Ozone estimates derived from Dobson direct sun measurements: effect of atmospheric temperature variations and scattering

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We have performed an analysis of the impact of the temperature sensitivity of the ozone absorption coefficients on estimates of total atmospheric ozone obtained by the Dobson spectrophotometer operating in direct sun mode. In general, the higher the mean ozone temperature the greater will be the tendency to overestimate the ozone amount. The spreads in ozone residuals over the temperature models we investigated were 3%, 4%, and 6% for the *A*, *C*, and *D* line pairs, respectively, whereas for coupled line pairs the spread was only about 2%. The *A-C-D* triplet showed a very small temperature effect, the spread being probably less than 2%. For the *A-D* system, currently recommended by the WMO, the computed spread was 2.4 ± 0.5%. A Monte Carlo model was applied to investigate the potential impact of scattered radiation entering the system. The effect has been computed for various conical fields of view. For clear sky conditions with no aerosols present, the error introduced appears to be less than 1%. When a tropospheric aerosol model was inserted, however, significant errors were observed. For the models we studied aerosol attenuation resulted in overestimates of total ozone up to 8%, but the impact of scattered radiation was to reduce the overestimate, and, in some cases, the scattering and attenuation effects may balance for a realistic Dobson system. Both effects increased from the *A* to the *C* to the *D* line pairs. The results indicate that line pair coupling reduces the combined error due to both sources to less than 1%.

Introduction

The Dobson spectrophotometer[1] has been employed as a standard over a number of decades for monitoring the total atmospheric ozone. Also, when employed in the Umkehr mode[2,3] it provides information relating to the vertical distribution of ozone. With growing concern over the possibility of ozone depletion by various mechanisms it has recently become increasingly important to have accurate ozone measurements so that any real changes in total ozone would not be masked by experimental uncertainty. It is therefore vital that any inherent errors in the Dobson related instruments be fully appreciated and some effort be made to evaluate their potential magnitude.

This paper addresses two sources of possible errors in the Dobson instrument measurements. First, we shall consider the impact of the temperature sensitivity of the ozone absorption coefficients,[4] and second, we shall make some estimates of the contribution of scattered radiation entering the aperture. Mechanisms for the reduction or elimination of both error sources will be discussed, including line pair combinations other than the currently recommended *A-D* system.

Measurement Concept and Analysis

The Dobson spectrophotometer is a specialized double beam selector which, when operating in the direct sun mode, determines the total atmospheric ozone by measuring the ratios of the intensities of two selected wavelengths of uv radiation in the solar spectrum. The difference in ozone absorption at the two wavelengths provides an indication of the total amount of ozone in the atmosphere, the objective of the differencing procedure being to reduce or eliminate unknown attenuation contributions from atmospheric aerosols.

The wavebands observed are dictated by the instrument slit characteristics and vary in base widths from 18 Å at the shorter wavelength to about 39 Å at the longer wavelength.[5] Vanier and Wardle[6] have shown that the finite slit widths have a negligible effect on the analysis.

The ozone amount computation is based on the equation

$$N_\lambda = (\alpha - \alpha')_\lambda \mu X + (\beta - \beta')_\lambda m + (\delta - \delta')_\lambda \sec Z, \qquad (1)$$

where, in our notation, N_λ is the log of the intensity ratio normalized by the solar constant ratio (see below), α is the ozone absorption coefficient, X is the total ozone (to

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be derived), β is the atmospheric molecular optical thickness (base 10), and δ is the corresponding aerosol optical thickness. The prime indicates the longer of the two wavelengths, and λ indicates a specific line pair. Z is the solar zenith angle at the observer, and μ and m are the weighted means of the local solar angle secant values along the observer–sun line in passing through the ozone layer and the molecular atmosphere, respectively.

The quantity N_λ is derived from the equation

$$N_\lambda = \log_{10}\left(\frac{I'}{I}\right) - \log_{10}\left(\frac{I_0'}{I_0}\right), \quad (2)$$

where I,I' are the measured intensities, and I_0,I_0' are the corresponding intensities at the top of the atmosphere.

