ATTENUATION OF VISIBLE ENERGY IN A POLLUTED ATMOSPHERE

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Atmospheric attenuation at visible wavelengths in polluted atmospheres cannot necessarily be predicted accurately from visibility statistics. This report discusses human vision under different lighting conditions. The eye has much less than its maximum sensitivity where molecular absorption by pollutants is strongest. However, it was concluded that molecular absorption at visible wavelengths is rarely large enough to be a serious problem. Scattering is the primary cause of low visibilities in the atmosphere. Scattering is also the main cause of really large extinction coefficients throughout the visible portion of the spectrum.
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I. INTRODUCTION

Atmospheric visibility statistics are useful but are not entirely reliable indicators of atmospheric attenuation at visible wavelengths. There are two main problems with statistics which are based on observations where the detector is the human eye. First, there are large variations in the sensitivity of the eye as a function of wavelength. The second problem is more complex. Atmospheric attenuation is caused by absorption and scattering. It can be shown that the contrast between an object and a background does not necessarily increase with an increase in attenuation if the added attenuation is pure absorption. These characteristics of visibility are discussed in Section II.

Scatterers and absorbers in the atmosphere may be molecules or larger particles. Molecular absorption by some trace gases varies considerably and in an uneven manner as a function of wavelength. Attenuation by larger particles generally varies smoothly and slowly with wavelength. Wavelength dependence of attenuation by several atmospheric constituents is examined in Sections III and IV, and conclusions from this study is in Section V.

II. VISIBILITY AND HUMAN VISION

The eye's ability to detect an object depends upon the contrast between the apparent brightness of the object and the apparent brightness of the background. This depends upon the nature of the object, atmospheric attenuation, and illumination. Observations of visibility are usually placed in one of two distinct categories, those made during daylight and those made at night [1]. This dichotomy ignores a considerable amount of time before sunrise and after sunset when important changes occur. There is a gradual variation between the photopic response in good illumination and the scotopic response of the dark-adapted eye [2,3]. Furthermore, molecular absorption may be more important at dusk than it is during the day.

A. Photopic Response

The wavelength of maximum sensitivity of the eye in good illumination is approximately 555 nm [4]. At the wavelength of maximum sensitivity the relative luminosity is unity. The relative luminosity is 0.995 or greater for all wavelengths in the band from 550 to 560 nm; it drops off for shorter and longer wavelengths [5]. The relative luminosity is only 0.503 at 510 and 610 nm. This means that the relative luminosity is less than half for all wavelengths outside a band slightly wider than 100 nm. The relative luminosity is only 0.00012 at 390 and 750 nm. The visible portion of the electromagnetic spectrum ranges from approximately 350 to 770 nm.

Photometric units are analogous to radiometric units. For example, luminous flux is the integral over visible wavelengths of the radiative flux weighted according to the absolute luminosity. At the wavelength of maximum sensitivity of the eye, the absolute luminosity is 680 lumens per watt (680 lm W\(^{-1}\)). At any other wavelength, the absolute luminosity is found by multiplying 680 lm W\(^{-1}\) by the relative luminosity at that wavelength. A point source which radiates 1 lm into a solid angle of one steradian (1 sr) has a luminous intensity of one candela (1 cd). A point source which emits isotropically and
has a luminous intensity of 1 cd emits a total flux of $4\pi$ lm. Details of the characteristics of the standard candela by which the lumen is defined may be found in standard references [2,5].

The luminance (photometric brightness) is usually expressed either in candelas per unit area or in lamberts (L). One lambert is equal to the uniform luminance of a diffuse surface which emits or reflects light at a rate of 1 lm cm$^{-2}$ (10000 lm m$^{-2}$). One millilambert (1 mL) is equal to $(10/\pi)$ cd m$^{-2}$. The lower limit of the photopic response occurs at a luminance of about 1 mL.

B. Mesopic and Scotopic Response

As luminance decreases below 1 mL, the wavelength of maximum sensitivity of the eye gradually changes [2,3]. The wavelength of maximum sensitivity decreases from 550 nm for a luminance of 0.1 mL (100 mL) to 520 nm for 1 mL. At a luminance of 0.01 mL, vision is scotopic, and the maximum relative luminosity occurs at a wavelength of 511 nm. The curve of relative luminosity for scotopic vision is narrower than the curve for photopic vision. The relative luminosities for scotopic vision are 0.456 and 0.365 at 460 and 560 nm, respectively. The maximum absolute luminosity for scotopic vision is 1746 lm W$^{-1}$ at 511 nm.

