# The Size of Particulate Trace Elements in the Atmosphere—A Review

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# The Sizes of Particulate Trace Elements in the Atmosphere—A Review

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Size distributions of 38 trace elements reported in the literature over the past two decades have been summarized. Those elements with aerodynamic mass median diameter less than 2 $\mu$m generally have bimodal distributions: the dominant peak occurs in the range 0.5–1 $\mu$m, with a smaller peak at about 3–5 $\mu$m. Elements with larger mass median diameter have a single peak, with relatively little mass below 1 $\mu$m. Overall, the individual distributions of many of the elements are surprisingly consistent, despite different sampling locations, time periods, and experimental methods.

Size and chemical composition are among the most important parameters influencing the way in which airborne particles interact with the environment. Deposition from the atmosphere onto soil, vegetation, and other surfaces is a function of particle size. Once deposited, the fate of the particles depends on their size and composition. The extent to which airborne particles penetrate the human respiratory system is determined mainly by size, with possible health effects resulting from the presence of toxic substances. Visibility degradation is known to be a function of both size and composition of airborne particles. Cloud formation, warming of the earth's surface by solar radiation, and other meteorological phenomena are also affected by particle characteristics.

Because of the importance of particle size and composition, a large number of studies have been devoted to airborne particle characterization. Many of these studies have focused on trace elements: over 60 separate investigations have produced roughly two thousand size distributions since 1960, including data for more than 40 elements. Previous literature reviews have summarized trace element size data up to the mid-1970s[1,2] but a wealth of new data has appeared since then.

In this article, we discuss trace element size distributions reported in the literature from some of the earliest studies up through 1985. Details of the measurement methods are presented first, focusing on experimental errors and resulting uncertainty in the data. Overall average size distribution plots for 38 elements are then given, with a detailed examination of the distributions for Al, Na, and Pb. Finally, the utility of these distributions is discussed; as examples, the data for several potentially toxic elements have been used to calculate deposition in the human lung, and dry deposition velocities for natural grassland have been calculated for all of the elements. A companion paper currently in preparation will discuss size distributions of airborne nitrate and sulfate.

## Measurement Methods and Experimental Error

Nearly all of the size distribution data reported in the literature have been obtained with cascade impactors. These devices collect atmospheric aerosols by inertial impaction, depositing particles of decreasing size on consecutively cascaded stages. A final backup filter is normally used to capture particles that are too small to be collected by inertial deposition. While providing a convenient method of fractionating aerosols for subsequent elemental analysis, impactors are highly imperfect.

Obtaining a representative sample requires that the impactor inlet be faced directly into the wind and that the inlet air speed be identical to the ambient wind speed (isokinetic sampling). Several investigators have shown that size distributions measured with commercial impactors tend to underestimate particle concentrations in the largest size ranges due to nonisokinetic sampling.[3-6] Supermicron particles are also more likely than smaller particles to deposit on walls of the inlet and on internal walls of the impactor.[7-10]

Particles may bounce off impaction surfaces, becoming reentrained in the flow and depositing on lower stages. This problem is usually minimized by applying adhesive coatings, although some particle bounce may still occur and the coatings may interfere with subsequent chemical analysis.[11,12] Recent studies have shown that the severity of bounceoff depends on particle characteristics, relative humidity, and other factors; for example, hygroscopic seaspray aerosols are retained on dry surfaces better than soil-derived elements.[5,13] Adhesive-coated surfaces have been used in many of the studies reported here, although few investigators have attempted to quantify the effect of bounceoff on their own data.

Aside from the difficulties discussed above, the fractionation of particles into desired size ranges is imperfect: small particles may be collected to a

certain extent on the upper stages, while some of the large particles may not be impacted until reaching the lower stages. Such problems are the result of nonideal air flow through the impactor, particularly variations in the air velocity across each jet.[14,15] To define their size ranges, many researchers have merely adopted the manufacturers' suggested cutoff diameters which are often based on ideal air flow. In only a few instances have investigators attempted to calibrate their impactors with monodisperse particles under conditions similar to those of their field experiments.