Linear combinations of Eq. (1) are often employed to further reduce the possibility of aerosol attenuation induced error. In general terms, if we assign a multiplier a_λ to the line pair indicated by λ, the resulting reduction equation is

$$\sum_\lambda a_\lambda N_\lambda = X\mu \sum_\lambda (\alpha - \alpha')_\lambda a_\lambda + m \sum_\lambda (\beta - \beta')_\lambda a_\lambda + \sec Z \sum_\lambda (\delta - \delta')_\lambda a_\lambda, \quad (3)$$

where the a_λ values are chosen such that the expectation of the last sum is small. Ideally, we would like the a_λ coefficients to satisfy

$$\sum_\lambda (\delta - \delta')_\lambda a_\lambda = 0 \quad (4)$$

for a broad range of aerosol properties.

In this analysis we have restricted the temperature dependence study to the *A, B, C,* and *D* line pairs, the *A-D, C-D,* and *A-C* doublets and the *A-C-D* triplet. The *B* line pair was excluded from the scattering study, simulations being applied only to the *A, C,* and *D* wavelength pairs. The World Meteorological Organization currently recommends the use of the *A-D* line pair doublet as the most reliable system.

Effect of Temperature

The values of the cross section differences, $(\alpha - \alpha')_\lambda$, employed in the International Ozone Commission standard reduction system are based on the estimates of Vigroux (1967)[5] for −50°C. The cross sections are temperature dependent, however, and therefore we might expect errors to be introduced in the ozone estimates since the mean ozone temperature can vary considerably from −50°C.

While the treatment of the temperature effect is difficult, at best on account of the sparseness of temperatures at which the ozone cross sections have been measured, the results of Walshaw *et al.*[7] at −42°C and Vigroux[5] at 18°C suggest that a linear variation in the cross sections is a reasonable assumption. The original results of Vigroux[8] indicated a tendency for the temperature sensitivity to increase as the temperature increased around −44°C, but these measurements were not made specifically for the Dobson system. Assuming, for the moment, the validity of the linear relationship, it is easy to show that the mean ozone absorption coefficient is merely that coefficient appropriate to the mean ozone temperature $\overline{T}$ given by

$$\overline{T} = \int_{H_1}^{H_2} T(h)\rho(h)dh \Big/ \int_{H_1}^{H_2} \rho(h)dh, \quad (5)$$

where $T(h)$ is the temperature at altitude h, $\rho(h)$ is the ozone density at altitude h, and H_1 and H_2 are the altitudes of the bounds of the ozone layer of interest.

Since, in general, neither $T(h)$ nor $\rho(h)$ will be known it will not be possible to compute $\overline{T}$ for any given experimental measurements. Thus, if the cross section difference terms of Eqs. (1) or (3) are temperature sensitive, it will not be possible to supply corrections. It follows that the most appropriate method for the elimination of the effect would be to select the multipliers a_λ such that the sum $\Sigma_\lambda a_\lambda (\alpha - \alpha')_\lambda$ of Eq. (3) is independent of temperature while retaining a reasonably large (constant) value. If d_λ is the temperature coefficient of $(\alpha - \alpha')_\lambda$, this condition can be expressed as

$$\sum_\lambda a_\lambda d_\lambda = 0. \quad (6)$$

Table I presents the cross section differences estimated by Vigroux (1967) at −50°C and 18°C for the *A, B, C,* and *D* lines. The results for −50°C are composite values based mostly on his direct measurements using the Dobson slits. The values for 18°C are those taken by the direct method. The results for the doublets and the triplet were computed by us. We also present the values we computed for the temperature sensitivity coefficients d_λ, together with the associated standard errors. The mean ozone temperature was computed for a number of vertical ozone distributions[9] and ten standard temperature profiles.[10] The values obtained ranged from −39°C to −62.3°C, the mean being −48°C. The corresponding spread in the cross section differences expressed as a percentage of the −50°C values are given in the last column of Table I. It can be seen that while the spread for the *A, B, C,* and *D* line pairs are about 3%, 4%, 4%, and 6%, respectively, the coupled line pairs show a spread around only 2%, and the *A-C-D* triplet has a negligible expected spread but with a larger standard error than that for the other cases.

For the sake of comparison we also present the percentage spreads computed from the temperature coefficients of Walshaw *et al.*[7] in Table I. These results were calculated on the basis of the Vigroux results[8] at −59°C and −44°C, and, while the agreement with the present results is good for the *C* line pair, somewhat lower spreads arose for the *A, B,* and *D* line pairs.

