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Correlations between urban atmospheric light extinction coefficients and fine particle mass concentrations

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RESUMEN

Se han medido coeficientes atmosféricos totales horizontales de extinción de luz así como concentraciones de masa de partículas atmosféricas en zonas céntricas de Santiago de Chile, una ciudad altamente contaminada. Las campañas de medición se han hecho en 1994 y en 1995. Las mediciones de extinción se han hecho por un método telefotométrico en cuatro bandas espectrales; las concentraciones de masa PM2.5 y PM10 se han medido con instrumentos del tipo de balanzas de masa oscilantes. Tales instrumentos no han estado disponibles durante trabajos anteriores. Las extensas mediciones continuas de concentraciones de masa PM2.5 son las primeras para Santiago de Chile. Se han encontrado fuertes correlaciones estadísticas, altamente significativas, entre coeficientes de extinción y concentraciones de masa, especialmente las concentraciones de partículas finas respirables PM2.5. Se han estimado también exponentes de Ångström y, en un caso, coeficientes másicos de extinción.

ABSTRACT

Total horizontal atmospheric light extinction coefficients as well as particle mass concentrations have been measured in downtown areas of Santiago de Chile, a heavily polluted city. Measurement campaigns were carried out in 1994 and in 1995. Extinction measurements were made by a telephotometric technique in four wavelength bands; oscillating mass balance type instruments were used to measure PM2.5 and PM10 mass concentrations. The latter type instrument had not been available heretofore. The extensive continuous PM2.5 measurements are the first for this city. Strong and highly significant statistical correlations were found between extinction coefficients and mass concentrations, especially with the fine respirable or PM2.5 mass concentrations. Angström exponents and, in one case, mass extinction coefficients have been estimated.

Key-word index: light extinction, Angström exponent, PM2.5 mass concentration, PM10 mass concentration.

1. Introduction

Light extinction in the atmosphere arises both from particles and from gas molecules (Middleton, 1952; van de Hulst, 1957). In the urban atmosphere scattering by fine particles tends to be the dominant effect, absorption by soot particles contributing. Absorption by gases such as nitrogen dioxide and ozone may also become significant (Horvath, 1993). Atmospheric light wazzu extinction coefficients as defined by the well-known Bouguer-Lambert-Beer exponential law (Middleton, 1952) can therefore be expected to vary with fine particle number and mass concentrations, yielding useful indicators of atmospheric pollution. Evidence to this effect exists in the literature (Charlson *et al.*, 1968; Horvath *et al.*, 1989; Horvath and Trier, 1993; White *et al.*, 1994). The present paper reports on total light extinction measurements carried out near the Santiago de Chile city center during 1994 and 1995 and on their correlations with fine particle mass concentrations as measured at one of the public network pollution monitoring stations. The city of Santiago spreads in a valley located on a southern latitude of 33°30' at an elevation of 550 [m] a.s.l., the altitude of city center. The extent of the city exceeds 800 sq. Km and it is surrounded by the Andes mountain range on the East and a secondary mountain range on the West. Ventilation of the Santiago valley is further restricted by ground-level and altitude thermal inversion phenomena. Unfortunately, vertical atmospheric temperature profiles are not available on a permanent basis for Santiago to date.

2. Experimental

Light extinction coefficients were determined by a telephotometric method perfected at University of Vienna (Horvath, 1981). The method involves horizontal measurements of the contrast of a small distant target in natural light. When a uniform atmosphere is assumed it can be shown (Horvath, 1981; Horvath and Trier, 1993) that the total linear extinction coefficient may be expressed as follows:

$$b = \frac{1}{D} \ln \frac{R_H - R_T}{R_H - R_{T0}} \qquad (1)$$

where ln denotes the natural logarithm. In this equation R_H, R_T and R_{T0} stand for the radiances of the horizon, of the target and of the target at close range, respectively, and D for the distance from instrument to target. The radiance of the target measured at close range is representative of the intrinsic target radiance, which would be zero for a true blackbody.

