Generalized treatment of particulate scattering in Dobson ozone spectrophotometer calculations

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SUMMARY

In the calculation of atmospheric total ozone from ultraviolet spectrometry, the particulate scattering term is usually regarded as a linear function of wavelength. A method due to R. E. Basher, in which it is treated as a quadratic polynomial, is here generalized to include a polynomial of any degree, and the quadratic approximation is seen to be somewhat arbitrary.

It is shown that the determination of the quadratic and higher coefficients from Dobson spectrophotometer observations is limited by systematic errors of measurement, and that these errors are doubled or trebled by attempting to correct even for the quadratic coefficient. It is concluded that Basher's method of calculation is at present inadvisable.

1. INTRODUCTION

The determination of total ozone by the Dobson spectrophotometer involves the measurement of \( N = L_0 - L \), where \( L \) is the logarithm of the ratio of the intensities at a pair of ultraviolet wavelengths in direct solar radiation received at the earth's surface, and \( L_0 \) is the value of \( L \) outside the atmosphere. Four wavelength pairs A, B, C and D can be used to obtain four independent determinations of total ozone, which do not in general agree with each other.

Basher (1976) has attributed this inconsistency entirely to neglect of the particulate scattering term in the calculation, and has developed a method for eliminating the scattering term in order to arrive at the true value of total ozone. The discrepancy may, however, arise from systematic errors in the measurement of \( N \) since neither \( L_0 \) nor \( L \) can be measured directly. In this case Basher's treatment cannot be expected to reduce the errors in total ozone, and may indeed magnify them.

2. PARTICULATE SCATTERING FUNCTION

The particulate scattering coefficient, \( \delta \), (Dobson 1957) may be approximated by a polynomial in wavelength, \( \lambda \),

\[
\delta = \delta_0 + \sum_{i=1}^{n} q_i G_i(\lambda)
\]  

where \( \delta_0 \) is a constant and \( G_i \) is a polynomial of degree \( i \). For a particular set of data the \( q_i \) will depend on the choice of \( n \) unless the \( G_i \) are mutually orthogonal over the set of wavelengths used. Since the Dobson spectrophotometer measures only the ratio of intensities at two wavelengths, \( \delta_0 \) cannot be found, and the condition for orthogonality is

\[
\sum_{k} H_{ik} H_{jk} = \begin{cases} 1, & i = j \\ 0, & i \neq j \end{cases}
\]

where

\[
H_{ik} = G_i(\lambda_k) - G_i(\lambda_i) = \Delta_k(G_i)
\]

and \( \lambda_i, \lambda_k \) are the shorter and longer wavelengths, respectively, of the \( k \) wavelength pair, \( k = A, B, C \) or \( D \).
The orthogonal polynomials of the first degree are simply

\[ H_{ik} = (\lambda_k - \lambda_0)/n_1 = \Delta_k \lambda/n_1 \]  

where the normalizing factor, \( n_1 \), is given by

\[ n_1^2 = \sum_k (\lambda_k - \lambda_0)^2 = \sum_k \Delta_k^2 \lambda \]  

The remaining \( H_{ik} \) may be generated from the polynomials \((\lambda - \lambda_0)^i\) or simply from \( \lambda^i \) by the relation

\[ n_i H_{ik} = \Delta_k (\lambda - \lambda_0)^i - \sum_{j=1}^{i-1} a_{ij} H_{jk}, \quad i > 1 \]  

where

\[ a_{ij} = \sum_k H_{jk} \Delta_k (\lambda - \lambda_0)^i \]  

and the normalizing factor, \( n_i \), is given by

\[ n_i^2 = \sum_k \Delta_k^2 (\lambda - \lambda_0)^i - \sum_{j=1}^{i-1} a_{ij}^2 \]  

The last term in Eq. (6) removes those parts of \( \Delta_k (\lambda - \lambda_0)^i \) which are already adequately represented by the orthogonal polynomials of degree less than \( i \), which ensures that the \( i \)th polynomial \( H_{ik} \) will itself be orthogonal to the rest.