In Table II we present the temperature sensitivities for the cross section difference ratios. The results are given as change per °C as a fraction of the value at −50°C, the capital letters referring to $\alpha - \alpha'$ for the appropriate line pairs. The present results are in acceptable agreement with those of Powell,[11] which were

Table I. Vigroux 1967 Cross Sections (Direct)

Line pair	X-section (−50°) (atm cm)$^{-1}$	18°C (atm cm)$^{-1}$	Temp. coefficient (atm cm°C)$^{-1}$	Percentage spread (present)	Percentage spread (Warshaw *et al.*)
A	1.750 ± 0.010	1.911 ± 0.013	2.37 ± 0.24 × 10^{-3}	3.14 ± 0.33	2.51
B	1.135 ± 0.008	1.264 ± 0.013	1.90 ± 0.22 × 10^{-3}	3.89 ± 0.44	2.20
C	0.800 ± 0.008	0.898 ± 0.011	1.44 ± 0.20 × 10^{-3}	4.19 ± 0.58	4.10
D	0.360 ± 0.005	0.425 ± 0.012	0.96 ± 0.19 × 10^{-3}	6.22 ± 1.23	2.81
A-D	1.390 ± 0.011	1.486 ± 0.018	1.41 ± 0.31 × 10^{-3}	2.35 ± 0.51	2.46
C-D	0.440 ± 0.009	0.473 ± 0.016	0.49 ± 0.27 × 10^{-3}	2.59 ± 1.42	5.19
A-C	0.950 ± 0.013	1.013 ± 0.017	0.93 ± 0.31 × 10^{-3}	2.28 ± 0.77	0.93
A-C-D	0.590 ± 0.013	0.588 ± 0.021	−0.03 ± 0.36 × 10^{-3}	−0.12 ± 1.42	−0.42

Table II. Comparisons of the Cross-Section Difference Ratio Temperature Sensitivities

	Temperature sensitivity (°C^{-1} × 10^4) at −50°C		
Line pair ratio	Vigroux (direct)	Powell	Walshaw *et al.*
A/D	−11.0 ± 4.5	−8.6 ± 1.9	−1.2
B/D	−8.4 ± 4.7	−6.5 ± 1.9	−2.6
C/D	−7.2 ± 5.0	−4.8 ± 1.8	−5.6

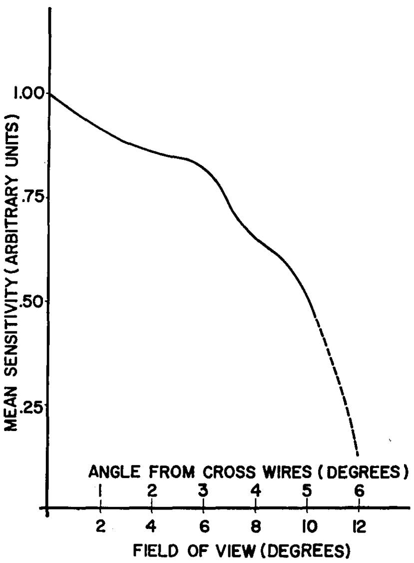

Fig. 1. Mean sensitivity of Dobson spectrophotometer 102 as function of angle from cross wires for longer *D* wavelength.

computed from measurements at −56.1°C and 20°C, but showed larger magnitudes for the *A/D* and *B/D* ratios than those estimated from the sensitivities given by Walshaw *et al.*[7] This discrepancy again reflects the differences between the temperature pairs employed for the evaluation.

The spread for the line pair doublets is of the same order, if not smaller, than those that might arise from other error sources so that it appears likely that, at this stage, the doublets provide satisfactory temperature effect elimination. While the *A-C-D* triplet probably has an even smaller temperature sensitivity, it must be remembered that this particular combination will not be effective as the doublets in eliminating the aerosol attenuation.

Effect of Scattered Radiation

The field of view of the Dobson spectrophotometer is considerably larger than the 0.5° extension of the solar disk so that the measured intensity is the sum of the attenuated direct sun and scattered radiation. Figure 1 presents estimates we have made of the mean sensitivity of the instrument within annuli of various radii centered at the cross wires. The results are based on the measurements of Olafson[12] for instrument No. 102. While the peak measured sensitivity was at a point approximately 3½° from the cross wires, our integration shows that the mean sensitivity decreases monotonically with increasing annulus radius. Some sensitivity might be retained as far as 6° from the cross wires, but an effective total field of view of about 8° would seem to apply. It must be remembered, however, that the effective field of view will probably be affected by the operating conditions since both a ground quartz diffusing plate and a focusing lens may be inserted in front of the slit.

