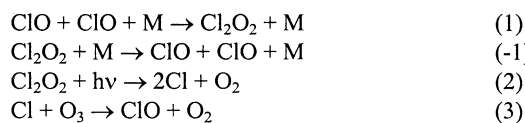# Sunset observations of ClO in the arctic polar vortex and implications for ozone loss

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Abstract. Chlorine oxide (ClO) was measured *in situ* in the perturbed arctic vortex from a balloon launched near Kiruna, Sweden, 67 °N, at sunset on January 27, 2000. Between 20 and 23 km, the time-dependent behavior of ClO agrees with the functional form for the kinetics of $ClO + ClO + M \rightarrow Cl_2O_2 + M$. The temporal change of ClO is described well by the integral of a rate expression that includes this reaction and thermal decomposition of Cl_2O_2. The value for the rate coefficient that best describes the observed decreases in ClO is consistent with the upper limit of the currently recommended value, and agrees well with the results of a recent laboratory study of ClO recombination at 190-195 K. These results reinforce the link between man-made chlorine compounds and ozone losses in the polar regions.

Introduction

Ozone loss in the wintertime polar stratosphere has received considerable attention since the discovery of the ozone hole over Antarctica by *Farman et al.* [1985]. These losses are believed to be due to photo-catalytic reactions involving the halogen oxide radicals, ClO and BrO. The following catalytic cycle accounts for more than half of the ozone loss:

$$ClO + ClO + M \rightarrow Cl_2O_2 + M \qquad (1)$$
$$Cl_2O_2 + M \rightarrow ClO + ClO + M \qquad (-1)$$
$$Cl_2O_2 + hv \rightarrow 2Cl + O_2 \qquad (2)$$
$$Cl + O_3 \rightarrow ClO + O_2 \qquad (3)$$

The rate of chemical ozone destruction can be quantified from the rate-determining step in this cycle as:

$$-\frac{dO_3}{dt} = 2J_2[Cl_2O_2] = 2\{k_1[ClO]^2 - k_{-1}[Cl_2O_2]\}[M] \qquad (4)$$

where J_2, k_1, and k_{-1} and are the rate coefficients for reactions (2), (1), and (-1), respectively.

Calculations constrained by observations of ClO over Antarctica have agreed well with observed ozone losses [*deZafra*, 1989, *Anderson et al.*, 1991, *Wu and Dessler*, 2001]. However, success for similar calculations for the Arctic has been mixed. Several studies found that the observed rates of ozone loss exceeded those calculated by as much as a factor of two [*Woyke et al.*, 1999, *Becker et al.*, 2000], whereas others found good agreement

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[*Lefevre et al.*, 1998, *Guirlet et al.*, 2000]. The reasons for the difficulties in balancing the arctic ozone budget remain unclear.

In sunlight, the balance between ClO and Cl_2O_2 is determined largely by reactions (1) and (2). At sunset, when solar zenith angles exceed 90°, photolysis of Cl_2O_2 becomes negligible [*Avallone and Toohey*, 2001] and daytime abundances of ClO rapidly decrease down to nighttime values at rates governed by reactions (1) and (-1). Atmospheric observations of the rate of change of ClO following sunset can provide a unique test of the validity of laboratory-determined rate parameters under relevant atmospheric conditions [*Shindell and deZafra*, 1996]. Because reactions (1) and (-1) are linked directly to the rate of ozone destruction via equation (4), these observations can serve to constrain our present understanding of this contribution to polar ozone loss.

Based on several laboratory measurements, the third-order rate coefficient for the recombination reaction of ClO (reaction (1)) is estimated to be $(7.8 \pm 2.0) \times 10^{-32}$ cm^6 $molecule^{-2}$ s^{-1} (1σ) under typical polar stratospheric conditions [*Sander et al.*, 2000]. However, a recent laboratory study has found the rate coefficient to be ~30% larger than this recommendation at temperatures ~200 K and below [*Bloss et al.*, 2001] , similar to values reported in one previous study [*Trolier et al.*, 1990]. One study has specifically examined the behavior of ClO in the atmosphere in comparison to this key reaction rate parameter. Based on ground-based observations from McMurdo Station, Antarctica (78° S), *Shindell and deZafra* [1996] found the diurnal behavior of ClO between 16 and 24 km was described well by currently recommended rate parameters, and argued that these results significantly reduced the uncertainties in the recommended rate coefficient for reaction (1).