Radiances were measured by means of a University of Vienna type telephotometer (Horvath, 1981) in four wavelength bins defined by interference filters of 50 [nm] bandwidth centered at 400, 450, 550 and 650 [nm]. The 550 [nm] bandwidth is closest to the maximum sensitivity of the human eye. The detector was a commercial photodiode/operational amplifier. The telephotometer was located on the helicopter terrace of Torre Santiago Centro at Av. B. O'Higgins 949, about 85 [m] above ground level, and targeted Torre Santa María at Los Conquistadores 1700, 3.4 Km to the NE. The solid angle subtended by the target at the telephotometer was about $2.5.10^{-6}$ [sr]. From measurements at close range the intrinsic radiance of the target was estimated to be 5% of the horizon radiance (Horvath and Trier, 1993). Measurements were typically made every 15 minutes between 11:00 and 13:00 local standard time or between 12:00 and 14:00 local daylight saving time. The extinction measurements were carried out under conditions of stable lighting only, which very often meant a cloudless sky. Extinction measurement campaigns were run from March 16 to April 26, 1994 on eleven days (austral autumn, designated as A94); from October 5 to November 15, 1994 on fifteen days (austral spring, designated as S94); from December 30, 1994 to March 10, 1995 on fifteen days (overlapping summer and autumn, designated as 95I); and from June 30 to October 31, 1995 on thirty-two days (overlapping winter and spring, designated as 95II).

Fine particle mass concentration measurements were carried out at ground level at one of the public monitoring stations located in a street canyon at Plaza Gotuzzo, about 100 [m] from Government House

(Palacio de la Moneda) and 600 [m] NW from Torre Santiago Centro. Commercial instruments of a continuous, mechanically oscillating mass balance type supporting a filter have been used. One of these has an inlet cutoff at 2.5 [μm] aerodynamic diameter (designated as "PM2.5"), the other at 10 [μm] (the standard "PM10"). These instruments yield half-hourly averaged mass concentration values expressed in [μg m^{-3}]. The instruments are designed so that the ambient air drawn in is dried to a centigrade temperature of 50 degrees while the temperature of the measurement enclosure containing the filter is set to 40 degrees.

3. Results

A. Time evolution of the extinction coefficients

Extinction coefficients were seen to increase during the A94 campaign; during the S94 and 95II campaigns they were observed to decrease. Such overall behavior is expected from the fact that atmospheric pollution indicators are found to peak in Santiago during the winter months of May through August. The extinction data are partially displayed in Figures 1A through 1D. It must be borne in mind that the data pertain to irregularly spaced days, and that between four and eight measurements are available for any single day. Figure 1A sequentially shows extinction coefficients in units of Km^{-1} for campaign A94. Figs.1B, 1C and 1D similarly show data for campaigns S94, 95I and 95II, respectively. High values for the extinction coefficients can be seen to occur in any season; they are an effective measure of impaired atmospheric visibility (Trier and Horvath, 1993).

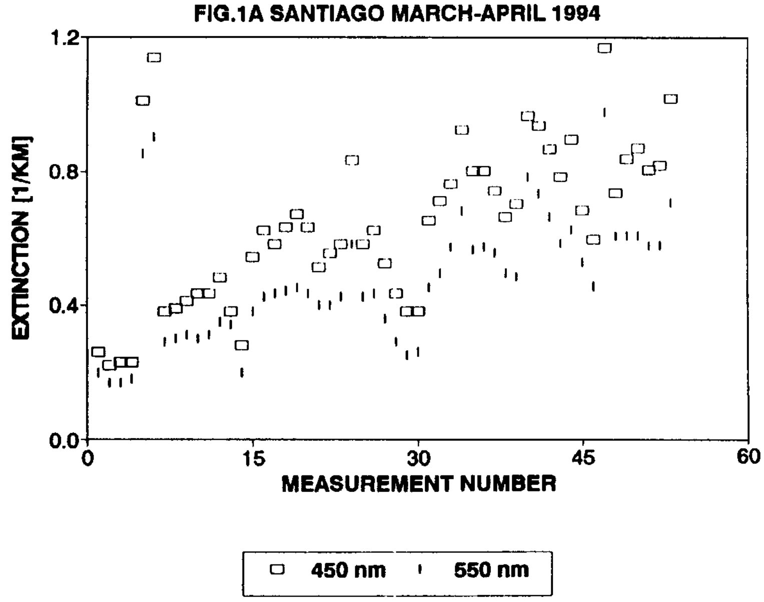

Fig.1A. Sequential presentation of the atmospheric light extinction coefficients measured in the 450 and 550 [nm] bands during the period spanning March 16 and April 26, 1994 (A94 campaign). Measurements 5 and 6 pertain to March 18.