C. Diurnal Variation

Both photometric brightness of the sky and illuminance (illumination) on horizontal surfaces vary by several orders of magnitude between noon and midnight at lower and middle latitudes [4,5].

1. **Midday.** During the day an object may be illuminated by direct sunlight or by diffuse energy scattered by the atmosphere. Nearly one-fifth of the illuminance at the surface on a clear day is from scattered sunlight. Illuminance on an object in direct sunlight when the sun is high in the sky is more than $10^5$ lm m$^{-2}$ on a clear day. Illuminance at the surface on an overcast day ranges from $10^2$ to $10^3$ lm m$^{-2}$ depending on the thickness of the clouds.

The luminance of the horizon sky during the middle part of the day may vary from $10^2$ cd m$^{-2}$ on a heavily overcast day to $10^4$ cd m$^{-2}$ on a clear day [6].

2. **Night.** The natural scene illuminance and the luminance of the horizon sky at night are only a small fraction of their daytime magnitudes [4,5,6]. Even when the moon is full, the illuminance is approximately 0.1 lm m$^{-2}$ at the surface and for a quarter moon it is only 0.01 lm m$^{-2}$. When all illumination is from starlight, the illuminance varies from $10^{-4}$ lm m$^{-2}$ for overcast conditions to $10^{-3}$ lm m$^{-2}$ for clear conditions. The horizon sky has luminances of $10^{-3}$ cd m$^{-2}$ on clear moonless nights and $10^{-4}$ cd m$^{-2}$ on overcast moonless nights. When moonlight is fairly bright, the luminance near the horizon is 0.01 cd m$^{-2}$.

3. **Twilight.** Astronomical twilight is the interval between sunrise or sunset and the time when the true position of the center of the sun is 18° below the horizon [1,3,5]. The center of the sun is 50° below the horizon at sunrise or sunset. Astronomical twilight lasts more than an hour in the morn-
The duration at the equator is 1 hr and 9 min at the equinoxes and 1 hr and 15 min at the solstices. Outside the tropics twilight lasts longer. At 40° N astronomical twilight lasts 2 hr and 3 min at the summer solstice and 1 hr and 38 min at the winter solstice. Minimum durations at 40° N are approximately 1 hr and 30 min from the last week in February to the middle of March and from the last week in September through the middle of October. At 50° N daylight lasts 16 hr and 23 min at the summer solstice, and twilight lasts all night. Astronomical twilight at 50° N lasts 2 hr and 0 min at the winter solstice, and minima in spring and fall are not less than 1 hr and 47 min.

Astronomical twilight is subdivided into shorter time periods. Nautical twilight exists between sunrise or sunset and the time when the true position of the center of the sun is 12° below the horizon. Civil twilight is the interval between sunrise or sunset and the time when the true position of the center of the sun is 6° below the horizon. Civil twilight lasts 22 ± 1 min each morning and evening at the equator. It is never more than half an hour at sites between the equator and 35° N. Civil twilight at 50° N has a maximum duration of 45 min at the summer solstice and minima of 32 min in spring and fall. Civil twilight lasts all night during at least part of the summer at latitudes above 61° N. Dusk is the part of twilight between the lower limit of civil twilight and the lower limit of astronomical twilight.

The illuminance on a horizontal surface on a relatively clear day decreases from 453 lm m⁻² at sunset to 6.51(10⁻⁴) lm m⁻² at the lower limit of astronomical twilight [5]. During civil twilight, sky illumination is sufficient to carry on normal activities out of doors. The lower limit of illuminance on a horizontal surface during civil twilight in clear weather is 3.40 lm m⁻². Illuminance changes rapidly during dusk. When the center of the sun is 12° below the horizon, the illuminance on a horizontal surface is only 8.31(10⁻³) lm m⁻².

Middleton [6] and Meinel and Meinel [7] have given information about the sky near the horizon. The luminance near the horizon at sunset on an overcast day is 10 cd m⁻² (3 mL). During clear weather in middle latitudes luminances are only 1 cd m⁻² one-fourth hour after sunset and 0.1 cd m² one-half hour after sunset.