We modeled the impact of the scattering phenomenon through the application of a Monte Carlo simulation code[13,14] which we applied to each of the six wavelengths of the *A,C,* and *D* line pairs. The model atmosphere was taken to be distributed in fifty homogeneous layers each 2 km thick, and the vertical molecular and ozone density distributions are presented in Fig. 2. The vertical aerosol distribution was taken to be of the Elterman type.[15] The molecular scattering cross sections were chosen to match the vertical optical thicknesses given in the Handbook of Geophysics, whereas the ozone cross sections at various temperatures were computed by linear interpolation based on the Vigroux results.[8] The vertical temperature distribution was taken from the U.S. Standard Atmosphere 30°N Spring/Fall model.

The aerosol size distribution and refractive index selection were somewhat arbitrary. We chose a refractive index of 1.55 and a Haze *C* size distribution,[16] i.e., we assumed that the distribution varied as D^{-4} for

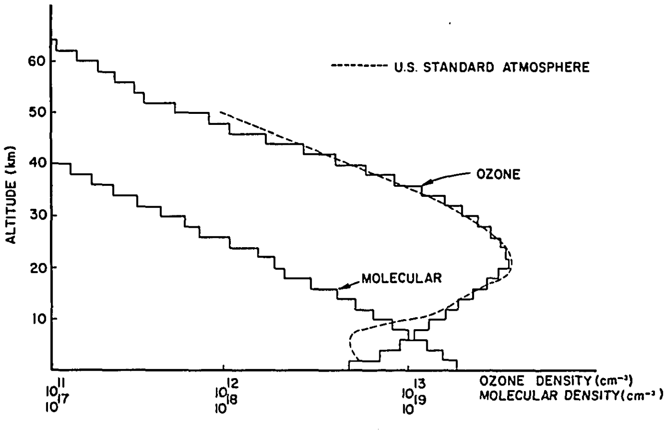

Fig. 2. Ozone and molecular densities of model atmosphere as function of altitude.

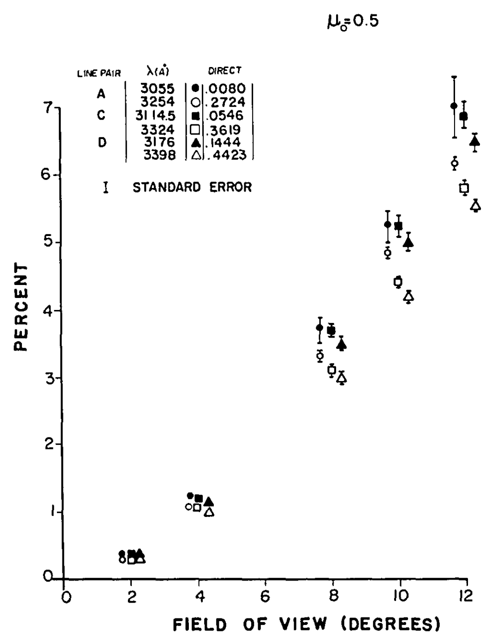

Fig. 3. Scattered radiation entering aperture as percentage of the direct (attenuated) radiation vs field of view for various Dobson line pairs.

diameters D between 0.2 μm and 10 μm and assumed a uniform probability distribution for diameters between 0.06 μm and 0.2 μm. The vertical optical thickness of the aerosol model approximated that in the Handbook of Geophysics[15] ranging form 0.263 (base e) at 3055 Å to 0.247 at 3398 Å.

While it would be possible to model exactly the effect of the sensitivities measured by Olafson,[12] they were determined for one specific line only. We chose, therefore, to model a uniform response within a set of fields of view. The selected set was 2°, 4°, 8°, 10°, and 12°, and at each scattering of our simulation we modeled random transfers into each of these fields of view. The results for each wavelength were normalized to an incident flux of π per unit area, so that in the analysis of the results, the term I_0'/I_0 of Eq. (2) was zero.

The single scattering intensity results of the Monte Carlo code were replaced by the analytical expression

$$I_s(\Omega) = \pi \exp(-\tau) \sum_{i=1}^{N} \tau_i P_i(\Omega), \tag{7}$$

where

τ_i = optical thickness (base e) of ith atmospheric scattering constituent along the path to the sun.

