Sensitivity of ozone to bromine in the lower stratosphere

R. J. Salawitch,[1] D. K. Weisenstein,[2] L. J. Kovalenko,[3] C. E. Sioris,[4] P. O. Wennberg,[3] K. Chance,[4] M. K. W. Ko,[5] and C. A. McLinden[6]

Received 15 September 2004; revised 23 November 2004; accepted 3 February 2005; published 9 March 2005.

[1] Measurements of BrO suggest that inorganic bromine (Br_y) at and above the tropopause is 4 to 8 ppt greater than assumed in models used in past ozone trend assessment studies. This additional bromine is likely carried to the stratosphere by short-lived biogenic compounds and their decomposition products, including tropospheric BrO. Including this additional bromine in an ozone trend simulation increases the computed ozone depletion over the past ~25 years, leading to better agreement between measured and modeled ozone trends. This additional Br_y (assumed constant over time) causes more ozone depletion because associated BrO provides a reaction partner for ClO, which increases due to anthropogenic sources. Enhanced Br_y causes photochemical loss of ozone below ~14 km to change from being controlled by HO_x catalytic cycles (primarily HO_2+O_3) to a situation where loss by the BrO+HO_2 cycle is also important. **Citation:** Salawitch, R. J., D. K. Weisenstein, L. J. Kovalenko, C. E. Sioris, P. O. Wennberg, K. Chance, M. K. W. Ko, and C. A. McLinden (2005), Sensitivity of ozone to bromine in the lower stratosphere, *Geophys. Res. Lett.*, *32*, L05811, doi:10.1029/2004GL021504.

1. Introduction

[2] Models used to quantify our understanding of ozone trends rely on estimates of stratospheric inorganic bromine (Br_y) based on the decomposition of the long-lived source gases methyl bromide (CH_3Br) and halons in the stratosphere [*World Meteorological Organization* (*WMO*), 2003]. For the assumed sources, the abundance of Br_y calculated in these models is close to zero at the tropopause, increasing with altitude as air photochemically ages.

[3] There have been many suggestions that non-zero levels of Br_y exist near the tropopause [e.g., *WMO*, 2003, chap. 2]. Possible contributions to Br_y from decomposition of short-lived halogens such as $CHBr_3$, CH_2BrCl, $CHBrCl_2$, CH_2BrCH_2Br [*Wamsley et al.*, 1998; *Dvortsov et al.*, 1999; *Schauffler et al.*, 1999; *Sturges et al.*, 2000] or the transport of BrO across the tropopause [*Ko et al.*, 1997; *Pfeilsticker et al.*, 2000] have been described. Estimates of upper stratospheric Br_y from balloon-borne observations of BrO are 6 ppt larger than the expected bromine content based on measurements of CH_3Br+halons [*WMO*, 2003, Figure 1–8].

[4] We present observations of BrO that suggest Br_y near the tropopause (termed Br_y^{TROP}) might be as high as 4 to 8 ppt. Possible source species are described. We quantify the effect of excess bromine in the lowermost stratosphere (LMS) on the photochemical budget and trends of ozone by increasing Br_y, within the AER 2D model, by specified amounts relative to abundances found using the *WMO* [2003] Ab baseline scenario for organic bromine source gases.

2. The Bromine Budget

[5] Measurements of total column BrO from space reveal much higher abundances than found from standard stratospheric models. The vertical column of BrO from GOME [*Chance*, 1998] during May 1997 far exceeds vertical BrO columns from the AER model (auxiliary material[1]). Much attention has focused on whether this discrepancy might be explained by a global, ubiquitous background level of 1 to 2 ppt of BrO in the free troposphere [*Platt and Hönninger*, 2003]. However, an examination of ground-based diffuse and direct sunlight over Lauder, NZ (45°S) indicates a mean value for tropospheric BrO of 0.2 ppt and an upper limit of 0.9 ppt [*Schofield et al.*, 2004].

