# Reports

## Atmospheric Aerosol: Does a Background Level Exist?

Abstract. *Measurements of light-scattering made with an integrating nephelometer at Point Barrow, Alaska, and Mount Olympus, Washington, are in agreement in magnitude, and both sets of measurements also are in agreement with other measurements of light-scattering and turbidity made in remote locations. This agreement suggests that a background level of aerosol exists and that the concept of a background is applicable.*

In recent years interest in a background level of atmospheric aerosol has increased dramatically. This is due, in part, to data implying rapid increases in atmospheric aerosol in the last two decades (*1*) and subsequent speculation on the effect of atmospheric aerosol on world climate (*2*). There is also considerable interest in background levels arising from efforts to control air pollution. Junge (*3*) and others have speculated that because of the highly mixed character of tropospheric air, a background level of atmospheric aerosol may exist analogous to a background level, already found, for $CO_2$. Such a background might be viewed as an equilibrium concentration, affected by both sources and sinks of particulate matter. Since the sinks for aerosol (for example, rainfall, sedimentation, and condensation) presumably change little with time, a change in the equilibrium concentration would imply a change in the source. If there were, indeed, an identifiable property of background atmospheric aerosol, long-term monitoring of this property of the atmosphere could be used as an indicator of changes in worldwide aerosol pollution. Short-term variations might provide evidence regarding the mixing time of the atmosphere relative to the residence time of the particulate matter in air. Special significance should be attached to the average of minima of the measured pollutant levels; they represent the least polluted situations and hence can be called "background" levels.

We report here preliminary measurements of the scattering component of the extinction coefficient of air ($b_{\text{scat}}$), taken with the angular integrating nephelometer in remote locations, which indicate the existence of a background level. These data also will be compared to published data obtained with a Volz sunphotometer (*4*).

The integrating nephelometer has been described by Ahlquist and Charlson (*5*). Essentially, it is a broad-band instrument, centered at 500 nm (*6*), which measures the scattering component of extinction of an air sample flow. It has proved to have sufficient sensitivity and stability for both short- and long-term studies of even the clearest atmospheric air. The instrument is calibrated by filling the scattering volume with various clean, filtered gases ($CO_2$, Freon 12, air). The relative accuracy is about 4 percent, and helium is used for approximating zero scatter.

The Volz sunphotometer has been described by Flowers *et al.* (*4*). This instrument measures turbidity *B* at 500-nm wavelength. Turbidity can be related to the extinction coefficient due to scattering in a vertical column of air between the observer and the sun:

$$\overline{b_{\text{scat}}} = \frac{2.3\,(R + B)\,m}{X}$$

where $\overline{b_{\text{scat}}}$ is the average of $b_{\text{scat}}$ over the air column, $m$ is the number of optical air masses ($m = 1$ for sun overhead), $R$ is the Rayleigh scattering coefficient (due to molecular scattering) integrated over an optical path of 1 optical air mass, and $X$ is the optical thickness of the atmosphere (in units of distance, for example, kilometers). This instrument is inexpensive and adequately accurate, although more difficult to calibrate than the integrating nephelometer. It operates only during daytime where there is little cloud cover. A great deal of information has been collected on the turbidity of the atmosphere. In fact, historical records on various types of turbidity go back for perhaps 70 years (*7*); however, a lack of standardization of either the method or the instrumental sensitivity forced Flowers *et al.* (*4*) to avoid comparison with such old data in their report for the period from 1961 to 1966.

A comparison of recent data taken

Table. 1. Background values of $b_{\text{scat}}/b_{\text{Rayleigh}}$. N, nephelometer; V, Volz sunphotometer; S, searchlight.

| Location | Date | Instrument | $b_{\text{scat}}/b_{\text{Rayleigh}}$ | Comments |
|---|---|---|---|---|
| Mount Olympus, Washington | 12 Feb. to 28 March 1968 | N | 1.5 | Geometric mean of continuous record at 500 nm |
| Point Barrow, Alaska | 10 to 25 March 1970 | N | 1.95 | Geometric mean of continuous record at 500 nm |
| Ocean City State Park, Washington | 7 to 8 Sept. 1967 | N | 2.8 | Two-hour averages of minima at 500 nm |
| Seattle, Washington | 1967–1970 | N | 2.0 | Minimum value at 500 nm |
| Altadena, California | 11 to 19 Dec. 1968 | N | 2.0 | Minimum value at 500 nm |
| Clearest location in Idaho | 1961–1966 | V (*4*) | 1.8 | Average for location at 500 mn |
| United States | 1961–1966 | V (*4*) | 1.32 | Minimum value at 500 nm |
| New Mexico | 1963–1964 | S (*12*) | 1.8 | Average for air at altitude of 3 to 5 km, clear, moonless nights at 550 nm |
| McMurdo Station, Antarctica | Nov. to Dec. 1966 | V (*13*) | 1.36 | Average value, near sea level, at 500 nm |