Another potential problem with the data reported here is the error associated with analytical results. Of primary importance is possible contamination during sampling, sample handling, and analysis. Recent work by Patterson and coworkers[16-18] has demonstrated that measurement of Pb concentrations in environmental samples is extremely difficult; minimizing contamination of air samples analyzed for other trace metals may also pose a challenge.[19] The potential for contamination is particularly high in impactor sampling, since the small amount of total airborne material is fractionated by size into even smaller samples for analysis. Other analytical problems include difficulties specific to the method of analysis. For example, atomic absorption analysis may be complicated by interferences from other metals or from organic material in the samples.[20,21] Neutron activation suffers from uncertainties in the position of the samples with respect to the detector, and from counting statistics limitations.[22] Both X-ray fluorescence and proton induced X-ray emission analyses are prone to errors if the sample is too thick or not uniformly deposited on the substrate.[23,24] All analytical methods are highly uncertain when the mass of material approaches the limit of detection, a situation often encountered during analysis of size-fractionated aerosol samples. Although some recent studies have included quality assurance procedures such as interlaboratory comparisons of analytical results, most of the studies summarized here contain little or no discussion of quality control.

Finally, the small number of experiments conducted in many of the studies suggests that the representativeness of the data must be questioned. Many of the investigations involved only one or two experiments. Even the most extensive studies included 10–20 separate sampling periods, a relatively small number compared with total airborne concentration monitoring programs.

All of these problems suggest that most of the size distribution data in the literature is subject to considerable un-

certainty. Widely varying sampling periods and locations, as well as differences in the aerosol collection and analysis techniques, further suggest the difficulty in averaging the results of the independent studies. Nevertheless, the data show consistencies which imply characteristic shapes in the distributions of certain elements. The next section presents the average distributions, and discusses characteristic spectra for several of the elements.

## Presentation of Average Size Distributions

Figure 1 shows overall average size distributions for 38 elements. The ordinate is the normalized mass distribution function $(\Delta C/C_T)/\Delta \log d_p$, where $\Delta C$ is the airborne mass concentration of the element in a given size range (which extends from $d_{p\ min}$ to $d_{p\ max}$), $C_T$ is the total concentration of the element in all size ranges, and $\Delta \log d_p$ is the difference $\log d_{p\ max} - \log d_{p\ min}$. The aerodynamic diameter of a particle $d_p$ represents the size of a unit density sphere with aerodynamic transport characteristics which are identical to those of the original particle. Note that the area under the curve between any two particle diameters is proportional to the fraction of airborne mass in that size interval.

For consistency, overall minimum and maximum aerodynamic diameters of 0.05 and 40 $\mu$m, respectively, have been assumed after Hidy[25] and Davidson.[3] Airborne particles as large as 40 $\mu$m have been documented in the literature,[3,26] although such large particles were probably sampled with low efficiency in the studies reported here. Much of the mass reported for the largest size ranges in Figure 1 may represent smaller particles collected by the nonideal upper impactor stages.

All distributions have been plotted as though the particles are uniformly distributed in $\log d_p$ in each size range. The resulting histograms are thus only approximations to the actual smooth-curve distributions. Although techniques for estimating the true size spectra have been reported in the literature,[27-29] this style of graphing has been chosen to allow direct observation of those size ranges containing the bulk of the airborne mass, and to emphasize differences in the shapes of the distributions.

Data to construct these graphs were obtained from differential or cumulative distribution plots, or from tables, in the original references. Personal communication with the authors was necessary in some instances to clarify or update the data. Sets of measurements including fewer than four size ranges were excluded, as were those which did not incorporate a backup fil-

ter (except where this omission was considered insignificant).

The final set of data from each separate investigation was used to construct a histogram plot for each element reported. The intervals of the composite histogram were defined by initiating a new interval at each cutoff diameter reported in any of the separate investigations. The values of $(\Delta C/C_T)/\Delta \log d_p$ for all of the distributions for a given element were then combined to provide an arithmetic average and standard deviation for each size range. The heavy line in each plot represents the average of $(\Delta C/C_T)/\Delta \log d_p$. The light lines show corresponding values one standard deviation above and below the average. Note that the elements are arranged in order of increasing aerodynamic mass median diameter (MMD). Values of MMD are shown on each graph, as are the number of the independent sets of size distributions (N) reporting data for that particular element. Only elements for which $N \geq 2$ have been included.

