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Project Summary

Haze Over Eastern North America: Part 1. Haze Properties

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The fundamental properties of atmospheric aerosols pertinent to atmospheric optics are the size, shape, and refractive index for the entire aerosol population at a given point. Once these properties are established, their interaction with visible radiation can be calculated, and the relevant optical properties can be measured. The most important properties are the concentration and size distribution of particles within the accumulation mode size range of 0.1 to 1.0 μm in diameter. The chemical composition of the aerosol population weakly influences optical properties by changing the refractive index, but it is vital for the identification of the origin of the light-scattering aerosol. This Summary reviews the properties of aerosols relevant to their optical behavior. Regularities in these properties suggest that relatively simple parameterizations can be developed that will relate optical properties to aerosol mass. These relationships can then be used with aerosol models to predict visibilty and with optical measurements to infer aerosol mass.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, North Carolina to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This summary is a review of the optical characteristics of atmospheric aerosols, the physical and chemical properties and behavior that influence optical properties, and the relationships between optical properties and chemical and physical properties. We search for regularities in aerosol properties that will assist us in parameterizing the optical behavior of the atmospheric aerosol. Such parameterizations are needed to transform aerosol mass calculated in regional or urban models into visual range and other visibility-related air quality parameters. Parameterizations are also needed to estimate aerosol mass loading from optical measurements such as those obtained from teleradiometers or from images taken by satellites.

Results

Aerosol Properties

Size distribution. The size of atmospheric aerosols ranges over five orders of magnitude. The smallest observed particles are on the order of 10° A in diameter, and they could well be called molecular clusters. At the other extreme, large dust particles of 100 μm or more may be suspended in the air for extended periods of time. Within the five decades of size range, there is a region in which the particle diameter is comparable to the wavelength of visible radiation (0.4 to 0.7 μm). Particles of this size interact strongly with visible light.

Recent intensive studies on the physical-chemical properties and behavior of man-made aerosols have revealed some important regularities. In a study of the characteristics of the Los Angeles smog aerosol, Whitby et al. (1) discovered and substantiated by a variety of data that

most of the atmospheric aerosol volume and mass is distributed bimodally; the lower mass mode is in the size range 0.1 to 1 μm, while the upper mode was over 5 μm. The saddle point between the two volume or mass modes is generally between 0.8 and 3 μm. Their finding of bimodal aerosol mass distribution is significant in that the two modes were subsequently identified as having distinctly different physical characteristics (particle shape, volatility) and chemical composition; ordinarily the two modes are produced by different sources; and finally the lower (fine) and upper (coarse) mass modes are associated with distinctly different effects.

Atmospheric optics is influenced almost exclusively by the accumulation mode aerosols in th 0.1- to 1-μm size range. Particles in this size range are the most efficient scatterers per unit mass; also, fine particles tend to accumulate in that size range, which prompted Whitby to call it the accumulation mode. The volume concentration in the accumulation mode ranges from 0.1$\mu m^3/cm^3$ for marine background aerosols (which corresponds to concentration of 0.1$\mu g/m^3$ at unit density) to about 100 $\mu m^3/cm^3$ in regional hazes. In spite of almost three orders of magnitude volume concentration variability, the mean size and the fitted logarithmic standard deviation of the accumulation mode aerosol have been found to be remarkably constant; the volume mean size normally ranges from 0.18 to 0.3 μm, while the standard deviation is between 1.84 and 2.11.

Chemical composition. The knowledge of the chemical composition of light-scattering aerosols is essential to the understanding of the cause of visibility impairment. It is not so much that the chemical composition of the aerosol changes the optical properties; rather, the chemical composition serves as a tracer of the probable origin of the light-scattering aerosol. In fact, for atmospheric haze in general, the chemical composition is the most important clue currently available regarding its probable orgin.

The chemical composition of the ambient aerosol may be used to trace its origin. Characteristic tracer elements such as vanadium (which comes primarily from fuel oil) and lead (which comes primarily from auto exhaust) can be used to tell how much fuel oil and auto exhaust, respectively, contribute to the ambient aerosol. This method is called chemical element balance and requires knowledge of source compositions. A second technique starts with the chemical composition and uses statistical techniques to infer source compositions. The composition of each identified source may be determined.

The first comprehensive study of the size-chemical composition of the haze aerosol was conducted in the Los Angeles air basin by the California Air Resources Board as part of the Aerosol Characterization Experiment (ACHEX). As part of this study of the nature and origins of visibility-reducing aerosols in Los Angeles, a chemical mass balance was constructed for the measured aerosol at seven locations in the basin. The key contributing species for the total aerosol mass concentration were nitrates, sulfates, organics, and other unidentified substances. Based on statistical analysis of b_{scat}, and chemical composition data, they concluded that sulfates are the most efficient scatterers among the measured chemical species.