Here we present new high-resolution *in situ* balloon-borne observations of ClO measured during and after sunset, under conditions where Cl_2O_2 photolysis has recently ceased. We examine how well the observed rate of decrease of ClO can be described by reactions (1) and (-1) under conditions appropriate for determining polar ozone loss rates.

Observations

Measurements were obtained from a 10^4 m^3 balloon launched from Esrange near Kiruna, Sweden (67.9 °N, 21.1 °E) at 12.21 UT on January 27, 2000. ClO and BrO were measured *in situ* on a gondola called HALOZ (HALogens and OZone loss) with an accuracy of 25% and 35% (2σ), respectively, using chemical conversion/resonance fluorescence [*Toohey et al.*, 1993, *Pierson et al.*, 1999]. Ozone was measured using an electrochemical concentration cell (ECC). Temperature, pressure, and winds were measured using a Vaisala RS80 radiosonde. Additional measurements included particles, CFC-11, latitude and longitude. Data from a frost-point hygrometer launched 30 min after the HALOZ payload were used to corroborate the latter temperature measurements.

Enhancements of ClO were observed up to a pressure level of roughly 25 hPa, with a peak in excess of 800 parts per trillion by volume (pptv) during ascent (Figure 1). Throughout this region, BrO abundances were below the detection limit of ~2 pptv for a
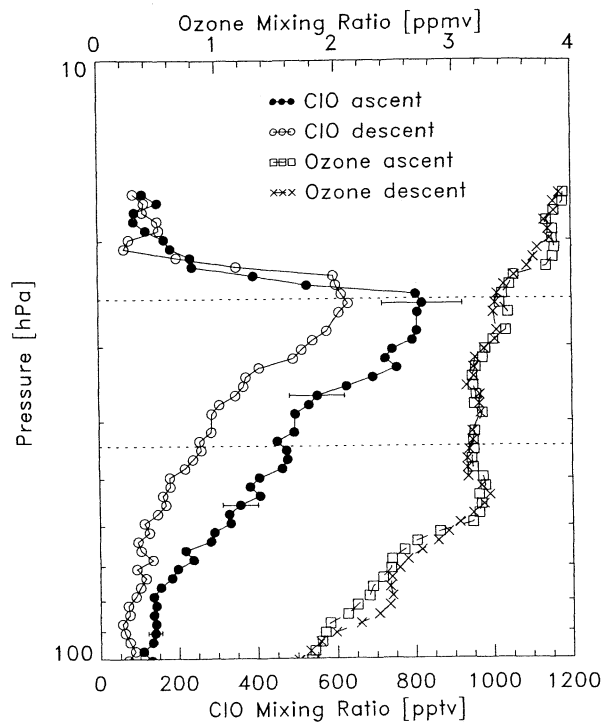
Figure 1. Ascent and descent profiles of ClO and ozone on January 27, 2000 from Kiruna, Sweden. The error bars indicate the 1σ uncertainties for the ClO measurements at representative points. Ozone errors are approximately the size of the data points. Horizontal dashed lines mark the region where the differences between the characteristics of air masses on ascent and descent are minimal, where photolysis of Cl_2O_2 is negligible, and ClO abundances on descent are far from equilibrium values.

300 s average, consistent with previous observations at high solar zenith angles [*Avallone and Toohey*, 2001 and references therein].

At 31 and 23 hPa on ascent, the balloon encountered strong temperature inversions, stalled, and descended ~200 m before reascending after 150 s and 240 s, respectively. Based on temporary increases in temperature, rising background signals, and decreases in ClO signals we believe that the instrument may have

aspirated its own exhaust during these stagnant periods [*Pierson et al.*, 1999], and these few observations have been discarded.

There were other occasions on ascent and descent when the temperature measured by the Vaisala sensor increased sharply by about 8K, without similar changes in the temperature measured by the ClO instrument (a less accurate measurement by ~ 1K). Because the latter instrument measured beyond the boundary layer of the gondola, we interpret these changes in the Vaisala temperature as thermal contamination of it only, and these points have been removed. Based on the excellent agreement between the remaining points and the near-coincident temperature profile measured by the frost-point hygrometer, we use the latter results to complete the HALOZ profile, which we estimate to be accurate to 2 K (2σ).

