

1 Attribution of recovery in lower-stratospheric ozone

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11 12 13 Abstract

14
15 Multiple satellite and ground-based observations provide consistent evidence that the
16 thickness of Earth's protective ozone layer has stopped declining since 1997, close to the
17 time of peak stratospheric halogen loading. Regression analyses with Effective Equivalent
18 Stratospheric Chlorine (EESC) in conjunction with further analyses using more
19 sophisticated photochemical model calculations constrained by satellite data demonstrate
20 that the cessation of ozone depletion between 18-25 km altitude is consistent with a
21 leveling off of stratospheric abundances of chlorine and bromine, due to the Montreal
22 Protocol and its amendments. However, ozone increases in the lowest part of the
23 stratosphere, from the tropopause to 18 km, account for about half of the improvement in
24 total column ozone during the past 9 years at northern hemisphere mid-latitudes. The
25 increase in ozone for altitudes below 18 km is most likely driven by changes in transport,
26 rather than driven by declining chlorine and bromine. Even with this evidence that the
27 Montreal Protocol and its amendments are having the desired, positive effect on ozone
28 above 18 km, total column ozone is recovering faster than expected due to the apparent
29 transport driven changes at lower altitudes. Accurate prediction of future levels of
30 stratospheric ozone will require comprehensive understanding of the factors that drive
31 temporal changes at various altitudes, and partitioning of the recent transport-driven
32 increases between natural variability and changes in atmospheric structure perhaps
33 related to anthropogenic climate change.

1 **1. Introduction**

2 Atmospheric ozone, which protects life on Earth's surface from damaging solar ultraviolet
3 radiation, exists mostly (~90% of the total column) in the stratosphere. The decrease in
4 stratospheric ozone and the character of its expected recovery have been the subject of intense
5 research [WMO, 2003]. Recently reported evidence for the first stage of recovery (i.e., a
6 slowdown in the ozone depletion rate) in the upper stratosphere at 35-45 km [Newchurch et al.,
7 2003b; Reinsel et al., 2002] has confirmed our understanding of ozone chemistry and the positive
8 effect of the Montreal Protocol and its amendments, which have led to a decline in stratospheric
9 halogen (chlorine and bromine) loading. However, the largest fraction of the ozone column
10 resides in the lower stratosphere, between approximately 10 and 25 km altitude [WMO, 1999].
11 The abundance of ozone in the lower stratosphere is the essential metric for confirming the health
12 of the ozone layer.

13 Stratospheric ozone is continually produced by photolysis of molecular oxygen and is
14 removed locally by both transport and chemical processes. In the upper stratosphere, transport
15 plays a minor role and there is a direct, almost linear anti-correlation between the abundances of
16 ozone and chlorine [e.g., figure 6-21, WMO, 1999]. The majority of stratospheric chlorine is
17 supplied by industrial pollutants, such as CFCs (chlorofluorocarbons). Ozone in the lower
18 stratosphere is sensitive to re-distribution by atmospheric transport, the abundance of volcanic
19 aerosols, and a complex set of non-linear chemical interactions involving anthropogenic chlorine
20 and bromine [chapter 7, WMO, 1999; chapter 4, WMO, 2003]. A number of recent studies, based
21 on examination of time series of total column ozone, have noted a turnaround in the recent
22 downward trend [Reinsel et al., 2005; Steinbrecht et al., 2005; Hadjinicolaou et al., 2005] that
23 may be evidence for the beginning of an ozone recovery due to declining halogen loading
24 [Reinsel et al., 2005]. However, Hadjinicolaou et al. [2005] attribute the recent turnaround in total
25 column ozone to effects of transport. Here, we examine changes in total column ozone as well as
26 partial ozone columns, in specific altitude regions, to better ascertain effects of halogen chemistry
27 (i.e., chlorine and bromine) and transport forcings on recent changes in stratospheric ozone. Our
28 focus is on changes in ozone that have occurred outside the polar regions; our analyses are

1 restricted to regions equatorward of 60° latitude. The long-term evolution of polar ozone is
2 sensitive to changes in stratospheric temperature that may be linked to climate change, as well
3 as evolving levels of chlorine and bromine, and is the subject of many other studies [*Austin et al.*,
4 2002; *Austin*, 2003; *Huck et al.*, 2005; *Newman et al.*, 2004; *Rex et al.*, 2004; *Shindell et al.*,
5 1998; *Solomon et al.*, 2005; *Yang et al.*, 2005]. However, the influence of polar ozone loss on the
6 extra-polar ozone time series [*Reinsel et al.*, 2005; *Weatherhead and Andersen*, 2005] is
7 considered in this study.

8 Recently, the International Ozone Commission [http://ioc.atmos.uiuc.edu/documents/](http://ioc.atmos.uiuc.edu/documents/Statement-QOS2004.pdf)
9 [Statement-QOS2004.pdf](http://ioc.atmos.uiuc.edu/documents/Statement-QOS2004.pdf) defined the first stage of ozone recovery as a ‘statistically significant
10 slowing of the downward trend’. Our study focuses on empirical evidence for this first stage of
11 ozone recovery that is evident from several independent measurement systems and networks
12 covering large portions of the global atmosphere during the past 25 years. These independent
13 observing techniques show a consistent slowdown in the loss rates in total ozone columns,
14 stratospheric ozone columns, and ozone columns between 18-25 km (near the ozone-layer
15 maximum). Our study focuses on the attribution of changes in ozone at mid-latitudes by
16 examining the role of chemistry and transport forcings on observed changes in partial column
17 ozone, for layers between 18-25 km and the tropopause to 18 km. The significance of these
18 changes is quantified by a cumulative sum of residuals analysis [*Newchurch et al.*, 2003b;
19 *Reinsel*, 2002]. A photochemical model, constrained by satellite observations of tracers of
20 atmospheric transport, volcanic aerosol loading, and numerous other chemical measurements, is
21 also used to quantify the expected increases in ozone due to declining levels of stratospheric
22 chlorine and bromine that have resulted from the Montreal Protocol and its amendments.

23

24 **2. Data**

25 The most comprehensive representation of changes in the global stratospheric ozone
26 layer is based on the consistent results of three independent satellite instruments and two
27 independent ground-based observing networks. We analyze the TOMS/SBUV satellite
28 measurements to characterize total-column ozone changes from 60°S to 60°N latitudes. From the

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1 well-calibrated ground-based networks, we use 36 Dobson/Brewer stations between 30°S-60°N
2 to corroborate the satellite total-column ozone results. We use both SAGE and HALOE satellite
3 measurements to characterize the global stratosphere above 18 km, between 60°S and 60°N.
4 These ozone data are area-weighted to compute near-global mean values. Because most of the
5 total-column ozone amount resides in the stratosphere and because the global mixing time is
6 significantly less than the decadal time frame important here, we expect to see broadly consistent
7 recovery signatures from all of these independent measurements.

8 The Stratospheric Aerosol and Gas Experiment I and II (SAGE I/II) instruments comprise
9 the longest (1979 to August 22, 2005, but with a discontinuity between November, 1981 and
10 October, 1984) and most widely analyzed source of global stratospheric ozone measurements
11 [*Cunnold et al.*, 2000; *Newchurch et al.*, 2000; *WMO*, 2003]. The complete version-6.2 data set
12 and details of the retrieval algorithm are available through <http://www-sage2.larc.nasa.gov>.

13 The version-19 Halogen Occultation Experiment (HALOE) data for 1991 to November 21,
14 2005 comprise a shorter, but equally accurate record of stratospheric ozone amounts, in addition
15 to measurements of other trace gases critical to partitioning the chemical and dynamical causes
16 of the improving ozone layer [*Russell III et al.*, 1993]. The HALOE data are available at
17 <http://haloedata.larc.nasa.gov>. Both SAGE and HALOE measurements have been extensively
18 validated [*Ackerman et al.*, 1989; *Attmannspacher et al.*, 1989; *Cunnold et al.*, 1989; *Cunnold et*
19 *al.*, 1996; *Gordley et al.*, 1996; *Hervig et al.*, 1996; *Newchurch et al.*, 1995; *Oberbeck et al.*, 1989;
20 *Russell III et al.*, 1996a,b; *Wang et al.*, 2002] and are widely accepted by the atmospheric
21 community for studies of ozone trends [*Harris et al.*, 1998; *WMO*, 1994; *WMO*, 2003].

22 We also analyze global total ozone data from the merged Total Ozone Mapping
23 Spectrometer (TOMS)/SBUV data (Merged Ozone Data, herein after referred to as the MOD),
24 which provide nearly continuous global coverage since 1979 [*McPeters et al.*, 1996; *McPeters*
25 *and Labow*, 1996; *Reinsel et al.*, 1994; *Stolarski et al.*, 1991] (details at
26 http://code916.gsfc.nasa.gov/Data_services/merged/). Total ozone measurements observed from
27 the ground-based Dobson [*Dobson*, 1931; *Dobson*, 1968; *Dobson and Harrison*, 1926; *Dobson et*
28 *al.*, 1928; *Komhyr et al.*, 1989; *Lloyd et al.*, 1999; *Newchurch et al.*, 2000; *Staelin et al.*, 1998;

1 *Staehelin et al.*, 1995; WMO, 2003] and Brewer [*Bais et al.*, 1996; *Hoegger et al.*, 1992; *Kerr et*
2 *al.*, 1988; *Lloyd et al.*, 1999; *McElroy and Kerr*, 1995; *Slusser et al.*, 1999; *Staehelin et al.*, 1995]
3 spectrophotometers are obtained from the World Ozone and Ultraviolet Radiation Data Centre
4 (WOUDC) (<http://www.msc-smc.ec.gc.ca/woudc>). These data are mostly selected based on table
5 4-4 of WMO [1999]: 26 Dobson/Brewer stations between 30-60°N (Kagoshima, Quetta, Sapporo,
6 Tateno, Bismarck, Caribou, Edmonton, Arosa, Camborne, Haute Provence, Potsdam, Uccle,
7 Vigna Di Valle, Toronto, Boulder, Belsk, Goose Bay, Churchill, Lisbon, Hradec Kralove,
8 Hohenpeissenberg, Nashville, Wallops Island, Cairo, Sestola, and Xianghe) and 10
9 Dobson/Brewer stations between 30°S-30°N (Kodaikanal, New Delhi, Mauna Loa, Varanasi,
10 Naha, Samoa, Cachoeira Paulista, Kunming, Singapore, and Natal). The selected data follow the
11 corrections recommended by WMO [1999, section 4.2]. Balloon-borne ozonesonde
12 measurements [*Newchurch et al.*, 2003a, *Oltmans et al.*, 1998; *Oltmans et al.*, 1996] from 11
13 stations between 30-60°N (Kagoshima, Sapporo, Tateno, Edmonton, Uccle, Boulder, Goose Bay,
14 Churchill, Hohenpeissenberg, Wallops Island, and Payerne), obtained from the WOUDC, are
15 used to derive reliable long-term trends of ozone from the surface to 27 km [page 4.14, WMO,
16 1999]. Ozone columns are calculated both in the lower stratosphere between the tropopause and
17 18 km (TP-18 km) and in the middle stratosphere (18-25 km near the maximum layer in ozone
18 concentration).

