



Supplement of

Quantification of the depletion of ozone in the plume of Mount Etna

L. Surl et al.

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1 Initial conditions for HSC calculations

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Species	low Br/S	high Br/S
$\begin{array}{ccccc} {\rm CO}_2 & 9.28{\rm e}{\rm -}02 & 3.90{\rm e}{\rm -}02 \\ {\rm N}_2 & 3.90{\rm e}{\rm -}02 & 3.90{\rm e}{\rm -}02 \\ {\rm NO} & 1.66{\rm e}{\rm -}05 & 2.00{\rm e}{\rm -}05 \\ {\rm NO}_2 & 4.31{\rm e}{\rm -}08 & 4.19{\rm e}{\rm -}08 \\ {\rm NO}_3 & 2.72{\rm e}{\rm -}15 & 2.80{\rm e}{\rm -}15 \\ {\rm HNO}_3 & 7.16{\rm e}{\rm -}13 & 6.02{\rm e}{\rm -}13 \\ {\rm HONO} & 1.95{\rm e}{\rm -}09 & 2.00{\rm e}{\rm -}09 \\ {\rm NH}_3 & 8.36{\rm e}{\rm -}15 & 2.08{\rm e}{\rm -}14 \\ {\rm SO}_2 & 1.60{\rm e}{\rm -}02 & 2.82{\rm e}{\rm -}02 \\ {\rm H}_2{\rm SO}_4 & 2.95{\rm e}{\rm -}07 & 2.96{\rm e}{\rm -}07 \\ {\rm SO}_3 & 2.32{\rm e}{\rm -}04 & 2.99{\rm e}{\rm -}05 \\ {\rm H}_2{\rm S} & 0.00{\rm e}{\rm +}00 & 0.00{\rm e}{\rm +}00 \\ {\rm SO} & 7.40{\rm e}{\rm -}10 & 3.10{\rm e}{\rm -}09 \\ {\rm O}_3 & 3.43{\rm e}{\rm -}13 & 4.24{\rm e}{\rm -}13 \\ {\rm CH}_4 & 1.03{\rm e}{\rm -}30 & 1.05{\rm e}{\rm -}29 \\ {\rm CO} & 8.23{\rm e}{\rm -}08 & 1.82{\rm e}{\rm -}07 \\ {\rm HCOOH} & 4.47{\rm e}{\rm -}14 & 9.17{\rm e}{\rm -}14 \\ {\rm OH} & 9.81{\rm e}{\rm -}06 & 1.46{\rm e}{\rm -}05 \\ {\rm HO}_2 & 2.10{\rm e}{\rm -}08 & 2.65{\rm e}{\rm -}08 \\ {\rm H}_2{\rm O}_2 & 3.51{\rm e}{\rm -}09 & 4.34{\rm e}{\rm -}09 \\ {\rm HCl} & 6.52{\rm e}{\rm -}03 & 1.36{\rm e}{\rm -}02 \\ {\rm HOCl} & 1.56{\rm e}{\rm -}07 & 3.21{\rm e}{\rm -}07 \\ {\rm Cl}_2 & 3.62{\rm e}{\rm -}07 & 1.29{\rm e}{\rm -}06 \\ {\rm Cl} & 5.74{\rm e}{\rm -}06 & 1.51{\rm e}{\rm -}05 \\ {\rm ClO} & 1.73{\rm e}{\rm -}08 & 4.05{\rm e}{\rm -}08 \\ {\rm HBr} & 7.32{\rm e}{\rm -}06 & 5.08{\rm e}{\rm -}05 \\ {\rm HOBr} & 1.75{\rm e}{\rm -}10 & 1.20{\rm e}{\rm -}09 \\ {\rm Br}_2 & 8.97{\rm e}{\rm -}10 & 2.85{\rm e}{\rm -}08 \\ {\rm BrCl} & 3.85{\rm e}{\rm -}08 & 4.08{\rm e}{\rm -}07 \\ {\rm Br} & 2.14{\rm e}{\rm -}06 & 1.57{\rm e}{\rm -}05 \end{array}$		8.33-01	8.17e-01