It is interesting to consider the distributions for Pb, Na, and Al in greater detail. These elements are commonly used as tracers of anthropogenic emissions, seaspray, and soil dust, respectively. For each of the three elements, the overall average distribution in Figure 1 has been divided into separate categories depending on sampling location. The average urban distribution represents data collected in populated regions or near industrial sources. "Nonurban continental" refers to rural and remote areas somewhat removed from major sources. The marine category pertains to coastal and island sampling sites and to data collected from ships, where seaspray aerosol is expected to dominate. The average values of $(\Delta C/C_T)/\Delta \log d_p$ for each category are shown in Figure 2.

Table I lists detailed information for the studies represented in the average distributions of Figures 1 and 2. The authors, sampling dates and locations, and elements analyzed for each study are given in the table.

## Discussion

Several features of the distributions in Figure 1 merit attention. The first 18 elements have MMD below 2 $\mu$m; many of these elements show bimodal spectra. The primary mode generally occurs in the range 0.5–1 $\mu$m, with a smaller peak at approximately 3–5 $\mu$m. The mass of these species is more broadly distributed than the mass of elements with larger MMD. The 20 elements with MMD greater than 2 $\mu$m generally show a dominant peak at 3–5 $\mu$m. Most elements in this category have relatively little mass below 1 $\mu$m.

