

Measurement-based modeling of bromine chemistry in the Dead Sea boundary layer – Part 2: The influence of NO₂ on bromine chemistry at mid-latitude areas

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Abstract. Understanding the interaction between anthropogenic air pollution and Reactive Halogen Species (RHS) activity has had only limited support from direct field measurements, due to the fact that past field measurements of RHS have been mainly performed in Polar Regions. The present paper investigates the interaction between NO₂ and Reactive Bromine Species (RBS) activity by model simulations based on extensive field measurements performed in the Dead Sea area, as described in a companion paper (Tas et al., 2006). The Dead Sea is an excellent natural laboratory for this investigation since elevated mixing ratios of BrO (up to more than 150 pptv) are frequently observed, while the average levels of NO₂ are around several ppb. The results of the present study show that under the chemical mechanisms that occur at the Dead Sea, higher levels of NO₂ lead to higher daily average mixing ratios of BrO_x. This is the result of an increase in the rate of the heterogeneous decomposition of BrONO₂, which in turn causes an increase in the rate of the “Bromine Explosion” mechanism. However, above a certain threshold level of NO₂ (daily average mixing ratios of 0.2 ppbv during RBS activity), the daily average mixing ratios of BrO_x decrease for a further increase in the NO₂ mixing ratios. This investigation shows that the influence of NO₂ on BrO_x production clearly reflects an enhancement of RBS activity caused by anthropogenic activity.

1 Introduction

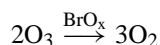
The destruction of ozone in the tropospheric boundary layer of Polar Regions by Reactive Halogen Species (RHS=X, XO, XnOm, HO_x, X₂, XY (X,Y=F,Cl, Br, I)) has been well documented during the last two decades (e.g., see Simpson et al., 2007 for an overview). It has been shown that activity of Reactive Bromine Species (RBS=Br, BrO, BrnOm, HOBr, Br₂), with BrO levels up to ~30 ppt, play a major factor in boundary layer ozone depletion events (ODE's) (Platt and Hoenninger, 2003). It has recently been recognized that RBS may lead to ozone destruction in the boundary layer also at mid-latitude areas. This was evident for the first time at the Dead Sea where very high BrO levels, above 150 ppt, were detected together with daytime depletion of O₃ from levels of above 120 ppb to below the detection limit of the instrument (<1 ppb) (Hebestreit et al., 1999; Matveev et al., 2001). Later, evidence for additional RBS activity has been found at other mid-latitude locations. At the Great Salt Lake, Utah (Stutz et al., 2002), north of the Canary Islands (Leser et al., 2003) and at Salar de Uyuni, Bolivia (Hoenninger et al., 2004).

A companion paper (Tas et al., 2006), presented a chemical mechanism that could account for the RBS activity observed at the Dead Sea. The efficient destruction of ozone through the gas phase was described by the following two well known cycles:

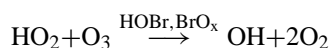


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Cycle 1 (BrO-cycle)



Cycle 2 (HOBr-cycle)

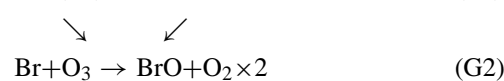
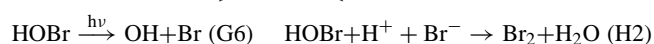


In these chemical cycles, ozone is catalytically destroyed by Br and BrO (collectively defined as BrO_x). At the Dead Sea, Cycle 1 is more efficient due to the high BrO levels prevalent in this area (Tas et al., 2006). Cycles 1 and 2 provide the chemical basis for the destruction of ozone within a time scale of a few hours, by RHS at concentrations three orders of magnitude smaller than ozone. However, it has been suggested (e.g., Lehrer et al., 2004) that the above mechanisms could not explain the observed O₃ destruction rate in the troposphere, if the loss reactions of BrO_x with hydrocarbons were also taken into account.

In order to account for the observed rates of BrO_x production and ozone destruction at the Dead Sea, more efficient recycling of bromine reservoirs via heterogeneous processes had to be included in the chemical mechanism. This is consistent with other studies (Fan and Jacob, 1992; Tang and McConnell, 1996; Sander et al., 1997; De Haan et al., 1999; Michalowski et al., 2000; Pszenny et al., 2004).

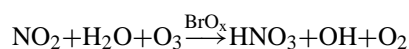
It has been shown that the inclusion of the heterogeneous decomposition of BrONO₂ on sulfate aerosols into the mechanism (Hanson and Ravishankara, 1995; Hanson et al., 1996; Sander et al., 1999) can significantly increase BrO_x formation through the production of HOBr. The inclusion of this heterogeneous process together with the "Bromine Explosion" mechanism (Mozurkewich et al., 1995; Vogt et al., 1996; Tang and McConnell, 1996; Platt and Moortgat, 1999) can account for the observed RBS activity at the Dead Sea. These two processes can be described by the following Cycle 3b (Tas et al., 2006):

Cycle 3

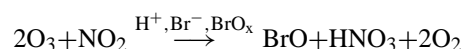


net:

Cycle 3a



Cycle 3b



Cycle 3b is important because it leads to a nearly exponential growth of Br production via reaction H2, which represents the "Bromine Explosion" mechanism. The importance of the heterogeneous decomposition of BrONO₂ is that it leads to the enhancement of reaction H2 (the rate limiting step in Cycle 3b) by producing HOBr approximately 4 times faster in comparison with reaction (G5). Based on kinetic considerations, the rate of Cycle 3b is enhanced by the concentrations of NO₂ and sulfate aerosols (Tas et al., 2006). This is of special importance since it represents the influence of anthropogenic activity on the rate of BrO_x production. In practice, the influence of NO₂ levels on the rate of Cycle 3b is more significant since, in general, its concentrations change more sharply with the distance from emission sources than those of SO₂.

The present research investigates the influence of NO₂ on the diurnal profile and total daily production of BrO_x and ozone destruction, caused primarily by the heterogeneous decomposition of BrONO₂. The sensitivity of BrO_x production to NO₂ levels via the heterogeneous decomposition of BrONO₂ has been investigated by Sander, et al. (1999), who showed that the increase in NO₂ did not necessarily lead to an increase in the production of BrO_x via the heterogeneous decomposition of BrONO₂. This issue is investigated based on simulations performed by Tas et al. (2006) in order to explain the RBS activity at the Dead Sea area.