19

20 **3. Statistical model**

21 We employ a stepwise linear regression model to remove solar and Quasi Biennial
22 Oscillation (QBO)-related signals from the ozone time series [*Newchurch et al.*, 2000; *Newchurch*
23 *et al.*, 2003b]. Variations in solar ultraviolet radiation due to the 11-year cycle of solar sunspots,
24 and changes in the direction of stratospheric winds in the tropics that vary on a roughly 2.5-year
25 period, are known to affect measured time series of stratospheric and total column ozone.
26 Because our emphasis is on the identification of variations in ozone due to changes in halogen
27 loading, a statistical model is used to account for, and remove, the effects of these processes on
28 the measured time series. Seasonal effects and the mean abundance of ozone over the time

1 period are also removed, providing a residual time series that is examined for evidence of ozone-
2 layer recovery.

3 The linear regression model is well accepted by the atmospheric sciences community
4 [*Harris et al.*, 1998] and is represented by

5

$$6 \quad [O_3]_t = \mu + \omega t + [\text{Seasonal terms}] + [\text{QBO periodic terms}] + \gamma [F10.7]_t + U_t \quad (1)$$

7

8 where μ is the mean level, ω is a linear trend coefficient, and the seasonal terms represent the
9 12-, 6-, 4-, and/or 3-months cosine terms each with a time lag to obtain the best estimate of its
10 coefficient. The QBO periodic terms consist of an ensemble of cosines with time lags to represent
11 the QBO signal with periods between 3 and 30 months excluding 12-, 6-, 4-, and/or 3-months
12 terms, which are included in the seasonal coefficients. $[F10.7]_t$ is the F10.7-cm radio flux density,
13 which is used to provide a proxy for variations in solar UV irradiance. γ is a solar signal
14 regression coefficient. U_t is the autocorrelated error term, representing a first-order
15 autoregressive process ($U_t = a_1 U_{t-1} + \varepsilon_t$).

16 Based on surface measurements of ozone depleting substances and the time lag (~3
17 years) involved in their rising to the altitude of the stratospheric ozone layer at mid-latitudes, we
18 choose the start of 1997 as the time to test for an inflection in the ozone time series [*Montzka et*
19 *al.*, 1999; *WMO*, 2003]. The Effective Equivalent Stratospheric Chlorine (EESC), a combined
20 measure of lower stratospheric abundances of inorganic chlorine and bromine, peaked in mid-
21 1996 [figure 1-23, *WMO*, 2003]. The effect of the autoregressive coefficient on the subsequent
22 uncertainty calculation is described in the appendix. Details of the treatment of exogenous
23 variables appear in *Newchurch et al.* [2003b].

24 An aerosol term is not included in the regression. Highly-elevated aerosol loading
25 following major volcanic eruptions interferes with the space-borne measurement of lower
26 stratospheric ozone [*Cunnold et al.*, 2000]. Of course, ozone depletion results from changes in
27 heterogeneous chemistry associated with enhanced aerosol loading following major volcanic
28 eruptions [e.g., *Dessler et al.*, 1993; *Fahey et al.*, 1993; *Wennberg et al.*, 1994; *Kinnison et al.*,

1994]. Changes in stratospheric heating associated with volcanic aerosols lead to additional short-term variations in ozone [e.g., *Kinne et al.*, 1992; *Kinnison et al.*, 1994; *Robock*, 2000]. We have omitted data collected up to 30 months following the eruption of Mt. Pinatubo from the SAGE and HALOE time series due to the aerosol influence on space-based ozone [*Cunnold et al.*, 2000] and also because our analysis is focused on long term changes in ozone for stratospheric aerosol conditions close to background. We also omit the merged TOMS/SBUV data, Dobson/Brewer total ozone, and ozonesonde ozone records for 1991.5-1994.0 to be consistent with the statistical treatment of the SAGE and HALOE satellite records and because our study is focused on near background aerosol conditions. The omission of data for time periods perturbed by enhanced volcanic aerosols is a common practice in regression based analyses of ozone time series: e.g., *Reinsel et al.* [2005] omit data influenced by Pinatubo, as explained in paragraph 10 of their paper. Here, we show data collected during the Pinatubo time period, plotted as open circles, but we do not include these data in our statistical analyses.

4. Photochemical Model

The attribution of changes in ozone is based independently on EESC regression and on more sophisticated photochemical model calculations constrained by observations of tracers of dynamical motion and stratospheric aerosol. The EESC time series is based on measurements of tropospheric total organic chlorine (CCl_y) and bromine (CBr_y). It is lagged relative to the surface by three years [pages 1.32 and 11.15, *WMO*, 1999 and page 1.19, *WMO*, 2003]. The efficiency of ozone loss due to bromine relative to chlorine, which is based on photochemical model simulations, is used to arrive at a single time series to represent the aggregate effect of halogens on ozone [alpha factor, page 1.69, *WMO*, 2003].

Many studies which have focused on attribution of ozone changes have used EESC to represent the effects of halogens on ozone [e.g., *Newman et al.*, 2004; *Huck et al.*, 2005; *Yang et al.*, 2005]. However, EESC is a simplistic representation of the influence of chlorine and bromine on ozone. Not all stratospheric air is three years old, as assumed in the formulation of EESC. Also, the relative influence of chlorine and bromine on ozone loss varies as a function of altitude,

1 latitude, season, and aerosol loading. The formulation of EESC assumes a single relative-
2 influence factor that has the same value at all latitudes and altitudes. However, the contribution of
3 halogens to ozone loss varies as a function of aerosol loading [e.g., *Dessler et al.*, 1993; *Fahey*
4 *et al.*, 1993; *Kinnison et al.*, 1994] and as a function of the abundance of HO_x (hydrogen oxide)
5 and NO_x (nitrogen oxide) radicals. In turn, HO_x and NO_x variations are also driven by changes in
6 H₂O, CH₄, and temperature [e.g., *Salawitch et al.*, 1994; *Wennberg et al.*, 1994]. Also, bromine
7 has a larger relative influence on ozone loss near the tropopause than at higher altitudes [e.g.,
8 *Salawitch et al.*, 2005].

9 We have used a photochemical model, constrained by satellite measurements of water
10 vapor (H₂O), ozone (O₃), methane (CH₄), and sulfate aerosols, to compute 24-hour-average
11 radical abundances (e.g., ClO, BrO, OH, HO₂, NO, and NO₂) for all altitudes, latitudes, and time
12 periods under consideration. The fractional contribution of halogens to total ozone loss found
13 from these calculated radical fields, termed LOSS_{MODEL}, is also used as a regression variable in
14 the analysis discussed in Section 5. The quantity LOSS_{MODEL}, described more fully below, can be
15 thought of as a more sophisticated version of EESC.

16 Here, we describe the procedure used to estimate LOSS_{MODEL}. We estimate the fraction
17 of ozone loss due to halogens for each month of the ozone time series, at 1-km intervals between
18 18 and 25 km, for latitudes of 55°N, 45°N, 35°N, 5°N, 5°S, 35°S, 45°S and 55°S. The model is
19 constrained by zonal, monthly mean values of H₂O, CH₄, and O₃, all observed by HALOE
20 [*Russell III et al.*, 1993]. Prior to the launch of HALOE, SAGE II measurements of O₃ are used.
21 Aerosol surface area is obtained from SAGE I and SAGE II observations [*Thomason and Poole*,
22 1997]. First, N₂O is calculated from HALOE zonal, monthly mean CH₄ using the formula of
23 *Michelsen et al.* [1998]. Different relations are used for tropical and mid-latitude regions. The
24 shapes of these relations are related to the relative lifetime of each species in the tropics and
25 mid-latitude regions, respectively. The ATMOS relations that covered several weeks of
26 observations at many latitudes have been shown to agree well with in situ [e.g., *Herman et al.*,
27 1998] and aircraft [e.g., *Chang et al.*, 1996a] observations of these relations, obtained at other
28 time periods. We allowed for growth in N₂O over time of 0.315% per year, relative to 1994.875

1 (the time of the *Michelsen et al.* [1998] ATMOS observations), which is obtained from data in
 2 table 1-12 of *WMO* [1999]. We allowed for growth of CH₄ of 5.0 ppbv/year from 1979 until 2000
 3 and of 2 ppbv/year from 2000 onward, again relative to 1994.875. These values are obtained
 4 from section 1.7.2 of *WMO* [2003]. These small growth rates were implemented so that the
 5 formula of *Michelsen et al.* [1998] could be incorporated more realistically into the model, which is
 6 driven ultimately by HALOE CH₄: e.g., prior to input to the *Michelsen et al.* formula, HALOE CH₄
 7 was converted to its equivalent value for 1994.875; a value of N₂O was found using the
 8 appropriate relation, based on latitude zone; then, the computed value of N₂O was scaled to the
 9 time of the actual CH₄ observation. The growth rates for N₂O and CH₄ are a minor part of the
 10 overall analysis and have no bearing on the final results.

11 Inorganic chlorine (Cl_y) is estimated based on the formulation derived from aircraft
 12 measurements of organic chlorine compounds that is described by *Woodbridge et al.* [1995]. As
 13 noted above, N₂O is estimated from HALOE CH₄, using the formula from *Michelsen et al.* [1998],
 14 allowing for the small temporal growth in both N₂O and CH₄ described above. For the estimate of
 15 Cl_y, the following relation with N₂O was used:

$$16 \quad [Cl_y] = 3.53876 - 2.57709 \times 10^{-3} [N_2O] - 1.91693 \times 10^{-5} [N_2O]^2 - 2.40584 \times 10^{-8} [N_2O]^3 \quad (2)$$

17 where [Cl_y] and [N₂O] are in ppbv. This relation is based on in situ measurements of a complete
 18 set of halocarbons obtained during the SOLVE campaign [*Schauffler et al.*, 2003]. All other
 19 aspects of the computation of Cl_y are based on the method described by *Woodbridge et al.*
 20 [1995], which allows for Cl_y to be computed for earlier time periods by adjusting the value of total
 21 chlorine in the troposphere [equation 11 of *Woodbridge et al.*, 1995].

22 Inorganic bromine (Br_y) is estimated based on a relation derived from aircraft
 23 measurements of the bromocarbon source gases and nitrous oxide (N₂O) [*Wamsley et al.*, 1998].
 24 For the estimate of Br_y, a correlation with CFC-11 is used, because the primary bromine source
 25 gas, CH₃Br, has a stratospheric lifetime somewhat similar to lifetime of CFC-11 [e.g., plate 1 of
 26 *Wamsley et al.*, 1998]. Equations 15 and 16 of *Wamsley et al.* [1998] are used to estimate CFC-
 27 11 from N₂O, based on whether data was obtained in the tropics of extratropics, respectively.