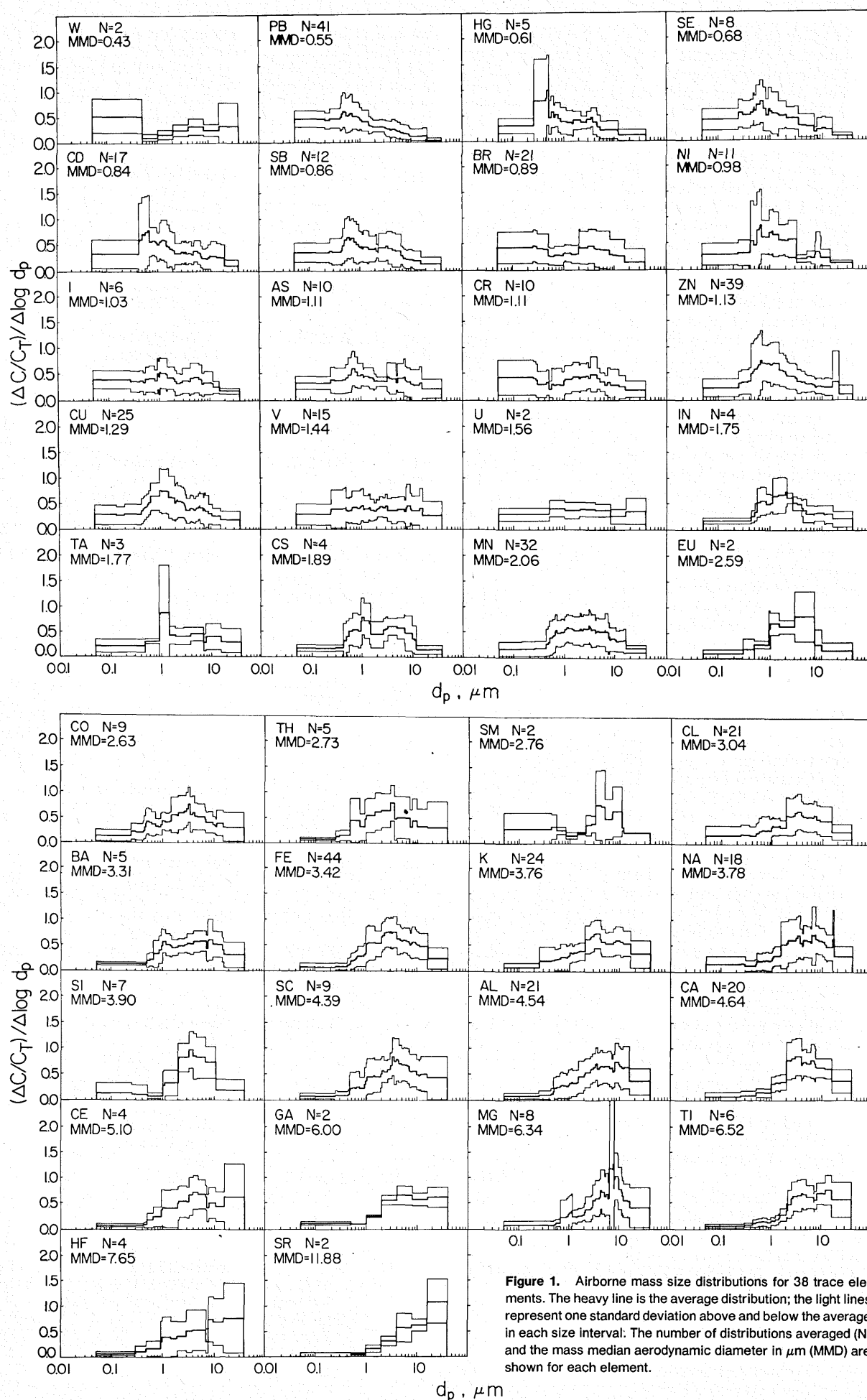The distributions in Figure 1 are

**Figure 1.** Airborne mass size distributions for 38 trace elements. The heavy line is the average distribution; the light lines represent one standard deviation above and below the average in each size interval. The number of distributions averaged (N) and the mass median aerodynamic diameter in $\mu$m (MMD) are shown for each element.

consistent with bimodal spectra for total aerosol mass reported in the literature.[30-34] The dominant peak generally occurs below 1 $\mu$m, with a second peak above 3 $\mu$m. The data of Figure 1 show that some elements contribute mainly to the submicron peak while other elements contribute primarily to the supermicron peak in total aerosol mass. It should be noted, however, that some of the most abundant contributors of submicron material, such as carbon, sulfur, and nitrogen species, are not included in Figure 1.

Many of the original investigations represented in Figure 1 have discussed sources of the various elements. Those with MMD smaller than about 2 $\mu$m are commonly associated with high temperature anthropogenic processes, such as welding and soldering, smelting of metals, and combustion of fossil fuels.[1,35,36] A variety of natural sources including combustion (e.g. forest fires and volcanic eruptions) and noncombustion processes (e.g. erosion of the earth's crust, production of seaspray aerosol, and biological mobilization) may also be significant.[2,37,38] In contrast, elements with MMD greater than 2 $\mu$m are emitted mainly by natural processes such as crustal erosion and production of seaspray. Soil erosion generally produces particles with mass distributions which peak in the range 1–20 $\mu$m.[39] Bubble bursting at the ocean surface produces particles of similar sizes.[40-42] Some anthropogenic activities may also contribute to airborne concentrations of large particles on a local scale; examples include agricultural and construction activities, material handling, and certain combustion processes.

Zoller et al.[37] have explained these different source categories in terms of relative volatilities. Elements with low boiling points are likely to be emitted as submicron particles or gases during combustion processes; many of the gases may later condense to form additional submicron particles. Elements with high boiling points, emitted as fly ash during combustion, are more likely to be contained by particulate control devices because of the larger particle sizes involved. Consistent with this discussion, the predominantly submicron elements in Figure 1 generally have lower boiling points than those with larger MMD.