$\begin{array}{llllllllllllllllllllllllllllllllllll$		9.12e-03	1.05e-02
$\begin{array}{c cccccc} NO_2 & 4.31e-08 & 4.19e-08 \\ NO_3 & 2.72e-15 & 2.80e-15 \\ HNO_3 & 7.16e-13 & 6.02e-13 \\ HONO & 1.95e-09 & 2.00e-09 \\ NH_3 & 8.36e-15 & 2.08e-14 \\ SO_2 & 1.60e-02 & 2.82e-02 \\ H_2SO_4 & 2.95e-07 & 2.96e-07 \\ SO_3 & 2.32e-04 & 2.99e-05 \\ H_2S & 0.00e+00 & 0.00e+00 \\ SO & 7.40e-10 & 3.10e-09 \\ O_3 & 3.43e-13 & 4.24e-13 \\ CH_4 & 1.03e-30 & 1.05e-29 \\ CO & 8.23e-08 & 1.82e-07 \\ HCOOH & 4.47e-14 & 9.17e-14 \\ OH & 9.81e-06 & 1.46e-05 \\ HO_2 & 2.10e-08 & 2.65e-08 \\ H_2O_2 & 3.51e-09 & 4.34e-09 \\ HCCl & 1.56e-07 & 3.21e-07 \\ Cl_2 & 3.62e-07 & 1.29e-06 \\ Cl & 5.74e-06 & 1.51e-05 \\ ClO & 1.73e-08 & 4.05e-08 \\ HBr & 7.32e-06 & 5.08e-05 \\ HOBr & 1.75e-10 & 1.20e-09 \\ Br_2 & 8.97e-10 & 2.85e-08 \\ BrCl & 3.85e-08 & 4.08e-07 \\ Br & 2.14e-06 & 1.57e-05 \\ \end{array}$	$\rm CO_2$	9.28e-02	9.09e-02
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N_2	3.90e-02	3.90e-02
$\begin{array}{llllllllllllllllllllllllllllllllllll$		1.66e-05	2.00e-05
$\begin{array}{llllllllllllllllllllllllllllllllllll$	NO_2	4.31e-08	4.19e-08
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	NO_3	2.72e-15	2.80e-15
$\begin{array}{llllllllllllllllllllllllllllllllllll$	HNO_3	7.16e-13	6.02e-13
$\begin{array}{c cccccc} SO_2 & 1.60e-02 & 2.82e-02 \\ H_2SO_4 & 2.95e-07 & 2.96e-07 \\ SO_3 & 2.32e-04 & 2.99e-05 \\ H_2S & 0.00e+00 & 0.00e+00 \\ SO & 7.40e-10 & 3.10e-09 \\ O_3 & 3.43e-13 & 4.24e-13 \\ CH_4 & 1.03e-30 & 1.05e-29 \\ CO & 8.23e-08 & 1.82e-07 \\ HCOOH & 4.47e-14 & 9.17e-14 \\ OH & 9.81e-06 & 1.46e-05 \\ HO_2 & 2.10e-08 & 2.65e-08 \\ H_2O_2 & 3.51e-09 & 4.34e-09 \\ HCCl & 1.56e-07 & 3.21e-07 \\ Cl_2 & 3.62e-07 & 1.29e-06 \\ Cl & 5.74e-06 & 1.51e-05 \\ ClO & 1.73e-08 & 4.05e-08 \\ HBr & 7.32e-06 & 5.08e-05 \\ HOBr & 1.75e-10 & 1.20e-09 \\ Br_2 & 8.97e-10 & 2.85e-08 \\ BrCl & 3.85e-08 & 4.08e-07 \\ Br & 2.14e-06 & 1.57e-05 \\ \end{array}$	HONO	1.95e-09	2.00e-09