1 We allow for variations in the age of air in the calculation of Cl_y and Br_y , as outlined by
2 *Woodbridge et al.* [1995] and *Wamsley et al.* [1998], using the relation between age and N_2O
3 given in figure 2.12 of *Park et al.* [1999]. This relation between age of air and N_2O is very similar
4 to an independent determination reported by *Engel et al.* [2002]. Finally, the temporal evolution of
5 CCl_y and CBr_y , which appear as factors in the formula for Cl_y and Br_y [e.g., *Woodbridge et al.*,
6 1995; *Wamsley et al.*, 1998], is based on the WMO 2003 Ab baseline scenario [e.g., table 1-16,
7 WMO, 2003]. This method for estimating Cl_y and Br_y from tracers has been used in many
8 empirical studies of balloon and aircraft data [e.g., *Chang et al.*, 1996a; *Salawitch et al.*, 1994;
9 *Salawitch et al.*, 2005 and references therein] and is a common tool for estimating time series of
10 halogens [e.g., *Engel et al.*, 2002].

11 A second set of calculations was conducted for the tropical region. The use of HALOE
12 CH_4 to prescribe model Cl_y and NO_y for 18 to 25 km in the tropics is a challenge, because
13 measured CH_4 lies close to its tropopause value. Hence, small uncertainties in measured CH_4
14 can lead to large relative errors in estimated Cl_y and NO_y . For this second set of calculations,
15 model HCl and NO_x was constrained to match the zonal, monthly mean HALOE observations of
16 these quantities by adjusted model Cl_y and NO_y to match the data. Both sunrise and sunset
17 observations were used, with the model matching the appropriate time of observation. Model Br_y
18 was scaled to preserve the Cl_y to Br_y ratio for the particular time of observation. Monthly mean
19 values of Cl_y , Br_y , and NO_y , normalized to year 1993.0, were computed for each latitude region
20 over the UARS time period. These monthly mean values were propagated backwards in time to
21 cover the time period between 1979 and the first data from HALOE, using the known temporal
22 changes in organic chlorine, organic bromine, and N_2O (e.g., WMO 2002 Ab scenario for CCl_y
23 and CBr_y , augmented by constant values of CH_2Br_2 and CH_2BrCl for Br_y ; NO_y growth of 0.315%
24 per year, based on the N_2O growth described above).

25 Estimates of NO_y are based on its relation with N_2O . For values of $N_2O < 150$ ppb, we
26 use the formula of *Rinsland et al.* [1999]. For $N_2O > 150$ ppb, the relation of *Popp et al.* [2001] is
27 used. The *Rinsland et al.* [1999] relation is based on measurements from ATMOS; the *Popp et al.*
28 [2001] relation is based on data from aircraft and balloons. The relation between NO_y and N_2O is

1 robust, displaying small variations outside the polar regions [e.g., *Sen et al.*, 1998; *Keim et al.*,
2 1997]. Indeed, various coupled climate and chemistry models, as well as 2D and 3D models,
3 display much larger variations in the NO_y vs N_2O relation (compared to either other models, or to
4 data) than is commonly seen in measurements from different instruments [e.g., *Chang et al.*,
5 1996b; *Park et al.*, 1999]. The good agreement between measured and modeled NO_x , illustrated
6 in Figure 1, again provides confidence in the fidelity of this approach. As for HCl, excellent
7 agreement is found for altitudes above 19 km. At 19 km and lower altitudes, small measurement
8 uncertainties in CH_4 have a large affect on the model results, because the tracer-tracer relations
9 are approaching tropopause values that lie close to zero. Similar comparisons between measured
10 and modeled NO_x are found for other latitudes (not shown).

11 The model is constrained by observations of CH_4 and H_2O , which are important for
12 calculating HO_x radicals. For the UARS time period, zonal, monthly mean observations from
13 HALOE are used. For the pre-UARS time period, we propagated back in time the monthly mean
14 value of H_2O , for the specific latitude and altitude point, derived from HALOE measurements and
15 assuming zero trend for H_2O . A similar treatment is used for CH_4 , except we allow for the small
16 temporal trend noted above. In other words, for all Januaries prior to the launch of UARS, the
17 same value of H_2O is used for the model grid point in question (function of altitude and latitude),
18 which is derived from a mean of all model grid points (at the same altitude and latitude) for times
19 when data are available. The trends in H_2O are uncertain, particularly prior to the launch of UARS
20 [SPARC, 2000]. However, the scientific results of this paper, the attribution of changes in ozone
21 to the leveling off of Cl_y and Br_y , are insensitive to any reasonable assumption regarding $d\text{H}_2\text{O}/dt$
22 over the pre-UARS time period. The reason for this insensitivity is that the abundance of HO_x
23 varies in proportion to changes in the square root of the concentration of H_2O . Finally, there are
24 occasional gaps in monthly, zonal mean HALOE and SAGE II data due to the sampling of the
25 respective instruments. For these occasions, which are rare in the overall analysis, values of
26 $\text{LOSS}_{\text{MODEL}}$ are not computed, and this information is treated as “not available” in the CUSUM
27 analysis of these model results.

1 Figure 1 compares modeled and measured HCl (sunrise and sunset) and NO_x (sunset) at
2 20 and 25 km, for three latitude regions. The good agreement between modeled and measured
3 HCl and NO_x demonstrates the reliability of the approach. A model calculation for the tropics,
4 based on specification of Cl_y and NO_y from measured CH₄, tends to simulate HCl and NO_x
5 reasonably well at 25 km (not shown). However, this model overestimates both HCl and NO_x at
6 20 km, because the HALOE CH₄ time series lies close to tropopause values of CH₄, which
7 introduces uncertainties in estimates of Cl_y and NO_y based on this “tracer-tracer” approach.
8 Hence, for the tropics, we show here and use in our CUSUM analysis the model calculation
9 constrained to match HALOE HCl and NO_x. The resulting CUSUMs of LOSS_{MODEL} for both of
10 these calculations in the tropics are remarkably similar, however, as discussed in Section 5.

11 Finally, since we are using the formula of *Wamsley et al.* [1998] to derive Br_y, the derived
12 values are ~2.4 ppt higher than values that would be derived from consideration of supply of
13 bromine from only CH₃Br and halons. Here, we assume CH₂Br₂ and CH₂BrCl are constant over
14 time. The values of Br_y in this model are smaller than values inferred from some measurements
15 of BrO [e.g., *Salawitch et al.*, 2005], possibly due to an important role for stratospheric supply of
16 bromine from biogenic bromocarbons. However, the role of biogenic bromocarbons on
17 stratospheric Br_y is a subject of active research [e.g., *Salawitch*, 2006]: retrievals of BrO from
18 SCIAMACHY by one group suggest a modest role for this source [*Sinnhuber et al.*, 2005], in line
19 with the approach used here, whereas retrievals from another group suggest a much larger role
20 for biogenic bromine [*Sioris et al.*, 2006]. An attempt to model the role of biogenic bromocarbons
21 is beyond the scope of this paper, although in Section 5 we comment about the possible affect of
22 these compounds on the attribution of ozone changes in the lowermost stratosphere.

23 Our approach allows us to calculate how ozone loss by halogens has evolved over time
24 in response to changes in chlorine, bromine, water, methane, HO_x, NO_x, and sulfate aerosol
25 loading as well as variations in atmospheric transport. Changes in transport are reflected in
26 changes in CH₄, which controls the input fields of NO_y, Cl_y, and Br_y. This model has been shown
27 to provide accurate simulations of hydrogen, nitrogen, and chlorine radical species under a
28 variety of aerosol loading, seasonal, and latitudinal conditions [*Osterman et al.*, 1997; *Salawitch*,

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1 2002; *Sen et al.*, 1999; *Sen et al.*, 1998]. Model results are integrated from 18 to 25 km, weighted
2 by the concentration of ozone at each altitude. Similar results are found if we were to use equal
3 weights for each altitude (this weighting is almost identical to a non-weighted average because
4 the ozone contents of each 1-km layer are almost all equal). The resulting time series is referred
5 to as $Loss_{MODEL}$. Plots of $Loss_{MODEL}$ for 7 latitude bands centered between 60°S and 60°N are
6 shown in Figure 2. The calculated increase in ozone loss by halogens between 1979 and 2005 is
7 consistent with the overall rise in stratospheric chlorine and bromine loading (top panel, Figure 2).
8 However, ozone loss by halogens peaked near 1992, which is expected based on known
9 photochemistry in the presence of highly elevated abundances of stratospheric aerosol following
10 the eruption of Mt. Pinatubo [*Dessler et al.*, 1993; *Fahey et al.*, 1993]. Figure 2 shows results for
11 $LOSS_{MODEL}$ in the tropics (10°S to 10°N) for the model constrained by measured HCl and NO_x ,
12 which is a more accurate empirical approach for this region of the atmosphere, where the tracer-
13 tracer relation approach introduces some uncertainty. Interestingly, however, nearly identical
14 results for $LOSS_{MODEL}$ are found for the tropics using the tracer-tracer approach. Ozone loss in
15 the tropics is found from a balance between halogen and HO_x photochemistry and decreases in
16 H_2O and CH_4 measured by HALOE since ~2002 result in the points for $LOSS_{MODEL}$, for the past 4
17 years, lying above the blue curve (EESC fit to $LOSS_{MODEL}$) by comparable amounts for both
18 simulations.

19 An outstanding scientific issue, which is not addressed in our study, is that even though
20 the effect of enhanced chemical loss of ozone due to Pinatubo aerosols is readily apparent from
21 various ozone datasets in the Northern Hemisphere, this same affect is not apparent from
22 measurements in ozone obtained in the Southern Hemisphere [section 4.6.6, *WMO*, 2003]. The
23 reason for this disparity is a subject of active research and is especially puzzling given the large,
24 Pinatubo induced decline in column NO_2 observed at Lauder, New Zealand [e.g., figure 4-21,
25 *WMO*, 2003]. We avoid this confounding issue by omitting in our analysis data collected during
26 times of highly perturbed aerosol loading.

27 Two time series are used independently for the attribution of ozone loss by halogens:
28 values of EESC (Figure 2) from *WMO* [2003] Ab baseline scenario and values of $Loss_{MODEL}$. The

1 EESC time series allows observed changes in O₃ to be related to well-established variations in
2 the abundance of stratospheric halogens. The Loss_{MODEL} time series is a refinement to the EESC-
3 based estimate, allowing the changes in O₃ to be related to the time evolution of ozone loss by
4 halogens accounting for “age of air” as well as observed changes in CH₄, H₂O, aerosol loading,
5 NO_x and HO_x radicals, in addition to variations in Cl_y and Br_y.

6

7 **5. Changes in ozone trends**

8 The three left panels in Figure 3 show the residual ozone time series from SAGE and
9 HALOE (top), Dobson/Brewer spectrophotometers (middle), and the merged TOMS/SBUV
10 satellite instruments (bottom) that remain after the mean, seasonal, QBO, and solar terms have
11 been removed, as described in Equation (1). The excellent agreement between the SAGE and
12 HALOE measurements of the temporal evolution of stratospheric ozone is apparent in the top left
13 panel. Likewise, the linear trends from 1979.0 to the end of 1996 (=1997.0) from SAGE ($-2.3 \pm$
14 0.2 %/decade with 2σ uncertainty), Dobson/Brewer (-2.1 ± 0.5 %/decade), and the MOD ($-1.6 \pm$
15 0.3 %/decade) are consistent over a broad portion of Earth’s atmosphere.