The effects of anthropogenic activity on RHS activity have had only limited support from direct field measurements, due mainly to the fact that past field measurements of RHS have been performed only in Polar Regions. The Dead Sea basin, therefore, provides a unique natural laboratory for investigating the interaction between RBS and photochemical pollutants, since very intensive RBS activity (BrO levels up to more than 150 pptv) is frequently observed in this area (Tas et al., 2003; Tas et al., 2005). In general, photochemical air pollution in this area can be characterized by average levels

of NO₂ and SO₂ around several ppb. The research summarized in this paper contributes to the overall understanding of the influence of anthropogenic activity on RBS activity and ozone destruction at mid-latitude areas.

2 Experimental

2.1 Model description

The core of the research analysis was done by a one dimensional Chemical Transport Model, UAHCTM 1D (Biazar, 1995). This model and its settings for the present study are essentially the same as used for a companion paper (Tas et al., 2006), and are described briefly here. The model includes an explicit gas phase chemical mechanism and takes into account the vertical motion of the different species based on diffusion and advection calculations and on deposition velocity values. For the present study the model used 27 levels from the surface to a height of 10 km with variable spacing, in order to represent the boundary layer with greater vertical resolution. Results are presented only for a height of 2 m, at which the chemical parameters were measured.

Fluxes were added for NO, NO₂ and 13 different hydrocarbons species, at heights between ground level and the base of the planetary boundary layer. The fluxes were determined from simulations based on field measurements from days when no significant activity of RBS was detected. Ozone fluxes were added in order to simulate the advection of “fresh” ozone into the evaporation ponds (see Sect. 3.1.1 in Tas et al., 2006). A very small flux of Br₂ of 10 molecules cm⁻² s⁻¹ was added for initiation of the bromine species activity, from ground level upwards.

Meteorological parameters representative of real conditions, including the planetary boundary height, were obtained by running the 1-D Meteorological Model (McNider and Pielke, 1981).

The deposition velocities of some bromine species were included based on Sander and Crutzen (1996). The deposition velocities for NO, NO₂, and 9 additional organic compounds were determined based on Trainer et al. (1987). The meteorological conditions, fluxes, solar data and heterogeneous parameterizations were updated every 15 min in all simulations.

The basic photochemical processes are described in the model by 166 gas-phase reactions based on the Trainer mechanism (Trainer et al., 1987), updated according to Atkinson et al. (2003). Thirty-one reactions, including five photochemical reactions were added to describe the bromine gas phase mechanism. The rate constant of each photochemical reaction was calculated by running the Tropospheric Ultraviolet and Visible Radiation model (Madronich et al., 1998).

Two heterogeneous processes, the heterogeneous decomposition of BrONO₂ (H1) and the “Bromine Explosion” mechanism (H2) were also included in the model. These two

reactions were added to the basic model using parameterization for their first order rate constant. The basic physical assumption for Reaction (H1) is that it takes place mainly on sulfate aerosols. This assumption is based on the relatively high efficiency of the heterogeneous decomposition of BrONO₂ on sulfate aerosols (Von Glasow et al., 2002; Hanson et al., 1996; Hanson and Ravishankara, 1995) together with the high levels of sulfate aerosols measured at the Dead Sea, averaging $\sim 8 \mu\text{g m}^{-3}$ (Andreae et al., 2002; Wanger et al., 2000; Formenti et al., 2001). Further, the heterogeneous decomposition rate of BrONO₂ is very efficient under dry conditions (Hanson and Ravishankara, 1995), such as exist at the Dead Sea.

Reaction (H2), the “Bromine Explosion”, is the most likely chemical mechanism for the release of bromine into the gas phase at the Dead Sea (Matveev et al., 2001; Tas et al., 2005). In the present simulation study, it was assumed that Br₂ was released solely from the sea salt aerosols. Even though this is not necessarily true, the model results support the assumption that the release from sea salt aerosols is the major contributor, since the solid salt depositions in the investigation region were very limited (Tas et al., 2006).

The total surface area of sulfate aerosols was determined based on direct measurements of sulfate aerosols at the Dead Sea (Matveev et al., 2001). Values between 50–65 $\mu\text{m}^2/\text{cm}^3$ were used for the total surface area of sulfate aerosols. A value of 0.75 was assumed for the uptake coefficient (Reaction H1) based on literature data (Atkinson et al., 2004; Hanson et al., 1996) and a comparison of model simulations with relevant measurements. The daily average value for the rate of reaction H2 was $1.35 \cdot 10^{-6}$ ppb/s.

2.2 Model simulations

All of the simulations presented in Sects. 3.1 and 3.2 are based on the methods and parameters that were used in the “FULL” and the “NOB” simulations presented in Tas et al. (2006), using the model described in Sect. 2.1. These simulations will be briefly described in the following. The “FULL” simulation is based on the parameters that were measured at the Dead Sea (Sect. 2.3) and lead to a relatively good agreement with measurements. The difference between the two simulations is that the “FULL” simulation includes the bromine chemistry while in the “NOB” simulation the bromine mechanism is absent.

All of the results and discussion presented in Sect. 3.1 are directly based on the “FULL” simulation. The results and discussion presented in Sect. 3.2 refer to a set of simulations based on the “FULL” simulation and on the “NOB” simulation, changing only the NO₂ fluxes, as described in more detail in Sect. 3.2.

It should be remarked that the Dead Sea works, which is the main anthropogenic air pollution source in the region, and located 5 km north of the field site, might influence the NO₂ measurements. However, unless noted otherwise, the

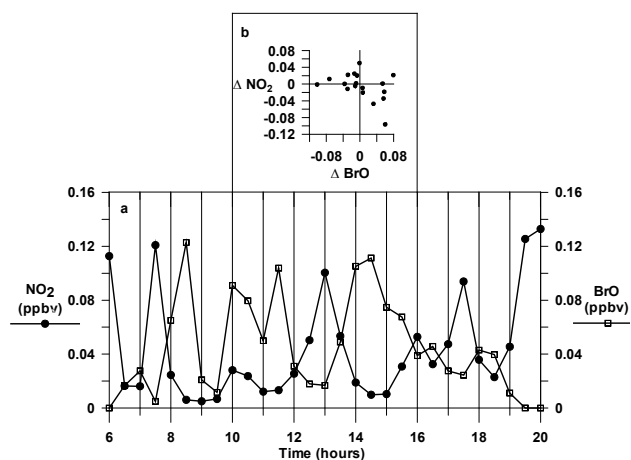


Fig. 1. Simulated mixing ratios of BrO and NO₂. (a) BrO and NO₂ diurnal profiles obtained for “FULL” simulation. (b) The difference in NO₂ mixing ratios between each two following time points was calculated and presented vs. the concurrent difference in BrO mixing ratios. The graph shows the data between 07:30–18:00 LT.

simulations presented in the paper were performed for those periods of time when there was no significant influence of the Dead Sea works on the RBS activity. Further information about the location, relevant features and the potential influence of the Dead Sea Works on RBS activity, can be found elsewhere (Hebestreit et al., 1999; Tas et al., 2005).