[6] Inconsistencies between stratospheric Br_y inferred from BrO and the delivery of bromine to the stratosphere by long-lived organic source molecules are indicated by data shown by *Wamsley et al.* [1998, Figure 7]. A photochemical model was used to compute Br_y from in situ aircraft observations of BrO in the LMS. For our Figure 1 we have taken those data from *Wamsley et al.* [1998] and added vertical error bars to represent a root-sum-of-squares (RSS) combination of the 2σ uncertainties in the BrO measurement and uncertainties in the computation of Br_y from BrO; horizontal error bars denote the standard deviation of measured CFC-11 (a tracer of photochemical aging) during the time the BrO data were obtained. Figure 1a compares Br_y derived from BrO to estimates of stratospheric bromine from the Wamsley organic relation, which assumes contributions to Br_y from CH_3Br, halons, CH_2Br_2 and CH_2BrCl. Also shown are estimates of Br_y found by applying Br_y^{TROP} offsets of 4 and 8 ppt to the Wamsley relation. This comparison suggests the 6 organic compounds considered by Wamsley do not supply the full burden of stratospheric Br_y.

[7] Figure 1b presents a similar comparison for Br_y from the AER model. This plot indicates the bromine content of the stratosphere is much larger than within the model for the WMO Br_y scenario (differences quantified in auxiliary

[1]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA.
[2]Atmospheric and Environmental Research, Inc, Lexington, Massachusetts, USA.
[3]California Institute of Technology, Pasadena, California, USA.
[4]Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, USA.
[5]NASA Langley Research Center, Hampton, Virginia, USA.
[6]Meteorological Service of Canada, Toronto, Ontario, Canada.

0094-8276/05/2004GL021504$05.00

[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2004GL021504.

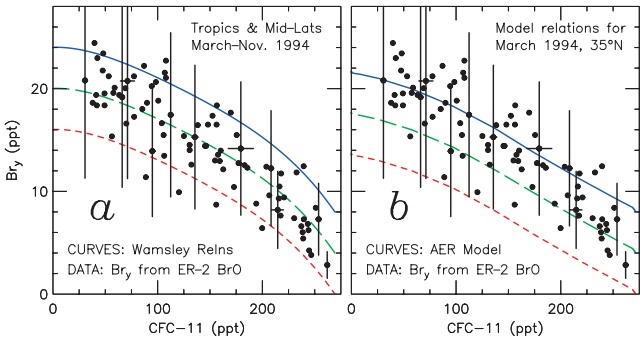

Figure 1. a. Calculated Br_y from in situ BrO (data points; see text for error bar description) plotted versus CFC-11 compared to the estimate of Br_y from measurements of the decomposition of CH_3Br, H-1211, H-1301, H-2402, CH_2Br_2, and CH_2BrCl (red short-dashed) given by *Wamsley et al.* [1998]. Also shown are estimates of Br_y from organics for Br_y^{TROP} of 4 ppt (green long-dashed) and 8 ppt (blue solid). b. Same as panel *a*, except Br_y is from the AER 2D model for 35°N, Sept. 1994, using source gases CH_3Br, H-1211, H-1301, H-2402, and H-1202 as described by the WMO Ab baseline scenario.

material). The discrepancy is larger than found for the Wamsley relation because the WMO scenario neglects contributions to Br_y from CH_2Br_2 and CH_2BrCl. These short-lived biogenic compounds deliver ~2.3 ppt of bromine to the LMS [*Wamsley et al.*, 1998].

[8] The only published profile of BrO in the tropics (22°S, Nov. 1997) indicates the presence of significant levels of BrO in the upper troposphere [*Pundt et al.*, 2002]. We have calculated Br_y from these balloon-borne, spectroscopic measurements of BrO as described in the auxiliary material. The resulting profile of Br_y is much larger than found within the AER model using the WMO Br_y scenario (Figure 2). The inferred Br_y profile suggests the conversion of organic bromine to inorganic forms below the tropopause, as noted by *Pundt et al.* [2002]. At higher altitudes, empirical Br_y is considerably larger than Br_y based solely on supply from CH_3Br+halons. This analysis suggests the contribution to Br_y from other species is ~8 ppt or perhaps larger. Also, vertical profiles of BrO retrieved from limb scatter radiances acquired by SCIAMACHY, between latitudes of 70°S and 60°N, indicate both the presence of significant levels of Br_y near the tropopause and a budget for middle stratospheric Br_y consistent with $Br_y^{TROP} \approx 8$ ppt [*Sioris et al.*, manuscript in preparation].