16 We calculate the cumulative departure of the measured ozone from the 1979-1996 trend
17 line (solid black line) extended forward to the time period 1997 to 2005, using the cumulative sum
18 (CUSUM) of residuals technique [Newchurch et al., 2003b; Reinsel, 2002]. If there is less ozone
19 depletion after 1997 than before, then ozone residuals after 1997 will show systematic positive
20 values above the projected trend line (black dotted line). The 95% confidence limits for unbiased
21 residuals appear as the black dotted traces in the right panels of Figure 3, where the limits
22 increase with time due to unresolved fluctuations and uncertainty in the trend estimates.

23 If the autocorrelation of the error terms (i.e., the AR(1) term) is significant, two problems
24 are expected in the ordinary least-squares fittings [e.g., see (8-56) and (8-60) of Johnston, 1984]:
25 (1) The estimated trend (ω) is unbiased, but the standard deviation for ω is underestimated and
26 (2) the variance of U_t is also underestimated. The underestimation of the variance of U_t is not
27 serious in this study because of the relatively large sampling size. The variances of mean level
28 and trend estimates, however, should be corrected by a correction factor (cf) = $(1+r)/(1-r)$, where r

1 is an autocorrelation parameter. In addition, the cumulative residuals tend to have more
 2 dispersion in the presence of a positive autocorrelation. Therefore, the variance of the cumulative
 3 ozone residuals (predicted) is calculated as (see Appendix),

4

5 $\text{VAR}\{\text{CUSUM}\}$

6

7 $= \text{VAR}\{\text{CUSUM residuals}\} + n_2^2 * \text{VAR}\{\text{mean}\} + [\sum_2 (t - t_0)]^2 * \text{VAR}\{\text{trend}\}$

8

9 $\approx \text{cf} \cdot \sigma^2 \{n_2 + n_2^2 / n_1 + [\sum_2 (t - t_0)]^2 / \sum_1 (t - t_0)^2\},$

10

11 where σ is a standard error of the residuals for 1979-1996, n_1 is number of data before the
 12 turnaround point (1997.0), n_2 is number of data after the turnaround point, t_0 is the mean value of
 13 t for 1979-1996 [see *Newchurch et al.*, 2003b]. The estimated autocorrelation parameters are
 14 ~ 0.5 for the MOD and ~ 0.4 for the ground Dobson/Brewer data in this study, resulting in inflations
 15 of CUSUM uncertainties by $\sim 70\%$ and $\sim 50\%$ for the MOD and Dobson/Brewer data. However,
 16 the autocorrelation parameter for the SAGE ozone residuals above 18 km is 0.08 so that its trend
 17 and CUSUM uncertainty are much less affected by these autoregressive processes. We expect
 18 the AR(1) parameter to be larger in the total ozone column than in the stratospheric column
 19 above 18 km because of the altitude dependence of the ozone lifetime (decreasing with altitude).

20 The CUSUMs plotted in the right panels of Figure 3 for the corresponding measurements
 21 are by definition equal to zero at the start of 1997; the small fluctuations prior to 1997 represent
 22 deviations from an assumption of linear ozone depletion over time. The CUSUMs increase
 23 starting in 1997.0, rising significantly above the 95% confidence limits indicated by the black
 24 dotted envelope for years after 1997. For example, the CUSUM metric for the SAGE data is 76%
 25 at the end of data (2005.5), while a CUSUM of only 29% would be considered a 2σ departure
 26 from the extended linear trend line if ozone loss over the 1979-1996 and 1997-2005 time periods
 27 had occurred at the same rate. The green parabolic traces show the expected CUSUM behavior
 28 for ozone levels held constant after 1997.0. The recovery signatures from both the

1 Dobson/Brewer networks and the MOD are highly significant, and reflect increases in total
2 column ozone since 1997. The Dobson/Brewer and MOD CUSUM values are larger than the
3 SAGE value, because the SAGE value is based on data acquired only above 18 km altitude. As
4 we show below, the region between the tropopause and 18 km (TP-18 km) contributes
5 significantly to trends in total column ozone. Recognizing the 2-sigma uncertainty envelopes
6 shown on Figure 3, we find that taken together, these independent measurements provide
7 compelling evidence that, outside of the polar regions, the decline in stratospheric ozone above
8 18 km has slowed down significantly since the beginning of 1997 and the decline in total-column
9 ozone has stopped entirely.

10 Figure 4 shows the SAGE/HALOE residual ozone time series between 18-25 km, for
11 northern mid-latitudes (30-60°N, top panels), tropics (10°S-10°N, middle panels), and southern
12 mid-latitudes (30-60°S, bottom panels). Because the HALOE ozone measurements are less
13 sensitive to aerosol loadings than the SAGE measurements, this combined ozone data set
14 consists of SAGE data before the Pinatubo eruption and HALOE data after the eruption. The
15 regression of the EESC time series (top panel, Figure 2) onto these ozone time series results in
16 the corresponding blue lines, representing an estimate of the ozone changes resulting from the
17 cessation of increasing levels of stratospheric halogens that occurred in approximately 1997. The
18 time series in the left panels and the CUSUM metrics in the right panels indicate close
19 correspondence between the observed ozone changes (black traces) and this estimate of ozone
20 changes due to the halogen loading (blue traces), for all three latitude regions.

21 Further confirmation that the changes in the ozone time series between 18-25 km are
22 due to changes in halogen loading is provided by model estimates of the fraction of ozone loss
23 due to halogens ($Loss_{MODEL}$) over the time period 1979 to present. The regression of $Loss_{MODEL}$
24 onto the ozone time series is shown by the red lines on the left hand panels of Figure 4. The
25 CUSUM of the regression is shown by the red lines on the right panels. For northern and
26 southern mid-latitudes, the CUSUMs for the SAGE/HALOE ozone time series, for EESC, and for
27 $Loss_{MODEL}$ provide an overall consistent picture of a change in linear trend near 1997, consistent

1 with the time of peak halogen loading. The slight sensitivity of these results to the year of change
2 in linear trend (1997 is used here) is described below.

3 The only deviation from this consistent picture is apparent, but with fewer data points, for
4 the tropical region from 2001 to present. Here, the CUSUM for residual ozone displays a lag of ~2
5 years relative to the CUSUM for EESC (black and blue lines, middle right panel, Figure 4).
6 Notably, the CUSUM for $LOSS_{MODEL}$ indicates that little change in the fractional loss of ozone due
7 to halogens is expected (red curve) between 1979 and present. This behavior of $LOSS_{MODEL}$ is
8 driven by a smaller relative contribution of halogens to total ozone loss compared to the other
9 latitude regions, because in the tropical lower stratosphere, inorganic chlorine and bromine have
10 yet to be fully released from their organic reservoirs. Loss of ozone by HO_x radicals exerts the
11 predominant chemical influence, and trends in ozone are sensitive to both dynamics and changes
12 in H_2O and CH_4 . As noted above, similar CUSUM curves for $LOSS_{MODEL}$ in the tropics are found
13 using a tracer-tracer approach, rather than the more empirical approach (e.g., model constrained
14 by measured HCl and NO_x) used for the curve shown in Figure 4. The disagreement between
15 CUSUMs for $LOSS_{MODEL}$ and EESC suggests a simple regression of residual ozone would not be
16 appropriate for the tropical lower stratosphere. This appears to be borne out by the ozone time
17 series, which does not display a statistically significant change in linear trend as is seen in the
18 other regions. Furthermore, time series of zonal, monthly mean HALOE H_2O and CH_4 in the
19 tropics exhibit significant long-term variability, with a tendency towards lower values since ~2002.
20 The HALOE H_2O and CH_4 data suggest the tropical lower stratosphere has undergone significant
21 recent change in the effect of both transport and thermodynamics on its overall composition.

22 To establish attribution of the improving ozone conditions, we examine measurements of
23 ozone collected in various altitude regions. Three altitude regions are considered: tropopause to
24 18 km, 18 to 25 km, and 25 km to the top of the atmosphere (TOA). Here, only data acquired in
25 the northern hemisphere mid-latitudes are shown. Changes in ozone as a function of altitude in
26 southern hemisphere mid-latitudes are challenging to define because SAGE I measurements
27 below 18 km altitude are unreliable (in both hemispheres) and Lauder ozonesonde observations
28 start in 1987. Figure 5 shows changes in ozone at 30-60°N for the three altitude regions noted

1 above, compared in this case to time series of EESC. The change in EESC is consistent with the
2 measured ozone behavior in the 18-25 km layer. This correspondence strongly suggests that
3 chemistry related to EESC changes, as opposed to dynamical changes, has been responsible for
4 the ozone changes in this layer. The correspondence between EESC and the ozone time series
5 and CUSUMs in Figure 4 support this conclusion.

6 Table 1 summarizes the estimated trends in ozone for the three altitude regions between
7 30-60°N, as well as the total column, based on various data sets. The decline in total column
8 ozone from 1979-1996 was -9.3 ± 3.3 (2σ) DU/decade in the MOD record and -8.7 ± 2.3 (2σ) in
9 the Dobson/Brewer networks (Table 1). Ozonesondes yield a value of -2.1 ± 1.6 DU/decade for
10 the change between the tropopause and 18 km. Trends of ozone in the 18-25 km layer are $-3.9 \pm$
11 0.9 based on only SAGE I/II, -4.7 ± 1.3 DU/decade based on the ozonesonde time series, and
12 -4.4 ± 1.2 DU/decade using the SAGE/HALOE record (all uncertainties throughout are 2σ
13 estimates). From 25 km to the TOA, SAGE indicates -4.3 ± 1.0 DU/decade was lost. Hence, we
14 find that ~20% of the decline of total ozone from 1979-1996 was due to changes between the
15 tropopause and 18 km, 38% of the drop occurred between altitudes of 18-25 km, and 42% of the
16 change occurred above 25 km.

17 The altitude partitioning of the improvement in the stratospheric ozone layer starting in
18 1997 is significantly different from the altitude partitioning of the decline (Table 1). The same data
19 sets described above yield an improvement in total ozone column of 16.3 ± 6.6 DU/decade from
20 1997-2005 with respect to the declining trend line, with 49% of the improvement occurring
21 between the tropopause and 18 km, 21% between altitudes of 18-25 km, and 30% due to ozone
22 increases above 25 km.