For several years an extensive air pollution monitoring program was conducted in St. Louis as part of project RAPS (Regional Air Pollution Study). Size-segregated aerosol samples were automaticaly collected by the dichotomous samplers and analyzed for the elemental composition and mass concentration of fine and coarse particles. The results from the ten-station monitoring network were analyzed to determine the distribution of the aerosol species within the St. Louis metropolitan area. Sulfur compounds were again the dominant species of the fine aerosol fraction, contributing about 60% of the mass. For stations within the central city, motor vehicle contribution was estimated to be about 10% of the fine particle mass. For the peripheral stations, 25 kms removed from the city center, the sulfate concentrations were comparable to those within the city, but motor vehicles accounted for only a few percent of the fine particle mass. It was concluded that the automobile contributions were of local origin, while the sulfate is distributed regionally, and the addition of the sulfate by the St. Louis metropolitan area is only 10-20% over the regional background.

In a mass balance analysis, it was possible to account for practically all the coarse particle mass by contributions of crustal shale and limestone. The fine particle mass concentration for a Smoky Mountain National Park site at Elkmont, Tennessee, was about 25$\mu g/m^3$, comparable to the values in the St. Louis region outside the city. Here again about 60% of the fine particle mass was contributed by sulfur compounds. The 40% of unknown compounds may include carbonaceous compounds, nitrates, and water. The coarse particle mass concentration at the Smoky Mountain site was only 6 $\mu g/m^3$, substantially below that in the St. Louis region.

More recent studies have shown that carbon particles, which contribute to extinction by both absorption and scattering, are important in urban areas. However, carbon particles are less important in rural areas unless the area is impacted by a forest fire.

Summary - Aerosol Properties. The atmospheric aerosol mass or volume distribution over the continental United States is generally bimodal, the fine particle volume mean diameter is almost invariant in size at about 0.3 μm. Most accumulation mode particles are spherical droplets. The chemical composition of the light-scattering aerosols provides a valuable clue regarding their probable sources. Sulfur compounds evidently contribute about half of the fine particle mass over most of the continental United States. They generally occur in the most effective light-scattering size range, 0.4 to 0.7 μm, and they contribute 50% or more of the light-scattering. From the above it is apparent that as far as optical effects are concerned, sulfur compounds constitute the most significant chemical component of the fine particle mass over the eastern United States.

Relationship Between Aerosol Number, Mass Concentration, and Optical Properties

Ever since John Aitken developed a condensation nuclei counter, a quest has been in progress to establish a generally applicable quantitative relationship between aerosol concentrations and size and aerosol effects on atmospheric optics.

By the 1970's, it was recognized that there are distinct advantages to monitoring the aerosol mass concentration in at least two size-segregated classes, the fine particle mass and the coarse particle mass. The separation size is normally set at the saddle point of the bimodal mass distribution (0.8 to 3 μm). From physical considerations, most of the light scattering by haze is contributed by fine particles. More recently, there has been statistical confirmation of the strong relationship between the fine particle mass and the light scattering coefficient measured by the integrating nephelometer. In various parts of the country, simultaneous monitoring of b_{scat} and FPM yielded correlation coefficients exceeding

0.9 and ratios b_{scat} to FPM of 3 to 4 m^2/g, as given in Table 1.

Table 1. Correlation of Fine Particle Mass with Light Scattering Coefficient

Location	$m^{2\#}/g$	r^{2*}	N^+
Riverside, CA		0.88	88
Los Angeles, CA	3.7	0.69	39
Oakland, CA	3.2	0.62	20
Sacramento, CA	4.4	0.96	6
Los Angeles, CA	3.2	0.83	58
Portland, OR	3.2	0.98	108
Mesa Verde, CO	2.9		5
Puget Isl., WA	3.0	0.94	26
Seattle, WA	3.1	0.90	58
Seattle, WA	3.2	0.94	64
Denver, CO	3.3	0.96	268
Houston, TX	3.3	0.88	88

$^{\#}m^2/g$ = ratio of b_{scat} to fine particle mass.
$^*r^2$ = coefficient of determination, square of correlation coefficient.
^+N = number of points.

The remarkable feature of these recent data sets is the narrow range of the ratio of b_{scat} to fine particle mass for various sampling locations, times, and mass concentrations. This ratio has units of square meters of light-scattering cross-section per unit mass of aerosol. It is thus a scattering efficiency factor, and its absolute magnitude is directly comparable to calculations of light scattering using Mie theory. The spatialtemporal invariance of the scattering efficiency factor has two possible explanations: either the size distribution of fine particles that contribute to light scattering is invariant or the scattering per unit mass of FPM is independent of particle size. As discussed in the full Project Report, it is a combination of both.

The above brief review, along with numerous reports not discussed here, reveals a century-long search for laws that describe the regularities of aerosol optics, aerosol size distributions, and their interdependence. However, at this time, generally applicable laws that consistently describe the size distribution and optical properties of atmospheric fine particles are not at hand. The increasing need for electro-optical information about the atmosphere along with the encouraging hints gathered over the past century dictates that the search be pursued.

