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An assessment of the total ozone mapping spectrometer for measuring ozone levels in a solid rocket plume

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Abstract. The question whether the total ozone mapping spectrometer (TOMS) is capable of measuring ozone levels in a solid rocket motor plume is examined. Simulated measurements were computed for a chemical kinetics and dispersion model of a Titan IV plume. The principal disadvantage of TOMS for measuring local plume ozone levels is that the detection field-of-view is typically much larger than the column area for ozone loss. A secondary problem is attenuation of backscattered light by plume species and particles that can distort the ozone measurement.

Introduction

The current understanding of rocket plume interactions with the stratosphere is very limited. In 1990, Prather and collaborators published a modeling study of the space shuttle's impact on the stratosphere that has generated a considerable amount of discussion [*Aftergood*, 1991; *McPeters et al.*, 1991]. They investigated the long term effects using global atmospheric chemistry and dispersion models, from which they concluded that at current launch rates, solid rocket motor exhaust does not impose a significant global impact on stratospheric chemistry. An attempt was also made to examine the transient chemical behavior and local impact. Although these investigators admit that the early stage of the launch is not adequately modeled, they argued a local column ozone hole should not occur because: (i) the chlorine is released predominantly as HCl, which requires considerable time to be converted to active forms of chlorine, (ii) the exhaust plume passing through the stratosphere is not aligned vertically, and (iii) the exhaust gases can disperse over a 1000 km range in a day.

In 1991 Aftergood challenged these conclusions raising two important points: (i) a U2 flying through the plume of a Titan III observed a 40% reduction in the ambient ozone level [*Pergament et al.*, 1977], although it was noted that this measurement is of uncertain reliability, and (ii) chlorine is not necessarily exhausted predominantly as HCl, but may contain large quantities of Cl_2 due to afterburning chemistry as predicted by an early plume model by Hoshizaki [1975]. More recently Zittel [1994], Denison *et al.* [1994], and Karol [1992] strengthened the evidence for afterburning chemistry using validated plume codes. Experimental verification has recently been obtained by Burke [1996]. The calculations of Denison *et al.* [1994], and Karol [1992] continued the plume exhaust kinetics to longer times and observed significant ozone depletion along the plume centerline. Brady and Martin [1996] carried out similar calculations using a comprehensive kinetics model including homogeneous and heterogeneous chemistry and also predicted significant ozone decomposition along the plume centerline. Ross [1992, 1996] calculated three-dimensional chemical profiles using a plume kinetics and dispersion model that also show significant ozone depletion. Jackman *et al.* [1996] recently updated the effects of Shuttle launches on the global ozone balance using a 2D photochemistry and transport model that included heterogeneous chemistry on stratospheric sulfuric acid aerosols. However, the work did not include heterogeneous effects involving aluminum oxide particle exhaust, or the local effect of ozone chemistry in the plume. The local and global effect of catalytic ozone decomposition on alumina was reported by Hanning-Lee *et al.* [1996].

Prather and collaborators rebutted the comment by Aftergood [1991] by citing total ozone mapping spectrometer (TOMS) results [*McPeters et al.*, 1991]. TOMS has a pixel size resolution of 40×40 km^2, which would limit the ability to accurately measure a local ozone hole. However, because the ozone measurement precision of TOMS is a few percent, a significant hole of small extent should be observable. By way of example, Prather explained that a 40% column reduction over a 20×20 km^2 area would appear as a 10% reduction for a single pixel, which is much greater than the detection limit of the TOMS instrument. The TOMS images of several Shuttle trajectories, ranging in time from 1 hour to 1 day after passage, give no indication of a transient ozone depletion.

In this paper, we examine the validity of using TOMS images to measure ozone content in a solid rocket motor plume. We consider two questions: (1) Is the TOMS pixel resolution and geometry of detection sufficiently good to detect ozone depletion in rocket plumes, and (2) how are ozone measurements perturbed by other plume species, particularly due to the presence of chlorine compounds that absorb light and aluminum oxide particles that scatter light in the same spectral region as ozone.

Background

TOMS is a remote passive downward looking absorption spectrometer that collects atmospheric backscattered radiation in six wavelength channels. Channels at 312.5, 317.5, 331.2, and 339.8 nm are used to determine total ozone column content. Two channels at 360 and 380 nm are used to determine ground and cloud reflectivity. TOMS provides a cross-wise sweep of 35 positions every 8 seconds. Global coverage is obtained by merging these scans with those from adjacent orbital tracks.