23 The ozone changes in the tropopause to 18 km layer since 1997.0, as shown in Figure 5
24 (bottom panel) and Table 1, are much larger than can be explained by known chemistry (i.e., the
25 EESC fit accounts for only approximately 50 CDU of the calculated 389 CDU change, where CDU
26 is cumulative DU). An analysis based on $Loss_{MODEL}$, using known photochemistry and established
27 tracer relations, similarly fails to account for the observed features of the ozone time series (not
28 shown). We should expect that some of the ozone change in the lower layer since 1997 results

1 from a change in the flux from the source layer above, because of the chemically induced ozone
2 change in the 18-25 km layer, even if there is no change in the dynamics. Based on an ozone
3 change of 249 CDU in the 18-25 km layer (average of 167 for SAGE, 309 for SAGE/HALOE and
4 271 for ozonesondes, see Table 1), and because there is approximately twice as much ozone in
5 this layer as in the tropopause to 18 km layer, a change of perhaps 124 CDU in the lower layer
6 might be related to this change of the downward flux without any change in the dynamics.
7 Combining this change with the EESC effect falls significantly short of accounting for the
8 observed change of 389 CDU relative to the pre-1997 trend. Therefore, transport changes
9 probably dominate the changes in ozone from 1997 to 2005, between the tropopause and 18 km,
10 for the 30-60°N region.

11 Because of the slowly-varying changes in ozone depleting substances at the ground and
12 the effect of mixing (which induces a spectrum to the mean age of air) [e.g., *Waugh et al.*, 2001;
13 *Engel et al.*, 2002], the expected turnaround point for ozone cannot be precisely defined. Figure 6
14 illustrates the sensitivity of the analysis to variations in the turnaround year, for residuals at 18-25
15 km, 30-60°N, for SAGE ozone (left panels) and ozonesonde ozone (right panels) residuals. The
16 late turnaround points in 1998 and 1999 result in more precise trend estimates and less
17 uncertainty of the CUSUM envelopes, which are balanced by the smaller CUSUM values due to
18 the smaller number of time steps for CUSUM calculations. Nonetheless, for turnaround in 1998 or
19 1999, the CUSUMs for SAGE and ozonesonde residuals approach or exceed the 95%
20 confidence intervals (black dotted lines) at the end of the time period. Assuming a turn around
21 point of 1995.0 (top panels, Figure 6) is the only case where the CUSUM values fails to exceed
22 the 95% confidence interval. In this case, the turn around point is close to the discontinuity
23 caused by the data exclusion during the Pinatubo period. Figure 6, therefore, shows shifts of the
24 turn around time by about one year forward from 1997.0, or two years after 1997.0, do not
25 change the conclusions of this study.

26

27

28

1 6. Relative roles of transport and chemistry

2 Support for the inferred relative roles of chemistry and transport in producing the
3 observed ozone changes since 1997.0 is provided by results shown in Figures 7 through 9. The
4 residual column ozone at 18-25 km and TP-18 km in Figure 5 has significant periodicities of 3-5
5 years. In order to show a clear long-term change in ozone, these ENSO-like signals are removed
6 from the ozone time series [e.g., *Steinbrecht et al.*, 2005] only in Figures 7 and 8 in this study.
7 Figure 7 displays results of the regression of EESC, temperature (T), tropopause height (TPH),
8 and potential vorticity (PV) onto residual ozone values smoothed with a 13-month filter. The
9 temperature, tropopause height, and potential vorticity are calculated at the same locations and
10 times as the ozonesonde measurements, using NCEP reanalysis data. The cause of long term
11 changes in temperature and tropopause height is difficult to assess, since each is sensitive to
12 climate change as well as ozone depletion [e.g., *Santer et al.*, 2003]. Indeed, *Santer et al.* [2003]
13 estimate, based on a climate model simulation, that declining ozone is the largest contributor to
14 rising tropopause height over the 1979 to 1999 time period. However, rising levels of greenhouse
15 gases are also expected to lead to significant increases in tropopause height. The changes in PV
16 illustrated in Figure 7 are likely indicative of changes in Rossby wave breaking events that can
17 clearly affect ozone time series in this region of the atmosphere [e.g., *Koch et al.*, 2002].
18 However, PV can also change due to variations in static stability, and hence is not uncoupled
19 from changes in tropopause height and temperature.

20 The analysis shown in Figure 7 indicates that variations of temperature, tropopause
21 height and PV explain more of the ozone variance from 1979 to 2005 in the lower layer
22 (tropopause to 18 km) than they explain in the 18 to 25 km region. The overall percentage of the
23 ozone variance explained by EESC, relative to T, TPH, and PV is much larger for the 18-25 km
24 region than the TP-18 km layer. However, as noted above, variations in T, TPH, and PV could be
25 due to feedbacks related to ozone changes, or could be driven by changes in transport ultimately
26 related to climate change.

27 To further explore the factors responsible for observed variations in ozone at different
28 atmosphere levels, we examine the relation between these quantities over shorter time periods.

1 Figure 8, using a 3-month filter on ozone residuals, shows the close correspondence of ozone
2 with T, TPH, and PV on time scales of a few months. We tested several proxies and found that
3 except for ENSO, their influences on the long-term changes in ozone at 18-25 km are negligible,
4 although the other proxies have some effects on the ozone below 18 km. The overall higher
5 correlations of T, TPH, and PV with ozone residuals below 18 km, relative to the correlation with
6 EESC, when residuals are examined for short term fluctuations provides further evidence that
7 changes in ozone below 18 km are not driven by halogen chemistry. The weak correlations
8 between these dynamical variables and ozone above 18 km, relative to the correlation of O₃ with
9 EESC, suggests a weak contribution from changes in dynamics (or climate) to long-term changes
10 in ozone above 18 km. Similarly, the weak correlation between EESC and ozone below 18 km
11 shown in Figure 8 is indicative of small contribution of ClOx/BrOx chemistry to the long-term
12 change in ozone below 18 km. Although temperature explains 48% and 38% of ozone variance at
13 18-25 km in Figures 7 and 8, the linear decrease of temperature over the entire time period does
14 not match the curved shape of the ozone residual at 18-25 km. The linear decrease of
15 temperature over time, different in shape from the ozone time series, seems consistent with
16 forcing from both changes in ozone and rising levels of greenhouse gases [e.g., *Santer et al.*,
17 2003].

18 It has been suggested that the turnaround year of 1997 might pose a complication due to
19 a number of cold Arctic winters that began in this time period [*Weatherhead and Andersen, 2005*].
20 To investigate the influence of polar ozone loss on the extra-polar ozone time series, we examine
21 the relation between residual ozone and the volume of air in the Arctic vortex exposed to polar
22 stratospheric clouds (V_{PSC}). It has been shown that V_{PSC} is a good proxy for chemical loss of
23 Arctic ozone [*Rex et al., 2004; Tilmes et al., 2004; Chipperfield et al., 2005*]. Figure 9 compares
24 the time series of residual ozone for various altitudes and latitudes, as indicated, to a time series
25 for V_{PSC} that is based on the same data points for each panel. The values of V_{PSC} are calculated
26 in the same manner as described by *Rex et al. [2004]*. The regressions of SAGE ozone residuals
27 with V_{PSC} appear as blue for regions showing negative correlations and are plotted as negative
28 values to visually emphasize the correlation; red is used for regions showing positive correlations

1 between residual ozone and V_{PSC} . A negative correlation between V_{PSC} and residual ozone
2 means that larger values of chemical loss of polar ozone are associated with decreases in the
3 ozone abundance at mid-latitudes, as hypothesized by *Weatherhead and Andersen* [2005].
4 Figure 9 shows the region of strong, negative correlations between V_{PSC} and SAGE ozone
5 variations for 50-60°N, below ~16 km. These results suggest horizontal transport of chemically
6 depleted ozone from the Arctic vortex might account for some of the observed negative trends in
7 ozone for this region of the atmosphere. But, this influence appears to be confined mainly to
8 altitudes below ~16 km, and latitudes poleward of 50°N. The regressions shown in Figure 9
9 demonstrate that, for the majority of the extra-polar data considered here, the dominant changes
10 in ozone are not driven by polar ozone chemical loss.

11 *Hadjinicolaou et al.* [2005] state “all of the observed upward trend [in total column ozone
12 from MOD] from 1994 to 2003 are reproduced by the [SLIMCAT] model which is forced only by
13 transport changes” [e.g., halogen levels are fixed at 1980’s levels]. This finding appears at first
14 glance to be different from our results, which require both chemical and dynamical forcings to
15 reproduce measured ozone residuals since 1997. Figure 1 and figure 2a in *Hadjinicolaou et al.*
16 [2005] show that (1) the negative trend in total column ozone for 1979-1993 is mostly due to the
17 increasing halogen loading for the same period and (2) the transport changes along with fixed
18 halogen loading is mostly responsible for the rise in column ozone for 1994-2003. Their results,
19 as shown in their figure 2a in particular, appear to us to require the existence of a substantial
20 change in halogen loading, between 1980 and 1994, in order to explain the changes in column
21 ozone over the entire time period. Note that their model with fixed halogen loading is predicting
22 larger ozone values in 2003 than in 1980, which is contrary to observations shown here.

23 Positive changes in ozone since 1996 were also obtained from the MOD, SBUV(/2), and
24 Dobson/Brewer total ozone data by *Reinsel et al.* [2005], who showed that the changes were
25 significant both with and without the dynamical considerations. Their result indicates that the
26 changes in total column ozone are attributable to chemistry as well as dynamics. Our study
27 compliments the analysis of *Reinsel et al.* [2005] by showing that the positive trend in ozone since

1 1996/1997 results both from the transport driven increases in ozone for the tropopause to 18 km
2 layer and from predominantly chemical driven increases in ozone for altitudes above 18 km.

3 Finally, *Salawitch et al.* [2005] noted that bromine supplied to the stratosphere from
4 biogenic bromine and tropospheric BrO could lead to larger amounts of ozone depletion, between
5 the tropopause and ~18 km, compared to models that consider supply of bromine only from
6 CH₃Br and halons. The effect of biogenic bromine on ozone trends is most notable during time of
7 elevated aerosol loading (figure 4 of *Salawitch et al.*). During periods of background loading, ClO
8 levels are too small, below 18 km, for ozone loss by the BrO+ClO cycle to be efficient. We have
9 conducted simulations using constant offsets to the Br_y relation based on the WMO Baseline Ab
10 scenario for CH₃Br and halons (not shown), and the resulting values of LOSS_{MODEL} are unable to
11 reproduce the large increases in ozone observed below 18 km since 1997. It is important to note
12 that these simulations assumed constant offsets to Br_y (e.g., that the supply of bromine from short
13 lived, biogenic bromocarbons and tropospheric BrO is constant over time). If the supply of
14 biogenic bromine to the stratosphere had varied over time, with a strong decrease after 1997,
15 then ozone levels would be expected to rise, due to the BrO+HO₂ cycle (figure 5 of *Salawitch et*
16 *al.*). However, values of Br_y inferred from balloon observations of BrO appear to exhibit a near
17 constant offset relative to the bromine content of CH₃Br+halons, data that spans stratospheric
18 entry dates of 1992 to 2002 [figure 1-8 of WMO, 2003; Dorf, 2005]. Therefore, we consider it
19 unlikely that biogenic bromine could be responsible for the rise in ozone observed between 18 km
20 and the tropopause since 1997.

