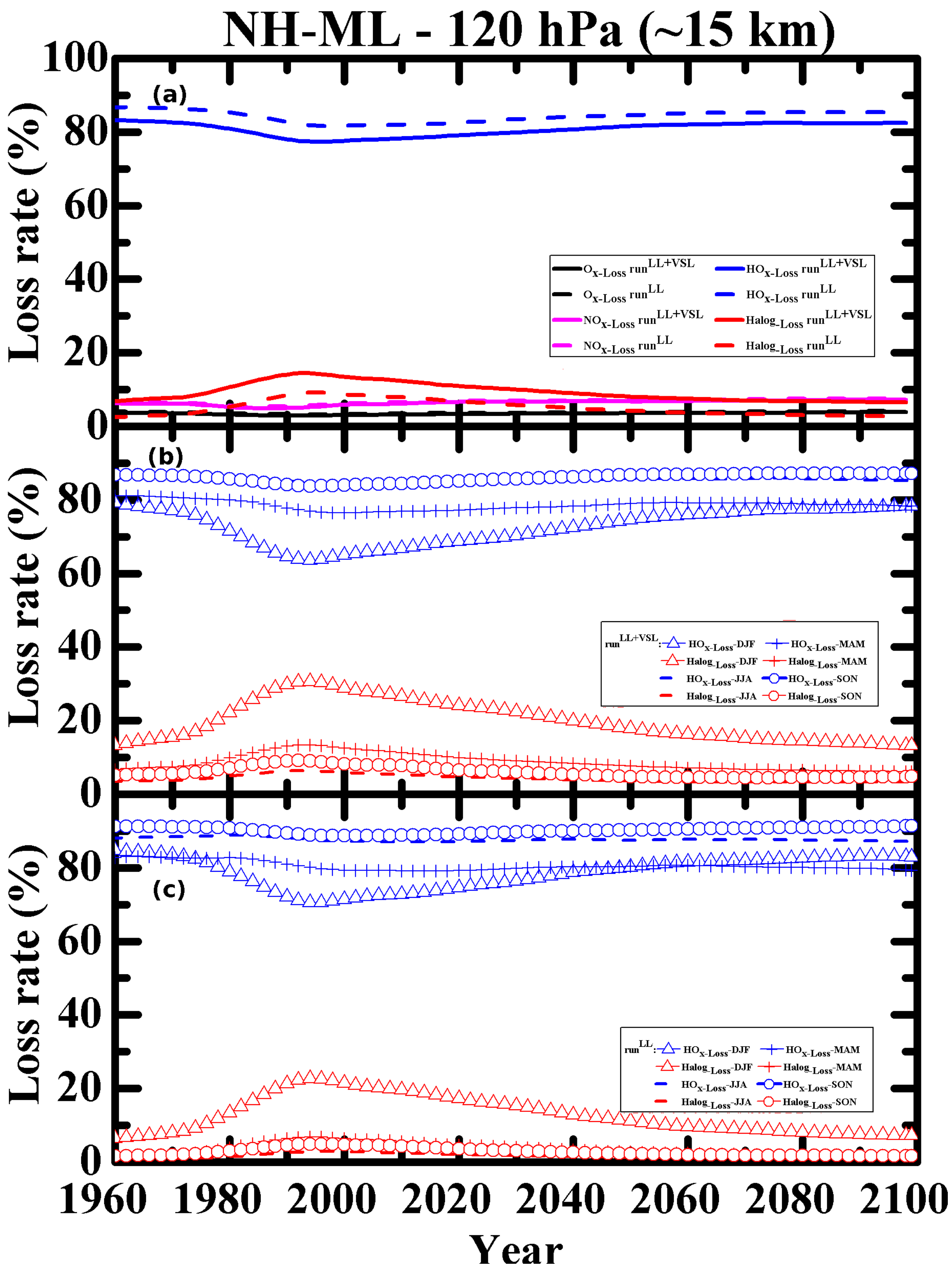

Figure S6: As Fig. 8 but for the lowermost stratosphere (120 hPa) at northern hemisphere mid-latitudes (NH-ML).