Note that in the paper, the magnitude $\frac{\Delta X}{\Delta t}$ represents the rate of reaction number X , as explained in Tas et al. (2006). This magnitude stands for the first derivative with time (t) of an inert species (X) that was added to the actual products of each reaction in the model. In this way, it provides a direct measure of the contribution of each reaction to the formation of its products in a similar way to what has been presented as the “counter species” method (Leone and Seinfeld, 1984).

2.3 Field measurements

The “FULL” and “NOB” simulations were based on a comprehensive set of atmospheric trace gas measurements and relevant meteorological parameters collected at the Dead Sea (Tas et al., 2006). The methods used for these simulations will be briefly described in the following. Continuous measurements of O₃, NO, NO_x, SO₂, particulate sulfates and nitrates, wind speed and direction, temperature, relative humidity, pressure and solar radiation, were conducted at the evaporation ponds using the techniques described by Matveev et al. (2001) during 2–12 August 2001. The differential optical absorption spectroscopy (DOAS) technique was employed to quantify BrO (detection limit ≤ 7 pptv) and NO₂ (detection limit ≤ 0.5 ppbv) (Matveev et al., 2001). NO_y species (NO_y=NO_x+HNO₃+2N₂O₅+NO₃+organic nitrates+particulate nitrate+...) were detected by the use of an appropriate converter located before the inlet of the NO_x moni-

tor. This, together with NO₂ data from the DOAS, was used to calculate the NO_z (NO_z=NO_y-NO_x) concentrations. During another campaign at the Ein Bokek site, canister samples were collected and analyzed for hydrocarbons using GCMS.

3 Results and discussion

3.1 The influence of NO₂ on the diurnal profiles of BrO_x, BrO and Br

The role of NO is not discussed in this section, because the NO levels measured during the field campaigns were usually very low, and frequently dropped below the detection limit (0.1 ppbv) during RBS activity. Additionally, the simulations showed that at these levels, the influence of NO on RBS activity was insignificant. In contrast, NO₂ plays a significant role in the RBS chemistry at the Dead Sea due to its relative high concentrations and its important contribution to the recycling of BrO_x.

The relationship between NO₂ and BrO during daytime is shown in Fig. 1a. An anti correlation trend between the two can be observed, shown more distinctly in the insert (Fig. 1b). The anticorrelation between the two is in agreement with measurements (Fig. 9 in Tas et al., 2006). The insert represents the time period between 07:30 and 18:00 local time (LT) in order to exclude the NO₂ peak occurring around 07:00 LT, due to advection from the Dead Sea Works, and the diminished BrO formation after 18:00 LT. The strong non-linear jagged shape of both NO₂ and BrO is very obvious. Both the anticorrelation between BrO and NO₂ and their jagged shape can be explained by the periodic two stage cyclic process previously described in detail in Tas et al. (2006), and summarized as follows: At the first stage an increase in ozone mixing ratios leads to an increase in the rate of BrO production via reaction (G2). This in turn leads to greater production of BrO_x, mainly through Cycle 3b, which then leads to the depletion of O₃ during the second stage of this periodic process. As O₃ levels drop below ~ 1 to 2 ppbv, Br levels decrease further, due to increased tendency to form terminator species, in competition with its reaction with O₃ (reaction G2; see Fig. 2). As a result of the decrease in Br mixing ratios, ozone mixing ratios increase due to advection, initiating the periodic two stage cyclic process again.

The increase in Br and BrO levels during the first stage leads to a decrease in the mixing ratios of NO₂. This is mainly due to a higher rate of consumption of NO₂ to form HNO₃ via Cycle 3b, and to a lesser extent due to an enhancement in the formation of BrONO₂ and BrNO₂ (Tas et al., 2006). Thus, during this stage of the periodic process, NO₂ tends to decrease while BrO tends to increase. During the second stage of the process a decrease in BrO and Br mixing ratios occurs and thus leads to a decrease in NO₂ consumption rate, due to a slower rate of formation of HNO₃, BrONO₂ and BrNO₂. Thus, during this stage of the periodic

process, NO₂ increases while BrO tends to decrease. Thus, the two-stage process leads to a jagged shape in the diurnal profiles of BrO and NO₂ with an anti-correlation between the two.

The relationship between BrO_x, ozone and NO_x during ozone depletion events, as described by the two stages periodic process, is not limited only to the Dead Sea area. A similar relationship between these species, during ozone depletion events at the Arctic boundary layer, was discovered by Evans et al. (2003) and was defined as “An Oscillatory System in Bromine-Catalyzed O₃ depletion”. Because of the relatively small area of the Dead Sea evaporation ponds and the high intensity of RBS activity, the time period of these oscillations in this area is expected to be small, in comparison with other areas. Thus, Evans et al. reported a much larger time period (3 days) for the oscillations at the Arctic, compared to the 1 to 3 h time period of the oscillations described in the present paper. The time period in the first case was long enough, so that a photochemical recovery of ozone occurred. In cases where the time period is short enough, advection of ozone is expected to be the main cause for ozone recovery, as was evident at the Dead Sea evaporation ponds.

The relationship between the termination reactions of RBS activity, represented by the terminator product HBr, and the mixing ratios of O₃, NO₂, Br and BrO is shown in Fig. 2. It can be seen that, with an analogy to the above explanations, when O₃ levels dip below ~2 ppbv, there is an increase in the mixing ratios of HBr (Fig. 2a and c), which is the main Br termination product. Figure 2c also shows that during intense RBS activity (between 08:00–18:30 LT), NO₂ correlates with HBr mixing ratios. The NO₂ peak around 07:00 LT, is a result of advection for that day, and is an exception. The correlation between NO₂ and HBr is the result of the tendency of these two species to increase as ozone mixing ratios drop below ~2 ppbv during the second stage of the periodic process, and to decrease during the first stage of the periodic process.