$\begin{array}{c ccccc} H_2SO_4 & 2.95e{-}07 & 2.96e{-}07 \\ SO_3 & 2.32e{-}04 & 2.99e{-}05 \\ H_2S & 0.00e{+}00 & 0.00e{+}00 \\ SO & 7.40e{-}10 & 3.10e{-}09 \\ O_3 & 3.43e{-}13 & 4.24e{-}13 \\ CH_4 & 1.03e{-}30 & 1.05e{-}29 \\ CO & 8.23e{-}08 & 1.82e{-}07 \\ HCOOH & 4.47e{-}14 & 9.17e{-}14 \\ OH & 9.81e{-}06 & 1.46e{-}05 \\ HO_2 & 2.10e{-}08 & 2.65e{-}08 \\ H_2O_2 & 3.51e{-}09 & 4.34e{-}09 \\ HCl & 6.52e{-}03 & 1.36e{-}02 \\ HOCl & 1.56e{-}07 & 3.21e{-}07 \\ Cl_2 & 3.62e{-}07 & 1.29e{-}06 \\ Cl & 5.74e{-}06 & 1.51e{-}05 \\ ClO & 1.73e{-}08 & 4.05e{-}08 \\ HBr & 7.32e{-}06 & 5.08e{-}05 \\ HOBr & 1.75e{-}10 & 1.20e{-}09 \\ Br_2 & 8.97e{-}10 & 2.85e{-}08 \\ BrCl & 3.85e{-}08 & 4.08e{-}07 \\ Br & 2.14e{-}06 & 1.57e{-}05 \\ \end{array}$	NH_3	8.36e-15	2.08e-14
$\begin{array}{llllllllllllllllllllllllllllllllllll$	SO_2	1.60e-02	2.82e-02
$\begin{array}{llllllllllllllllllllllllllllllllllll$	H_2SO_4	2.95e-07	2.96e-07
$\begin{array}{c ccccc} {\rm SO} & 7.40{\rm e}{-}10 & 3.10{\rm e}{-}09 \\ {\rm O}_3 & 3.43{\rm e}{-}13 & 4.24{\rm e}{-}13 \\ {\rm CH}_4 & 1.03{\rm e}{-}30 & 1.05{\rm e}{-}29 \\ {\rm CO} & 8.23{\rm e}{-}08 & 1.82{\rm e}{-}07 \\ {\rm HCOOH} & 4.47{\rm e}{-}14 & 9.17{\rm e}{-}14 \\ {\rm OH} & 9.81{\rm e}{-}06 & 1.46{\rm e}{-}05 \\ {\rm HO}_2 & 2.10{\rm e}{-}08 & 2.65{\rm e}{-}08 \\ {\rm H}_2{\rm O}_2 & 3.51{\rm e}{-}09 & 4.34{\rm e}{-}09 \\ {\rm HCl} & 6.52{\rm e}{-}03 & 1.36{\rm e}{-}02 \\ {\rm HOCl} & 1.56{\rm e}{-}07 & 3.21{\rm e}{-}07 \\ {\rm Cl}_2 & 3.62{\rm e}{-}07 & 1.29{\rm e}{-}06 \\ {\rm Cl} & 5.74{\rm e}{-}06 & 1.51{\rm e}{-}05 \\ {\rm ClO} & 1.73{\rm e}{-}08 & 4.05{\rm e}{-}08 \\ {\rm HBr} & 7.32{\rm e}{-}06 & 5.08{\rm e}{-}05 \\ {\rm HOBr} & 1.75{\rm e}{-}10 & 1.20{\rm e}{-}09 \\ {\rm Br}_2 & 8.97{\rm e}{-}10 & 2.85{\rm e}{-}08 \\ {\rm BrCl} & 3.85{\rm e}{-}08 & 4.08{\rm e}{-}07 \\ {\rm Br} & 2.14{\rm e}{-}06 & 1.57{\rm e}{-}05 \end{array}$	SO_3	2.32e-04	2.99e-05