21 We conclude that observed ozone changes in the 18-25 km layer since 1979 are
22 consistent with chemical effects driven by increases in halogens. However, increases in ozone
23 observed after 1997 between the tropopause and 18 km likely have had a significant transport
24 component. About half of the observed increase in ozone since 1997 has occurred between the
25 tropopause and 18 km.

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27
28

1 **7. Conclusions**

2 Analyses of monthly stratospheric and total-column ozone values from three independent
3 satellite instruments and two ground-based networks of sensors comprising combinations of the
4 SAGE I/II, HALOE, merged TOMS/SBUV satellites, the Dobson/Brewer ground-based networks,
5 and the global ozonesonde network indicate that the thickness of Earth's stratospheric ozone
6 layer stopped declining after about 1997. Regression analyses of both EESC (effective equivalent
7 stratospheric chlorine) and of more sophisticated photochemical calculations independently
8 indicate that the temporal signature of the observed changes in ozone above 18 km altitude is
9 consistent with the timing of peak stratospheric halogen abundances, which occurred mid-way
10 through 1997. These results confirm the positive effect of the Montreal Protocol and its
11 amendments on limiting the growth of stratospheric chlorine and bromine, and in protecting
12 Earth's ozone layer.

13 Increases in stratospheric ozone at NH mid-latitudes since the mid-1990s are also
14 observed for altitudes below 18 km. These increases appear to be driven principally by changes
15 in atmospheric dynamics. The changes in ozone for this height region exhibit positive correlations
16 with dynamical proxies such as potential vorticity and tropopause height, and do not bear the
17 signature of expected long-term change due to stratospheric halogens. The rise in total column
18 ozone since 1997, for NH mid-latitudes (30–60°N), appears to be caused by ~50% contribution
19 from increases in ozone below 18 km altitude, and ~50% contribution from rising ozone above 18
20 km. Hence, both chemical and dynamical forcings appear to be responsible for the observed rise
21 in column ozone at NH mid-latitudes since 1997. Much work remains in order to understand
22 whether the dynamically driven changes are due to natural variability or due to changes in
23 atmospheric structure related to anthropogenic climate change. Furthermore, the recent
24 observations of stratospheric ozone were obtained during a time of unusually low levels of
25 stratospheric aerosol loading. Chemical reactions initiated by volcanic aerosol that penetrates the
26 stratosphere, should a major eruption occur, will almost certainly lead to short periods of lower
27 ozone due to ozone destruction by anthropogenic halogens in the presence of those aerosols.

1 We conclude by noting that our paper represents the complete data record from the
2 remarkable SAGE and HALOE instruments. SAGE I commenced observations in 1979 and
3 SAGE II ceased operating on August, 22 2005. HALOE ceased operating on December 14, 2005.
4 The SAGE I/II and HALOE instruments documented ozone depletion due to rising CFCs, the start
5 of the recovery of ozone (above 18 km) due to declining CFCs, and an unanticipated significant
6 increase in ozone since 1997 (between the tropopause and 18 km) due most likely to changes in
7 stratospheric transport. The data record provided by HALOE and SAGE played an important role
8 in quantifying the effect of human activity on the ozone layer that led to the passage of the
9 Montreal Protocol and its amendments that restricted the production of CFCs. The HALOE and
10 SAGE II teams should be especially proud that these instruments recorded the beneficial effects
11 of this landmark international legislation.

12
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18 contract with National Aeronautics and Space Administration. SAGE and HALOE data for this
19 study were obtained from the NASA/LaRC data center. Dobson/Brewer total ozone and
20 ozonesonde ozone data were provided by the World Ozone and Ultraviolet Data Center
21 (WOUDC) in Toronto, Canada and by the Swiss Meteorological Service. The merged
22 TOMS/SBUV data were provided by NASA/GFSC. EESC data were provided by S.
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24 criticism, and Markus Rex for sharing values of V_{PSC} used in this study. This work is dedicated to
25 the memory of Professor Greg Reinsel.

1 **Figure Captions**

2

3 Figure 1. Comparison of modeled and measured HCl and NO_x. Time series of zonal, monthly
 4 mean HCl and NO_x measured by HALOE (black circles) at 20 and 25 km, for indicated
 5 latitude regions, compared to calculated values of HCl and NO_x (red dots). Data and
 6 model results for HCl include sunrise and sunset points. Data and model results for NO_x
 7 are shown only for sunset. The comparisons for sunrise (not shown) are comparable, but
 8 both measured and modeled NO_x are lower than sunset values, due to the diurnal cycle
 9 of NO_x. The simulations for the equatorial regions are constrained to measured HCl and
 10 NO_x during the UARS time period (Cl_y and NO_y are adjusted in the model); for earlier time
 11 periods, monthly mean values of Cl_y and NO_y normalized to 1993 are propagated
 12 backwards, using the known temporal changes in organic chlorine and N₂O.

13

14 Figure 2. Time series of Equivalent Effective Stratospheric Chlorine, EESC, (upper) and fractional
 15 ozone loss rate due to halogens (lower). The fractional ozone loss rate (Loss_{MODEL})
 16 results from photochemical model calculations that are constrained by observations as
 17 described in the text. Fractional ozone loss rate is the ozone loss rate due to halogens
 18 divided by total ozone loss rate integrated from 18 to 25 km weighted by the ozone
 19 concentrations at each altitude in 7 latitude bands. The blue lines show the EESC series
 20 fitted to the fractional loss rates whose data are excluded during the Pinatubo period.

21

22 Figure 3. Time series of monthly average ozone residuals plus linear trend (left) and cumulative
 23 sum (CUSUM) of residuals (right) in % for the SAGE(black)/HALOE(red) stratospheric
 24 ozone columns above 18 km between 60°S-60°N (top panels), Dobson/Brewer total
 25 ozone columns 30°S-60°N (middle panels), and merged TOMS/SBUV (MOD) total ozone
 26 columns 60°S-60°N (bottom panels). The SAGE, HALOE, Dobson/Brewer, and merged
 27 TOMS/SBUV monthly residuals are all independently obtained by removing the seasonal,
 28 solar, and QBO terms from their respective ozone series. The trend line indicates the

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1 ozone trend calculated from observations for 1979-1996 (solid line) and forecasted
2 linearly afterward (dotted line). Linear trends and 95% confidence intervals for 1979-1996
3 are listed. The ozone residuals during the Pinatubo period are shown in open circles, but
4 they are excluded from the trend calculations. The last value in the cumulative residual
5 time series represents the cumulative difference of all monthly residuals after 1997.0 with
6 respect to the predicted trend line. The green line represents the hypothetical case where
7 the ozone values remained at their 1997.0 value until 2005. The black dotted lines in the
8 right panels indicate the 95% confidence envelopes of departure from natural variability
9 and model uncertainty.

10

11 Figure 4. Time series of monthly ozone residuals plus linear trend (black trace in the left panels)
12 and cumulative sum of residuals (black trace in the right panels) for the SAGE/HALOE
13 data integrated from 18 to 25 km for 30-60°N (top panels), 10°S-10°N (middle panels),
14 and 30-60°S (bottom panels). Tabulated trends correspond to 1979-1996 (black line in left
15 panels) projected to 2005 (dotted black lines, left panels). The SAGE data are used for
16 the period before the Pinatubo volcanic eruptions and HALOE data afterwards. The blue
17 lines represent the ozone change estimated by the EESC fit (left) and its cumulative sum
18 (right). The red lines show the ozone evolution expected from the photochemical
19 calculations (left panels) and the cumulative sum of the ozone change estimated by the
20 calculated fractional loss rate (right panels). The black dotted lines in the right panels
21 indicate the 95% confidence envelopes of departure from natural variability and model
22 uncertainty

23

24 Figure 5. Time series of monthly ozone residuals plus linear trends from SAGE (red traces in the
25 left panels) and ozonesondes (black traces) at 30-60°N; cumulative sum in the right
26 panels in DU. Top panels display SAGE I/II values above 25 km and the associated
27 EESC fit. Middle panels display ozonesonde values from 11 stations (black), SAGE I/II
28 (red) and EESC fit (blue) at 18-25 km. The ozone residuals during the El Chichon and

1 Pinatubo period are shown in open circles, but they are excluded from the trend
2 calculations. Bottom panels display ozonesonde values (black) and SAGE II (red) with
3 EESC fit to ozonesonde values (blue) between tropopause and 18 km.

4

5 Figure 6. CUSUM calculations for the SAGE (left panels) and ozonesonde (right panels) ozone
6 residuals between 18-25 km, 30-60°N. The turnaround points are selected at 1995.0,
7 1996.0, 1997.0, 1998.0, and 1999.0 (top to bottom panels, respectively).

8

9 Figure 7. Ozonesonde residuals plus trend (black traces) between tropopause-18 km (left panels)
10 and 18-25 km (right panels) when additional ENSO-like signals (periodicities of 31-60
11 months) are removed from the ozonesonde measurements between 30-60°N in Figure 5.
12 Similarly, the respective residuals are calculated for temperature, tropopause height, and
13 potential vorticity. These residuals are smoothed by a 13-month running mean to show
14 their long-term changes. The ozone residuals are separately regressed against the EESC
15 series (first panel) and temperature residuals (second panel), tropopause-height
16 residuals (third panel), and potential-vorticity residuals (fourth panel). The estimated
17 ozone responses are shown in blue lines for EESC, T, TPH, and PV, respectively. The
18 percentage of the ozone variance explained individually by the exogenous variable is
19 shown in the individual panels.

20

21 Figure 8. Same as in Figure 7, but smoothed by a 3-month (instead of 13-month) running mean to
22 show the short-term fluctuations of ozone, EESC, temperature, tropopause height, and
23 potential vorticity.

24

25 Figure 9. Time series of the volume of polar stratospheric air containing Polar Stratospheric
26 Clouds (Vpsc) and SAGE ozone residuals at 50-60°N, 40-50°N, and 30-40°N from 10 to
27 24 km. The ozone residuals for March and April are regressed onto the Vpsc values. The
28 negative of the Vpsc series is plotted when the correlations are negative (blue line) in

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1 order to visually emphasize the correlations. The negative correlation coefficient is
2 significant only below 18 km at 50-60°N.

3

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1 **Table 1.** Altitude distribution of decreasing trends, uncertainties, and fractional altitude
 2 partitioning (1979-1996) from five different ozone records between 30-60°N and corresponding
 3 average accumulation rates**, uncertainties, and altitude partitioning (1997-2005).

4
 5
 6

Altitude Range	Instrument	Trend 1979-1996 [DU/decade]	Trend Uncertainty 2σ	% of Total 1979-1996	CUSUM 1997-2005 CDU(2σ)	Average Accumulation Rate [DU/decade]	Accumulation Rate Uncertainty 2σ	% of Total 1997-2005
25 km-TOA	SAGE	-4.3	1.0	42	238 (141)*	4.9	2.9	30
18-25 km	Ozonesonde	-4.7	1.3	38	271 (206)	5.6	4.2	21
	SAGE	-3.9	0.9		167 (138)*	3.4	2.8	
	SAGE/HALOE	-4.4	1.2		309 (174)*	6.4	3.6	
	Average	-4.3	0.7		5.1			
TP-18 km	Ozonesonde	-2.1	1.6	20	389 (256)	8.0	5.3	49
Σ layers	SAGE/SAGE/sonde	-10.3	2.1		794 (323)	16.3	6.6	
Total	D/B	-8.7	2.3		845 (399)	17.4	8.2	
Column	MOD	-9.3	3.3					

7 * mean ozone deviations assumed for missing data points.