[9] We return to the GOME observations of column BrO. Figure 3 shows the estimated stratospheric contribution to the BrO column measured by GOME, if 1 ppt of BrO had been uniformly distributed throughout the troposphere (1 ppt tropos. BrO $\approx 2.2 \times 10^{13}$ molecules/cm^2 at 35°N; details and discussion of "Enhanced Tropospheric BrO" feature in auxiliary material). Figure 3 suggests an overall level of consistency can be achieved between satellite measurements of total BrO, aircraft and satellite measurements of stratospheric BrO, and ground-based upper limits for tropospheric BrO assuming both a stratospheric (Br_y^{TROP} of 4 to 8 ppt) and tropospheric contribution (1 ppt) to the high values of BrO measured by GOME.

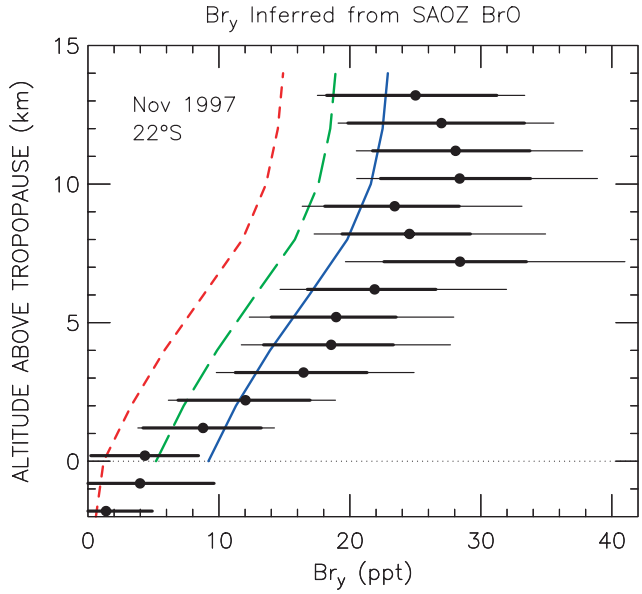

Figure 2. Profile of Br_y inferred from SAOZ BrO [*Pundt et al.*, 2002] at 22°S, Nov 1997 compared to profiles from the AER model for 20°S, Nov. 1997 using Br_y^{TROP} of 0, 4, and 8 ppt (same line types as Figure 1). Profiles are plotted relative to the local tropopause of measurement (16.8 km) and model (16.0 km). Thick error bars denote 1σ uncertainty in Br_y due just to the total measurement uncertainty for BrO. Thin error bars denote the overall 1σ uncertainty for Br_y, found from a RSS combination of the kinetic uncertainties involved in computing Br_y from BrO and the measurement uncertainty for BrO. At the lowest altitudes, overall uncertainty is dominated by the BrO measurement precision and the thin and thick error bars completely overlap. Details of the inferred Br_y calculation are given in the auxiliary material.

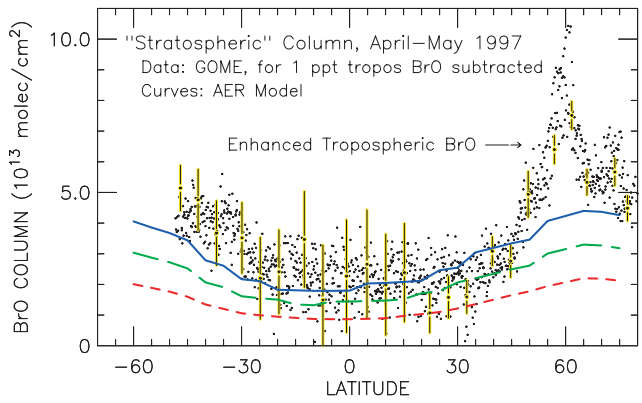

Figure 3. Estimated stratospheric BrO column from GOME for May 2, 1997 assuming a 1 ppt, uniform distribution of BrO in the troposphere (close to the upper limit of 0.9 ppt reported by *Schofield et al.* [2004]) compared to the stratospheric column from the model (mid-April, 1997), found by integrating above a chemical tropopause defined by the $O_3 = 0.1$ ppm level, for Br_y^{TROP} of 0, 4, and 8 ppt. Error bars (1σ total uncertainty) [*Chance*, 1998] are shown every 50th point, for clarity. All data and model results are restricted to SZA < 70° so that diurnal variation of the BrO column cannot be responsible for any significant portion of the model-measurement differences.