$\begin{array}{c ccccc} O_3 & 3.43e{-}13 & 4.24e{-}13 \\ CH_4 & 1.03e{-}30 & 1.05e{-}29 \\ CO & 8.23e{-}08 & 1.82e{-}07 \\ HCOOH & 4.47e{-}14 & 9.17e{-}14 \\ OH & 9.81e{-}06 & 1.46e{-}05 \\ HO_2 & 2.10e{-}08 & 2.65e{-}08 \\ H_2O_2 & 3.51e{-}09 & 4.34e{-}09 \\ HCl & 6.52e{-}03 & 1.36e{-}02 \\ HOCl & 1.56e{-}07 & 3.21e{-}07 \\ Cl_2 & 3.62e{-}07 & 1.29e{-}06 \\ Cl & 5.74e{-}06 & 1.51e{-}05 \\ ClO & 1.73e{-}08 & 4.05e{-}08 \\ HBr & 7.32e{-}06 & 5.08e{-}05 \\ HOBr & 1.75e{-}10 & 1.20e{-}09 \\ Br_2 & 8.97e{-}10 & 2.85e{-}08 \\ BrCl & 3.85e{-}08 & 4.08e{-}07 \\ Br & 2.14e{-}06 & 1.57e{-}05 \\ \end{array}$	H_2S	0.00e+00	0.00e+00
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	SO	7.40e-10	3.10e-09
$\begin{array}{c ccccc} CO & 8.23e{-}08 & 1.82e{-}07 \\ HCOOH & 4.47e{-}14 & 9.17e{-}14 \\ OH & 9.81e{-}06 & 1.46e{-}05 \\ HO_2 & 2.10e{-}08 & 2.65e{-}08 \\ H_2O_2 & 3.51e{-}09 & 4.34e{-}09 \\ HC1 & 6.52e{-}03 & 1.36e{-}02 \\ HOC1 & 1.56e{-}07 & 3.21e{-}07 \\ Cl_2 & 3.62e{-}07 & 1.29e{-}06 \\ Cl & 5.74e{-}06 & 1.51e{-}05 \\ ClO & 1.73e{-}08 & 4.05e{-}08 \\ HBr & 7.32e{-}06 & 5.08e{-}05 \\ HOBr & 1.75e{-}10 & 1.20e{-}09 \\ Br_2 & 8.97e{-}10 & 2.85e{-}08 \\ BrCl & 3.85e{-}08 & 4.08e{-}07 \\ Br & 2.14e{-}06 & 1.57e{-}05 \\ \end{array}$	O_3	3.43e-13	4.24e-13
$\begin{array}{llllllllllllllllllllllllllllllllllll$	CH_4	1.03e-30	1.05e-29
$\begin{array}{llllllllllllllllllllllllllllllllllll$	CO	8.23e-08	1.82e-07
$\begin{array}{llllllllllllllllllllllllllllllllllll$	HCOOH	4.47e-14	9.17e-14
$\begin{array}{ccccc} H_2O_2 & 3.51e{-}09 & 4.34e{-}09 \\ HCl & 6.52e{-}03 & 1.36e{-}02 \\ HOCl & 1.56e{-}07 & 3.21e{-}07 \\ Cl_2 & 3.62e{-}07 & 1.29e{-}06 \\ Cl & 5.74e{-}06 & 1.51e{-}05 \\ ClO & 1.73e{-}08 & 4.05e{-}08 \\ HBr & 7.32e{-}06 & 5.08e{-}05 \\ HOBr & 1.75e{-}10 & 1.20e{-}09 \\ Br_2 & 8.97e{-}10 & 2.85e{-}08 \\ BrCl & 3.85e{-}08 & 4.08e{-}07 \\ Br & 2.14e{-}06 & 1.57e{-}05 \\ \end{array}$	OH	9.81e-06	1.46e-05
$\begin{array}{llllllllllllllllllllllllllllllllllll$	HO_2	2.10e-08	2.65e-08
$\begin{array}{c ccccc} HOCl & 1.56e{-}07 & 3.21e{-}07 \\ Cl_2 & 3.62e{-}07 & 1.29e{-}06 \\ Cl & 5.74e{-}06 & 1.51e{-}05 \\ ClO & 1.73e{-}08 & 4.05e{-}08 \\ HBr & 7.32e{-}06 & 5.08e{-}05 \\ HOBr & 1.75e{-}10 & 1.20e{-}09 \\ Br_2 & 8.97e{-}10 & 2.85e{-}08 \\ BrCl & 3.85e{-}08 & 4.08e{-}07 \\ Br & 2.14e{-}06 & 1.57e{-}05 \\ \end{array}$	H_2O_2	3.51e-09	4.34e-09