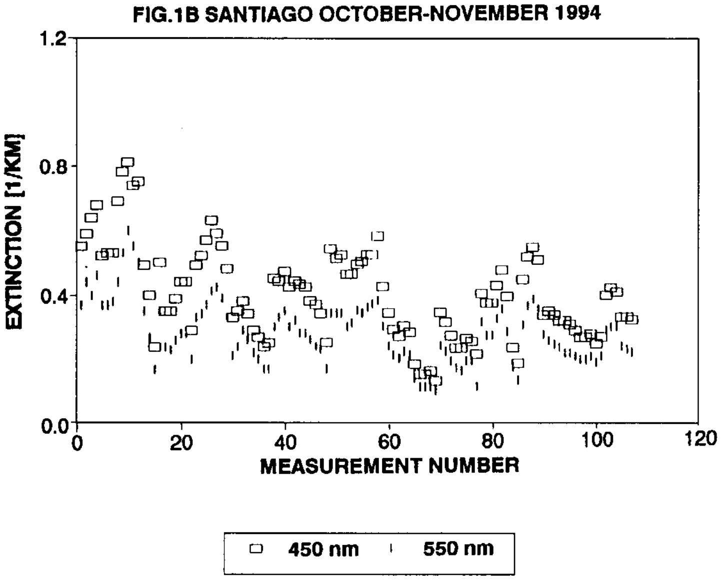

Fig.1B. Sequential presentation of the atmospheric light extinction coefficients measured in the 450 and 550 [nm] bands during the period spanning October 5 and November 15, 1994 (S94 campaign).

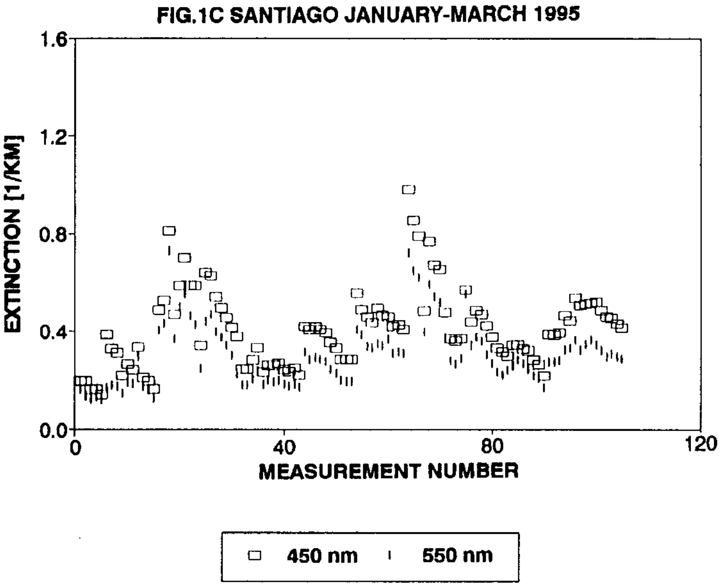

Fig.1C. Sequential presentation of the atmospheric light extinction coefficients measured in the 450 and 550 [nm] bands during the period spanning December 30, 1994, and March 10, 1995 (95I campaign).

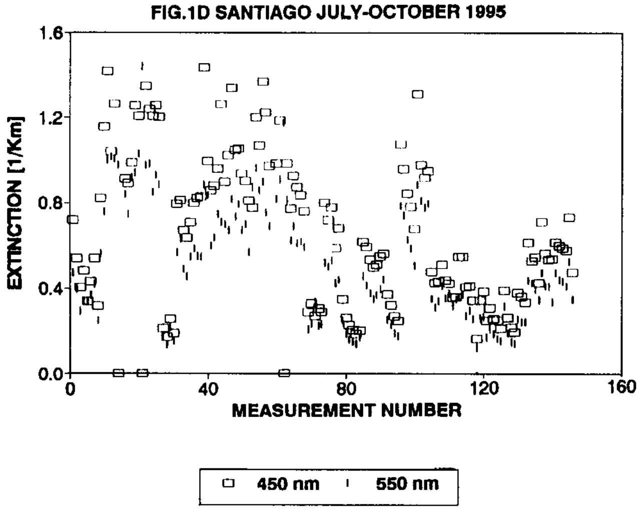

Fig.1D. Sequential presentation of the atmospheric light extinction coefficients measured in the 450 and 550 [nm] bands during the period spanning June 30 and October 31, 1995 (95II campaign). Measurements 25 through 28 were taken on a day following a heavy rainstorm. Points on the axis reflect partially missing data.

