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ERROR IN TOTAL OZONE MEASUREMENTS ARISING FROM AEROSOL ATTENUATION

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ABSTRACT

A generalized least squares method for deducing both total ozone and aerosol extinction spectrum parameters from Dobson spectrophotometer measurements has been developed. An error analysis applied to this system indicates that there is little advantage to additional measurements once a sufficient number of line pairs have been employed to solve for the selected detail in the attenuation model. It is shown that when there is a predominance of small particles (less than about 0.35 microns in diameter) the total ozone from the standard AD system is too high by about one percent. When larger particles are present the derived total ozone may be an overestimate or an underestimate but that serious errors occur only for narrow polydispersions.

INTRODUCTION

In estimating total ozone from the atmosphere's attenuation of solar radiation, it is necessary to use empirical methods to deal with the very variable and poorly known component of the attenuation due to scattering by particles, i.e., by dust, haze aerosols, etc. The current standard estimation method is the Dobson AD double bandpair method,¹ which is equivalent to assuming particulate attenuation to be spectrally linear.

As an intended advance on the standard method, Basher² proposed that the particulate attenuation spectrum be explicitly represented by a finite polynomial series. This concept was later generalized by Gardiner in terms of orthogonal polynomials but it was also shown by Gardiner that as one attempts to derive more information about the aerosol attenuation spectrum the result is to magnify the impact of other systematic measurement errors.

The objective of the work reported here was twofold. Firstly, we generalized the interpretation procedures in a new direction by defining solutions for overdetermined systems. This permitted goodness to fit estimates to be made giving some judgement as to when the detail of the aerosol attenuation model was excessive. Secondly, we developed estimates of actual errors in total ozone as

a function of aerosol particle size when each of the derived inversion procedures was applied. By means of these results, aerosol attenuation errors can be computed for arbitrary size distributions.

Generalized Multiple Line-pair Ozone Reduction System

When the particulate attenuation spectrum is represented by an arbitrary polynomial, the relative attenuation for the k th bandpair, at λ_1 and λ_2 , is

$$\Delta\delta_k = \delta(\lambda_1) - \delta(\lambda_2) = \sum_{i=1}^M g_i G_i \quad (1)$$

where

$$G_i = (\lambda_1 - \lambda_0)^i - (\lambda_2 - \lambda_0)^i \quad (2)$$

and where λ_0 is an arbitrarily chosen reference wavelength ($\lambda_0 = 333.55$ nm was chosen here), the g_i are the unknown coefficients of the polynomial representation and M is the chosen order of the representation. The bandpair's observation of ozone, X_k , can then be written

$$X_k = X + \Delta\alpha_k^{-1} \sum_{i=1}^M g_i G_i \quad (3)$$

where X is the actual ozone value, and $\Delta\alpha_k$ is the bandpairs' relative ozone absorption coefficient. The set of N ($\geq M+1$) such linear equations in turn can be expressed in matrix form as

$$P = AQ \quad (4)$$

where P is the column vector of the set of observed X_k , Q is the column vector of the quantities X and the g_i 's to be estimated, and A is the matrix which relates the vectors as described by equation 3. A least squares technique is employed to solve these equations.

Results For Ozone Reduction Coefficients

The analysis was applied to the data cited by Basher². In constructing the variance-covariance matrix, we assumed that the error in total ozone was inversely proportional to the ozone absorption cross-section difference $\Delta\alpha_k$, and the errors for different line pairs were uncorrelated. The numerical values of the parameters employed are summarized in Table 1. The ozone estimates are averages of large numbers of data and were given by Dobson and Normand⁴.

Table 1. Parameters Employed In The Calculations

Line Pair	A	B	C	D
λ_1 (n.m.)	325.4	329.1	332.4	339.8
λ_2 (n.m.)	305.5	308.8	311.45	317.6
$\Delta\alpha_k$ (atm.cm) ⁻¹	1.744	1.157	0.809	0.356
X_k (atm.cm)	0.3526	0.3492	0.3461	0.3483

Solutions were obtained for all possible subsets of the line pairs A, B, C and D and the more interesting results are in Table 2.