**TABLE 1**

<table>
<thead>
<tr>
<th>Wavelength pair ( k )</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_{1k} )</td>
<td>-0.47680</td>
<td>-0.48638</td>
<td>-0.50316</td>
<td>-0.53191</td>
</tr>
<tr>
<td>( H_{2k} )</td>
<td>0.59766</td>
<td>0.26046</td>
<td>-0.02441</td>
<td>-0.75593</td>
</tr>
<tr>
<td>( H_{3k} )</td>
<td>-0.59136</td>
<td>0.32967</td>
<td>0.63499</td>
<td>-0.37203</td>
</tr>
<tr>
<td>( H_{4k} )</td>
<td>0.25643</td>
<td>-0.76417</td>
<td>0.58568</td>
<td>-0.08512</td>
</tr>
<tr>
<td>( H_{5k} )</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**TABLE 2**

<table>
<thead>
<tr>
<th>Wavelength pair ( k )</th>
<th>A</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_{1k} )</td>
<td>-0.54570</td>
<td>-0.57586</td>
<td>-0.60877</td>
</tr>
<tr>
<td>( H_{2k} )</td>
<td>0.71230</td>
<td>0.06391</td>
<td>-0.69896</td>
</tr>
<tr>
<td>( H_{3k} )</td>
<td>-0.44141</td>
<td>0.81505</td>
<td>-0.37531</td>
</tr>
<tr>
<td>( H_{4k} )</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**TABLE 3**

<table>
<thead>
<tr>
<th>Wavelength pair ( k )</th>
<th>A</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_{1k} )</td>
<td>-0.66748</td>
<td>-0.74463</td>
</tr>
<tr>
<td>( H_{2k} )</td>
<td>0.74463</td>
<td>-0.66748</td>
</tr>
<tr>
<td>( H_{3k} )</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The computation can be made easier by choosing \( \lambda_0 \) with care, but the \( H_{ik} \) do not depend on the choice. The values of the functions \( H_{ik} \) are given in Table 1 for the full set of wavelength pairs A, B, C, D; in Table 2 for the partial set A, C, D since the B wavelengths are not widely used at the present; and in Table 3 for the set A, D. The wavelengths are A = 305.5, 325.4 nm; B = 308.8, 329.1 nm; C = 311.4, 332.4 nm; D = 317.6, 339.8 nm.
Eq. (1) may now be written
\[ \delta_k^* - \delta_k = \Delta \delta_k = \sum_{i=1}^{n} h_i H_{ik} \]  \hspace{1cm} (9)

The coefficients \( h_i \) are independent of the degree of approximation required, but depend on the wavelength pairs used. Since the \( H_{ik} \) are orthonormal
\[ h_i = \sum_k \Delta \delta_k H_{ik} \]  \hspace{1cm} (10)

A further account of orthogonal polynomials may be found in many elementary textbooks on numerical analysis, e.g.Ralston (1965).

3. Determination of Coefficients

Using Basher’s notation, \( X_k \) is the ozone as calculated from an observation on the \( k \) wavelength pair, neglecting \( \delta \), and \( X \) is the true ozone. If the possibility of systematic errors in the measurement of \( N_k \) is ignored, then
\[ \Delta \alpha_k X_k = (N_k - \Delta \beta_k m) / \mu \]  \hspace{1cm} (11)

and
\[ \Delta \alpha_k X = (N_k - \Delta \beta_k m) / \mu - \Delta \delta_k \sec z / \mu \]  \hspace{1cm} (12)

Omitting \( \sec z / \mu \sim 1 \) for the sake of clarity,
\[ \Delta \delta_k = \Delta \alpha_k (X_k - X) \]  \hspace{1cm} (13)

Hence from Eq. (10)
\[ h_i = \sum_k \Delta \alpha_k H_{ik} (X_k - X), \quad i = 1, 2, \ldots, n \]  \hspace{1cm} (14)

Since the true ozone \( X \) is not yet determined, there are \( n \) equations in \( n + 1 \) unknowns. The simplest way out of this difficulty is to assume that one of the \( h_i \), say \( h_e \), is equal to zero. The true ozone is then given by
\[ X = \frac{\sum_k \Delta \alpha_k H_{ek} X_k}{\sum_k \Delta \alpha_k H_{ek}} \]  \hspace{1cm} (15)

and the remaining \( h_i \) can all now be found.