At noontime O₃ mixing ratios tend to drop to nearly zero as some of the main bromine terminator species (i.e., HO₂ and CH₂O) reach maximal mixing ratios. As a result, the depletion of BrO around noontime was repeatedly detected at the Dead Sea area (Tas et al., 2006, Fig. 5). The relatively high rate of reaction of Br with its terminators during noon time causes the sharp increase in HBr between 10:30 a.m. and 12:30 p.m., simultaneous with Br and BrO depletion and NO₂ increase, as a part of the periodic process (Fig. 2b and c). This contradicts the predictions by von Glasow and Sander (2002) that at the Dead Sea, in contrast to other sites, depletion of BrO will not occur during noontime due to the high BrO levels. Their assumption might still be correct for other areas of the Dead Sea, in which the depletion in O₃ is not as intense as it is at the evaporation ponds.

Cycle 4, in addition to Cycle 3, is another important chemical pathway for the recycling of BrO_x via interaction with NO₂:

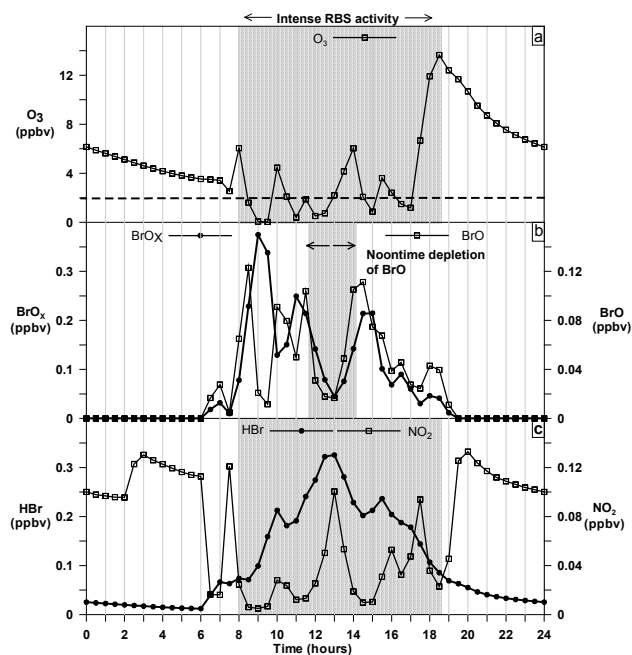
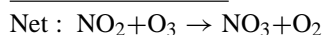


Fig. 2. The influence of O₃ depletion below ~1–2 ppbv on BrO, BrO_x and NO₂ diurnal profiles*. (a) When O₃ levels are reduced below ~1–2 ppbv, mixing ratios of HBr increase, indicating an increase in the rate that Br undergoes termination reactions (c). (b) This in turn causes the decrease in Br and BrO mixing ratios, and hence leads to lower BrO_x levels. (c) The decrease in Br and BrO mixing ratios as O₃ dip below ~1–2 ppbv leads to an increase in NO₂ mixing ratios, due to lower consumption rate by Br and BrO. This is the reason for the positive correlation between NO₂ and HBr. The increase in the mixing ratios of NO₂ and HBr is most significant during the noontime, as the mixing ratios of Br and BrO are depleted.

* All presented diurnal profiles were obtained during “FULL” simulation. The shaded area in (a) and (c) refers to intensive RBS activity, while the shaded area in (b) refers to noontime (see Sect. 3.1).

Cycle 4



Model simulations show that under the conditions prevalent at the Dead Sea, the rates of cycles 4 and 3a are about the same. Cycles 4 and 3a are less important, in terms of O₃ destruction, compared to Cycle 3b, which leads to an exponential net production of Br. However, these cycles (4 and 3a) are important due to their contribution to recycling of BrO_x, while preserving the bromine in the form of BrO, so that it can continue to react through Cycle 3b. The direct reaction of NO₂ with Br via reaction G9 leads to a null

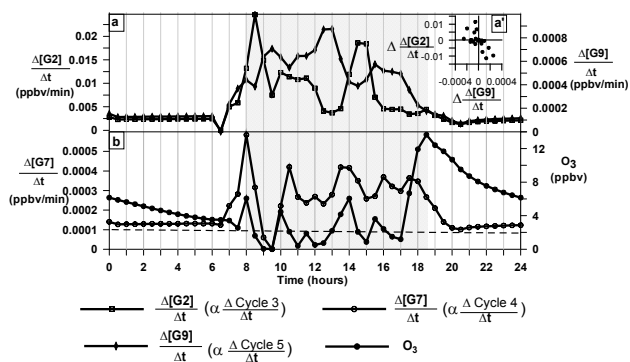
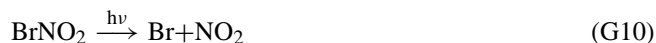


Fig. 3. The influence of ozone levels on the relative tendencies of NO₂ to react through cycles 3, 4 and 5*. (a) During the second stage of the periodic process as intensive RBS take place (indicated by the shaded areas in plots a and b) a decrease in the rate of reaction G2 and an increase in the rate of reaction G9 occur, as a result of the decrease in ozone mixing ratios and a consequent increase in the ratio [Br]/[BrO]. This, in turn, leads to a decrease in the rate of reactions through Cycle 3, and an increase of reactions through Cycle 5, respectively. The insert 3.a' presents the difference in reaction rate G2 between each two following time points versus the compatible differences in the values of the rate of reaction G9. This graph relates only to values that were obtained during RBS activity (06:00–20:00 LT). (b) The phenomena described above occur most significantly as a decrease in ozone mixing ratios below the threshold level of ~1 to 2 ppbv occurs. Due to the increase in the ratio [Br]/[BrO] during the second stage, the rate of reaction G7 also decreases parallel to the decrease in the rate of reaction G2 and the increase in the rate of reaction G9. The decrease in the rate of reaction G7 cause a decrease in the rate of Cycle 4.