B. Correspondence between extinction coefficients and fine particle mass concentrations

Since mass concentrations are available in the form of half-hourly averages the extinction measurements were first similarly reduced to half-hourly values. Figures 2A through 2D exemplify the correspondence between both classes of data in the form of scatter plots of the extinction coefficients in the 450 and 550 [nm] wavelength bands versus PM2.5 fine particle mass concentrations. Note that there is a large number of mass concentration data missing for the 95I campaign. It may be inferred from the scatter plots that relations between these variables will be poorly represented by linear models.

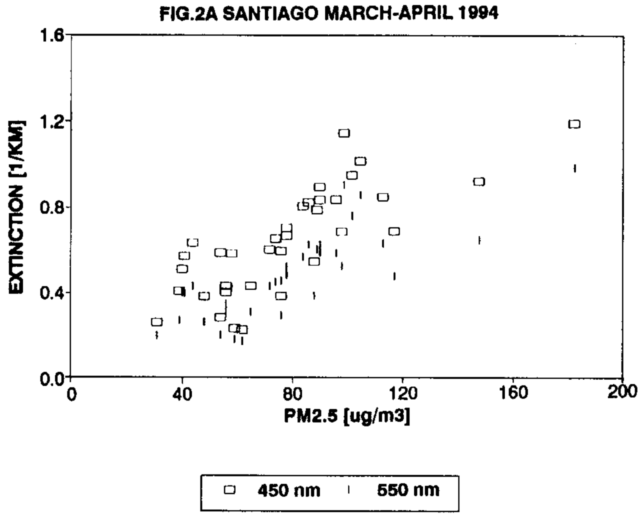

Fig.2A. Scatter plot of the light extinction coefficients measured in the 450 and 550 [nm] bands versus the fine respirable particle mass concentrations. A94 campaign.

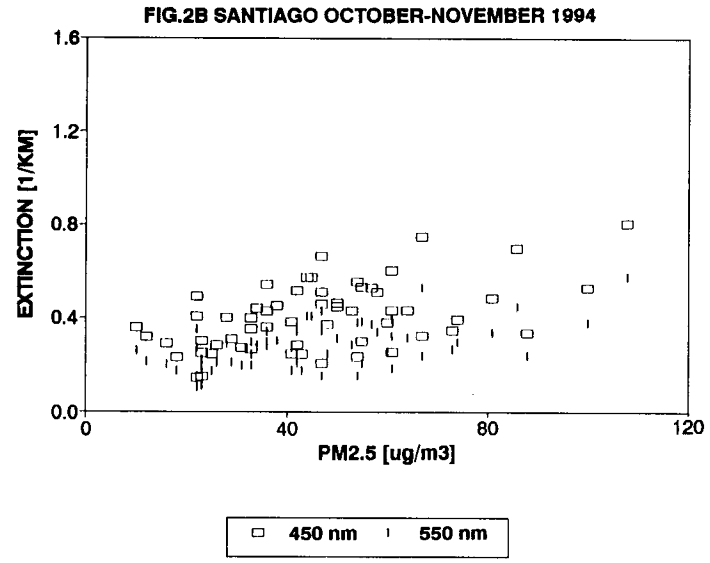

Fig.2B. Scatter plot of the light extinction coefficients measured in the 450 and 550 [nm] bands versus the fine respirable particle mass concentrations. S94 campaign.