The TOMS instrument measures the directional albedo of the Earth's atmosphere at each wavelength. Using the notation of Herman *et al.* we define this property as

$$A(\lambda)=\frac{I(\lambda)}{F_0(\lambda)} \quad (1)$$

where $I(\lambda)$ and $F_0(\lambda)$ are the true backscattered radiance and true solar irradiance, respectively. To minimize calibration errors and wavelength independent effects, TOMS reports ratios of albedo for wavelength pairs, the values being defined as $N_p = -100$

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Table 1. Wavelength pairs used by TOMS

Pair (nm)	Designation	Separation (nm)	Sensitivity, $\Delta N_p/\Delta\Omega$ [a]	
			radiative transfer[b]	This model[c]
312.5 / 331.2	A	18.8	0.125	0.168
317.5 / 331.2	B	13.8	0.063	0.080
331.2 / 339.8	C	8.5	0.010	0.011
312.5 / 317.5	A'	5.0	0.062	
317.5 / 339.8	B'	22.3	0.073	0.088

[a] $N_p = -100 \log_{10}[A(\lambda_1)/A(\lambda_2)]$ and the ozone column total Ω is in Dobson units (DU) where 1000 DU = 1 atm-cm. $\Delta N_p/\Delta\Omega$ values are for the range 325-375 DU and for vertical solar zenith and viewing angle. [b] From radiative transfer calculations [*Herman et al.*, 1991]. [c] From single-scattering radiation model used in this report.

$\log_{10}[A(\lambda_1)/A(\lambda_2)]$. The wavelength pairs that are used by TOMS are summarized in Table 1. Atmospheric ozone content is determined by comparing the measured directional albedo ratios to computed tables representing inverse solutions of a multiple scattering (Rayleigh) radiative transfer equation [*Klenk*, 1982]. These tables depend on total ozone Ω, ozone latitude dependence, solar zenith angle θ, atmospheric pressure at scattering altitudes, and other climatology conditions. A typical set of data are compiled in Table 1. The sensitivity for measuring total ozone for a particular wavelength pair is proportional to the slope of the N_p vs Ω curve.

TOMS data analysis assumes that the backscattered radiance $I(\lambda)$ is attenuated by ozone absorption and Rayleigh scattering. Methods have been developed to deal with the effect of aerosols on the estimation of total column ozone (Dave, 1978; Torres et al., 1992; Bhartia et al., 1993); however, not for the case of an alumina-laden plume. Nor are absorbing species considered other than those which exist in the ambient atmosphere. In the following discussion we consider how the measured value of $I(\lambda)$ is affected by the presence of plume constituents. Since we cannot carry out a full radiative transfer calculation, we instead use a simpler single scattering expression to calculate how the detected backscattered radiance is modified by the presence of the plume species and how it affects the estimation of the total ozone column. This simpler approach is valid because we are working with a model atmosphere and calculating how well TOMS measures *changes* in ozone levels in the presence of plume species. A typical set of N_p values calculated by the model described below is presented in Table 1.

Model of Scattered Radiation

The transmission of solar irradiance through the atmosphere and, consequently, the depth of penetration, depends strongly on wavelength, primarily due to absorption by ozone. One can define a scattering depth profile that relates the distribution of altitude from earth from which photons are scattered back to space. In the present analysis, we consider a zenith sun angle $\theta = 0^\circ$ and a TOMS viewing angle of $\alpha = 0^\circ$. Under these conditions, the scattering distribution for wavelengths 312.5 nm and longer lies below an altitude of 10 km for these conditions, which allows us to make the simplifying assumption that all backscatter originates from a narrow effective scattering layer below the ozone layer and plume track [*Syage*, 1995]. One then obtains the equation

$$I(\lambda) = \kappa(\lambda)\exp\left\{-2\left[\tau_R(\lambda)+\tau_{O_3}(\lambda)\right]-\sum_i \tau_i(\lambda)\right\} \qquad (2)$$

where

$$\tau_R(\lambda) = \sigma_R(\lambda)\int_{z_0}^{\infty} dz\; n_R(z) = \sigma_R(\lambda)\bar{N}_R$$

$$\tau_{O_3}(\lambda) = \sigma_{O_3}(\lambda)\int_{z_0}^{\infty} dz\; n_{O_3}(z) = \sigma_{O_3}(\lambda)\bar{N}_{O_3}$$

$$\tau_i(\lambda) = \sigma_i(\lambda)\int_{-x_0}^{x_0}\int_{-y_0}^{y_0} dx\,dy\int_{z_0}^{\infty} dz\; n_i(x,y,z) \qquad (3)$$

$$= \sigma_i(\lambda)\int_{-x_0}^{x_0}\int_{-y_0}^{y_0} dx\,dy\, N_i(x,y) = \sigma_i(\lambda)\bar{N}_i$$