* All presented diurnal profiles were obtained during “FULL” simulation.

chemical pathway, since the produced BrNO₂ is rapidly photolyzed to give the original reactants as shown in Cycle 5:

Cycle 5



In contrast to cycles 3a and 4, Cycle 5 preserves the bromine in the form of Br, and thus tends to decrease the formation rate of BrO_x via Cycle 3b. During the second stage of the periodic process, the rate of reaction G9 increases in parallel with a simultaneous decrease in the rate of ozone destruction (reaction G2) (Fig. 3a and insert 3.a'), reflecting the increase of cycle 5 at the expense of cycles 3 and 4. The rate of reaction G9 increases because less ozone is available to react with Br, and also because of the increase in the ratio [Br]/[BrO]. Because, at this stage, NO₂ has a greater tendency to react with Br than with BrO, the rate of reaction G7 also decreases, in parallel with the increase in reaction G9 and the decrease in reaction G2 (Fig. 3b). Figure 3 shows that the depletion in

the rates of reactions G2 and G7 and the increase in reaction G9, are most significant when O₃ mixing ratios drop below the threshold level of about 1 to 2 ppbv.

The influence of O₃ levels on the relative rates of reactions G7 and G9 has an important influence on the way that NO₂ interacts with BrO_x. A decrease in O₃ leads to an increase in the ratio [Br]/[BrO], a consequent increase in the rate of reaction G9 relative to the rate of reaction G7, and therefore to a lower rate of reactions through cycles 3 and 4 relative to the rate of reactions through Cycle 5. This leads to a decrease in the growth of BrO_x mixing ratios and therefore a decrease in the destruction rate of O₃, and a lower rate of increase in the mixing ratios of NO₂ (Fig. 2). In contrast, an increase in O₃ levels leads to a higher rate of NO₂ reaction via cycles 3 and 4 relative to the rate of reactions through Cycle 5. This results in an increase in the mixing ratios of BrO_x, and therefore an increase in the destruction rate of O₃ and a simultaneous decrease in the mixing ratios of NO₂ (Fig. 2).

3.2 The influence of NO₂ on the daily average levels of BrO_x

As discussed in the previous section, the tendency of NO₂ to react, during daytime, through Cycles 3b, 3a and 4, rather than Cycle 5, greatly enhances the formation of BrO_x and ozone destruction. In this section the investigation is limited only to the influence of NO₂ mixing ratios on the average mixing ratios of BrO, Br, BrO_x and O₃ obtained during daytime RBS activity (06:00–20:00 LT). Its influence on the diurnal profile of these species is ignored.

The influence of different levels of NO₂ on BrO_x mixing ratios was examined for 11 simulations with various levels of NO₂ fluxes. These simulations were based on the parameters of the “FULL” simulation (Sect. 2) as a base case scenario, and changing only the NO₂ flux levels. For each of these 11 simulations, the value of the NO₂ flux obtained in the “FULL” scenario was multiplied by a single multiplication factor, *n*, at each update time (every 15 min). For each simulation, a different value for *n* was used, varying from 0.1 to 100.

Each of the 11 simulations was run again under the same conditions, except that the bromine mechanism was excluded. Thus, for example, a simulation that was run with *n*=1, represents the “FULL” simulation if the bromine mechanism was included and the “NOB” simulation (Sect. 2.2) if the bromine mechanism was not included. *n*=40 denotes NO₂ fluxes 40 times larger than those given by the “FULL” or “NOB” base case simulations. Table 1 shows the daily average mixing ratios of some species and NO₂ fluxes during RBS activity (06:00–20:00 LT) obtained for the different simulations.

Figure 4 shows the results for the 11 simulations relating to the variations in BrO_x, Br and BrO levels with increasing NO₂ levels obtained for the 11 simulations that are based on the “FULL” simulations. Roughly, for Br and

Table 1. Average mixing ratios of various species obtained for different NO₂ flux values over the time period 06:00–20:00 LT.

Multiplication factor (<i>n</i>) for NO ₂ fluxes*	BrO (ppbv)	Br (ppbv)	NO ₂ (ppbv)	O ₃ (ppbv)	NO ₂ ** (NOB) (ppbv)	O ₃ ** (NOB) (ppbv)
0.1	0.0444	0.0523	0.0424	4.81	0.795	70.3
0.125	0.0444	0.0526	0.0425	4.80	0.797	70.4
0.167	0.0444	0.0531	0.0426	4.77	0.798	70.5
0.25	0.0444	0.0541	0.0430	4.71	0.801	70.6
0.5	0.0445	0.0575	0.0436	4.44	0.809	71.0
1	0.0445	0.0651	0.0439	4.20	0.825	72.0
2	0.0445	0.0824	0.0450	3.60	0.857	73.7
4	0.0438	0.121	0.0518	2.80	0.922	76.9
6	0.0412	0.153	0.0631	2.02	0.984	79.8
8	0.0406	0.184	0.0767	1.33	1.05	82.5
10	0.0395	0.193	0.0964	1.08	1.11	85.0
20	0.0381	0.199	0.211	1.02	1.47	95.4
40	0.0328	0.223	0.194	1.52	2.05	109
60	0.0294	0.211	0.921	2.25	76.9	229
80	0.0250	0.196	1.39	2.98	98.3	213
100	0.0238	0.182	1.89	3.69	115	198

* The *n* factors represent the values by which the NO₂ fluxes included in the “FULL” simulation were multiplied (see Sect. 3.2). The average NO₂ flux used for “FULL” simulation is $3.61 \cdot 10^{13}$ molec m⁻² s⁻¹ during RBS activity (06:00–20:00 LT).

** Mixing ratios obtained during “NOB” simulation.

BrO_x, the results of these simulations show two distinct zones of influence with respect to the NO₂ levels, separated at $\approx n=40$. In the lower zone, the Br and BrO_x mixing ratios increase sharply until $n=10$ and less strongly until $n=40$, reaching peak values of 0.2 and 0.25 ppb, respectively. From this point onwards there is a slow decrease in mixing ratios for both Br and BrO_x. In contrast, the BrO shows a continuous decrease in levels from a value of around 0.04 ppb at $n=0.1$, to half that value at $n=100$. Thus, the increase in BrO_x at the lower zone is due to the strong increase in Br that more than compensates for the decrease in BrO (see Table 1 and Fig. 4).