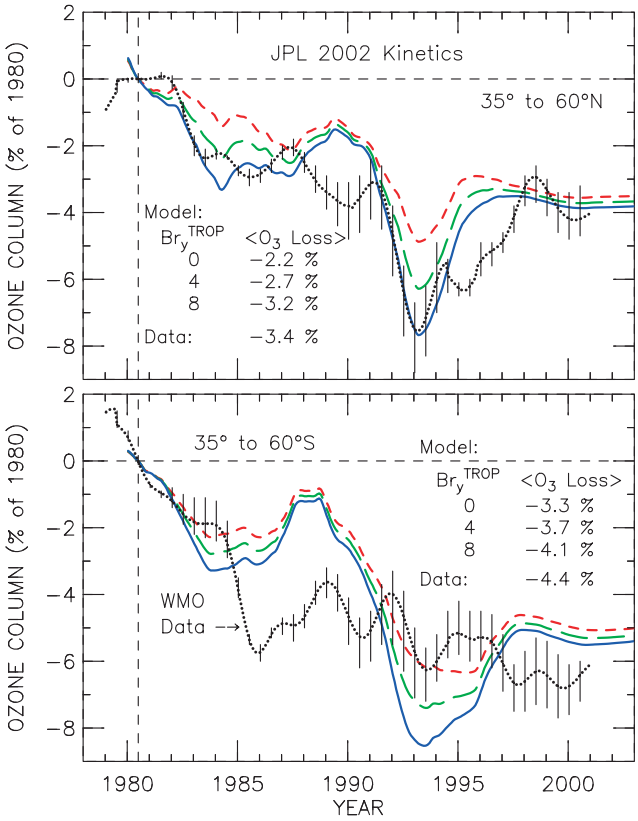

Figure 4. Calculated change in column ozone relative to 1980 levels found using the AER model for Br_y^{TROP} of 0, 4, and 8 ppt (same line types as Figure 1) for 35–60°N (top) and for 35–60°S (bottom) compared to observed trends in column ozone (black dotted lines) [*WMO*, 2003]. Each panel includes numerical values for the average of the modeled and measured ozone depletion, from the start of 1980 to the end of 2000 (details in auxiliary material).

[10] Numerous very-short lived (VSL) compounds likely contribute to Br_y at the tropical tropopause [*WMO*, 2003]. Bromoform ($CHBr_3$) levels as high as 1 ppt exist in the tropical mid-troposphere [*Schauffler et al.*, 1999; *Sturges et al.*, 2000] and this compound has the capacity to increase Br_y in the LMS by ~2 ppt [*Dvortsov et al.*, 1999]. Ethylene dibromide ($C_2H_4Br_2$) has been measured to be ~1 ppt at the South Pole [*Khalil and Rasmussen*, 1985] and ~5.0 ppt in urban areas [*Pratt et al.*, 2000], has anthropogenic sources [*Khalil and Rasmussen*, 1985], and has the potential to deliver significant amounts of Br_y to the tropopause. Decomposition products from C_2H_5Br, $CHBr_2Cl$, and C_3H_7Br provide a possible additional contribution of ~0.7 ppt to Br_y^{TROP} [*Pfeilsticker et al.*, 2000; *WMO*, 2003]. These abundances, combined with the 2.3 ppt from CH_2Br_2 and CH_2BrCl and the possible ~1 to 2 ppt background BrO (albeit, this might be supplied by the above mentioned species), are consistent with our 4 to 8 ppt estimate for Br_y^{TROP} based on measured BrO.

[11] The mechanism for supply of Br_y to the tropopause requires further study. Since HBr and HOBr are soluble, we might expect inorganic species produced by the decomposition of VSL biogenic compounds to rain out before reaching the stratosphere. However, heterogeneous reactions on tropospheric aerosol might liberate bromine back to the gas phase, allowing for delivery of Br_y derived from these organic compounds to the stratosphere [*Platt and Hönninger*, 2003].

[12] Many prior studies have examined the bromine budget. *Avallone et al.* [1995] used airborne observations of BrO and organic source gases to report a BrO/Br_y ratio of ~40% compared to a calculated value of ~55% based on kinetics circa 1994. This result contradicts our findings in that Br_y inferred from their BrO would be smaller than Br_y from organics. However, they focused on data collected above 19 km and north of 25°N, where the fractional increase in Br_y due to VSL species is relatively small.