The parameters are defined as follows:

- $\kappa(\lambda)$ - constant that includes $F_0(\lambda)$, scattering functions, instrument functions, and any other factors that are invariant to the plume properties,
- σ_R, σ_{O3}, σ_i - cross sections for Rayleigh scattering by air, absorption by O_3, and absorption and scattering of plume species, respectively,
- $n_R(z)$, $n_{O3}(z)$, $n_i(x,y,z)$ - molecular or particle density for air, O_3, and plume species as a function of atmospheric coordinates,
- $N_i(x,y)$ - Column total for plume species as a function of horizontal position,
- $\bar{N}_R$, $\bar{N}_{O3}$, $\bar{N}_i$ - Column totals for air, O_3, and plume species, averaged over the TOMS FOV.
- z, z_0 - vertical distance from the Earth's surface and altitude of assumed scattering layer, respectively,
- x, y, x_0, y_0 - horizontal atmospheric coordinates and size of TOMS pixel resolution, respectively.

The τ terms are attenuation factors. The ozone depletion in the plume is included in the sum of plume species and is represented by a negative density that gets subtracted from the ambient ozone density. There is a factor of 2 in the first exponent of Eq. (2) because the detected light makes two passes through the atmosphere. This factor is lacking in the second exponent because it is assumed for the common situation where $\theta \neq \alpha$ (even for small inequivalence), that the detected light makes just one pass through the plume. If TOMS is directly viewing the plume then this pass occurs only on the backscatter.

The calculated attenuation due to particle scattering may be overestimated (by as much as 50%) because the scattering tends to be in the forward direction and not isotropic. We assume that Rayleigh scattering is due to air and the n_R and n_{O3} distributions of the ambient atmosphere are uniform in the horizontal dimension. Ross [1992, 1996] has computed 3D spatial profiles $n_i(x,y,z)$ for chemical species and ozone depletion in SRM plumes using representative wind flow fields at different launch sites and for different times of the year. Horizontally-resolved column depletions for ozone $N_{O3}(x,y)$ are presented in Figure 1 for a one hour old plume from a Titan IV launched from Cape Canerval under summer-like conditions. A summary of the peak and FOV averaged column totals are given in Table 2. Ab-

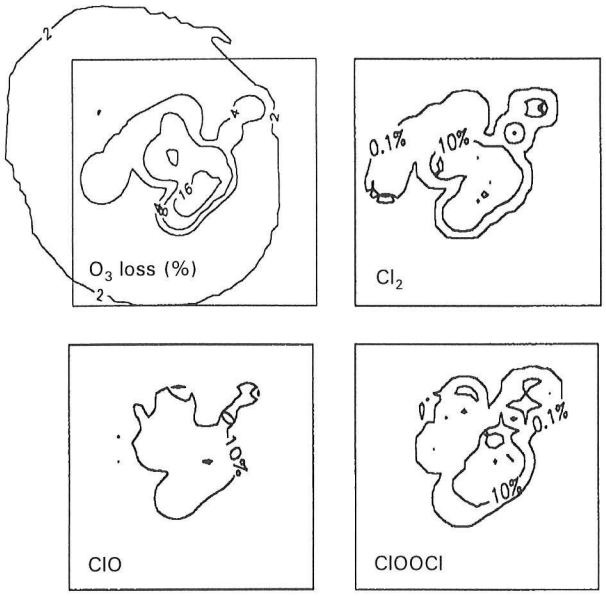

Figure 1. 2D column totals for O_3, Cl_2, ClO, and ClOOCl. Contour lines are expressed as percent of peak density (Table II). The rectangle superimposed on the data represents the TOMS FOV of 40×40 km.

sorption cross sections for the relevant plume species at the TOMS observing wavelengths are compiled in Table 3.

Results and Discussion

Simulated TOMS measurements of ozone levels for the plume properties in Fig.1 are summarized in Table 4. Results are presented that examine the effect of plume attenuation by uv absorption (by ClO, Cl_2, etc.) and particle scattering on the detected TOMS signal. If we ignore these interferences, then TOMS measures an ozone depletion of 6.5 DU (Case III, Table 4). This is exactly half the actual ozone column loss averaged over the TOMS FOV, and results because the TOMS algorithm assumes a double pass through an air parcel, when in fact a single pass through the plume is more likely, as discussed earlier. It is evident in Table 4 that adding the chemical species and the particles distorts the TOMS measurement (Cases I and II), but only moderately, assuming the plume model of Ross [1992, 1996]. Similar results are obtained for a 4 hr plume. At later times, the column ozone deficit diminishes. The following points constitute the major trends and observations:

1. Because the typical plume width and calculated ozone depletion is signficantly smaller than the TOMS FOV, the measured change in total ozone $\Delta\Omega$ understates the true ozone change.
2. ClO has a differential absorption similar to ozone and therefore causes an underestimate of the ozone loss. Conversely, Cl_2, has a differential absorption for the A, B, and B' wavelength pairs that is opposite to that of ozone. Because it looks like "anti-ozone," it, exaggerates the apparent ozone loss. For these wavelength pairs, the ClO and Cl_2 interferences somewhat offset each other, though Cl_2 dominates. For the C pair, Cl_2 has a differential absorption similar to ozone, thus underestimating the ozone loss. These interferences are relatively minor assuming the plume model of Ross [1992, 1996]. However, the distortion is about a factor of 2-3 greater using the model of Brady and Martin [1996] mainly because of a greater predicted density of Cl_2 [*Syage*, 1995].
3. The effect of particle attenuation on the TOMS reading is relatively minor assuming the particle size distribution determined by Beiting [1995]. However, the distortion can increase significantly if the actual particle size distribution has a large component near the wavelength of detected light (namely 0.3 μm) [*Syage*, 1995].

Table 3. Absorption cross sections of plume species (units of 10^{-20} cm^2)[a].

Species	312.5 nm	317.5 nm	331.2 nm	339.8 nm
O_3	7.40	3.76	0.50	0.12
Cl_2	19.8	22.3	25.4	23.6
ClO	10	2[b]	-	-
ClOOCl	37.5	28.6	16.0	12.1
air	1.40×10^{-6}	1.31×10^{-6}	1.11×10^{-6}	1.00×10^{-6}
particle model[c]				
0.056μ particle	4.95×10^{6}	4.48×10^{6}	4.01×10^{6}	3.54×10^{6}
1.0μ particle	2.47×10^{12}	2.46×10^{12}	2.45×10^{12}	2.43×10^{12}
3.6μ particle	4.32×10^{13}	4.38×10^{13}	4.45×10^{13}	4.52×10^{13}

[a] from DeMore *et al* [1994]. [b] Difficult estimate because of structured spectrum. [c] Cross sections for log normal particle distributions were determined from tables in Beiting (1995).

Table 2. Peak and FOV averaged column totals (atm-cm) for UV absorbing species (Titan IV launch).[a]

Species	Peak	Avg.
O_3	-0.069[b]	-0.013[b]
Cl_2	3.0×10^{-3}	1.1×10^{-4}
ClO	2.6×10^{-3}	1.6×10^{-4}
ClOOCl	1.6×10^{-3}	3.5×10^{-5}
particle model[c]		
0.056μ particle	5.3×10^{-10}	3.9×10^{-11}
1.0μ particle	1.3×10^{-13}	6.9×10^{-15}
3.6μ particle	1.4×10^{-13}	7.5×10^{-15}

[a] Conversion to units of cm^{-2} obtained by multiplying by 2.8×10^{19} $atm^{-1}cm^{-3}$. [b] Relative to ambient ozone total of 0.355 atm-cm. [c] Sauter mean diameter for log normal distribution, evaluated by Beiting (1995).

Table 4. Simulated TOMS measurement of ozone column depletion (DU units) for different plume conditions.[a]

Wavelength	$\Delta\Omega_{peak} = -69$ DU[b]		
Pair	I	II	III
A	-6.20	-6.37	-6.50
B'	-6.05	-6.40	-6.50
B	-6.17	-6.44	-6.50
C	-5.04	-6.06	-6.50

[a] Case I - plume molecules and trimodal particle distribution,
II - plume molecules and no particles,
III - no plume molecules nor particles.
[b] Peak vertical column depletion in the plume. For comparision Ω = 355 DU for the undisturbed atmosphere in our calculation.

The present assessment indicates that, in principle, TOMS could measure a local ozone depletion in a rocket plume. However, for the plume model given here, in which a 20% column ozone loss extends over several kilometers in radius, TOMS would measure a 2% decrease that would register in only one pixel. The measured loss could be enhanced by choosing a viewing angle α that is aligned along the plume axis, to maximize the pathlength and overlap with the plume centerline. We have carried out calculations that show the potential for a factor of three enhancement assuming an aligned plume unperturbed by differential wind velocities [*Syage*, 1995]. In reality, winds will randomize much of the initial alignment.

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References

Aftergood, S.,"Comment on 'The space shuttle's impact on the stratosphere' by M. J. Prather et al.," *J. Geophys. Res., 96*, 17,377 (1991).

Beiting, E. J., "Characteristics of alumina particles from solid rocket motor exhaust in the stratosphere," The Aerospace Corporation, TR-95(5231)-8 (Sept. 15, 1995).