In the lower zone, the increase in NO₂ leads to an increase in the rate of reactions through Cycle 3b and hence to an increase in the mixing ratios of Br and BrO_x. An analysis following the “counter species” method (Leone and Seinfeld, 1984) showed that there is an overall increase of a factor of ~ 4.2 in the production of Br via Cycle 3b due to an increase of a factor of ~ 2 in the rate of reaction H2. The reason for the decrease in the production rate of Br and BrO_x in the lower zone for ($10 < n < 40$), and for the decrease in their mixing ratios at the higher zone ($n > 40$), is related to the increase in the tendency of NO₂ to react through Cycle 5 relative to its tendency to react through cycles 3 and 4 for higher NO₂ fluxes. As was explained in Sect. 3.1, the tendency of NO₂ to react through cycles 3 and 4, relative to the rate of reactions through Cycle 5, is determined mainly by the [Br]/[BrO] ratio, which is highly sensitive to variations in O₃ levels. For $n < 10$ the ozone mixing ratios are still high and thus the ratio

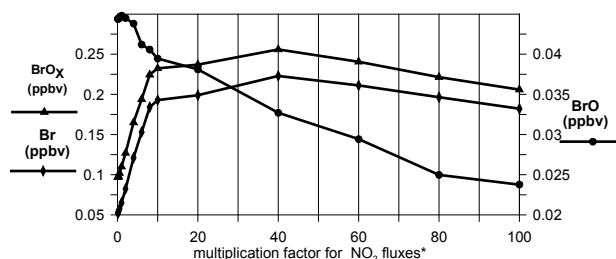


Fig. 4. Br, BrO and BrO_x mixing ratios as a function of NO₂ flux magnitude. The mixing ratios of Br, BrO and BrO_x obtained for the 11 simulations based on the “FULL” simulation are presented versus the multiplication factor for NO₂ fluxes, *n**. Two zones can be observed for changes in Br and BrO_x mixing ratios, separated in the graph at $n=40$. In the lower zone Br and BrO_x increase sharply until $n=10$. In contrast, BrO concentrations decrease sharply from $n \leq 1$.

* See additional information on the multiplication factor, *n*, in Sect. 3.2.

[Br]/[BrO] (Fig. 5b) is relatively low, and the rate of reactions through Cycles 3 and 4 is high relative to the rate of reactions through cycle 5. Thus, in this range a sharp increase in the mixing ratios of Br and BrO_x occurs as a result of the increase in NO₂ fluxes (Fig. 4 and Table 1). However, Fig. 6 shows that this ratio constantly increases for higher *n* values, and hence an increase in the formation of BrNO₂ occurs at the expense of BrO_x production via Cycle 3b. In the higher zone, the rate of reactions through Cycle 3b increases by about 10%, while the rate of reactions through Cycle 5 increase by more than 110%, reflecting an increase of about 12% in the ratio Br/BrO.

The question raised at this stage is the reason for the increase in the ratio [Br]/[BrO] and the consequent decrease in Br and BrO_x mixing ratios, for increasing *n* values at the higher range. Figure 5 shows that an increase in the ratio [Br]/[BrO] cannot be solely the result of the increase in ozone levels, since above $n=20$ this ratio increases in parallel with the ozone mixing ratios (Fig. 5a). The increase in the ratio [Br]/[BrO] is the result of the production of Br at the expense of BrO, due to the higher rate of reactions through Cycle 3b as the NO₂ levels are higher. The increase in the ratio [Br]/[BrO] leads to an increase in the rate of reactions through Cycle 5 relative to the rate of Cycles 3 and 4, and thus to an enhancement of the production of BrNO₂ at the expense of BrONO₂. Thus, the increase in the mixing ratios of NO₂ cannot lead to an unlimited increase in the mixing ratios of Br and BrO_x, since the increase in the formation of Br leads to production of BrNO₂ at the expense of BrO_x production, above a certain level of NO₂.

Figure 5 further demonstrates the complex influence of NO₂ on BrO_x levels. Figure 5c shows the variation in mixing ratios of BrONO₂ and BrNO₂ with increasing NO₂ flux. The increase in the ratio [BrNO₂]/[BrONO₂] for higher *n*

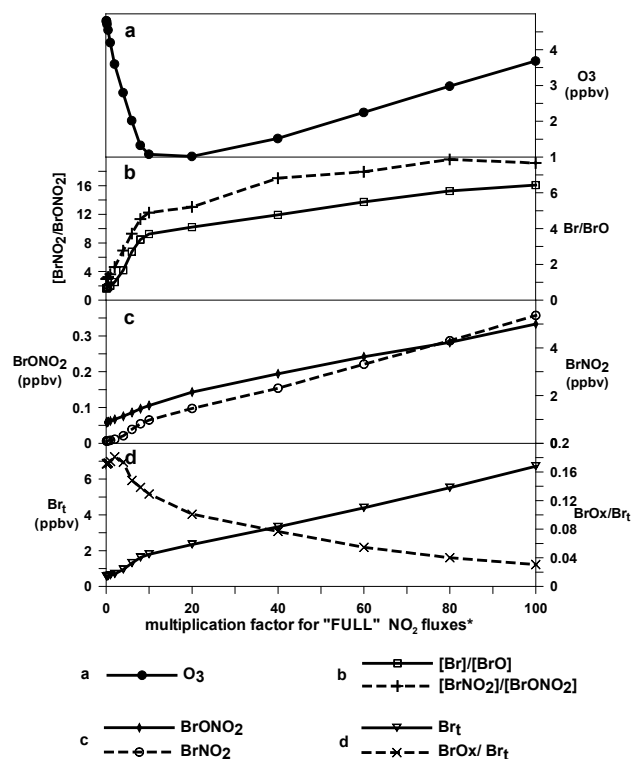


Fig. 5. Production of BrO_x and total bromine species as a function of NO₂ fluxes. (a) O₃ mixing ratios obtained for the 11 simulations that included the “FULL” bromine mechanism. O₃ mixing ratios decrease for an increase in n values until around $n^*=20$. The increase in the mixing ratios of O₃ for $n \geq 20$ indicates that the ratio [Br]/[BrO] is not influenced only by the O₃ mixing ratios. (b) The ratio [Br]/[BrO] constantly increases for an increase in n levels, mainly as a result of the higher rate of reactions through cycle 3b that leads to production of Br at the expense of BrO. The increase in the ratio [Br]/[BrO] leads to an increase in the ratio [BrNO₂]/[BrONO₂], for higher n values. This reflects an increase in the rate of reactions through Cycle 5 relative the rate of reactions through cycles 3 and 4. This, in turn, leads to a faster production of BrNO₂ via Cycle 5 at the expense of BrO_x production and recycling via cycles 3b and 3a and 4, respectively. At a certain stage the ratio [Br]/[BrO] is high enough, to cause a decrease in the mixing ratios of Br and BrO_x for an increase in n values. (c) Both the mixing ratios of BrNO₂ and BrONO₂ constantly increase for an increase in n values. (d) The continuous increase in the mixing ratios of BrONO₂ leads to a continuous increase in Br_T, for an increase in n values, due to an increase in the rate of Cycle 3b. The increase in the ratio [BrNO₂]/[BrONO₂] leads to an increase in the ratio [Br_T]/[BrO_x] above $n \geq 4$, due to an increase in the rate of Cycle 5 relative the rates of cycles 3 and 4.