The important quantities for this analysis are listed in Table 1 as roughly 1.5 hPa (~80 s) averages. The balloon trajectory was well inside the polar vortex (potential vorticity (PV) ≥ 60 PV units at $\Theta = 490K$), with generally weak horizontal winds. Important aspects of the air between 23 and 44 hPa were that the winds were nearly zonal (latitude varied from 67.65°N to 67.60°N) and that parcels encountered by the balloon on ascent can be traced to ~16 km or less of the balloon position on descent. These distances are too small to be meaningfully resolved in potential vorticity fields and they are a few percent of distances traveled by the solar terminator between the ascent and descent measurements, such that we can adequately use the elapsed time between the ascent and descent measurements to assess the kinetics of ClO decays.

Comparing ascent and descent within the 23-44 hPa region, differences in temperature and mixing ratios of ozone were uniformly small (~1 K and ~1%, respectively), indicating that these air masses had comparable photochemical histories. However, at pressures greater than 44 hPa these quantities diverged noticeably. As demonstrated later, at these lower altitudes ClO abundances on descent had sufficiently approached equilibrium, and we cannot infer accurate rate information in this region. Because the trajectory analysis indicates a significant increase in the airmass separation below 44 hPa and because ozone below this level shows a significant difference between ascent and descent, we restrict our analysis to the region between 44 hPa and the ClO peak at 25 hPa (~19.5-22.5 km), which is denoted by the dashed lines in Figure 1.

Table 1. Selected data for the ascent and descent profile on January 27, 2000.

P	Time [GMT]		Lon [°] [1]		SZA [°] [2]		ClO [pptv]		T [K]		Δx [3]	$k_1[M]$ [4]	$f_{th.d.}$ [5]	σ [6]
[hPa]	asc.	desc.	asc.	desc.	asc.	desc.	asc.	desc.	asc.	desc.	[km]	10^{-13} cm^{3}s^{-1}	[%]	[%]
25.5	14:15	14:49	23.89	24.95	95.3	98.4	819	632	193	194	5	0.92	6	13
28.3	14:11	14:50	23.77	24.99	95.0	98.5	806	577	192	192	8	1.03	5	13
30.4	14:08	14:51	23.70	25.01	94.7	98.6	743	514	192	193	4	1.06	5	13
32.6	14:04	14:52	23.60	25.05	94.4	98.7	754	407	191	191	6	1.65	5	13
35.0	14:01	14:54	23.52	25.09	94.2	98.9	626	367	190	191	6	1.43	6	14
37.5	13:59	14:55	23.48	25.12	94.0	99.0	532	306	187	189	12	1.50	5	14
41.7	13:57	14:58	23.42	25.19	93.9	99.2	494	285	189	189	16	1.35	5	15
44.7	13:55	14:59	23.38	25.22	93.7	99.3	475	259	193	192	42	1.59	13	20
48.0	13:54	15:00	23.36	25.24	93.6	99.4	464	218	196	193	50	2.06	17	24

[1]The latitude ranged from 67.65° to 67.60°. [2]Solar zenith angle. [3]Distance between the gondola during descent and the airmass that was originally encountered during ascent. [4]Rate of decay inferred from the ClO measurements. [5]Percentage contribution of the thermal dissociation of Cl_2O_2 to $k_1[M]$. [6]1σ uncertainty for $k_1[M]$.
The shaded rows are outside the region where we expect the analysis to yield results with high confidence.
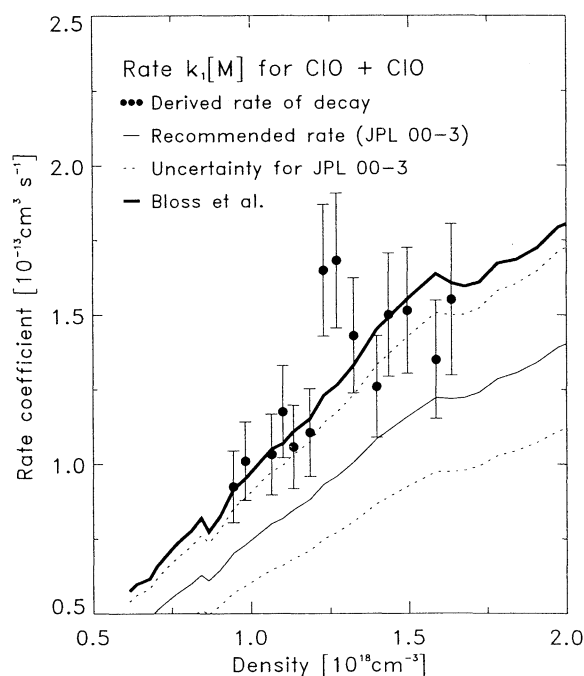
Figure 2. Derived rate of decay (points with 1σ error bars), the most recent JPL recommendation (thin solid line), its uncertainties (dashed lines), and a recent laboratory study by *Bloss et al.* [2001] (thick solid line). For clarity, the uncertainties from the Bloss et al. study are not shown; they are approximately the same size as those for the results based on the ClO observations.