4. Contrast. The ability of the eye to detect an object depends upon the contrast between the apparent luminance (photometric brightness) of the object and the apparent luminance of the background. Detailed derivations associated with this topic may be found in McCartney (4] and Middleton [6].

The inherent contrast \( C_0 \) between an object and the horizon is defined by

\[
C_0 = \frac{B_o - B_h}{B_h} \tag{1}
\]

where \( B_o \) is the intrinsic luminance of the object and \( B_h \) is the luminance of the horizon. The inherent contrast of an ideal black body against the horizon sky is -1. There is no upper limit of the contrast of a light source which is seen against a night sky.
The apparent luminance of an object changes along a path for two reasons: first, it decreases by extinction (\(\sigma\)) and second, it increases by forward scattering of airlight. This may be written in the formula for a change in luminance between distances \(r\) and \(r + dr\) along a path:

\[
\frac{dB(r)}{dr} = -\sigma B(r) + B_a(r)
\]  

(2)

where \(B(r)\) is the apparent luminance of the object at distance \(r\) and \(B_a\) is the luminance of a lamina of air caused by forward scattering. If the atmosphere is homogeneous along the path and there are no shadows, \(B_a\) is not a function of \(r\).

If one assumes that the luminance of the horizon does not change as one moves toward or away from it, then from Equation (2),

\[B_h = \frac{B_a}{\sigma}.\]  

(3)

The following formula was developed in Reference 6:

\[C_R = C_0 \exp(-\sigma R),\]  

(4)

where \(C_R\) is the apparent contrast between an object at distance \(R\) and the horizon sky. Substitute Equation (3) into Equation (1) and put the resulting expression for \(C_0\) into Equation (4) which yields

\[C_R = \left(\frac{B_0 \sigma}{B_a} - 1\right) \exp(-\sigma R).\]  

(5)

Interesting results are obtained if extinction changes by pure absorption with no change in scattering. Then \(B_a\) is a constant if both sides of Equation (5) are differentiated with respect to \(\sigma\) to obtain

\[
\frac{dC_R}{d\sigma} = \left(\frac{1}{\sigma}(1 + C_0) - C_0 R\right) \exp(-\sigma R).\]  

(6)

The quantity in brackets in Equation (6) must be positive if a positive contrast is to increase in magnitude, and it must be negative if the absolute value of a negative contrast is to increase. Appropriate manipulation of either inequality yields

\[R < \sigma^{-1}(1 + C_0^{-1})\]  

(7)

as the condition for the magnitude of the contrast to increase as a function of \(\sigma\). If the object is brighter than the background, the contrast may actually increase with the addition of pure absorption. An example of such an object is a snow-covered mountain. The magnitude of the contrast of a dark object against a brighter background never increases with increased attenuation. This follows from Inequality 7 because \(R\) cannot be negative, and \(C_0\) cannot be less than \(-1\).

Daytime visibility is the greatest distance in a given direction at which it is just possible to see and identify a prominent dark object against the sky at the horizon [1]. The threshold of brightness contrast for these
conditions has traditionally been taken to be 0.02 in meteorological literature. The meteorological observer is seeing and identifying a familiar object. Some investigators prefer to use larger contrast thresholds such as 0.05 or 0.06 for other purposes.

Nighttime visibilities are determined from suitably spaced, unfocused lights of moderate intensity.

III. MOLECULAR ABSORPTION

Molecular absorption of visible energy by atmospheric gases is not always negligible even though such absorption is small compared to infrared and ultraviolet absorption. Largest molecular absorption of visible wavelengths is not in the portion of the visible spectrum where the eye is most sensitive.

A. Nitrogen Dioxide (NO₂)

NO₂ is one of the most important absorbers at visible wavelengths. Nitrogen dioxide and aerosols are the only factors which cause low visibilities when humidity is low according to Friedlander [8, pp. 144 and 304]. A simplified absorption cross section was developed for NO₂ by Luther [9]. The absorption cross section of a molecule of nitrogen dioxide in the range 300-475 nm is assumed to have the constant value 5.0(10⁻¹⁹) cm². For 475-710 nm the absorption cross section is 2.99 (10⁻¹⁵) exp(-0.0185λ) cm² where λ is in nm. This approximation is particularly good at the shorter wavelengths where the difference between on-line and off-line absorption is no more than a factor of 2 [10]. Burrows et al. [11] reported a cross section of 6.0(10⁻¹⁹) cm² mol⁻¹ at 400 nm. At longer wavelengths there is more fine structure according to Ortgies and Comes [12]. Their reported absorption of 1(10⁻²⁰) cm² at 616 nm is about one-third as large as the prediction by Luther's [9] formula.