$\begin{array}{c cccc} Cl_2 & 3.62\text{e-}07 & 1.29\text{e-}06 \\ Cl & 5.74\text{e-}06 & 1.51\text{e-}05 \\ ClO & 1.73\text{e-}08 & 4.05\text{e-}08 \\ HBr & 7.32\text{e-}06 & 5.08\text{e-}05 \\ HOBr & 1.75\text{e-}10 & 1.20\text{e-}09 \\ Br_2 & 8.97\text{e-}10 & 2.85\text{e-}08 \\ BrCl & 3.85\text{e-}08 & 4.08\text{e-}07 \\ Br & 2.14\text{e-}06 & 1.57\text{e-}05 \\ \end{array}$	HCl	6.52 e- 03	1.36e-02
$\begin{array}{c cccc} Cl & 5.74e\text{-}06 & 1.51e\text{-}05 \\ ClO & 1.73e\text{-}08 & 4.05e\text{-}08 \\ HBr & 7.32e\text{-}06 & 5.08e\text{-}05 \\ HOBr & 1.75e\text{-}10 & 1.20e\text{-}09 \\ Br_2 & 8.97e\text{-}10 & 2.85e\text{-}08 \\ BrCl & 3.85e\text{-}08 & 4.08e\text{-}07 \\ Br & 2.14e\text{-}06 & 1.57e\text{-}05 \\ \end{array}$	HOCl	1.56e-07	3.21e-07
$\begin{array}{c cccc} ClO & 1.73e\text{-}08 & 4.05e\text{-}08 \\ HBr & 7.32e\text{-}06 & 5.08e\text{-}05 \\ HOBr & 1.75e\text{-}10 & 1.20e\text{-}09 \\ Br_2 & 8.97e\text{-}10 & 2.85e\text{-}08 \\ BrCl & 3.85e\text{-}08 & 4.08e\text{-}07 \\ Br & 2.14e\text{-}06 & 1.57e\text{-}05 \\ \end{array}$		3.62 e- 07	1.29e-06
$\begin{array}{c cccc} HBr & 7.32e{-}06 & 5.08e{-}05 \\ HOBr & 1.75e{-}10 & 1.20e{-}09 \\ Br_2 & 8.97e{-}10 & 2.85e{-}08 \\ BrCl & 3.85e{-}08 & 4.08e{-}07 \\ Br & 2.14e{-}06 & 1.57e{-}05 \\ \end{array}$	Cl	5.74e-06	1.51e-05
$\begin{array}{c ccc} HOBr & 1.75e{-}10 & 1.20e{-}09 \\ Br_2 & 8.97e{-}10 & 2.85e{-}08 \\ BrCl & 3.85e{-}08 & 4.08e{-}07 \\ Br & 2.14e{-}06 & 1.57e{-}05 \end{array}$	ClO	1.73e-08	4.05e-08
$\begin{array}{c cccc} Br_2 & 8.97\text{e-}10 & 2.85\text{e-}08 \\ BrCl & 3.85\text{e-}08 & 4.08\text{e-}07 \\ Br & 2.14\text{e-}06 & 1.57\text{e-}05 \end{array}$	HBr	7.32e-06	5.08e-05
BrCl3.85e-084.08e-07Br2.14e-061.57e-05	HOBr	1.75e-10	1.20e-09
Br 2.14e-06 1.57e-05	Br_2	8.97e-10	2.85e-08
	BrCl	3.85e-08	4.08e-07
BrO 2.80e-10 2.02e-09	Br	2.14e-06	1.57e-05
	BrO	2.80e-10	2.02e-09