* See additional information on the multiplication factor, n , in Sect. 3.2.

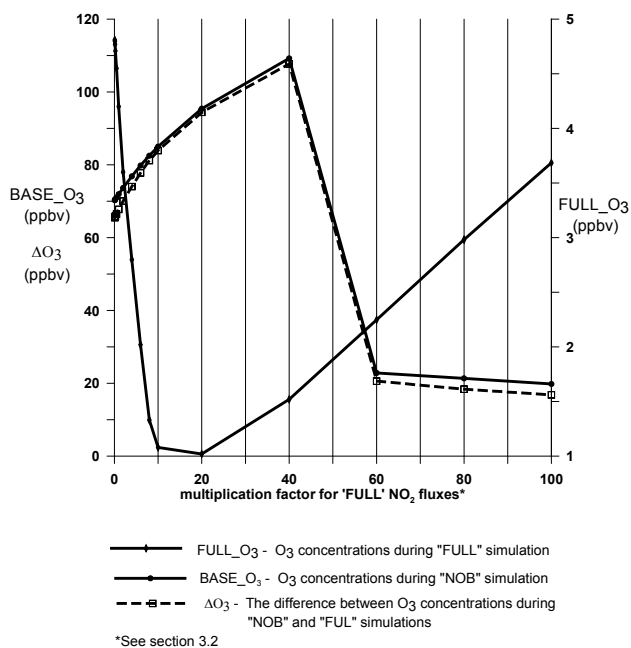


Fig. 6. Destruction of ozone by RBS activity as a function of NO₂ flux magnitude. Presented are the O₃ mixing ratios obtained for the 11 simulations that include the “FULL” bromine mechanism (FULL-O₃), the O₃ mixing ratios that were obtained during the 11 simulations that didn’t include the bromine mechanism (BASE-O₃), and the difference between these two categories (ΔO₃). The “FULL-O₃” mixing ratios decrease for n values smaller than 20 due to an increase in BrO_x mixing ratios as a result of the increase in the rate of Cycle 3b. For these n values the “FULL-O₃” decrease although the “BASE-O₃” production is NO_x limited in terms of photochemical ozone production. Between $n^*=20$ and $n=40$ an increase in “FULL-O₃” mixing ratios occurs although BrO_x mixing ratios increase too. This should be the result of the more intense effect of NO₂ to increase O₃ due to the limited NO_x conditions in terms of photochemical ozone production, compared to its effect to reduce O₃ as a result of increase in BrO_x production.

* See additional information on the multiplication factor, n , in Sect. 3.2.

values (Fig. 5b), is the result of the increase in the ratio [Br]/[BrO], and reflects an increase in the formation of the reservoir BrNO₂ through Cycle 5, at the expense of the enhancement of BrO_x production through cycle 3, and BrO recycling through cycle 4. At a certain stage Cycle 5 becomes predominant relative to Cycle 3b. This leads to a decrease in the growth of Br and BrO_x mixing ratios above $n=10$ and to a decrease in their mixing ratios above $n=40$.

The constant increase in BrONO₂ reflects the constant increase in the rate of reactions through Cycle 3b for higher n values, which leads to the increase in the mixing ratios of the total bromine (Br_T) species (Fig. 5d). However, although Br_T increases at higher n values, the increase in the formation of BrNO₂ via Cycle 5 dominates the BrO_x production above $n \sim 4$, and leads to a decrease in the ratio [BrO_x]/[Br_T].

The increase in NO₂ mixing ratios influences ozone destruction via BrO_x production, as demonstrated in Fig. 6, which shows the average ozone mixing ratios with and without the effect of bromine chemistry. Under the full bromine chemistry conditions the average ozone levels show a continuous drop for increases in *n* values, reaching minimum levels (~1 ppb) at *n*=20. It should be remarked that the reduction in O₃ levels in this lower NO₂ zone occurs under NO_x limited conditions in terms of the efficiency of photochemical ozone production. Above *n*=20, ozone levels continuously increase due to the decrease in BrO_x levels. Between *n*=20 and 40 there is an increase in O₃ levels, although the BrO_x levels increase. This increase is due to the greater contribution of NO₂ to form O₃ via photochemical processes, in comparison with its contribution to O₃ destruction as a result of BrO_x formation. In contrast, when no bromine chemistry is active, the ozone mixing ratios increase with increasing NO₂, since the system is NO_x limited. However from levels above *n*=40 a sharp decrease in ozone levels is observed, due to titration between O₃ and NO. From this point forward the ozone mixing ratios remain almost constant.

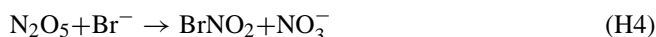
The analysis presented in this section shows that an increase in the growth of BrO_x, as a result of an increase in NO₂ levels, occurs for a wide range of NO₂ mixing ratios, representing a wide range of anthropogenic pollution levels (see Table 1). Thus, in other areas, in which the heterogeneous decomposition of BrONO₂ and the “Bromine Explosion” mechanism occur efficiently enough, an increase in NO₂ mixing ratios should also result in an increase in BrO_x mixing ratios and a consequent depletion in ozone mixing ratios.

In other cases for which these two processes do not occur efficiently enough, the increase in the concentrations of NO_x can lead to continuous decrease in the concentrations of BrO_x. For example, several studies (e.g., Beine et al., 1997; Sander et al., 1999; Ridley and Orlando., 2003) have showed that an increase in the concentrations of NO_x impedes the destruction of ozone due to an increase in the concentrations of bromine-containing nitrogen reservoirs. Thus, simultaneous depletions in ozone and NO_x during ODE's were explained by the higher impact of RBS activity on the reduction in ozone levels, due to a decreased tendency to form bromine-containing nitrogen reservoirs, as the NO_x levels are lower. It should be remarked that these simultaneous depletions in NO_x (representing mainly depletion in NO₂) and ozone concentrations might also be the result of the heterogeneous decomposition of BrONO₂ that may lead to both NO₂ depletion (e.g., Tas et al., 2006; Morin et al., 2007) and ozone destruction via BrO_x formation. The significant influence of heterogeneous recycling of BrONO₂ on the way that an increase in the NO_x concentrations affects RBS activity was also demonstrated by von Glasow et al. (2003). Their study showed that when the total surface area of particles available for the recycling of BrONO₂ and HBr is high enough,

the transformation of RBS into bromine-containing nitrogen reservoirs is significantly reduced.