Relationships Among the Optical Parameters

Spectral extinction. Spectral extinction data from the early 1900's show that the blue/green extinction ratio and the red/green extinction ratio converge systematically to unity as the extinction coefficient increases from near Rayleigh scattering to fog. Thus, the spectral extinction of aerosol (defined by Middleton as air and particles) becomes increasingly "white" with larger values of extinction. An interesting abrupt transition from spectral to white scattering at bext = $0.5km^{-1}$ may be used to define "mist", i.e., the transition phase betwen haze and fog.

Aerosol phase function. The regularities of the aerosol phase function (variation in scattering intensity with scttering angle) have also been examined. Various workers have observed a systematic shift of light scattering toward forward angles with increasing extinction coefficient (decreasing visual range). An impressive systematic investigation of this phenomena was conducted by Barteneva (2) at five locations in the Soviet Union, also showing the elongation of the phase function with decreasing visual range. These regularities of phase function have also been confirmed in a measurement program conducted by the United States Air Force in the United States and Europe using a polar nephelometer.

Backscattering. One of the more convenient means of monitoring the light-scattering by aerosols is detection of the light scattered backwards to the light source, whether the source is coherent or incoherent. The back-scattering intensity (R) has been simultaneously measured with the visual range (V) and gives a remarkably well-defined relationship for several sites in the United States: $V = \text{constant}/R^{1.5}$. An equally consistent relationship between total extinction and backscattering has been observed in the Soviet Union. These two data sets are consistent in that both the phase function and backscattering data show that with increasing extinction coefficient the backscatterng phase function declines systematically.

Inversion of Optical Data Using Interactive Graphics

Aerosol size distributions can be fitted iteratively to measured phase function data. An attractive data set for illustration and other purposes is the set measured and tabulated by Barteneva (2).

The phase function data for eight classes of haze from light haze (class, #1) to heavy haze (class, #2), have been fitted to various size distributions using Center for Air Pollution Information and Trends Analysis's interactive graphics capabilities. This numerical fitting process illustrates that for light hazes the choice of the real refractive index is not crucial. For heavy haze (#8), on the other hand, a fit can only be obtained with n = 1.4 or 1.33 but not with 1.5 or 1.6, suggesting a major contribution by water. The best fit size distributions also show that for light haze (#4 and #5) an appreciable quantity of 0.15-μm size particles is required in addition to Rayleigh scattering in order to obtain the measured amount of backscattering. Heavy hazes (#7 and #8) can be fitted with a narrower size distribution with the volume mean diameter centered at the wavelength of light.

Regularities

There are two regularities emerging from the extensive aerosol-optical data sets on fine particles: the systematic forward elongation of the aerosol phase function with increasing extinction coefficient (2) and the existence of the accumulation mode, i.e., condensation-coagulation aerosol growth into a relatively narrow size range (1). For some time it has been felt that the fine particle mass mode is rather invariant in volume mean diameter. This, however, is inconsistent with the inverted size distributions from Barteneva's phase function data (2). In order to fit this data, it was necessary to increase the volume mean diameter from 0.3 to 0.6 μm, corresponding to light and heavy haze, respectively. Thus, there appears to be an additional regularity - a systematic increase in volume or mass mean diameter as the mass concentration increases.

Conclusions

The atmospheric aerosol exhibits regularities in its physical, chemical, and optical properties. These regularities should permit relatively straight-forward parameterization of optical properties based on the total aerosol mass and the relative humidity. Because of the importance of sulfate for scattering and carbon for absorption, knowledge of the concentration of these two species, along with relative humidity, should provide a useful first estimate of optical extinction from which visual range may be inferred.

The idea of the self-preserving size distribution must be replaced by that of the accumulation mode in which atmospheric particulate matter piles up on accumulation. The accumulation mode of well-aged particulate matter does have a relatively constant mass mean diameter. However, as the total mass concentration increases there appears to be a small increase in the mass mean diameter and a

corresponding shift in the phase function toward more scattering in the forward direction. Information on phase function variations are important for calculating aerosol mass from optical properties, for determining changes in visual air quality such as contrast in objects at distances less than the visual range, and for estimating changes in haze color and intensity as a function of viewing angle. The regularities in these relationships appear to be adequate to permit parameterization of phase function in terms of aerosol mass loading.

Recommendations

It is recommended that the visibility research program proceed to develop parameters that relate optical extinction and phase function to aerosol mass; to use these parameters to calculate visibility from predictive aerosol models; and to estimate aerosol mass loading from satellite imagery.

References

1. Whitby, K.T., Husar, R.B. and Liu, B.Y.H. (1972) The aerosol size distribution of Los Angeles smog. J. Colloid Interface Sci. 39, 177-204.
2. Barteneva, O.D. (1960) Scattering functions of light in the atmospheric boundary layer. Izv. Akad. Nauk SSSR, Ser. Geofiz. 1852-1865.

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The complete report, entitled "Haze Over Eastern North America: Part 1. Haze Properties" (Order No. PB 85-181 857/AS; Cost: $8.50, subject to change) will be available only from:

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