8 **The CUSUM value is the cumulative (consecutive) sum of the ozone residual deviations from
 9 the projected trend line in the left panels of Figures 3 through 5. For a 1979-1996 trend estimate
 10 of ω_1 , assuming a linear trend, ω_2 , after 1997.0, the ozone deviations from the 1979-1996 trend
 11 line will follow the line, $(\omega_2 - \omega_1) * t$, with random fluctuations. Therefore, $[CUSUM]_t = \text{Integral of}$
 12 $(\omega_2 - \omega_1) * t = \frac{1}{2} * (\omega_2 - \omega_1) * t^2$, where t is months. For example, $[CUSUM]_t = 309 \text{ CDU}$ at $t = 108$
 13 months (9 years * 12 months/year) in the upper panel of Figure 4. Then, $309 = \frac{1}{2} * (\omega_2 - \omega_1) * t^2$
 14 and $(\omega_2 - \omega_1) = 6.4 \text{ DU/decade}$. With $\omega_1 = -4.4 \text{ DU/decade}$ in Figure 4, $\omega_2 = 2.0 \text{ DU/decade}$.
 15 Therefore, the 1997-2005 average accumulation rate estimated by the CUSUM value is +2.0
 16 DU/decade. This result is not a trend calculation, but rather an average accumulation rate with
 17 the starting point (1997.0) fixed to the value of 1979-1996 trend line at 1997.0 with all data are
 18 equally weighted. From this argument, however, it is clear that the change in trend at 1997.0 is
 19 proportional to the CUSUM value.

20

1 **Appendix:**

2 When the error terms in the regression model are positively correlated, the ordinary least
3 squares (OLS) estimates suffer the following two problems (e.g., *Johnston*, 1984).

4

5 1. The estimated regression coefficients are unbiased, but their error estimates could be
6 underestimated.

7 2. The variance of ozone residuals is underestimated.

8

9 The second problem is not serious in this study because of large sampling size (~200). The
10 variance of a cumulative sum of residuals, however, increases due to a positive autocorrelation of
11 ozone residuals (see Section C).

12

13 A. AR(1) term in time series data

14 The typical trend model for ozone can be described as

15

$$16 \quad [O_3]_t = c + \omega t + \alpha [S]_t + \beta [QBO]_t + \gamma [Solar]_t + U_t \quad (A1)$$

17

18 where c and ω are constant and linear trend terms and $[S]_t$, $[QBO]_t$, and $[Solar]_t$ represent ozone
19 variations due to season, QBO, and solar variations, respectively. Ozone trend plus error terms
20 are now obtained by subtracting season, QBO, and solar variations from the original ozone time
21 series, leading to the following expression:

22

$$23 \quad [O_3]'_t = c + \omega t + U_t \quad (A2)$$

24

25 where $u_t = \rho u_{t-1} + \varepsilon_t$ and ε_t is a white noise process (i.e., sequential errors are independent of
26 each other). Even after removing ozone signals with phase (seasonal, QBO, and solar terms), the
27 error term often shows a first-order autoregressive process, AR(1). The autocorrelated
28 disturbance could be attributed mostly to missing explanatory variables, misspecification of the

1 form of regression, or characteristics of a data set. If the AR(1) parameter, ρ , is positive, the
 2 estimates (c and ω) in Equation (A2) are unbiased but their standard errors are underestimated
 3 [e.g., *Pindyck and Rubinfeld, 1998*].

4

5 In particular, at $t-1$, the above ozone series can be written as

6

$$7 \quad [O_3]_{t-1}' = c + \omega(t-1) + u_{t-1} \quad (A3)$$

8

9 Then,

10

$$11 \quad \text{using } u_t = \rho u_{t-1} + \varepsilon_t,$$

12

$$13 \quad [O_3]_t' - c - \omega t = \rho \{ [O_3]_{t-1}' - c - \omega(t-1) \} + \varepsilon_t.$$

14

15 When introducing transformed variables, $[O_3]_t^*$, c^* , and t^* , we obtain

16

$$17 \quad [O_3]_t^* = c^* + \omega^* t^* + \varepsilon \quad (A4)$$

18

19 where

$$20 \quad [O_3]_t^* = [O_3]_t' - \rho [O_3]_{t-1}' = (1 - \rho B) [O_3]_t',$$

21

$$22 \quad c^* = c(1 - \rho) = (1 - \rho B) c,$$

23

$$24 \quad t^* = t - \rho(t-1) = (1 - \rho B) t, \text{ and}$$

25

26 B is a backward shift operator, i.e., $B[O_3]_t' = [O_3]_{t-1}'$.

27

1 In order to estimate the autocorrelation parameter ρ , we use the Hildreth-Lu procedure which
 2 minimizes the error sum of squares in the transformed regression model (A4) [Neter et al., 1996].
 3 The estimate of ρ is denoted here as r . The transformation reported by (A4) is the same as the
 4 transformation used by the Yule-Walker procedure [Pankratz, 1983] and the results obtained here
 5 are similar to the results obtained using that procedure.

6

7 B. Variance of CUSUM without an AR(1) term

8 If there is no AR(1) term in the regression model (A2), and if the ozone trend after the
 9 turnaround point (T_o) is the same as that before T_o (same-trend hypothesis), the variance of the
 10 predicted ozone time series ($[O_3]_t'$) after T_o is [Makridakis et al., 1983; Draper and Smith, 1998]:

11

$$\begin{aligned}
 & \text{Variance of predicted } [O_3]_t' \\
 & = \text{VAR}\{\text{residuals}\} + \text{VAR}\{\text{mean estimate}\} + \text{VAR}\{\text{trend estimate}\} \\
 & = \sigma_u^2 \left\{ 1 + 1/n_1 + (t - \tau_1)^2 / \sum_1 (t - \tau_1)^2 \right\}. \tag{B1}
 \end{aligned}$$

17

18 where

19 $\text{VAR}\{\text{residuals}\} = \sigma_u^2,$

20

21 $\text{VAR}\{\text{mean estimate}\} = \sigma_u^2 / n_1,$

22

23 $\text{VAR}\{\text{trend estimate}\} = \sigma_u^2 / \sum_1 (t - \tau_1)^2 = \sigma_u^2 / [(t_1 - \tau_1) + (t_2 - \tau_1) + \dots + (t_{n_1} - \tau_1)]^2,$

24

25 $n_1 =$ number of data prior to $T_o,$

26

27 $n_2 =$ number of data from T_o onward,

28

1 $\tau_1 =$ mean value of t prior to T_o , and

2

3 $\tau_2 =$ mean values of t after T_o .

4

5 The first term in the right hand side of Equation (B1) arises from random noise and the second
6 and third terms result from uncertainties in regression coefficients of mean and trend estimates.

7

8 The variance of CUSUM is a variance of the cumulative predicted- $[O_3]_t'$ such that

9

10 CUSUM variance of predicted $[O_3]_t'$

11

12 $= E\{[\sum_2 ([O_3]_t' - E[O_3]_t')]^2\}$

13

14 $= n_2 \cdot \text{VAR}\{\text{residuals}\} + n_2^2 \cdot \text{VAR}\{\text{mean estimate}\} + \sum_1 (t - \tau_1)^2 \cdot \text{VAR}\{\text{trend estimate}\}$

15

16 $= \sigma_u^2 \{n_2 + n_2^2 / n_1 + [\sum_2 (t - \tau_1)]^2 / \sum_1 (t - \tau_1)^2\},$ (B2)

17

18 where n_1 is the number of data prior to T_o and $E[x]$ is the expected value of x . The variance of
19 CUSUM after T_o increases with t , t^2 , and t^4 due to random fluctuations, uncertainty in mean level,
20 and uncertainty in trend estimate, respectively [*Newchurch et al.*, 2003b].

21

22 C. CUSUM variance with an AR(1) term

23 If the residuals are correlated in an AR(1) process, the regression model (A2) does not
24 provide the correct uncertainty in the trend estimate. Instead, the regression model (A4)
25 estimates an unbiased standard error of the ozone trend. Comparing models (A2) and (A4), we
26 can see that the independent variable t^* converges to t when $r \rightarrow 0$. Since we are interested in
27 ozone variations for actual time step (t), (A4) divided by $(1-rB)$ leads to,

28

$$1 \quad [O_3]_t' = c \frac{*}{1-r} + \omega * t + \frac{\varepsilon}{(1-r)B} \quad (A4')$$

2

$$3 \quad \text{VAR}\{\text{predicted } [O_3]_t'\}$$

4

$$5 \quad = \text{VAR}\{\text{residuals}\} + \text{VAR}\{\text{mean estimate}\} + \text{VAR}\{\text{trend estimate}\}$$

6

$$7 \quad \approx \sigma_u^2 \{1 + 1/n_1 \cdot cf + (t - \tau_1)^2 / \sum_1(t - \tau_1)^2 \cdot cf\} \quad (B1')$$

8

9 where

10

$$11 \quad \sigma_u^2 = \sigma_\varepsilon^2 / (1-r^2) \text{ from the relation } u_t = \rho u_{t-1} + \varepsilon_t,$$

12

$$13 \quad \text{VAR}\{\text{residuals}\} = \text{VAR}\{\varepsilon_t / (1-r)B\} = \text{VAR}\{(1 + rB + r^2B^2 + r^3B^3 + \dots) \varepsilon_t\} = \sigma_\varepsilon^2 / (1-r^2),$$

14

$$15 \quad \text{VAR}\{\text{mean estimate}\} = \sigma_\varepsilon^2 / (1-r)^2 / n_1, = \sigma_u^2 \cdot (1-r^2) / (1-r)^2 / n_1 = cf \cdot \sigma_u^2 / n_1,$$

16

$$17 \quad \text{VAR}\{\text{trend estimate}\} = \sigma_\varepsilon^2 / \sum(t^*)^2 = \sigma_\varepsilon^2 / [(1-r)^2 \sum(t)^2] = cf \cdot [\sigma_\varepsilon^2 / (1-r^2)] / \sum(t)^2,$$

18

$$19 \quad \text{and } cf = (1+r) / (1-r).$$

20

21 Due to the positive autocorrelations seen in most ozone time series, the ozone residuals

22 in the next step tend to follow the previous residual disturbances, resulting in more dispersion

23 from their expectation value. Indeed, a larger variance of CUSUM residuals is estimated if the

24 autocorrelation parameter r is positive.