4. Special cases of the theory

Basher’s two methods can now be seen as special cases of the general treatment given above. If \( w \) is the number of wavelength pairs in use, then Basher’s first method (his Eq. (5)) is the case \( w = n = e = 2 \), and the second method (his Eq. (7)) is the case \( w = n = e = 3 \). This equivalence can be verified by rearranging Basher’s equations in the form
\[ X = \sum_k b_k X_k \Delta \alpha_k / \sum_k b_k \Delta \alpha_k \]  \hspace{1cm} (16)

The first method gives \( b_A = 1 / \Delta \lambda_A \) and \( b_D = -1 / \Delta \lambda_D \), and these are proportional to \( H_{2A} \) and \( H_{2D} \) in Table 3. The second method gives, after some manipulation, \( b_A = (\Sigma \lambda_C - \Sigma \lambda_D) / \Delta \lambda_A \), \( b_C = (\Sigma \lambda_D - \Sigma \lambda_A) / \Delta \lambda_C \), and \( b_D = (\Sigma \lambda_A - \Sigma \lambda_C) / \Delta \lambda_D \), which are proportional to \( H_{3A}, H_{3C}, H_{3D} \) in Table 2. In both cases, therefore, Eq. (16) yields the same value of \( X \) as Eq. (15). It is clear that the corresponding special case to be used when four wavelength pairs are available is the case \( w = n = e = 4 \).
5. Test Case

The test case used by Basher, which is taken from Dobson and Normand (1962), can now be analysed by the general treatment described in section 3. Eq. (14) and Table 1 are applied to the values of $X_k$ and $\Delta \alpha_k$ reproduced in Table 4.

<table>
<thead>
<tr>
<th>Wavelength pair $k$</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_k$</td>
<td>0.3526</td>
<td>0.3492</td>
<td>0.3461</td>
<td>0.3483</td>
</tr>
<tr>
<td>$\Delta \alpha_k$</td>
<td>1.744</td>
<td>1.157</td>
<td>0.809</td>
<td>0.356</td>
</tr>
</tbody>
</table>

The results are displayed in Fig. 1. The coefficients $h_i$ are shown as a function of the true ozone $X$, which cannot be determined until the $h_i$ are constrained. If this is to be done by setting one of the $h_i$ equal to zero, it can be seen that the choice will seriously affect $X$.

![Graph showing particulate scattering coefficients $h_i$ calculated from the test case data.](image)

Figure 1. Particulate scattering coefficients $h_i$ calculated from the test case data.

If $\delta$ is thought to be linear in $\lambda$, then $h_2$ will be set to zero, giving $X = 0.353 \text{ atm-cm}$, and $h_3$ and $h_4$ must be regarded as experimental error or noise. If $\delta$ is to be quadratic in $\lambda$, then $h_3 = 0$, $X = 0.368 \text{ atm-cm}$, and $h_4$ is noise. If $\delta$ is cubic in $\lambda$, $h_4 = 0$ and $X = 0.361 \text{ atm-cm}$.

The choice must be based on prior knowledge of the behaviour of particulate scattering in the atmosphere. Without such prior knowledge it is not correct to argue, for example, that since $h_3$ is small it must be zero.

Basher has pointed out that the test case data show excellent agreement with a parabolic model of particulate scattering, i.e. a model in which $h_3$ and $h_4$ are zero. The reason for this agreement may be seen in Fig. 1: at $X = 0.368 \text{ atm-cm}$, $h_3$ is zero and $h_4$ is very small. It can be shown that the ordinate in Basher’s ‘graph of the second type’ is given by

$$X_{\text{II}} = X + (h_2/n_2)(1/\delta_{k_2}) + h_4 \frac{(H_{4k}/\Delta \lambda_k - H_{4\lambda}/\Delta \lambda_i)}{(\Delta \alpha_k/\Delta \lambda_k - \Delta \alpha_i/\Delta \lambda_i)}$$