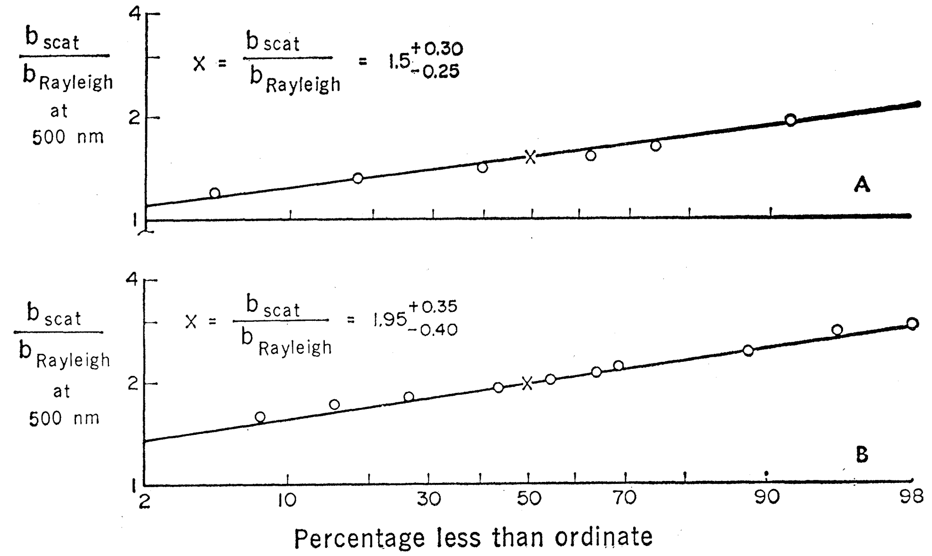

Fig. 1. Logarithmic probability plot of the ratio of observed scattering ($b_{\mathrm{scat}}$) to Rayleigh scattering by air ($b_{\mathrm{Rayleigh}}$) at 500 nm. (A) Mount Olympus, Washington, 1400 hourly averages, February to March 1968; (B) Point Barrow, Alaska, 650 hourly averages, March 1970. Shown on the ordinate is the ratio; values along the abscissa represent the percentage less than the ordinate value. In this plot the ordinate value corresponding to the abscissa value of 50 percent is the geometric mean, and the slope gives the geometric standard deviation.

with the integrating nephelometer at Point Barrow, Alaska (March 1970), and Mount Olympus, Washington (February to March 1968), with turbidity data suggests that there is indeed a background level of atmospheric aerosol. The Point Barrow and Mount Olympus sites had the following local characteristics.

The nephelometer was installed in a remote micrometeorological hut, located 5 km northeast of the village of Point Barrow. This location is, essentially, directly upwind from the village, and negligible effects on the measurements could be ascribed to human sources. After study of the wind direction during the period of record, we assumed that a Distant Early Warning (DEW) station located 3 km to the north-northwest and the Naval Arctic Research Laboratory located 2.5 km to the north-northeast would have an insignificant effect on the measurements. The Beaufort Sea and the Arctic Ocean were covered with ice ~ 3 m thick so that there was little open water, which presumably made the influence of sea-salt aerosol on the measurements negligible. Measurements of sodium concentrations made simultaneously were in support of this presumption. Data on $CO_2$ concentrations taken in this location over an extended period by Kelley (*8*) indicate that this site is highly representative of the arctic atmosphere.

The station on Mount Olympus is located on a precipice (altitude, 2025 m) on the northwest side of this mountain (2430 m high), which is located on the sparsely populated Olympic Peninsula. This area is upwind of virtually all urban and industrial aerosol sources in Washington and British Columbia. The mountain itself is a massif rising perhaps 1000 m above the surrounding foothills and is entirely covered with snow, rime ice, or glacial ice at this time of year. The prevailing winds in winter are dominated by cyclonic activity over the Pacific Ocean and have a persistent westerly component. This situation provides maritime air with little history of contact with even the ocean surface, and certainly with no fresh anthropogenic aerosols (*9*).