Spatial variations of concentration of nitrogen dioxide are quite large. Johnston and McKenzie [13] measured mixing ratios from 10 to 1360 parts per trillion by volume (pptv) in rural New Zealand, and most of these measurements were less than 800 pptv. Levine's [14] standard reference states that concentrations are in the range 10-300 pptv. In maritime air on the coast of northern Germany concentrations have been measured in the range 2.3-75 parts per billion by volume (2.3-75 ppbv), and most were below 30 ppbv [15]. Concentrations of NO₂ in polluted urban areas are typically in the range 20-200 ppbv [16, 17, 18, and 19]. Above a chemical factory, concentrations may be a few parts per million by volume and reach 1170 ppmv at the exit of the stack [20].

Nitrogen dioxide in a typical polluted urban atmosphere will have an absorption coefficient of 0.03-0.30 km⁻¹ at visible wavelengths below 475 nm. Absorption at 555 nm, where the eye is most sensitive, should be 0.006-0.060 km⁻¹ in a highly urbanized area.

B. Ozone (O₃)

Ozone is another important molecular absorber at visible wavelengths. In fact, it is the only molecular absorber which is considered for the range 0.25-0.70 μm in one authoritative work [21, p. 36]. The Chappuis bands provide semicontinuous absorption by ozone over most of the visible spectrum [21, 22, and 23]. Maximum absorption occurs near 605 nm where the cross section is
4.85(10^{-21}) \text{ cm}^2 \text{ mol}^{-1}. \text{ Some other absorption cross sections are } 1.66(10^{-21}) \text{ cm}^2 \text{ mol}^{-1} \text{ at } 505 \text{ nm}, 1.25(10^{-21}) \text{ cm}^2 \text{ mol}^{-1} \text{ at } 685 \text{ nm}, \text{ and } 3.68(10^{-22}) \text{ cm}^2 \text{ mol}^{-1} \text{ at } 465 \text{ nm}, \text{ and } 5.69(10^{-22}) \text{ cm}^2 \text{ mol}^{-1} \text{ at } 725 \text{ nm}.

Concentrations of ozone observed near the surface are usually within the range 10-100 ppbv \cite{14, 21, 24}. In very polluted regions, concentrations of 196 ppbv \cite{17} or even 240 ppbv \cite{16} may be reported. The latter value is for Los Angeles about one-half hour after sunset. Concentrations of ozone decreased during the night in this heavily polluted area to about 40 ppbv near sunrise.

Maximum ozone concentration generally occurs in the spring in middle latitudes. In the past, this was usually explained as the result of increased downward transport from the stratosphere in spring. A new photochemical model, Liu et al. \cite{25}, suggests that anthropogenic factors may be more important in the lower troposphere. Both ozone and the nitrogen compounds from which it is produced have long lifetimes in winter. These long lifetimes permit transport to less urbanized areas. A gradual accumulation of O3 in most of the northern hemisphere during winter produces a maximum in spring. The model in Reference \cite{25} is supported by data from eight rural stations in the United States.

Delany et al. \cite{26} have shown that large-scale fires affect ozone concentrations. Each year in Brazil 4\times10^5 \text{ km}^2 of vegetation are burned during the dry season. Measured ozone concentrations were 45-50 ppbv near the surface over the fire and only 22-30 ppbv in an area surrounding the fire. The corresponding concentrations at 2 km altitude were 55-65 ppbv and 38-44 ppbv. Thus, ozone production by large-scale fires is less than production in heavily polluted urban areas.

Dickerson et al. \cite{27} have recently shown that pollution can be carried to higher levels by thunderstorms. Measurements in and near a thunderstorm showed ozone concentrations greater than 80 ppbv at 10 km. Their detailed analysis of all the data indicated that this was influenced by photochemical reactions with anthropogenic pollutants as well as by some ozone brought down from the stratosphere.