Results and Discussion

ClO abundances following sunset are governed by an expression similar to (4), with an additional term that accounts for the ClO+BrO reaction:

$$\frac{dClO}{dt} = 2\{k_{-1}[Cl_2O_2] - k_1[ClO]^2\}[M] - k[ClO][BrO] \qquad (5)$$

Since BrO abundances are much smaller than those of ClO and are rapidly consumed (as confirmed by measurements of BrO), the third term on the right hand side of (5) vanishes. An equilibrium is eventually established between ClO and Cl_2O_2, such that ClO abundances in darkness are governed entirely by temperature, pressure and abundances of Cl_2O_2 [*Avallone and Toohey*, 2001]. Assuming that abundances of Cl_2O_2 are nearly constant with time, equation (5) can be integrated to give:

$$k_1[M] = \frac{1}{4[ClO]_{eq}(t_1 - t_0)} \ln(\frac{([ClO]_{t1} + [ClO]_{eq})([ClO]_{t0} - [ClO]_{eq})}{([ClO]_{t1} - [ClO]_{eq})([ClO]_{t0} + [ClO]_{eq})}) \qquad (6)$$

where $[ClO]_{eq} = \sqrt{[Cl_2O_2]/K_{eq}}$ is the value of [ClO] at equilibrium and $K_{eq}=k_1/k_{-1}$. Although a slightly more complex equation can be derived without the assumption that Cl_2O_2 is constant in time, the contributions from the thermal decomposition of Cl_2O_2 are small, and equation (6) is sufficiently accurate for this analysis.

Calculations of the right-hand side of equation (6) based on the observations are listed in Table I and plotted versus density in Figure 2. $[ClO]_{eq}$ is based on the equilibrium constant inferred from ER-2 observations [*Avallone and Toohey*, 2001], where we assumed that $[Cl_2O_2] \sim 1.3$ parts per billion by volume (ppbv) based on a total inorganic chlorine budget derived from coincident measurements of CFC-11 [*Robinson et al.*, 2001]. Figure 2 also includes values and ranges of uncertainty for $k_1[M]$ from the

most recent JPL recommendation [*Sander et al.*, 2000]. The rate of decay inferred from the observations follows the behavior expected for a termolecular process over the density range (0.9-1.8)×10^{18} cm^{-3}. Furthermore, the results are consistent with the upper limit for k_1 as currently recommended at pressures and temperatures encountered during the flight. A recent laboratory study [*Bloss et al.*, 2001] of reaction (1) at low temperatures found a larger rate coefficient than recommended by JPL. Figure 2 shows that our results agree well with those of this study. A weighted average of the ratio of the inferred rate coefficient to the JPL-recommended value using all the points in Figure 2 yields a value of 1.33 ± 0.40 (2σ). A similar value relative to the *Bloss et al.* results is 1.01 ± 0.30 (2σ).