[13] *Pfeilsticker et al.* [2000] found that an additional 3.1 ppt of bromine is needed to reconcile the budget based on balloon-borne profiles of BrO and organic compounds. Their formulation of Br_y^{org} included a contribution of 2.6 ppt from $C_nH_mBr_yCl_x$ compounds. Had they used the WMO definition of Br_y^{org}, their budget discrepancy would have been 5.7 ppt, consistent with our results.

[14] *Sinnhuber et al.* [2002] and *Schofield et al.* [2004] reported good agreement between column BrO and values found by the SLIMCAT model, for total model Br_y equal to 20 and 21 ppt, respectively, reflecting a 5 to 6 ppt contribution from VSL species. Within SLIMCAT, decomposition of CH_3Br is a surrogate for supply of all stratospheric Br_y. Considering that CH_3Br is shorter lived than halons in the LMS and model Br_y was increased by ~30% relative to WMO Br_y, our results are generally consistent with these

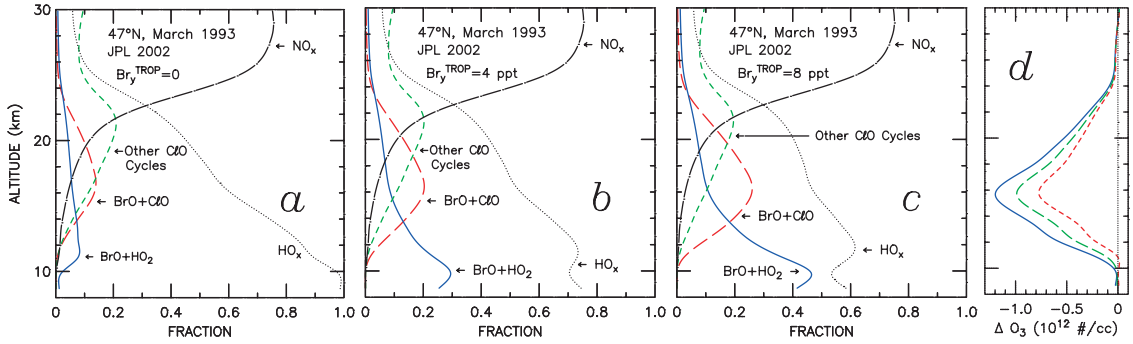

Figure 5. Fraction of odd oxygen loss by various catalytic cycles within the AER model at 47°N, March 1993, for model runs with Br_y^{TROP} of 0, 4, and 8 ppt (panels *a*–*c*, as indicated). d. Difference between the ozone profile at 47°N, March 1993 and the profile at 47°N, March 1980 for runs with Br_y^{TROP} of 0, 4, and 8 ppt (same line types as Figure 1).

two studies. As shown in the auxiliary material, the stratospheric vertical column of BrO given by *Schofield et al.* [2004] is consistent with values of Br_y^{TROP} between 4 and 8 ppt when compared to calculations of column BrO from the AER model.

3. Ozone Trends

[15] Figure 4 compares observed trends in column ozone between 35–60°N and 35–60°S to computed trends from the AER 2D model for three scenarios: Br_y^{TROP} of 0, 4, and 8 ppt. No trend is imposed on the Br_y^{TROP}, since presumably the sources are mainly biogenic. Rather, the model is run using the WMO Ab scenario for time evolution of Br_y, Cl_y, CH_4, aerosols, etc, with Br_y then increased by either 4 or 8 ppt at each model level and all times. Although use of a constant Br_y offset is a simplification, it captures the essence of what appears to be occurring. Most of the bromine from VSL gases that cross the tropopause is likely released below 16 km, where the computed effect on ozone trends is largest (Figure 5d). Also, a constant offset is straightforward to implement in global models. Ozone column data, smoothed as described in the report, are from *WMO* [2003, Figure 4–33]. Calculations from the AER model are identical to those presented by *WMO* [2003, chap. 4] except we use reaction rates from the most recent compendium [*Sander et al.*, 2003]. Use of the latest rate constants reduces the computed ozone depletion by about 13% relative to results presented in *WMO* [2003] (auxiliary material).