25

26 At $t = n_1 + 1$ (first data point after T_o),

$$27 \quad E[u_t \cdot u_t]$$

$$\begin{aligned}
 1 \quad &= E[(\epsilon_{n1+1} + r \epsilon_{n1} + r^2 \epsilon_{n1-1} + r^3 \epsilon_{n1-2} + \dots) \cdot (\epsilon_{n1+1} + r \epsilon_{n1} + r^2 \epsilon_{n1-1} + r^3 \epsilon_{n1-2} + \dots)] \\
 2 \quad &= E[(\epsilon_{n1+1}^2 + r^2 \epsilon_{n1}^2 + r^4 \epsilon_{n1-1}^2 + r^6 \epsilon_{n1-2}^2 + \dots)] \\
 3 \quad &= \sigma_\epsilon^2 + r^2 \sigma_\epsilon^2 + r^4 \sigma_\epsilon^2 + r^6 \sigma_\epsilon^2 + \dots \\
 4 \quad &= 1 \cdot \sigma_\epsilon^2 / (1-r^2)
 \end{aligned}$$

5

6 At $t = n_1 + 2$ (second data point after T_0),

$$\begin{aligned}
 7 \quad &E[(u_t + u_{t-1}) \cdot (u_t + u_{t-1})] \\
 8 \quad &= E[\{(\epsilon_{n1+2} + r \epsilon_{n1+1} + r^2 \epsilon_{n1} + r^3 \epsilon_{n1-1} + \dots) + (\epsilon_{n1+1} + r \epsilon_{n1} + r^2 \epsilon_{n1-1} + r^3 \epsilon_{n1-2} + \dots)\} \cdot \{(\epsilon_{n1+2} + r \\
 9 \quad &\epsilon_{n1+1} + r^2 \epsilon_{n1} + r^3 \epsilon_{n1-1} + \dots) + (\epsilon_{n1+1} + r \epsilon_{n1} + r^2 \epsilon_{n1-1} + r^3 \epsilon_{n1-2} + \dots)\}] \\
 10 \quad &= E[(\epsilon_{n1+2}^2 + (1+r)^2 \epsilon_{n1+1}^2 + r^2 (1+r)^2 \epsilon_{n1}^2 + r^4 (1+r)^2 \epsilon_{n1-1}^2 + \dots)] \\
 11 \quad &= \sigma_\epsilon^2 + (1+r)^2 / (1-r^2) \cdot \sigma_\epsilon^2 \\
 12 \quad &= (2+2r) \cdot \sigma_\epsilon^2 / (1-r^2)
 \end{aligned}$$

13

14 At $t = n_1 + 3$ (third data point after T_0),

$$\begin{aligned}
 15 \quad &E[(u_t + u_{t-1} + u_{t-2}) \cdot (u_t + u_{t-1} + u_{t-2})] \\
 16 \quad &= E[\{(\epsilon_{n1+3} + r \epsilon_{n1+2} + r^2 \epsilon_{n1+1} + r^3 \epsilon_{n1} + \dots) + (\epsilon_{n1+2} + r \epsilon_{n1+1} + r^2 \epsilon_{n1} + r^3 \epsilon_{n1-1} + \dots) + (\epsilon_{n1+1} + r \\
 17 \quad &\epsilon_{n1} + r^2 \epsilon_{n1-1} + r^3 \epsilon_{n1-2} + \dots)\} \cdot \{(\epsilon_{n1+3} + r \epsilon_{n1+2} + r^2 \epsilon_{n1+1} + r^3 \epsilon_{n1} + \dots) + (\epsilon_{n1+2} + r \epsilon_{n1+1} + r^2 \epsilon_{n1} + r^3 \epsilon_{n1-1} \\
 18 \quad &+ \dots) + (\epsilon_{n1+1} + r \epsilon_{n1} + r^2 \epsilon_{n1-1} + r^3 \epsilon_{n1-2} + \dots)\}] \\
 19 \quad &= E[(\epsilon_{n1+3}^2 + (1+r)^2 \epsilon_{n1+2}^2 + (1+r+r^2)^2 \epsilon_{n1+1}^2 + r^2 (1+r+r^2)^2 \epsilon_{n1}^2 + r^4 (1+r+r^2)^2 \epsilon_{n1-1}^2 + \dots)] \\
 20 \quad &= \sigma_\epsilon^2 + (1+r)^2 \cdot \sigma_\epsilon^2 + (1+r+r^2)^2 / (1-r^2) \cdot \sigma_\epsilon^2 \\
 21 \quad &= (3+4r+2r^2) \cdot \sigma_\epsilon^2 / (1-r^2)
 \end{aligned}$$

22

23 At $t = n_1 + 4$ (fourth data point after T_0),

$$\begin{aligned}
 24 \quad &E[(u_t + u_{t-1} + u_{t-2} + u_{t-3}) \cdot (u_t + u_{t-1} + u_{t-2} + u_{t-3})] \\
 25 \quad &= E[\{(\epsilon_{n1+4} + r \epsilon_{n1+3} + r^2 \epsilon_{n1+2} + r^3 \epsilon_{n1+1} + \dots) + (\epsilon_{n1+3} + r \epsilon_{n1+2} + r^2 \epsilon_{n1+1} + r^3 \epsilon_{n1} + \dots) + (\epsilon_{n1+2} + r \\
 26 \quad &r \epsilon_{n1+1} + r^2 \epsilon_{n1} + r^3 \epsilon_{n1-1} + \dots) + (\epsilon_{n1+1} + r \epsilon_{n1} + r^2 \epsilon_{n1-1} + r^3 \epsilon_{n1-2} + \dots)\} \cdot \{(\epsilon_{n1+4} + r \epsilon_{n1+3} + r^2 \epsilon_{n1+2} + r^3 \\
 27 \quad &\epsilon_{n1+1} + \dots) + (\epsilon_{n1+3} + r \epsilon_{n1+2} + r^2 \epsilon_{n1+1} + r^3 \epsilon_{n1} + \dots) + (\epsilon_{n1+2} + r \epsilon_{n1+1} + r^2 \epsilon_{n1} + r^3 \epsilon_{n1-1} + \dots) + (\epsilon_{n1+1} + r \\
 28 \quad &\epsilon_{n1} + r^2 \epsilon_{n1-1} + r^3 \epsilon_{n1-2} + \dots)\}]
 \end{aligned}$$

$$\begin{aligned}
 &= E[(\epsilon_{n_1+4}^2 + (1+r)^2 \epsilon_{n_1+3}^2 + (1+r+r^2)^2 \epsilon_{n_1+2}^2 + (1+r+r^2+r^3)^2 \epsilon_{n_1+1}^2 + r^2 (1+r+r^2+r^3)^2 \epsilon_{n_1}^2 + r^4 \\
 &(1+r+r^2+r^3)^2 \epsilon_{n_1-1}^2 + \dots)] \\
 &= \sigma_\epsilon^2 + (1+r)^2 \cdot \sigma_\epsilon^2 + (1+r+r^2)^2 \cdot \sigma_\epsilon^2 + (1+r+r^2+r^3)^2 / (1-r^2) \cdot \sigma_\epsilon^2 \\
 &= (4+6r+4r^2+2r^3) \cdot \sigma_\epsilon^2 / (1-r^2)
 \end{aligned}$$

5 .
6 .
7 .

8 At $t = n_1 + n_2$ (last data point),

$$\begin{aligned}
 &E[(u_t + u_{t-1} + u_{t-2} + u_{t-3} + \dots) \cdot (u_t + u_{t-1} + u_{t-2} + u_{t-3} + \dots)] \\
 &= E\{[(\epsilon_{n_1+n_2} + r \epsilon_{n_1+n_2-1} + r^2 \epsilon_{n_1+n_2-2} + r^3 \epsilon_{n_1+n_2-3} + \dots) + (\epsilon_{n_1+n_2-1} + r \epsilon_{n_1+n_2-2} + r^2 \epsilon_{n_1+n_2-3} + r^3 \\
 &\epsilon_{n_1+n_2-4} + \dots) + \dots] \cdot [(\epsilon_{n_1+n_2} + r \epsilon_{n_1+n_2-1} + r^2 \epsilon_{n_1+n_2-2} + r^3 \epsilon_{n_1+n_2-3} + \dots) + (\epsilon_{n_1+n_2-1} + r \epsilon_{n_1+n_2-2} + r^2 \epsilon_{n_1+n_2-3} + \\
 &r^3 \epsilon_{n_1+n_2-4} + \dots) + \dots]\} \\
 &= E[(\epsilon_{n_1+n_2}^2 + (1+r)^2 \epsilon_{n_1+n_2-1}^2 + (1+r+r^2)^2 \epsilon_{n_1+n_2-2}^2 + \dots + (1+r+r^2+\dots+r^{n_2})^2 \epsilon_{n_1+1}^2 + r^2 \\
 &(1+r+r^2+\dots+r^{n_2})^2 \epsilon_{n_1}^2 + r^4 (1+r+r^2+\dots+r^{n_2})^2 \epsilon_{n_1-1}^2 + \dots)] \\
 &= \sigma_\epsilon^2 + (1+r)^2 \cdot \sigma_\epsilon^2 + (1+r+r^2)^2 \cdot \sigma_\epsilon^2 + (1+r+r^2+r^3)^2 \cdot \sigma_\epsilon^2 + \dots + (1+r+r^2+\dots+r^{n_2})^2 / (1-r^2) \cdot \sigma_\epsilon^2 \\
 &= \{n_2 + 2(n_2-1)r + 2(n_2-2)r^2 + 2(n_2-3)r^3 + \dots + 2(1)r^{n_2-1}\} \cdot \sigma_\epsilon^2 / (1-r^2) \\
 &\approx \{n_2 + 2n_2r / (1-r)\} \cdot \sigma_\epsilon^2 / (1-r^2) \\
 &= n_2 \cdot (1+r) / (1-r) \cdot \sigma_\epsilon^2 / (1-r^2) \\
 &= \sigma_\epsilon^2 / (1-r^2) \cdot n_2 \cdot cf
 \end{aligned}$$

21 Because of the sufficiently large number of n_2 in this study (108 months from 1997 to 2005), the
22 variance of the CUSUM residuals approaches $\sigma_\epsilon^2 / (1-r^2) \cdot n_2 \cdot cf$. Therefore, the variance of the
23 CUSUM is calculated as

$$\begin{aligned}
 &VAR\{\text{cumulative predicted-[O}_3\text{]}_t'\} \\
 &= VAR\{\text{CUSUM residuals}\} + n_2^2 \cdot VAR\{\text{mean estimate}\} + [\sum_2 (t - \tau_1)]^2 \cdot VAR\{\text{trend} \\
 &\text{estimate}\}
 \end{aligned}$$

1

2
$$\approx \text{cf} \cdot \sigma_u^2 \{n_2 + n_2^2 / n_1 + [\sum_2 (t - \tau_1)]^2 / \sum_1 (t - \tau_1)^2\} \quad (\text{B2}')$$

3

4 In the above derivations, we neglect uncertainty in an estimated r . Compared to the CUSUM
5 variances without an AR(1) term, (B2') now shows that the variances increase by a correction
6 factor, $(1+r)/(1-r)$.

7

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