The inferred rate coefficient, the contribution of the term due to thermal decomposition of Cl_2O_2, and total uncertainties in the calculations are listed in Table 1. The uncertainties were determined by combining, as uncorrelated errors, the accuracies in the ClO measurements and the corrections for thermal decomposition of Cl_2O_2. The latter were determined by independently varying temperature by 2 K, reducing abundances of Cl_2O_2 by 50%, and increasing K_{eq} to the value recommended in the JPL compendium. At pressures below 50 hPa, ClO abundances on descent are far from equilibrium, such that the uncertainties in the term $[ClO]_t-[ClO]_{eq}$ have very little impact on the total errors. However, above 50 hPa these uncertainties increase rapidly as the ClO abundances observed on descent approach equilibrium. Therefore, we cannot draw meaningful quantitative conclusions regarding the rates of decay of ClO at these higher pressures. Coincidentally, these are the pressure altitudes below which air mass differences (based on trajectories, ozone, and temperatures) become significant.

The contribution of Cl_2O_2 decomposition to the inferred rate coefficient highlights several important points. First, at the lowest pressures within the perturbed layer this term has a minor effect on observed ClO loss rates. The ascent and descent positions are most coincident in time, such that the calculations based on data in this region are the least subject to air mass differences. Consequently, these results are the most significant ones in our analysis, so it is not surprising that the inferred rate coefficients exhibit the least amount of scatter here. Second, in the limit that $[Cl_2O_2]/K_{eq} \to 0$ this term vanishes, and equation (6) is equivalent to:

$$k_1[M] = \frac{1}{2*(t_1 - t_0)} * \left(\frac{1}{[ClO]_{t1}} - \frac{1}{[ClO]_{t0}} \right) \qquad (7)$$

Thus, the present JPL recommendation for k_1 could adequately explain our results if our measurements are an underestimate of the true ClO abundances by ~35%. This is larger than the 2σ (or 95% confidence level) upper limit for our measurements. Because it neglects a process that produces ClO, equation (7) necessarily provides underestimates for the inferred rate coefficients. Furthermore, the non-linearities with increasing time that result from use of this incomplete equation are evidence of the contribution by thermal decomposition of Cl_2O_2 to the observed rates of ClO decay. The uncertainties in the rate parameters are too large to use the ClO observations to estimate abundances of Cl_2O_2 to better than 50%.

Our conclusions differ somewhat from those of *Shindell and deZafra* [1996], who found very good agreement between the sunset behavior of ClO at 20 km measured remotely from McMurdo Station, Antarctica and models using the recommended values for reactions (1) and K_{eq} for $Cl_2O_2 \leftrightarrow ClO + ClO$. Several studies using *in situ* data have concluded that K_{eq} is ~50% smaller than recommended at 190-200 K [*Pierson, et al.*,

1999 and *Avallone and Toohey*, 2001]. It is possible that the observations of *Shindell and deZafra* [1996] are consistent with models that include the combination of a larger value for k_1 and a smaller one for K_{eq}. It would be useful to revisit the calculations of *Shindell and deZafra* [1996] to determine whether or not the combination of these separate *in situ* results can adequately explain their observations.

Our results have important implications for polar ozone losses. They confirm that the atmospheric behavior of ClO in the winter polar regions is consistent with proposed photochemical mechanisms, and they constrain ozone loss rates determined from equation (4). For example, *Bloss et al.* [2001] show that calculated ozone loss rates based on observations of ClO and their larger rate coefficient for reaction (1) increase by only 15% relative to calculations employing the present JPL recommendation. This is because reaction (1) is responsible for about half of the ozone loss rate due to ClO (the other half being due to the reactions of ClO with BrO, O, and HO_2). Our results suggest that an error in k_1 is not the source for the large discrepancies between observations and calculations of ozone losses in the Arctic found in some studies [*Becker et al.*, 2000 and *Woyke et al.,* 1999].

Conclusions

Balloon-borne observations in the perturbed arctic vortex at sunset on January 27, 2000 find the time-dependent behavior of ClO between 44 and 25 hPa to be consistent with the proposed kinetics of ClO. In particular, the rates of decrease of ClO agree well with an analytical expression derived from the termolecular recombination of ClO and thermal decomposition of Cl_2O_2, the difference of which is equivalent to the rate determining step for ozone loss due to the ClO/ClO catalytic cycle. The rate coefficient for the recombination of ClO that best describes the observed changes in ClO is consistent with the upper limit of the currently recommended value based on laboratory studies, and it agrees well with the results of a recent laboratory study at 190-195 K [*Bloss et al.,* 2001].