Table S1: Initial conditions (in mol/mol) from HSC calculations for the subset of species that have been used in the model runs presented in this paper. Note that HOBr is not included in HSC. It has been calculated from HBr using the HOCl/HCl ratio as determined by HSC. H₂S has been set to 0., as there are strong indications from field measurements (Aiuppa et al., 2007) that equilibrium models and kinetic models do not capture the chemistry of H₂S. On the times scales considered here, H₂S is considered inert. "Low Br/S" refers to volcanic volatile measurements taken in June 2012, "high Br/S" refers to the composition used in von Glasow, 2010. For more details see text.

2 Plots relating to "High Br/S" initialisation

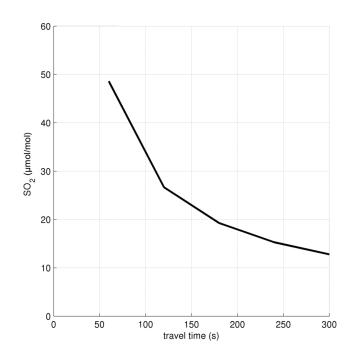


Figure S1: Modelled SO_2 mixing ratio in the plume core ("high Br/S" initialisation).

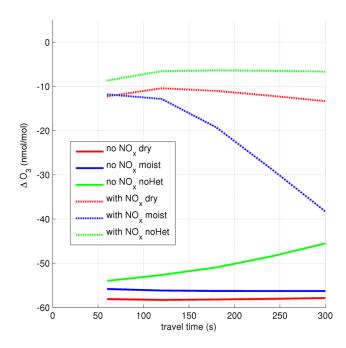


Figure S2: Evolution of ΔO_3 in the core of the plume for the six model scenarios discussed in the text ("high Br/S" initialisation).

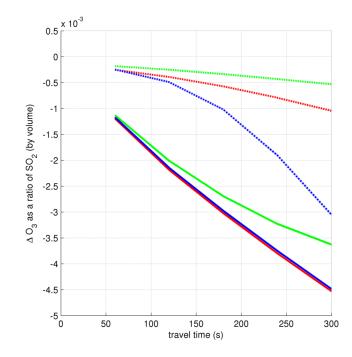
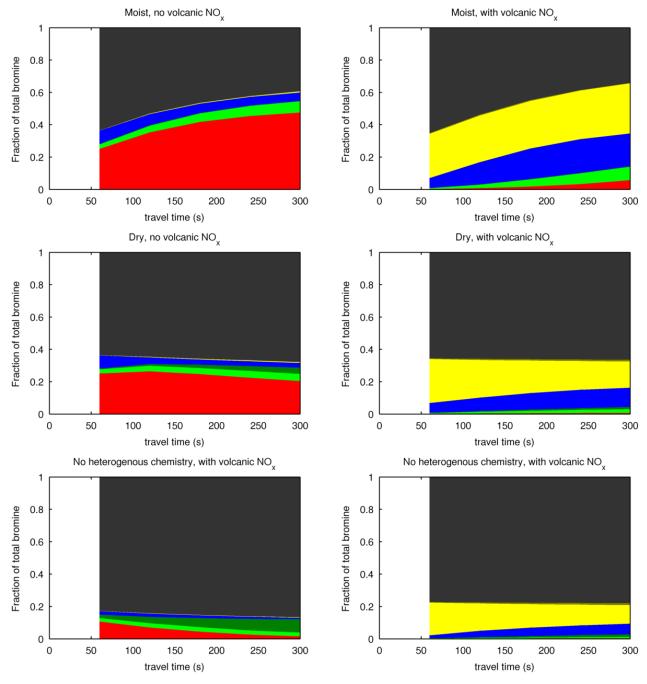


Figure S3: Evolution of $\Delta O_3/SO_2$ in the core of the plume for the six model scenarios discussed in the text ("high Br/S" initialisation). The colour code is the same as in Figure S2.



Speciation of bromine within the plume core

Figure S4: Speciation of bromine for the six model scenarios discussed in the text ("high Br/S" initialisation). Red - Br; Light Green - BrO; Dark Green - HOBr; Blue - Br_2 ; Yellow - $BrNO_2$; Dark Yellow - $BrNO_3$; Grey - HBr.

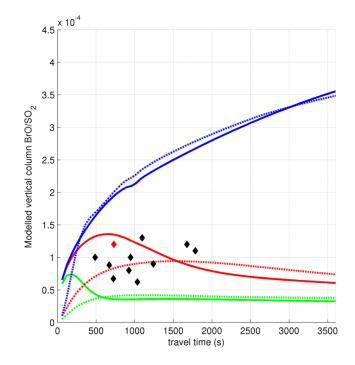


Figure S5: Evolution of vertical column BrO/SO_2 for the six model scenarios discussed in the text ("high Br/S" initialisation). The colour code is the same as in Figure S2. The diamonds represent the spectroscopic measurements, the red diamond represents a measurement contemporaneous with near-crater measurements of both O_3 and SO_2 .