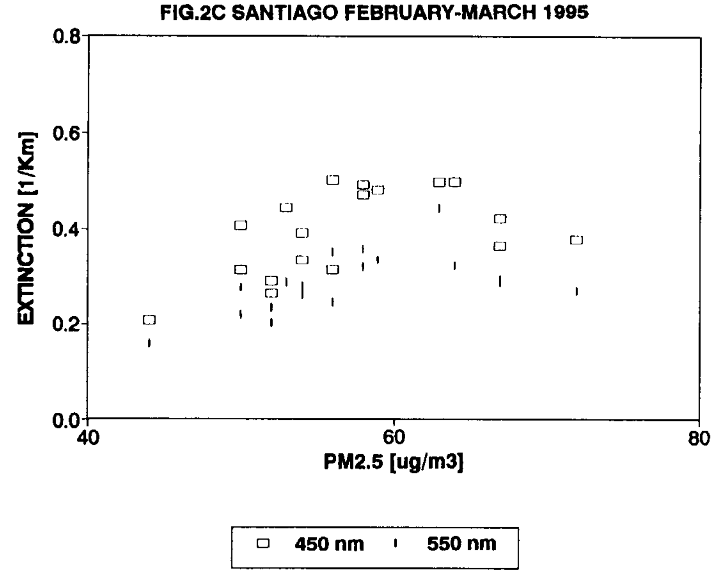

Fig.2C. Scatter plot of the light extinction coefficients measured in the 450 and 550 [nm] bands versus the fine respirable particle mass concentrations. Because of missing PM2.5 data only part of the 95I campaign can be shown.

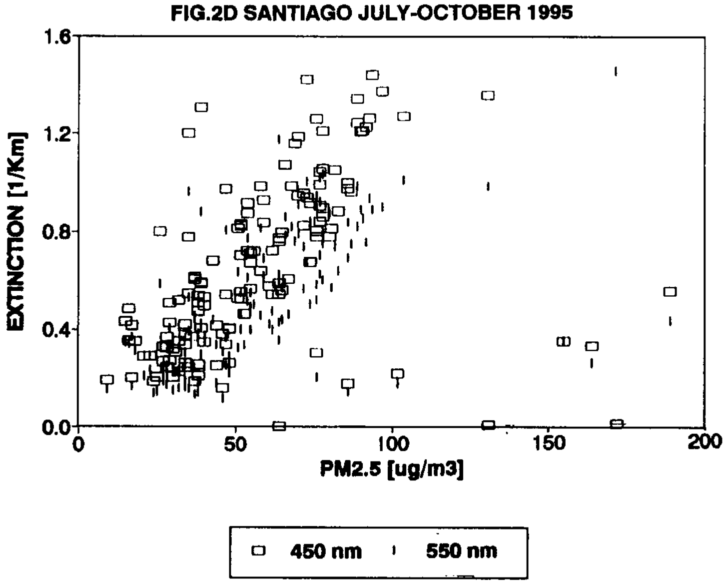

Fig.2D. Scatter plot of the light extinction coefficients measured in the 450 and 550 [nm] bands versus the fine respirable particle mass concentrations. 95II campaign. The anomalous values appearing above 150 [ug m^{-3}] may be due to polluting perturbations close to the measuring station at Plaza Gotuzzo. Points on the axis reflect partially missing data.

C. Statistical correlations

Statistical correlations have been examined between the following classes of data: atmospheric extinction coefficients, fine particle mass concentrations, and meteorological variables including ambient temperature T, wind strength WS and, for the 1995 data, relative air humidity RH and wind direction WD. The meteorological data were secured from the public monitoring network and have been taken at station B which is located close to the intersection of Av. Providencia and calle Seminario, about equally distant from the telephotometer station and the target. They are not available at Plaza Gotuzzo.

The measure for paired association of the variables has been taken to be the rank difference (Spearman) correlation coefficients. The calculation of these coefficients, and of their statistical significance, involves no assumptions regarding the distributions of the data. The correlations reported on below are significant at the 1% level. It must be borne in mind that the extinction data are of the nature of extensive or area measurements, while all other data are the result of local or point measurements.

The investigation of statistical correlations demonstrated in many cases the existence of time lag effects between the extinction coefficients and the mass concentration data, in the following sense: when extinction coefficients were correlated with mass concentration measured at the same time (time lag zero), one hour previously and two hours previously, the highest correlation coefficients were obtained for a time lag of one hour. This occurred both with PM2.5 and PM10 mass concentrations.

Table I lists correlation coefficients for the datum pairs shown. b450 designates the linear atmospheric extinction coefficient measured in the 450 [nm] wavelength band, and so forth. WS designates wind speed in [m s^{-1}], T stands for centigrade ambient temperature and RH for % relative air humidity.