so that if $h_4$ had been zero at $X = 0.368 \text{ atm-cm}$, the points would have fallen on a straight line with slope $h_2/n_2$ and intercept $X$, and the agreement would have been perfect. Since
\( \Delta \lambda_k \) and \( \Delta \lambda_i \) are nearly equal, the departure from the straight line is approximately
\[ h_k (H_{4k} - H_{4i})/(\Delta \lambda_k - \Delta \lambda_i). \]
The point farthest from the line is therefore \( X'_{\text{BC}} \). In the test case \( h_k = -0.00004 \) at \( X = 0.368 \text{ atm-cm} \), so that \( X'_{\text{BC}} \) lies above the line by about 0.0002.
This can be seen in Basher's graph.

The agreement of the experimental data with the parabolic model is therefore illusory. The gradient of the \( h_k \) line in Fig. 1 is independent of the observed data, and is so small that \( h_k \) will have practically the same value for all reasonable values of \( X \). If \( h_k \) is close to zero, the experimental data can always be fitted to the parabolic model by setting \( h_3 = 0 \). If, on the other hand, \( h_k \) is not near zero, one of two conclusions must follow: either \( h_k \) is correct, in which case \( \delta \) is at least a fourth-degree function of wavelength, and there is no reason to suppose that \( h_3 = 0 \); or \( h_k \) is affected by experimental errors in the measurement of \( N_k \), in which case \( h_3 \) will also be affected and no test of the parabolic model can be made. It follows that the quadratic approximation advocated by Basher is not supported by the experimental data, and the ozone value which it produces, 0.368 atm-cm, is no more reliable than the value of 0.353 atm-cm produced by the linear approximation.

The difficulty in deciding which, if any, of the \( h_i \) is to be constrained to zero does not arise from a random error of measurement, and therefore cannot be resolved by examining the statistical behaviour of the \( h_i \) in a series of observations. For example, if in Fig. 1 the lines for \( h_1 \) and \( h_2 \) remained the same throughout the series, while that for \( h_3 \) moved up and down at random, it would still not be correct to infer \( h_3 = 0 \).

### 6. Systematic errors of measurement

It has been shown above that the true ozone, \( X \), cannot be determined until the \( h_i \) are constrained, but even a constraint soundly based on knowledge of particulate scattering in the atmosphere will leave systematic errors of measurement out of account. If the recorded values of \( N_k \) are systematically low by \( \Delta N_k \), then the true ozone is given by

\[
\mu \Delta \lambda_k X = N_k + \Delta N_k - \Delta \beta_k m - \Delta \delta \text{sec} z
\]  \hspace{1cm} (18)

With \( \Delta N_k \) neglected, the inferred value of \( \Delta \delta_k \) will be reduced by \( \Delta N_k /\text{sec} z \), and Eq. (10) shows that the calculated value of each \( h_i \) will then be too low by \( \Delta h_i \), given by

\[
\Delta h_i = \sum_k \Delta N_k H_{ik}/\text{sec} z
\]  \hspace{1cm} (19)

Since the slope of the \( h_i \) line in Fig. 1 is \( -\sum_k \Delta \lambda_k H_{ik}/z \), the value of \( X \) obtained by setting \( h_i \) equal to zero will be too low by \( \sum_k \Delta N_k H_{ik}/\mu \sum_k \Delta \lambda_k H_{ik} \). If, on the other hand, \( X \) is calculated from an AD observation by the orthodox method

\[
X = (N_A - N_D)/(\Delta \lambda_A - \Delta \lambda_D) - (\Delta \beta_A - \Delta \beta_D)/(\Delta \lambda_A - \Delta \lambda_D)
\]  \hspace{1cm} (20)

then \( X \) will be too low by \( (\Delta N_A - \Delta N_D)/(\Delta \lambda_A - \Delta \lambda_D) \). The misinterpretation of a systematic error in \( N_A \) will therefore magnify its effect by \( H_{iA}(\Delta \lambda_A - \Delta \lambda_D)/\sum_k \Delta \lambda_k H_{ik} \). For \( i = 3 \), this magnification factor is about 3.1 and the corresponding factor for a systematic error in \( N_D \) is about 1.9. Ozone values calculated from four wavelength pairs will suffer also from systematic errors in \( N_B \) and \( N_C \), whereas those from orthodox AD observations will not.