These results add confidence to calculations of chemical ozone loss over the polar regions, and reinforce the conclusions of those studies that have shown that the ozone budget over Antarctica is largely understood. The shortfalls in some ozone loss calculations for the Arctic remain unresolved.

References

Anderson, J. G., D. W. Toohey, and W. H. Brune, Free radicals within the antarctic vortex: The role of CFCs in antarctic ozone loss, *Science, 251,* 39-46, 1991.

Avallone, L. W. and D. W. Toohey, Tests of halogen photochemistry using *in situ* measurements of ClO and BrO in the lower polar stratosphere, *J. Geophys. Res. 106,* 10411-10421, 2001.

Becker G., R. Müller, D. S. McKenna, M Rex, K. S. Carslaw, and H. Oelhaf, Ozone loss rates in the arctic stratosphere in the winter 1994/1995: Model simulations underestimate results of the Match analysis, *J. Geophys. Res., 105,* 15175-15184, 2000.

Bloss, W. J., S. L. Nickolaisen, R. J. Salawitch, R. R. Friedl, and S. P. Sander, Kinetics of the ClO self-reaction and 210 nm absorption cross section of the ClO dimer, *J. Phys. Chem.,* in press, 2001.

DeZafra, R. L., M. Jaramillo, J. Barret, L. K. Emmons, P. M. Solomon, and A. Parrish, New observations of a large concentration of ClO in the springtime lower stratosphere over Antarctica and its implications for ozone-depleting chemistry, *J. Geophys. Res., 94,* 11423-11428, 1989.

Farman, J. C., B. G. Gardiner, and J. D. Shanklin, Large losses of total ozone in Antarctica reveal seasonal ClOx/NOx interaction, *Nature, 315,* 207, 1985.

Guirlet, M., M.P. Chipperfield, J.A. Pyle, F. Goutail, J.-P. Pommereau, E. Kyrö, Modeled arctic ozone depletion in winter 1997/1998 and comparison with previous winters, *J. Geophys. Res., 105,* 22185-22200, 2000

Lefevre F., F. Figarol, K. S. Carslaw, and T. Peter, The 1997 arctic ozone depletion quantified from three-dimensional model simulations, *Geophys. Res. Lett.,* 25, 2425-2428, 1998.

Pierson, J. M., K. A. McKinney, D. W. Toohey, J. Margitan, U. Schmidt, A. Engel, and P. A. Newman, An investigation of ClO photochemistry in the chemically perturbed arctic vortex, *J. Atmos. Chem., 32,* 61-81, 1999.

Robinson A. D., et al., Ozone loss derived from balloon-borne tracer measurements and the SLIMCAT CTM, J. Geophys. Res., submitted.

Sander, S. P., R. R. Friedl, W. B. DeMore, D. M. Golden, M. J. Kurylo, R. F. Hampson, R. E. Huie, G. K. Mortgat, A. R. Ravishankara, C. E. Kolb, M. J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, supplement to evaluation 12: update of key reactions, Jet Propulsion Laboratory publication 00-3, Pasadena, CA, 2000.

Shindell, D. T and R. L. deZafra, Chlorine monoxide in the antarctic spring vortex 2: A comparison of measured and modeled diurnal cycling over McMurdo Station, 1993, *J. Geophys. Res., 101,* 1475-1487, 1996.

Toohey, D. W., L. M. Avallone, N. T. Allen, J. N. Demusz, J. N. Hazen, N. L. Hazen, and J. G. Anderson, The performance of a new instrument for *in situ* measurements of ClO in the lower stratosphere, *Geophys. Res. Lett., 20,* 1791-1794, 1993.

Trolier, M., R. L. Mauldin, III and A. R. Ravishankara, Rate coefficient for the termolecular channel of the self-reaction of ClO, *J. Phys. Chem., 94,* 4896-4907, 1990.

Woyke, T, R. Müller, F. Stroh, D. S. McKenna, A. Engel, J. J. Margitan, M. Rex, and K. S. Carslaw, A test of our understanding of the ozone chemistry in the arctic polar vortex based on *in situ* measurements of ClO, BrO, and O_3 in the 1994/1995 winter, *J. Geophys. Res., 104,* 18755-18768, 1999.

Wu, J and A. E. Dessler, Comparisons between measurements and models of antarctic ozone loss, *J. Geophys. Res., 106,* 3195-3201, 2001.

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