Figure 1 is a logarithmic probability graph which shows the distribution of the total scattering coefficient $b_{\mathrm{scat}}$ divided by the component due to air with no aerosol ($b_{\mathrm{Rayleigh}}$) from data taken at Mount Olympus and Point Barrow. The ratio was chosen both to indicate the relative importance of particulate matter and gas and to establish an absolute dimensionless magnitude.

Figure 1 illustrates that these two exceedingly different locations are similar with respect to the geometric mean and the geometric standard deviation, or slope, on this particular plot. The 90 percent confidence interval for both locations is about ± 30 percent from the geometric mean, and the two values of 1.5 and 1.95 for the ratio are similar in magnitude.

Aerosol exhibits a higher variability than $CO_2$. This variability seems reasonable in view of the shorter lifetime (perhaps of the order of a month) of aerosol in the troposphere, a time which may be of the same magnitude as the mixing time. In contrast, the lifetime of $CO_2$ is much longer than the mixing time, with the result that there is a slowly varying atmospheric concentration in remote locations.

The ~ 25 percent difference in the ratio between the two locations might be due to random fluctuation; alternatively, it might (in an extreme view) represent the cumulative effect of 2 years of aerosol production. The difference in altitude seems a more likely explanation, since most aerosol sources are near sea level, and since the top of the troposphere bounds on the ultraclean (comparatively) stratosphere.

Table 1 presents a comparison of data collected up to now in various locations with the nephelometer and the sunphotometer. Both Seattle, Washington, and Altadena, California, had cleanest days that were almost the same, despite a large difference in average pollution levels. The cleanest air sampled with the nephelometer occurred at Mount Olympus on three separate occasions when the value of $b_{\mathrm{scat}}/b_{\mathrm{Rayleigh}}$ reached 1.05 (that is, almost completely molecular light-scattering). The similarity of the mean values of $b_{\mathrm{scat}}/b_{\mathrm{Rayleigh}}$ in remote locations to minimum values in urban areas suggests the existence of a background level of atmospheric aerosol which is augmented by pollution sources when the surrounding air is not well mixed. The agreement of the integral (sunphotometer) measurement with the point (nephelometer) measurement implies that light absorption and multiple scattering are both small, since the nephelometer senses neither of these quantities and the sunphotometer senses both.

From previous studies in which Charlson *et al.* correlated atmospheric aerosol mass concentration and $b_{\mathrm{scat}}$ measured by the nephelometer (*10*), the mean aerosol mass concentrations at Point Barrow and Mount Olympus were estimated to be approximately 8 and 4 $\mu$g/m$^3$, respectively. The upper and lower limits [based on Charlson *et al.* (*6*)], if 90 percent confidence limits are used for the correlation of mass concentration with $b_{\mathrm{scat}}$, would be from 1.6 to 16 $\mu$g/m$^3$. This range is in agreement with typical minimum values of ~ 10 $\mu$g/m$^3$ measured by the National Air Sampling Network (*11*). These results are also consistent with data from searchlight probing of the lower atmosphere on clear nights in New Mexico (*12*).

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14. Support for the work at Mount Olympus was provided under grant GA 780 from the Atmospheric Science section of the National Science Foundation and contract 14-06-D-5970 from the U.S. Department of Interior, Office of Water Resources. Support for the work at Point Barrow was provided under contract No. N0014-67-A-0103-0007 from the Office of Naval Research (Arctic Program) and grant GA 17381 from the Atmospheric Science section of the National Science Foundation. Support for the design of the nephelometer and the measurements was provided under grant AP00336-07 from the National Air Pollution Control Administration, U.S. Public Health Service.