[16] Enhanced Br_y in the LMS increases computed ozone depletion, particularly during times of elevated aerosol loading due to volcanic activity. The model accounts for ~65% and ~75% of the observed depletion in the 35–60°N and 35–60°S regions, respectively, for $Br_y^{TROP} = 0$. Better overall agreement, ~92% of measured ozone loss in each hemisphere, is achieved for runs using $Br_y^{TROP} = 8$ ppt, a value consistent with the BrO observations presented above. The AER model, like most other models used in the *WMO* [2003] assessment, is less capable of describing year-to-year variations of ozone in the 35–60°S region, which might be due to poor representation within models of ozone-depleted air exported from the vortex or to improper aliasing of the 11-yr solar cycle, the QBO, and volcanic aerosol effects in the smoothing of O_3 column data performed by WMO (R. Stolarski, private communication, 2004). Regardless, model calculations presented here demonstrate that ozone depletion is increased by the presence of enhanced bromine in the LMS, as suggested by *WMO* [2003] (pg 4.46–4.47).

[17] Figure 5 provides a look into the model photochemistry and O_3 loss. Contributions to O_3 loss by catalytic cycles at 47°N (March 1993) are shown, as well as the change in O_3 profile at 47°N between March 1980 to March 1993. Increased O_3 depletion associated with enhanced bromine is due mainly to a greater role for catalytic loss by the BrO+ClO cycle. Larger BrO concentrations provide a reaction partner for ClO, which in March 1993 was enhanced by increased aerosol following the Mt. Pinatubo eruption. For non-zero Br_y^{TROP}, ozone loss below ~14 km changes from being dominated by pure HO_x photochemistry to a situation where loss by the BrO+HO_2 cycle is considerable. Enhanced loss by the BrO+HO_2 cycle in the LMS occurs for all years of the simulation; this feature is not driven by volcanic aerosol.

[18] Reductions in the O_3 profile revealed by the time slice in Figure 5d peak at 16 km, the altitude where fractional contribution to O_3 loss by the BrO+ClO cycle also maximizes. Observations reveal that loss of O_3 peaked near 16 km over the time period 1980–1996 [*WMO*, 2003, Figure 4–13]. Calculated trends in O_3 are small at altitudes where loss from the BrO+HO_2 cycle peaks because we have assumed constant Br_y^{TROP}.

4. Concluding Remarks

[19] Enhancements to lower stratospheric Br_y are probably due primarily to biogenic gases. Many of these compounds are produced by coastal seaweed populations that might be affected by processes such as El Niño or changes in ocean temperature, circulation, and nutrient supply [*Carpenter and Liss*, 2000]. The delivery of Br_y to the tropopause depends on the interaction of convective and chemical processes in the upper troposphere [*WMO*, 2003] that might vary interannually. It is important to quantify the source gases and processes that appear to be responsible for supply of Br_y to the tropopause and to understand possible, associated climate-chemistry interactions [*Quack et al.*, 2004].

[20] **Acknowledgments.** We thank R. Schofield for helpful discussions and sharing results prior to publication, W. Randel for sharing O_3 trend data files, F. Goutail for providing SAOZ BrO data files, and the reviewers for constructive comments. Research at the Jet Propulsion Laboratory, California Institute of Technology, is performed under contract with the National Aeronautics and Space Administration (NASA). Research at the Smithsonian Astrophysical Observatory is supported by NASA and the Smithsonian Institution. Work at AER is funded by the NASA ACMAP and SOSST programs.

References

Avallone, L. M., D. W. Toohey, S. M. Schauffler, W. H. Pollock, L. E. Heidt, E. L. Atlas, and K. R. Chan (1995), In situ measurements of BrO during AASE II, *Geophys. Res. Lett.*, *22*, 831–834.

Carpenter, L. J., and P. S. Liss (2000), On temperate sources of bromoform and other reactive organic bromine gases, *J. Geophys. Res.*, *105*, 20,539–20,547.

Chance, K. (1998), Analysis of BrO measurements from GOME, *Geophys. Res. Lett.*, *25*, 3335–3338.

Dvortsov, V. L., M. A. Geller, S. Solomon, S. M. Schauffler, E. L. Atlas, and D. R. Blake (1999), Rethinking reactive halogen budgets in the lower stratosphere, *Geophys. Res. Lett.*, *26*, 1699–1702.