It has been shown in this section, that even in cases where the two heterogeneous processes, the “Bromine Explosion” and the heterogeneous decomposition of BrONO₂, take place in the chemical mechanism, increasing NO₂ cannot continue to increase the mixing ratios of BrO_x indefinitely. Above a certain threshold value of NO₂, the mixing ratios of BrO_x are predicted to decrease. According to the present research, under conditions typical of the Dead Sea, this threshold value averages 0.2 ppbv during 06:00–20:00 LT time period (Table 1). This value is equivalent to an average NO₂ concentration of about 2.1 ppbv, for the same conditions without the bromine mechanism. This threshold value is influenced by many factors. Basically, a decrease in BrO_x, for an increase in NO₂ levels, is predicted to occur only if O₃ levels are low enough in order to enable a low enough [Br]/[BrO] ratio. The [Br]/[BrO] ratio, and hence also the threshold value, are sensitive to other parameters, including the total surface area available for heterogeneous decomposition of BrONO₂, the rate of bromine release into the gas phase, etc. Thus, the threshold level of NO₂ could be different at other locations.

An earlier study (Sander et al., 1999) suggested that an increase in NO₂ levels would not result in a higher contribution to BrO_x production by the heterogeneous decomposition of BrONO₂. The reason given for that was that the higher levels of NO₂ would lead to a significant increase in the reaction rates of NO₃ and N₂O₅ with Br⁻ via the heterogeneous reactions (H3) and (H4):



In order to investigate the effect of these reactions on the analysis described in the present paper, their potential influence on BrO_x levels should be evaluated, based on the NO₂ fluxes used in the present study. For this purpose the rate of reactions H3 and H4 should be compared with these of the rate limiting step reactions of cycles 3a, 3b, 4 and 5. The rate of reaction H2 is the slowest of all limiting rate reactions of these cycles. The rate of reaction H2 was compared to the calculated rates of reactions H3 and H4, assuming uptake coefficients (γ) of 0.16 for reaction H3 (Seisel et al., 1997), and 0.023 for reaction H4. The calculations show that the daily average rates (06:00–20:00 LT) of reactions H3 and H4 are lower than the rate of reaction H2, by at least 1.5 and 3.5 orders of magnitude, respectively, for all of the simulations described in the present study. Thus, it appears that the influence of reactions H3 and H4 on BrO_x production can be neglected, under the conditions used for the present study. However, it should be remarked that reactions H3 and H4 are expected to have higher influence on BrO_x production and NO₂ lost during nighttime, and also in cases that the available salt surface area is large enough for significant surface reaction rates.

4 Summary

The influence of NO₂ on both the diurnal profiles and daily average production of Br and BrO was investigated in this study, based on measurements performed at the Dead Sea evaporation ponds. It has been shown that the ratio [Br]/[BrO] has a significant influence on the way that NO₂ influences both the diurnal profiles and the average daily production of Br and BrO. Higher levels of [Br]/[BrO] lead to a decrease in the mixing ratios of BrO_x during the day and on a daily average basis. This is because higher levels of [Br]/[BrO] lead to higher rates of reactions of NO₂ through Cycle 5 relative to the rate of reactions through cycles 3 and 4. During the daytime, higher levels of ozone were the major factor causing an increase in the production of BrO_x by decreasing the ratio [Br]/[BrO]. However, for higher NO₂ levels and on a daily average basis, the NO₂ mixing ratios were the major factor to influence the BrO_x mixing ratios by changing the [Br]/[BrO] ratio, while ozone had only a secondary effect on this ratio.

The present study shows that the influence of NO₂ on the daily average BrO_x production can be divided into two main zones of NO₂ levels, separated by a certain threshold value of NO₂ mixing ratios. According to the present research, under the Dead Sea conditions this threshold value equals about 0.2 ppbv on a daily (06:00–20:00 LT) average. This value is equivalent to a daily average concentration of NO₂ of about 2.1 ppbv, for the same conditions excluding the bromine mechanism. In other geographical locations the value of this threshold level is expected to be different because it depends on many parameters, including the total surface area available for heterogeneous decomposition of BrONO₂, among other factors.

In the lower zone, below the threshold level of NO₂, an increase in NO₂ leads to a higher production of BrO_x, which results in more intensive destruction of O₃, as a result of an increase in the rate of reactions through cycles 3 and 4 relative to the rate of reactions through Cycle 5. For higher NO₂ levels the rate of Cycle 5 relative to cycles 3 and 4 becomes higher until, above a certain threshold level of NO₂, an additional increase in NO₂ levels leads to a decrease in BrO_x levels and O₃ destruction. It is demonstrated by the present study that, on a daily average basis, above a certain threshold level of NO₂, an increase in the mixing ratios of NO₂ leads to a decrease in the BrO_x mixing ratios, in a self-terminating process.

One of the most significant contributions of the present study refers to the relation between anthropogenic activity and RBS activity. It was shown that an increase in the mixing ratios of NO₂ leads to an enhancement of ozone destruction via an increase in the mixing ratios of BrO_x for a relatively wide range of NO₂ levels, reflecting different levels of anthropogenic activity. Similar influence of anthropogenic activity on RBS activity is expected to occur in other areas, in which the heterogeneous decomposition of BrONO₂ and

the release of bromine into the gas phase activated by HOBr are involved in the chemical mechanism. It should be remarked that in other areas, in which these two processes are not significant enough, the increase in NO_x levels may cause a decrease in ozone destruction rates due to the formation of bromine-containing nitrogen reservoirs.

The present study shows that, on a daily average basis and for all levels of NO₂ that were investigated, the levels of the total bromine species in the gas phase increase for higher NO₂ levels, as the result of an absolute increase in the rate of Cycle 3b. In the higher zone, the formation of BrNO₂ is favored at the expense of BrO_x. Once the ozone mixing ratios increase again, this reservoir may undergo fast photolysis during daytime, thereby increasing the mixing ratios of BrO_x.

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