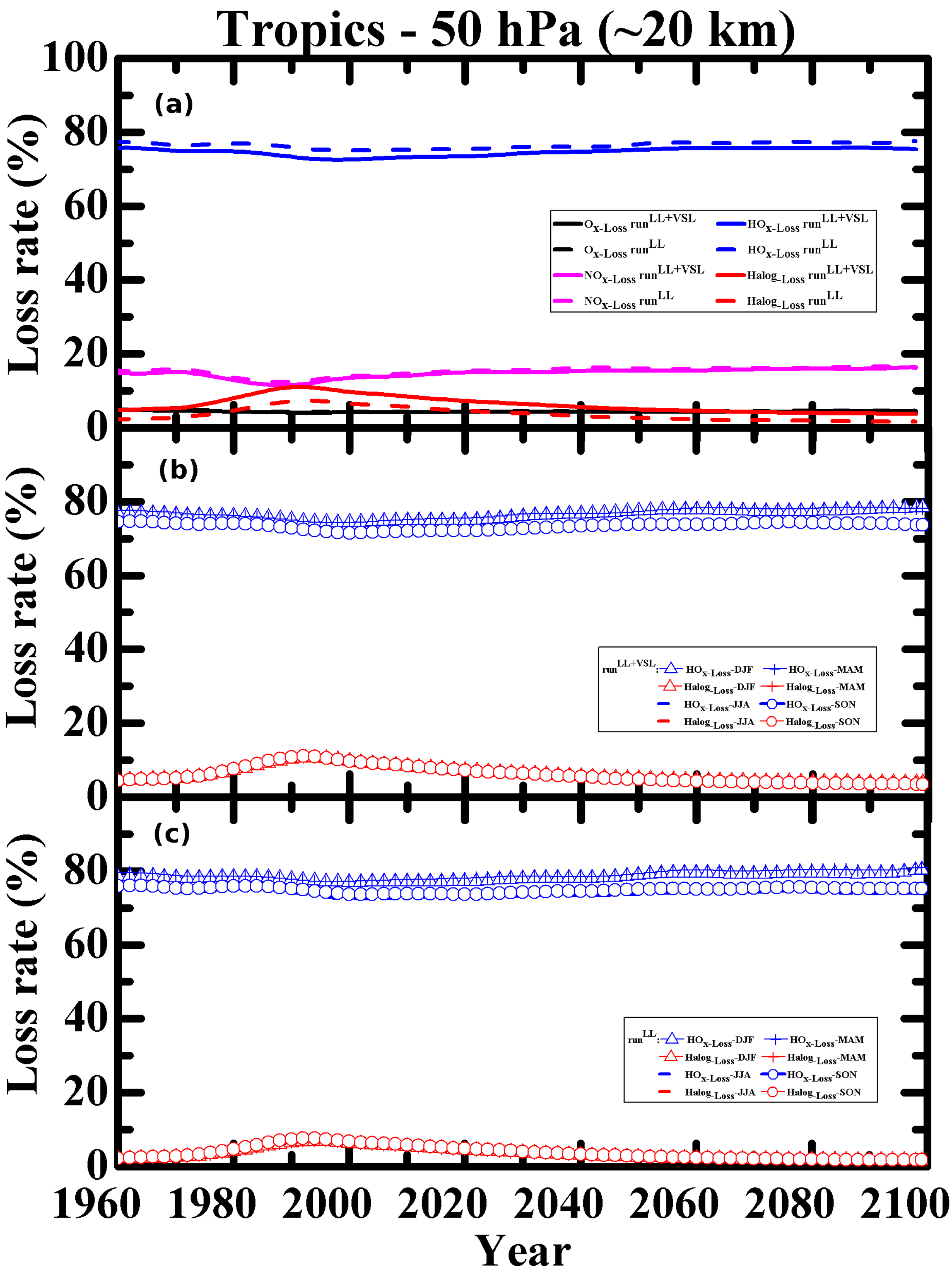

Figure S7: As Fig. 8 but for the lower stratosphere (50 hPa) at tropics.