Khalil, M. A. K., and R. A. Rasmussen (1985), The trend of $CBrClF_2$ and other Br-containing gases at the South Pole, *Antarct. J. U. S.*, *19*, 206–207.

Ko, M. K. W., N.-D. Sze, C. J. Scott, and D. K. Weisenstein (1997), On the relation between stratospheric chlorine/bromine loading and short-lived tropospheric source gases, *J. Geophys. Res.*, *102*, 25,507–25,517.

Pfeilsticker, K., W. T. Sturges, H. Bösch, C. Camy-Peyret, M. P. Chipperfield, A. Engel, R. Fitzenberger, M. Müller, S. Payan, and B.-M. Sinnhuber (2000), Lower stratospheric organic and inorganic bromine budget for the arctic winter 1998/99, *Geophys. Res. Lett.*, *27*, 3305–3308.

Platt, U., and G. Hönninger (2003), The role of halogen species in the troposphere, *Chemosphere*, *52*, 325–338.

Pratt, G. C., et al. (2000), An assessment of air toxics in Minnesota, *Environ. Health Perspect.*, *108*, 815–825.

Pundt, I., J.-P. Pommereau, M. P. Chipperfield, M. Van Roozendael, and F. Goutail (2002), Climatology of the stratospheric BrO vertical distribution by balloon-borne UV–visible spectrometry, *J. Geophys. Res.*, *107*(D24), 4806, doi:10.1029/2002JD002230.

Quack, B., E. Atlas, G. Petrick, V. Stroud, S. Schauffler, and D. W. R. Wallace (2004), Oceanic bromoform sources for the tropical atmosphere, *Geophys. Res. Lett.*, *31*, L23S05, doi:10.1029/2004GL020597.

Sander, S. P., et al. (2003), JPL 2002: Chemical kinetics and photochemical data for atmospheric studies, *JPL Publ.*, *02–25*.

Schauffler, S. M., E. L. Atlas, D. R. Blake, F. Flocke, R. A. Lueb, J. M. Lee-Taylor, V. Stroud, and W. Travnicek (1999), Distributions of brominated organic compounds in the troposphere and lower stratosphere, *J. Geophys. Res.*, *104*, 21,513–21,535.

Schofield, R., K. Kreher, B. J. Connor, P. V. Johnston, A. Thomas, D. Shooter, M. P. Chipperfield, C. D. Rodgers, and G. H. Mount (2004), Retrieved tropospheric and stratospheric BrO columns over Lauder, New Zealand, *J. Geophys. Res.*, *109*, D14304, doi:10.1029/2003JD004463.

Sinnhuber, B.-M., et al. (2002), Comparison of measurements and model calculations of stratospheric bromine monoxide, *J. Geophys. Res.*, *107*(D19), 4398, doi:10.1029/2001JD000940.

Sturges, W. T., D. E. Oram, L. J. Carpenter, S. A. Penkett, and A. Engel (2000), Bromoform as a source of stratospheric Br_y, *Geophys. Res. Lett.*, *27*, 2081–2084.

Wamsley, P. R., et al. (1998), Distribution of halon-1211 in the upper troposphere and lower stratosphere and the 1994 total bromine budget, *J. Geophys. Res.*, *103*, 1513–1526.

World Meteorological Organization (WMO) (2003), Global ozone research and monitoring project, in *Scientific Assessment of Ozone Depletion: 2002*, *Rep. 47*, Geneva.

K. Chance and C. E. Sioris, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138–1516, USA.

M. K. W. Ko, NASA Langley Research Center, Mail Stop 401B, Hampton, VA 23681-2199, USA.

L. J. Kovalenko and P. O. Wennberg, Division of Geological and Planetary Sciences, California Institute of Technology, Mail Stop 150-21, Pasadena, CA 91125, USA.

C. A. McLinden, Meteorological Service of Canada, 4905 Dufferin Street, Toronto, ON, Canada ON M3H 5T4.

R. J. Salawitch, Jet Propulsion Laboratory, California Institute of Technology, MS 183-601, Pasadena, CA 91106, USA. (ross.j.salawitch@jpl.nasa.gov)

D. K. Weisenstein, Atmospheric and Environmental Research, Inc, 131 Hartwell Avenue, Lexington, MA 02421–3126, USA.