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## Humic Substances: Fulvic Acid–Dialkyl Phthalate Complexes and Their Role in Pollution

Abstract. *Fulvic acid is a water-soluble humic material with relatively low molecular weight that occurs widely in soils and waters. It can combine with lyophobic organic compounds such as alkanes, fatty acids, and dialkyl phthalates to form stable "complexes" that are soluble in water. Fulvic acid in an aquatic environment may act as a vehicle for the mobilization, transport, and immobilization of organic compounds, some of which may be toxic pollutants.*

Humic substances are among the most widely distributed natural products of plant decomposition on the earth's surface, occurring in soils, lakes (*1*), rivers (*2*), and the sea (*3*). In spite of their extensive distribution, little is known about their chemical structure and synthesis or mechanisms of their degradation and adsorptive properties. Of special interest are fulvic acids which are water-soluble, relatively low-molecular-weight humic materials that can form stable complexes with metal ions and hydrous oxides (*4*), can interact with clay minerals (*4*), and are physiologically active (*5*). Although interactions between fulvic acid and inorganic soil constituents have been investigated, very little is known about reactions of fulvic acid with organic compounds of concern to man, especially with those that are environmental pollutants.

We recently reported the isolation from a fulvic acid of small amounts of normal and branched cyclic alkanes and of fatty acids, ranging from $C_{14}$ to $C_{36}$, that account for 0.25 percent of its dry, ash-free weight (*6*). Less than 10 percent of the alkanes and fatty acids could be extracted by organic solvents from untreated fulvic acids; the remainder was extractable only after methylation of the fulvic acid and adsorption on neutral aluminum oxide (*6*). Even though the nature of the molecular forces that hold the alkanes and fatty acids to the fulvic acid is still a matter for conjecture, results from infrared spectroscopy indicate that methylation reduces hydrogen bonding in the fulvic acid. This, in turn, may change the conformation of the fulvic acid polymer in such a manner as to make these compounds extractable by organic solvents. We report here the isolation and identification of small amounts of dialkyl phthalates in fulvic acid and suggest a possible role of fulvic acid in pollution.

The fulvic acid was extracted from the Bh horizon of a podzol soil in Prince Edward Island. Methods of extraction, purification, and drying as well as several physical and chemical characteristics of the fulvic acid have been described (*4*). Briefly, the fulvic acid is a chemically and biologically stable polyelectrolyte with a number-average molecular weight (measured by vapor-pressure osmometry) of 951 and contains 9.1 meq of COOH, 6.9 meq of total OH, and 3.1 meq of C=O groups per gram (*4*). In the present investigation 100 g of air-dry fulvic acid (1.0 percent ash) was extracted for 24 hours in a Soxhlet apparatus first with 1 liter of *n*-hexane, then with 1 liter of benzene, and finally with 1 liter of ethyl acetate. The *n*-hexane extract contained small amounts of alkanes and fatty acids, but none of the extracts contained dialkyl phthalates. The remaining fulvic acid (98.5 g) was then methylated with silver oxide–methyl iodide (*7*). Four successive methylations increased the methoxyl content from 0.2 to 28.2 percent. The methylated fulvic acid (75.0 g) was refluxed with 1 liter of *n*-hexane. The *n*-hexane extract contained trace amounts of dialkyl phthalates. The methylated fulvic acid was then dissolved in benzene. The benzene-soluble material (41.3 g) was chromatographed over neutral aluminum oxide (2000 g) and eluted successively with 3000 ml of *n*-hexane, benzene, benzene–ethyl acetate (9:1 by volume), and benzene–ethyl acetate (1 : 1 by volume). Each extract was further fractionated by repeated thin-layer chromatography on $Al_2O_3$ and silica gel. Only the benzene–ethyl acetate (1 : 1) extract was found to contain dialkyl phthalates. The procedure employed for their isolation was as follows: The benzene–ethyl acetate (1:1) extract (0.51 g) was first separated by preparative thin-layer chromatography on $Al_2O_3$ with toluene–ethyl acetate (3:1 by volume) as solvent. The material near the solvent front was removed from the plates, extracted with ethyl acetate, and refractionated on $Al_2O_3$ plates with toluene–ethyl acetate (9 : 1); the yield was 0.04 g of extract. The location of phthalates on the plates was detected by examination under an ultraviolet lamp and by spraying a guide strip with hydroxylamine-ferric reagent (*8*). Four fractions were scraped off the thin-layer chromatographic plates; these fractions were eluted with ethyl acetate and further separated by preparative gas chromatography (Hewlett-Packard model 402 flame ionization detector, 122 × 3 mm glass column packed with 3 percent OV-17 on Chromosorb W HMDS, 60 to 80 mesh, programmed from 200° to 300°C at a rate of 7.5°C per minute). Materials representing the four major peaks, I, II, III, and IV, were eluted from the gas chromatographic column, collected in capillary tubes, and identified by ultraviolet spectroscopy, infra-