In Figure 25 of the report by McClatchey et al. \cite{21}, the maximum ozone absorption coefficient is about 0.15 per (cm-atm)STP at about 605 nm. Figure 23 of the same report shows the average ozone amounts for different idealized atmospheres are in the range 0.002-0.003 (cm-atm)STP per km. This yields absorption coefficients of 3.0-4.5(10^{-4}) \text{ km}^{-1}. This agrees well with Thompson's \cite{23} cross section per ozone molecule of 4.85(10^{-21}) \text{ cm}^2 at 605 nm if a typical concentration of 30 ppbv is used. One cm$^3$ of air is assumed to contain 2.69(10^{19}) \text{ molecules} \cite{21}, or there are 2.69(10^{19}) \text{ mol} \text{ cm}^{-2} \text{ in one (cm-atm)STP. For very polluted atmospheres the absorption by ozone near 600 nm could be of the order of } 10^{-3} \text{ km}^{-1}.

C. Nitrogen Trioxide (NO$_3$)

Nitrogen trioxide absorbs more strongly at 662 and 623 nm and a little less strongly at 627 nm \cite{11 and 17}. Measured absorption cross sections per molecule at 662 nm vary from 1.21(10^{-17}) \text{ cm}^2 to 1.90(10^{-17}) \text{ cm}^2. Cross sections at 623 nm are in the range from 0.92(10^{-17}) \text{ cm}^2 \text{ mol}^{-1} \text{ to } 1.28(10^{-17}) \text{ cm} \text{ mol}^{-1}. Reported cross sections of nitrogen trioxide at 627 nm are from 0.57 (10^{-17}) \text{ cm}^2 \text{ mol}^{-1} \text{ to } 0.76(10^{-17}) \text{ cm}^2 \text{ mol}^{-1}.
Diurnal variation of NO$_3$ is quite large. Below 630 nm absorption leads to dissociation and nitrogen dioxide lasts only a few seconds in the presence of daylight [11]. Maximum concentrations usually occur between 1 and 2 1/2 hr after sunset [16, 17, 28], and then amounts decrease rapidly to the concentrations that existed at sunset. Maxima are typically less than 100 pptv, but much higher values have been measured in very polluted areas. On 18 September 1979, in the Los Angeles basin, NO$_3$ concentrations reached 355 pptv [17].

Maximum absorption coefficients at 662 nm in an urban area would typically be between $10^{-3}$ and $10^{-2}$ km$^{-1}$.

D. Water Vapor (H$_2$O)

Some information about water vapor is appropriate in this report on polluted atmospheres even though water vapor also exists in unpolluted air. Molecular absorption of visible energy by water vapor is strongest at the longest visible wavelengths and absorptions are stronger in the near infrared [29]. Absorption bands consist of very narrow and closely spaced lines. Long [30] studied a few individual lines in the range 0.693316-0.694521 $\mu$m. Very little is known about the fine structure in most of the spectrum and reliable details about absorption bands are not available.

Zuev [31], Goody [32], and Goldberg [33] have listed some information on bands. No strong bands of water vapor exist in the visible portion of the spectrum. The shortest wavelength where a strong water vapor absorption band is centered is 0.9419 $\mu$m. There are two bands of medium strength below 0.700 $\mu$m: 0.5915 $\mu$m and 0.6981 $\mu$m. Weak bands exist at 0.5436 $\mu$m, 0.5918 $\mu$m, 0.5942 $\mu$m, and 0.6314 $\mu$m. Very weak bands have centers at 0.5714 $\mu$m and 0.6513 $\mu$m.

Tomasi et al. [34] made low resolution measurements of water vapor absorption coefficients at some visible wavelengths where they expected weak absorptions. The shortest visible wavelength in their table was 0.648 $\mu$m where the photopic sensitivity of the eye is only 12 percent of its maximum. The absorption coefficient at 0.648 $\mu$m was 0.076 per centimeter of precipitable water vapor at standard temperature and pressure (0.076 (cm STP)$^{-1}$). An absolute humidity of 10 grams per cubic meter (10 g m$^{-3}$) corresponds to 1 cm STP of precipitable water vapor per kilometer. Other attenuations found by Tomasi et al. [34] were 0.041 (cm STP)$^{-1}$ at 0.665 $\mu$m, 0.037 (cm STP)$^{-1}$ at 0.682 $\mu$m, and 0.042 (cm STP)$^{-1}$ at 0.700 $\mu$m. Additional details about these measurements may be found in a later article [35]. The photopic sensitivity of the eye at 0.700 $\mu$m is only 0.4 percent of its maximum.