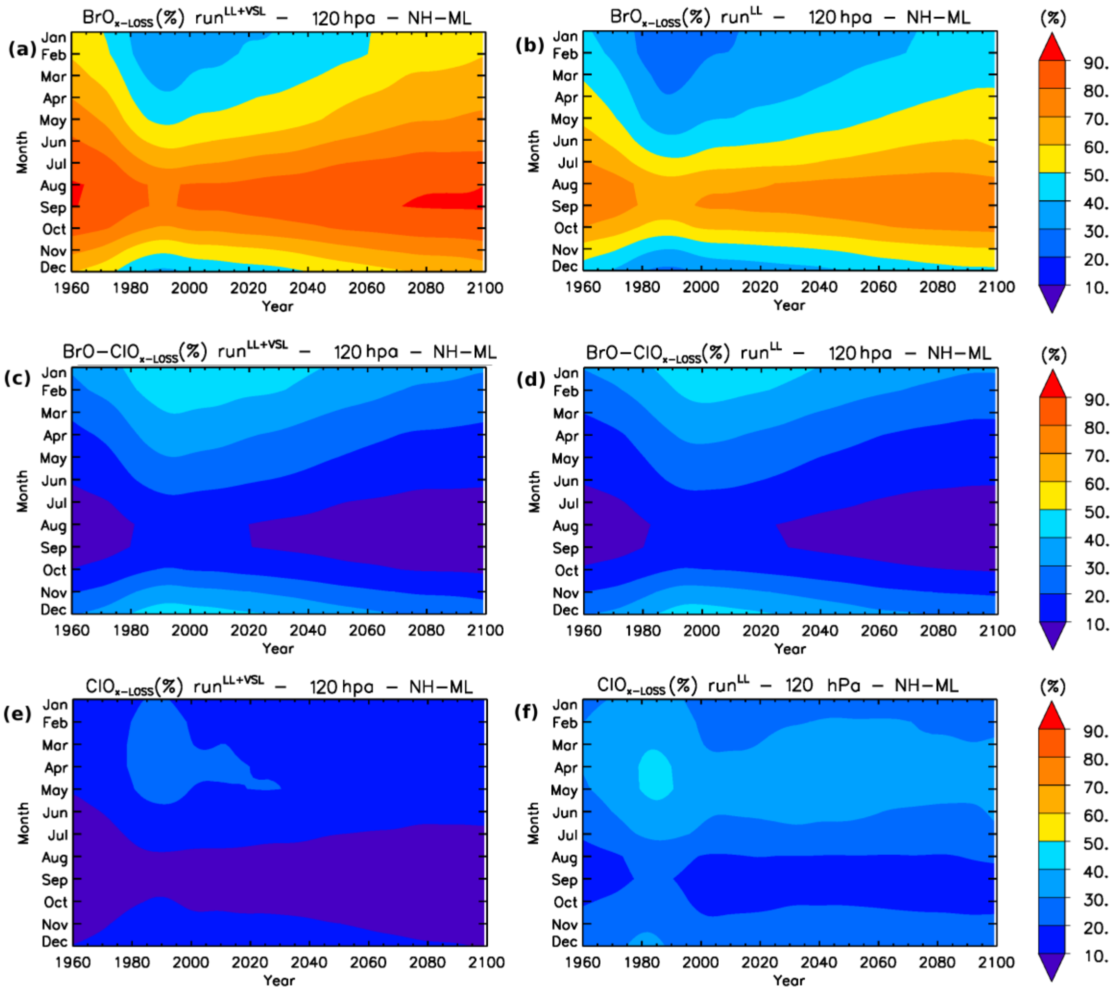

Figure S8: As Fig. 9 but for the lowermost stratosphere (120 hPa) at northern hemisphere mid-latitudes (NH-ML).