Table I. Rank difference correlation coefficients
* time lagged correlations (see text)
++ correlation not significant at the 0.01 level

Campaign	A94	S94	95I	95II
Paired variables				
b400 / PM2.5	0.79*	0.44*	++	0.81
b450 / PM2.5	0.82*	0.46*	++	0.85
b550 / PM2.5	0.82*	0.47*	0.57*	0.86
b650 / PM2.5	0.82*	0.46*	0.58*	0.86
b400 / PM10	0.70*	0.43*	++	0.72
b450 / PM10	0.67*	0.46*	0.43	0.75
b550 / PM10	0.68*	0.48*	0.41	0.76
b650 / PM10	0.68	0.47*	0.41	0.77
b400 / WS	++	-0.68	-0.36	-0.32
b450 / WS	++	-0.69	-0.42	-0.34
b550 / WS	++	-0.69	++	-0.35
b650 / WS	++	-0.66	-0.37	-0.35
b450 / T	++	0.34	-0.39	++
b550 / T	++	0.33	-0.40	++
b650 / T	++	0.37	-0.49	++
b450 / RH			0.35	-0.29
b550 / RH			0.42	++
b650 / RH			0.43	++

D. Wavelength dependence of the extinction coefficients

Following Ångström (Ångström, 1929) and in agreement with previous work (Trier and Horvath, 1993) we have found that for a large number of cases the wavelength dependence of the extinction coefficients can be represented by a statistical model of form

$$\log b = F - a \log \lambda \tag{2}$$

where F is a parameter depending, among other factors, on particle number concentration, and a is called the Angström exponent of wavelength dependence. For molecular scattering in dry air this exponent is expected to be very close to 4 (van de Hulst, 1957). For large particles, i.e. in the diffraction limit, no wavelength dependence is expected.

We have estimated the exponents for the 1994 campaigns by linear regression, keeping only those results where the regression coefficient R was calculated to be no less than 0.99. The average values and their standard deviations for the measurement campaigns A94, S94, 95I and 95II were found to be a = 1.42 (±0.23), a = 1.52 (±0.23), a = 1.39 (±0.21) and a = 1.43 (±0.26), respectively.

E. Mass extinction coefficients

A mass extinction coefficient, m, can be defined by writing the Bouguer-Lambert-Beer extinction law in terms of atmospheric mass per unit light beam cross section area. Instead of the linear extinction coefficient, quoted in this paper in [Km^{-1}], one then quotes a mass extinction coefficient in [m^2g^{-1}]. The coefficient m pertaining to any given wavelength band can be estimated from a linear regression of the corresponding linear extinction coefficient on mass concentration. This exercise has been carried out for the 550 [nm] band. It turns out that because of the wide scatter of the data a useful estimate can only be obtained from the fine respirable (PM2.5) mass concentrations during the A94 campaign. This linear regression, with $R^2 = 0.60$, yielded a mass extinction coefficient $m = 4.93$ (±0.69) [m^2g^{-1}]; in all other cases the linear regression models turned out to be highly unsatisfactory.

4. Discussion

The results presented here confirm that total light extinction in the urban atmosphere of Santiago, Chile, is dominated by effects due to particles; this is perhaps most clearly shown by the wavelength dependence of the extinction coefficients, i.e. the values of the Angström exponent. The correlations measured between extinction coefficients and fine particle mass concentrations indicate that the former may be taken as statistical indicators of atmospheric pollution by particles. The strength of the correlations observed for the A94 and 95II measurement campaigns also indicates the dominance of particle effects in the extinction. However, it is not possible to make useful predictions of one of these variables from a knowledge of the other. It is seen from Table I that the statistical correlations tend to be better with the respirable (or PM2.5) mass concentrations than with the inhalable (or PM10) concentrations. This can be expected on general physical grounds: on a mass basis smaller particles are much more effective light scatterers (Hinds, 1982). However, at this time unexplained seasonal differences are seen in this general trend; they may be related to local atmospheric stability. Statistical correlations of the extinction coefficients with available meteorological measurements turned out to be weak when significant at all, wind speed being somewhat exceptional in this respect. Because light extinction coefficients as measured in this work are indicators of extensive or area effects in contrast to local or point measurements, they can be taken to give a better representation of urban air pollution.

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LIST OF SYMBOLS

a	Ångström exponent
b	linear extinction coefficient [Km^{-1}]
D	telephotometric target distance [Km]
l	wavelength [nm]
m	mass extinction coefficient [m^2 g^{-1}]
R_H	radiance of horizon beyond target [W sr^{-1} m^{-2}]
R_T	perceived radiance of the telephotometric target [W sr^{-1} m^{-2}]
R_{T0}	target radiance at close range (intrinsic radiance) [W sr^{-1} m^{-2}]