Amounts of water vapor in the atmosphere are quite variable because the capacity of the air to hold water increases almost exponentially with temperature. Air at 20 °C can hold approximately 100 times as much vapor as air at -40 °C. Maximum vapor content at -40 °C is only 0.1757 g m$^{-3}$, and at 0 °C it is 4.847 g m$^{-3}$. Absolute humidities are therefore low during cold air outbreaks in middle latitudes in winter. On the other hand, absolute humidities are quite high along the coast of and above the Persian Gulf (also called the Arabian Gulf) and the Red Sea where dew points above 32 °C have been recorded in summer. Maximum absolute humidities can reach 37 g m$^{-3}$ or 38 g m$^{-3}$ [36, 37] in this region.
In addition to large natural variations, water vapor content in the air is often increased considerably due to anthropogenic activity. Although relative humidity is usually lower in a metropolitan area than in the surrounding countryside because of the higher temperature, absolute humidity frequently has a maximum over an urban area [38-44].

Combustion of fuel produces water vapor. This is often very significant at higher latitudes. Hage [45] compared data from the 1968-69 winter at Edmonton, Alberta, with data from an earlier study of the 1949-50 winter [46]. The population increased from 159,000 in 1950 to 410,000 in 1969, and the area of gas consumption increased from 46 km² to 170 km². Hage concluded that total production of water vapor in the Edmonton metropolitan area on a cold day in the 1968-69 winter was seven times as large as in the 1949-50 winter. Principal sources of water vapor in the area were the combustion of natural gas and evaporation from cooling towers. About 2.5 percent resulted from combustion of motor vehicle fuel.

Absorption at visible wavelengths by water vapor is normally expected to be less than 0.3 km⁻¹. This high value could occur only at very long visible wavelengths and with very high absolute humidities.

E. Oxygen (O₂)

Molecular oxygen has absorption bands at visible wavelengths [31, 33, 47]. Pollution has little effect, and concentration of molecular oxygen does not vary much from one location to another. Therefore, if a test works well in one location and poorly in another, oxygen cannot be the cause of poor performance. If all tests are poor, information on oxygen may be needed. Centers of absorption bands of molecular oxygen are located at 0.5384 μm, 0.5796 μm, 0.6288 μm, 0.6379 μm, 0.6884 μm, 0.6970 μm, and 0.7621 μm. Line structures are not well known for most bands.
IV. SCATTERING

Scattering in the atmosphere is governed by Mie scattering theory. The importance of different aspects of the theory depend upon the size of the scattering particles.

A simplified theory called Rayleigh scattering may be used when the scatterers are spherical particles with radii less than approximately one-tenth the wavelength of the scattered radiation. Rayleigh theory is much simpler than Mie theory. It states that scattering is inversely proportional to the fourth power of the wavelength. Rayleigh theory applies well to the scattering of visible energy by molecules of air [48]. Therefore, energy of wavelength 500 nm is scattered twice as much as energy of wavelength 600 nm. Scattering at 450 nm is more than four times as great as scattering at 650 nm.

The wavelength dependence is not as strong for larger particles. The exponent of the reciprocal of wavelength is 4 for Rayleigh scattering and is 0 in rain at visible wavelengths. In haze the exponent is generally between 0.12 and 2.3. Fogs contain a wide variety of drop-size distributions [49], but the wavelength dependence at visible wavelengths is usually much smaller than the dependence in haze. Clay and Lenham [50] measured attenuation at 0.53 \( \mu \text{m} \) and 0.65 \( \mu \text{m} \), and the ratio of attenuation at 0.53 \( \mu \text{m} \) to 0.65 \( \mu \text{m} \) was typically slightly larger than unity. The range was from 0.91 to 1.25.

V. CONCLUSION

Scattering in the atmosphere is the main cause of low visibilities, and molecular absorption is rarely large enough at any visible wavelength to be a problem.
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