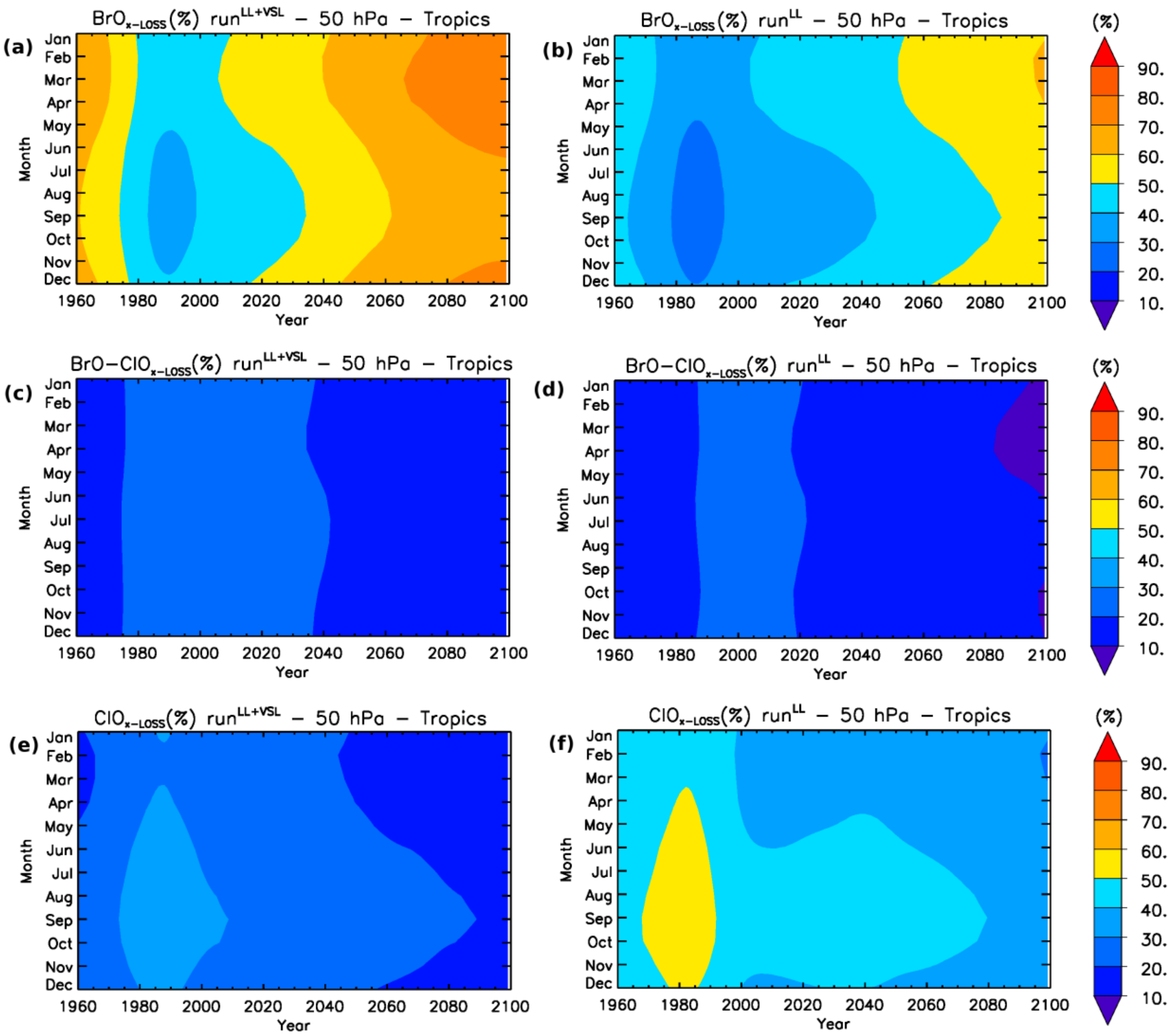

Figure S9: As Fig. 9 but for the lower stratosphere (50 hPa) at tropics.

References

Kinnison, D. E., Brasseur, G. P., Walters, S., Garcia, R. R., Marsh, D. R., and Sassi, F., Harvey, V. L., Randall, C. E., Emmons, L., Lamarque, J. F., Hess, P., Orlando, J. J., Tie, X. X., Randel, W., Pan, L. L., Gettelman, A., Granier, C., Diehl, T., Niemeier, U., and Simmons, A. J.: Sensitivity of chemical tracers to meteorological parameters in the MOZART-3 chemical transport model, J. Geophys. Res.112, D20302, doi:10.1029/2006JD007879, 2007.

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