Bhartia, P. K., J. Herman, R. D. McPeters, and O. Torres, "Effect of Mount Pinatubo aerosols on total ozone measurements from backscatter ultraviolet (BUV) experiments," *J. Geophys. Res., **98**,* 18,547-18,554 (1993).

Brady, B. B., and L. R. Martin, "Modeling solid rocket booster exhaust plumes in the stratosphere with SURFACE CHEMKIN," The Aerospace Corporation, TR-95(5231)-9 (1996).

Burke, M. L., and P. F. Zittel, "Laboratory generation of free chlorine from Hcl under stratospheric afterburning conditions," The Aerospace Corporation, TR-96(1306)-3 (1 March 1996), submitted to *Comb. Flame*.

Dave, J. V., "Effect of aerosols on the estimation of total ozone in an atmospheric column from the measurements of its ultraviolet radiance," *J. Atmos. Sci., 35,* 899-911 (1978).

DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, "Chemical kinetics and photochemical data for use in stratospheric modeling," Evaluation number 11, JPL Publication 94-26 (December 15, 1994).

Denison, M. R., J. J. Lamb, W. D. Bjorndahl, E. Y. Wong, and P. D. Lohn, "Solid rocket exhaust in the stratosphere: Plume diffusion and chemical reaction," *J. Spacecraft & Rocket, 31*, 436 (1994).

Hanning-Lee, M. A., B. B. Brady, L. R. Martin, and J. A. Syage, "Ozone decomposition on alumina: Implications for solid rocket motor exhaust," *Geophys. Res. Lett., 23,* 1961-1964 (1996).

Herman, J. R., R. Hudson, R. McPeters, R. Stolarski, Z. Ahmad, X.-Y. Gu, S. Taylor, and C. Wellemeyer, "A new self-calibration method applied to TOMS and SBUV backscattered ultraviolet data to determine long-term global ozone change," *J. Geophys. Res., 96,* 7531-7545 (1991).

Hoshizaki, H. (chairman), "Aircraft wake microscale phenomena," in *The Stratosphere Perturbed by Propulsion Effluents, CIAP Monogr.* 3, chap. 2., pp. 60-73, Climatic Impact Assessment Program, U.S. Dept. of Transportation, Washington D. C., Sept. 1975.

Jackman, C. H., D. B. Considine, and E. L. Fleming, "The space shuttle's impact on the stratosphere: An update," *J. Geophys. Res., 101,* 12,523-12,529 (1996).

Karol, I. L., Y. E. Ozolin, and E. V. Rozanov, "Effect of space rocket launches on ozone," *Ann. Geophysicae, 10,* 810 (1992).

Klenk, K. F., P. K. Bhartia, A. J. Fleig, V. G. Kaveeshwar, R. D. McPeters, and P. M. Smith, "Total ozone determination from the backscattered ultraviolet (BUV) experiment," *J. Appl. Meteorol., 21,* 1672-1684 (1982).

McPeters, R., M. Prather, and S. Doiron, "Reply," *J. Geophys. Res., 96,* 17,379 (1991).

Pergament, H. S., R. I. Gomberg, and I. G. Poppoff, "NO_x deposition in the stratosphere from the space shuttle rocket motors," Appendix G to *NASA Tech. Memo.* X-58198, G-3, Jan. 1977.

Prather, M. J., M. M. Garcia, A. R. Douglass, C. H. Jackman, M. K. W. Ko, and N. D. Sze, "The space shuttle's impact on the stratosphere," *J. Geophys. Res., 95,* 18,583-18,590 (1990).

Ross, M. N. "Potential impact of solid rocket exhaust on stratospheric ozone," The Aerospace Corporation, TOR-92(2565)-2 (1992).

Ross, M., "Local effects of solid rocket motor exhaust on stratospheric ozone," *J. Spacecraft & Rocket, 33,* 144-153 (1996).

Syage, J. A., "Can the total ozone mapping spectrometer (TOMS) measure ozone depletion in rocket plumes," The Aerospace Corporation, TR-95(5231)-4 [AFSMC Report SMC-TR-95-31] (1 June 1995).

Torres, O., Z. Ahmed, and J. R. Herman, "Optical effects of polar stratospheric clouds on the retrieval of TOMS total ozone," *J. Geophys. Res., 97,* 13,015-13,024 (1992).

Zittel, P. F., "Computer model predictions of the local effects of large, solid-fuel rocket motors on stratospheric ozone," The Aerospace Corporation, TR-94(4231)-9 (SMC-TR-94-36) (Sept 10, 1994).

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