$P_i(\Omega)$ = probability that a scattering by the ith species would generate a photon within the field of view Ω of the receiver.

$$\tau = \tau_{oz} + \sum_{i=1}^{N} \tau_i,$$

the total optical thickness (including that of ozone) along the path to the sun.

N, the total number of scattering constituents was two, of course, $i = 1$ referring to Rayleigh and $i = 2$ to aerosol scattering. Note that the percentage error in the signal due to single scattering is a linear function of the atmospheric turbidity.

The simulations showed that when the aerosols were absent the scattering contribution for a solar zenith angle of 60° and fields of view up to and including 8° were less than 1% of the attenuated direct sun. In this case the multiple scattering contribution was of the same order as the single scattering contribution, but the resulting error in total ozone reached a maximum of only 1%.

The introduction of tropospheric aerosol into the model had a significant effect in increasing the error however. Figure 3 presents our estimates of the scattered radiation as a percentage of the attenuated direct sun for the five fields of view, and it can be seen that, for the model we considered, the percentage contribution for the shorter wavelengths was significantly larger than that for the longer wavelengths. This had the effect of reducing N_λ and therefore could cause underestimates of the total ozone.

In reducing the N_λ values we employed the ozone absorption cross sections relevant to the assumed ozone and temperature profiles, thus eliminating the temperature induced error in this part of the study. The results for the percentage deviations between the total ozone derived from the A, C, and D line pairs and the model value of 0.36607 atm cm are plotted in Fig. 4. It can be seen that estimates increased from the A to the C to the D line pair, whereas the standard errors in the estimates increased in the opposite direction. The results for zero field of view reflect the impact of aerosol attenuation. It can be seen that the aerosol attenuation caused overestimates of the total ozone, but that the effect of scattering was to reduce this error. Thus, while it would be possible to reduce considerably the error contribution due to scattering by limiting the field of view to 2°, or so, the resultant error in this case might well be larger than that for a larger field of view where scattering is important. The results computed on the

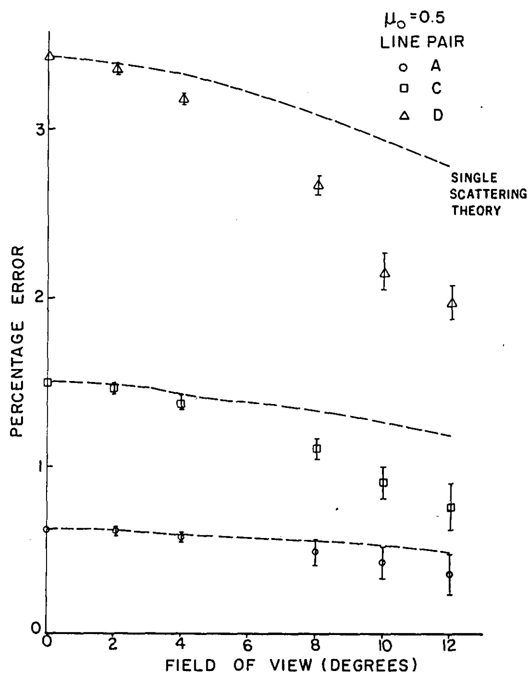

Fig. 4. Percentage error in total ozone arising from scattering and attenuation by molecules and aerosols vs field of view for various Dobson line pairs.

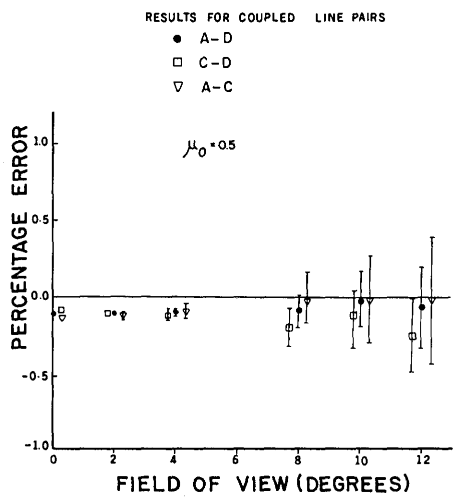

Fig. 5. Percentage error in total ozone arising from scattering and attenuation by molecules and aerosols vs field of view for coupled line pairs.

basis of single scattering alone are given by the dashed lines, and it is clear that this approximation is not adequate for error evaluation. The multiple scattering contribution ranged from about 20% of the single scattering contribution for a field of view of 2° to about 40% at 12°.