TABLE 2. SUMMARY OF MULTIPLYING FACTORS REQUIRED TO ESTIMATE THE TOTAL OZONE AND RELATED RESULTS

N	M	LINE PAIRS USED				XA COEFF	XB COEFF	XC COEFF	XD COEFF	X ERROR(PC)
2	1	A	B			2.860	-1.860	0.0	0.0	4.005
2	1	A	C			1.788	0.0	-0.788	0.0	2.466
2	0	A	D			0.960	0.0	0.0	0.040	0.980
2	1	A	D			1.224	0.0	0.0	-0.224	1.644
2	1	B	C			0.0	3.101	-2.101	0.0	6.509
2	1	B	D			0.0	1.392	0.0	-0.391	2.842
2	1	C	D			0.0	0.0	1.710	0.710	5.069
3	1	A	B	C		1.875	-0.151	-0.724	0.0	2.450
3	2	A	B	C		9.713	13.748	5.035	0.0	25.330
3	1	A	B	D		1.113	0.126	0.0	-0.239	1.627
3	2	A	B	D		5.498	-4.859	0.0	0.361	9.327
3	1	A	C	D		1.290	0.0	-0.091	-0.198	1.625
3	2	A	C	D		3.193	0.0	-2.752	0.558	7.272
3	1	B	C	D		0.0	1.296	0.118	-0.413	2.825
3	2	B	C	D		0.0	6.734	-6.566	0.832	17.889
4	0	A	B	C	D	0.589	0.259	0.127	0.025	0.768
4	1	A	B	C	D	1.156	0.182	-0.129	-0.209	1.594
4	2	A	B	C	D	3.932	-1.558	-1.870	0.495	6.566

The results for the weighting coefficients are not only applicable to the estimate of total ozone, but are also the error magnification coefficients. Thus while the sum is always unity their magnitudes increase as M increases, confirming Gardiner's hypothesis of error magnification.

The parameter indicating expected percentage error was computed assuming a random error of 0.0035 (about 1%) in X_A . The propagated uncertainty for the quadratic M=2 cases varies considerably depending on the band combination, and is smallest for the ABCD and ACD combinations. Comparison of these combinations demonstrates the important point that the addition of the extra B bandpair to the ACD combination gives negligible reduction

in the propagated uncertainties in both ozone and particulate components. Comparison of the AD, ACD, and ABCD combinations for the linear $M=1$ cases shows a similar result. In other words, with respect to propagation of uncertainty there is virtually no advantage in using more than the minimum number of bandpairs needed for the given polynomial representation.

The choice of estimation method is essentially between the A bandpair with the constant $M=0$ particulate representation and a unit magnification of uncertainty, the AD combination with the linear $M=1$ representation and 1.6 magnification of uncertainty, and the ACD combination with the quadratic $M=2$ representation and a 6.8 magnification of uncertainty. The impact of any given level of X_k uncertainty on a particular ozone estimate can be directly determined from these magnifications.

Numerical Modeling

Empirical descriptions of particulate attenuation are needed because the physical parameters of atmospheric particulates upon which the attenuation depends vary very widely and are at best poorly known at a given place and time. There is, however, information available on the typical values and bounds of the parameters from which typical values and bounds of the attenuation can be assessed.

The procedure developed here is to describe the attenuation effects for a set of quasi-monodisperse distributions which span the particle size range of interest, with the understanding that the attenuation effects for actual atmospheric polydispersions can be found by simply integrating the computed effect, e.g., ozone error in X_{AD} for the quadratic method, over the appropriate size distribution. In this way the route along which the error generates is more clearly and usefully described.

The calculations of extinctions or attenuation used Mie theory applied to spherical particles of constant refractive index $1.55-0.005i$, equivalent to spherical aerosols such as are found in hazes. Averaging the extinctions over the Dobson slit transmittance functions was performed, but was found to have little effect owing to the ratio of slitwidth to center wavelength, at about $1/300$, being so small.

A review of the reduction equations reveals that the residual between the estimate X_k and the true ozone, X , can be written approximately as

$$X_k - X = \frac{\Delta\delta_k}{\Delta\alpha_k} \quad (5)$$

Thus if we compute $\Delta\delta_k$ using Mie theory the right hand side of equation (5) yields the actual error in the ozone estimate X_k . The related error in estimations for multiple line pairs can then be obtained by applying the appropriate coefficients given in Table 2 to these errors.