Systematic errors encountered in practice are not negligible. Table 5, reproduced from Dziewulska-Losiowa and Walshaw (1975), shows that when ten Dobson spectrophotometers from all over the world were compared at Belsk, Poland, in 1974, six of them differed systematically from the reference instrument (No. 83) by more than 0.020 in at least one of the wavelength pairs A, C, and D. The root mean square of all the entries
TABLE 5

<table>
<thead>
<tr>
<th>Instrument No.</th>
<th>$\Delta N_C$</th>
<th>$\Delta N_A$</th>
<th>$\Delta N_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>0.006</td>
<td>0.002</td>
<td>-0.014</td>
</tr>
<tr>
<td>64</td>
<td>-0.012</td>
<td>0.084</td>
<td>-0.024</td>
</tr>
<tr>
<td>77</td>
<td>-0.003</td>
<td>-0.017</td>
<td>0.006</td>
</tr>
<tr>
<td>83</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>84</td>
<td>0.016</td>
<td>0.046</td>
<td>-0.010</td>
</tr>
<tr>
<td>96</td>
<td>-0.031</td>
<td>-0.054</td>
<td>-0.056</td>
</tr>
<tr>
<td>101</td>
<td>-0.007</td>
<td>0.001</td>
<td>-0.017</td>
</tr>
<tr>
<td>108</td>
<td>-0.012</td>
<td>-0.015</td>
<td>-0.040</td>
</tr>
<tr>
<td>110</td>
<td>-0.023</td>
<td>0.018</td>
<td>-0.033</td>
</tr>
<tr>
<td>112</td>
<td>-0.025</td>
<td>-0.030</td>
<td>-0.006</td>
</tr>
</tbody>
</table>

in Table 5 is 0.028. However, some of the instruments were already known to be out of calibration, and the intercomparison must have greatly reduced their systematic errors. If the three instruments with the smallest differences from No. 83 are typical of instruments with up-to-date calibrations, then the root-mean-square value of $\Delta N$ for one wavelength pair can be taken as 0.010.

Suppose, for example, $\Delta N_A = 0.020$ while $\Delta N_B = \Delta N_C = \Delta N_D = 0$, and $\sec z = 2$. Then $\Delta h_3 = \Delta N_A H_{3A} / \sec z = -0.0059$. Fig. 1 shows that a change of this size is not trivial. If the true ozone, $X$, is calculated by assuming $h_3 = 0$, then $X$ will be too low by 0.022 atm·cm. This is nearly the same as the error which Basher attributes to neglect of the quadratic expansion coefficient of particulate scattering.

If the true ozone is arrived at by assuming $h_2 = 0$ (this is practically the same as the orthodox method), the standard error in $X$ due to the $\Delta N_k$ is only about a quarter of that for $h_3 = 0$, because the $h_2$ line in Fig. 1 is about four times as steep as the $h_3$ line, while the sum of the squares of the $H_{ik}$ remains at unity. On the other hand, the slope of the $h_4$ line is so small that systematic errors would be magnified enormously if $X$ were to be calculated by assuming $h_4 = 0$.

7. CONCLUSIONS

It has been shown that Dobson spectrophotometer observations cannot be used to measure both ozone and particulate scattering in the atmosphere unless the polynomial expansion coefficients of the particulate scattering term are subjected to a mathematical constraint. Such a constraint cannot therefore look to the same observations for support. It can be justified only by a detailed analysis of other knowledge of particulate scattering.

Even with such justification, however, the determination of the particulate scattering term cannot be taken very far. In its polynomial expansion with wavelength, the quadratic and higher coefficients will be masked by systematic errors of measurement currently encountered in practice, and the effect of these errors on the ozone value will in general be magnified by attempting to eliminate the quadratic or higher coefficients.

It therefore appears inadvisable to reduce Dobson spectrophotometer observations by the method advocated by Basher (1976) unless systematic errors of measurement can be significantly reduced.

REFERENCES