Figure 5 presents the results for coupled line pairs. In all cases, the resultant error was very small indeed and certainly less than 1%. It appears, therefore, that the line pair coupling procedure is not only effective in reducing the aerosol attenuation error, but also in eliminating errors due to scattering processes.

In order to evaluate the variation in the errors as a function of the solar zenith angles we computed the errors for an 8° field of view for zenith angle secants of 1.0 (0.5) 3.0, i.e., for zenith angles ranging from 0° to 70.5°. The results, plotted in Fig. 6, indicate only a weak dependence on solar position, with a tendency for the scattering contribution to increase slowly with increasing zenith angle thus reducing the ozone overestimate. This effect is entirely due to multiple scattering and, for our model, had the effect of essentially eliminating the resultant error for the *A* line pair at large zenith angles.

We investigated the effect of variations in atmospheric turbidity by multiplying the aerosol densities of our standard model by various factors from 0 to 2.5. The results are shown in Fig. 7. The errors appear to be approximately proportional to the turbidity factor, but increase more slowly than would be expected on the basis of attenuation alone or attenuation coupled with single scattering. The results for attenuation alone are exactly linear, of course, and intersect the origin, whereas the results for single scattering are very nearly linear with an intercept on the error axis equal to the error for single scattering by molecules.

Conclusions

It would appear that the temperature and scattering effects might cause errors of the order of 5% to be present in the total ozone estimated from individual line pairs. The temperature effect may be effectively removed by taking linear combinations of line pairs, and for the doublets studied, the effect was satisfactorily small. The errors due to the scattering effect are important only when aerosols are present, and for the model studied they tend to compensate for errors due

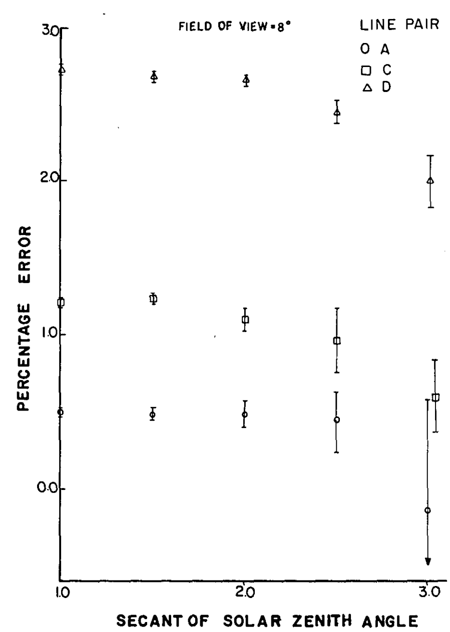

Fig. 6. Percentage error in total ozone vs secant of solar zenith angle for 8° field of view and various Dobson line pairs.

to aerosol attenuation. The error due to both scattering and attenuation is effectively eliminated by the line pair coupling system. In particular, the *A-D* system showed negligible sensitivity to aerosol induced effects. While the percentage error in total ozone due to the temperature effect is independent of the solar zenith angle, that due to scattering increases slowly with the secant of the solar zenith angle and approximately linearly with the aerosol loading factor.

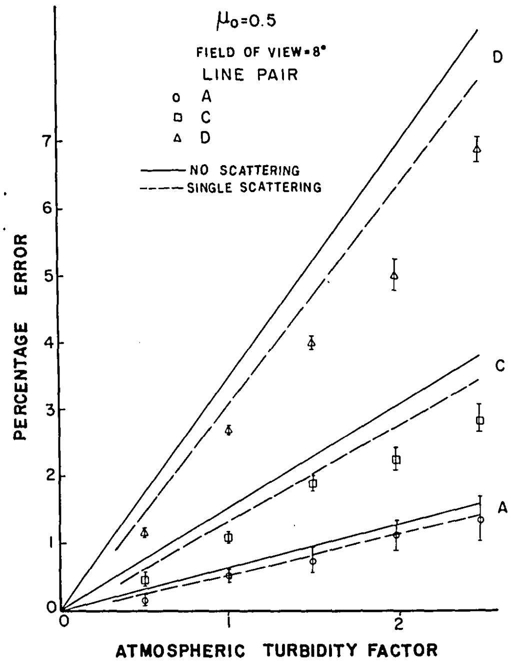

Fig. 7. Percentage error in total ozone vs atmospheric turbidity factor for $\mu_0 = 0.5$, a field of view of 8° and various Dobson line pairs.

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