All the attenuations and ozone errors presented below are

normalized to an optical depth of 0.1 (base 10) at 305.5 nm. compatible with standard aerosol descriptions. Values for other optical depths are in simple proportion to the optical depth. Calculations were done for all possible bandpair combinations and polynomial representations, and for the observation variance model described earlier. The results for the A, B, C and D line pairs are given in Figure 1. It is clear that the error magnitudes are proportional to $\Delta\alpha_k$, increasing from A to D. For small particles (less than 0.35 microns in diameter) an overestimate always occurs in agreement with the earlier analysis of Thomas and Holland. To compute the results for an arbitrary polydispersion, $f(D)$, we must perform the integration

$$\epsilon = 10 \int_0^{\infty} \frac{f(D)}{N(D)} e(D) dD \quad (6)$$

where $N(D)$ is the column count required to produce unit optical depth (to base 10) and $e(D)$ is the plotted error.

For the AD system we performed estimations for both the $M=0$ and $M=1$ (standard) case and the results are given in Figure 2. While the error for small particles is reduced from about 6% to 1% by fitting one aerosol coefficient, the error amplitude for larger particles is not significantly reduced. However the frequency of the oscillations increases for $M=1$ so that the effect of integrating these results over the polydispersions likely to occur in nature will be to reduce the resultant error.

Figure 3 presents results for the (A,B,C,D) combination with $M=0, 1$ and 2 . It can be seen that for $M=2$ the effect is to increase the oscillation magnitude. However, the oscillation frequency also increases so that the actual error for a broad polydispersion may be smaller. For small particles, the $M=2$ solution reduced the error to only 0.1%.

CONCLUSIONS

The goodness of fit estimates that we have performed indicate that the data of Dobson and Normand⁴ is compatible with the hypothesis of a quadratic spectral dependence of the aerosol attenuation and very low values of other systematic and random errors. However, the results can also be explained by simpler spectra if other systematic errors are present.

The evaluation of errors arising from spherical aerosol particles indicates that the practical application of a quadratic model would only be justified in the presence of aerosol with large optical depth or the presence of very narrow polydispersions with particle diameter greater than about 0.5 microns. The evaluation of the statistical characterization of aerosols at a Dobson site could, with the aid of the results developed, greatly clarify the magnitude of the errors in the total ozone arising from the aerosol attenuation spectrum.

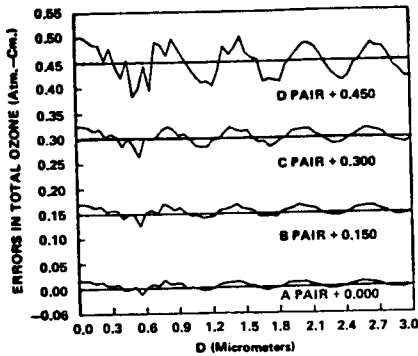


FIGURE 1. ERRORS IN TOTAL OZONE FOR SINGLE LINE PAIRS AS FUNCTION OF AEROSOL PARTICLE DIAMETER. (VERTICAL OPTICAL DEPTH TO BASE $10^{-0.1}$)

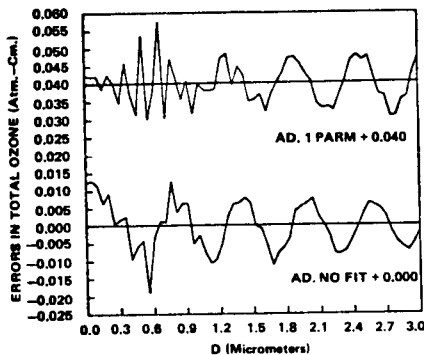


FIGURE 2. ERRORS IN TOTAL OZONE FOR MULTIPLE LINE PAIRS AND VARIOUS AEROSOL ATTENUATION MODELS AS FUNCTION OF AEROSOL PARTICLE DIAMETER. (VERTICAL OPTICAL DEPTH TO BASE $10^{-0.1}$)

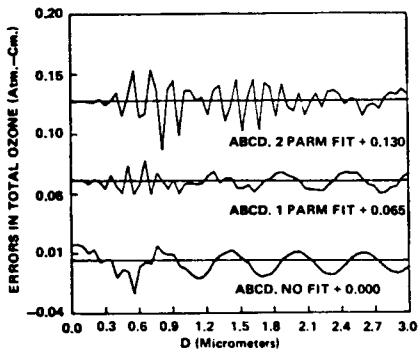


FIGURE 3. ERRORS IN TOTAL OZONE FOR MULTIPLE LINE PAIRS AND VARIOUS AEROSOL ATTENUATION MODELS AS FUNCTION OF AEROSOL PARTICLE DIAMETER. (VERTICAL OPTICAL DEPTH TO BASE $10^{-0.1}$)

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