The relative influences of natural and anthropogenic sources of airborne trace elements can be assessed through the mobilization factor MF and the crustal enrichment factor EF. The former is defined by[43]:

$$MF = \frac{\text{Total emission rate from anthropogenic sources}}{\text{Total emission rate from natural sources}}$$

**Table I.** Summary of the individual studies contributing to the average distributions in Figures 1 and 2. Only those dates, locations, and elements analyzed which have been used to construct Figures 1 and 2 are given in this listing; some of the studies included additional data which have been excluded for various reasons (see text).

| Reference No. | Authors | Sampling dates | Sampling locations | Elements analyzed |
|---|---|---|---|---|
| 64 | Andreae, 1982 | Sept. 1979 | Cape Grim, Tasmania; Townsville, Queensland | Br,Ca,Cl,K,Si |
| 65 | Appel et al., 1980a | Jul.–Oct. 1973 | Los Angeles, CA, average of 4 sites | Br,Ca,Fe,K, Mn,Ni, Pb,Ti |
| 66 | Berg and Winchester, 1977 | Mar. 1976 | Gulf of Mexico, 4 km from N. Florida shore | Cl |
| 67 | Bernstein and Rahn, 1979 | Aug. 1976 | New York, NY, roof of 10-story building | Al,As,Ba,Br, Cl,Co,Cr,Cs, Cu,Fe,Hg, I,In,K,Mn, Na,Pb,Sb, Sc,Se,Sm, Ti,V,Zn |
| 68 | Boueres and Patterson, 1981 | May 1979 | Kosovo, Yugoslavia, downwind of industrial complex | Na,Ca |
| 69 | Caruso et al., 1981 | 1977–1979 | Milan, Italy | Br,Ca,Fe, Pb,V,Zn |
| 70 | Cawse et al., 1974 | Jul.–Dec. 1973 | Chilton, England | Fe,Mn,Pb, Zn |
| 71 | Cholak et al., 1968 | Apr. 1968 | Cincinnati, OH, average from three sites, 3.3–10.4 km from I-75 | Pb |
| 72 | Crecelius et al., 1980 | May–Sept. 1975 | Colstrip, MT | Al,As,Br, Co,Cr,Cs, Eu,Fe,Hf, K,Mn,Na, Sc,Se,Th, V,Zn |
| 73 | Daines et al., 1970 | 1968 | New Brunswick, NJ | Pb |
| 3 | Davidson, 1977 | May and Jul. 1975 | Pasadena, CA, roof of 4-story building | Cd,Pb,Zn |
| 74 | Davidson et al., 1981a | Jul.–Sept. 1979 | Pittsburgh, PA | As,Cd,Cu, Fe,Mn,Ni, Pb,V |
| 75 | Davidson et al., 1981b | Dec. 1979 | Nepal, Himalayas, elevation 3962 m | Pb |
| 76 | Davidson et al., 1983 | Jun. 1980 | Export, PA | Al,As,Ba, Cd,Cu,Fe, Mg,Mn,Ni, Pb,V,Zn |
| 77 | Davidson et al., 1985 | Jul. 1980 | Olympic National Park, Hurricane Ridge; Packwood, WA; Gifford Pinchot Natl. Forest; Great Smoky Mountains National Park, Clingman's Dome | Al,Ca,Cd, Cu,K,Mg, Mn,Na,Pb, Zn |
| 78 | Duce et al., 1976 | May–Jul. 1975 | Bermuda | Al,As,Cd, Co,Cu,Fe, Hg,Na,Pb, Sb,Sc,Se, Th,Zn |
| 51 | Duce et al., 1983 | Apr.–May, 1979, wet season; Jun.–Aug., 1979, dry season | Marshall Islands, Enewetok Atoll, Bokandretok Islands | Al,Ba,Br, Ca,Ce,Cl, Co,Cs,Cu, Eu,Fe,Hg, I,K,Mn, Mg,Na,Pb, Sb,Sc,Se, Ta,Th,V,Zn |

**1252**

**Table I.** *Continued.*

| Reference No. | Authors | Sampling dates | Sampling locations | Elements analyzed |
|---|---|---|---|---|
| 79 | Gillette and Winchester, 1972 | Oct. 1968 | Ann Arbor, MI; Chicago, IL; Lincoln, NE | Pb |
| 80 | Hardy et al., 1976 | Summer 1974 | Miami, FL | Fe,Mn,Zn |
| 81 | Harrison et al., 1971 | Apr. 1968 | Ann Arbor, MI | Cd,Cu,Pb |
| 82 | Harrison and Williams, 1982 | Apr. 1978– Mar. 1979 | Hazlerigg, England; Lancaster, England | Cd,Pb,Zn |
| 83 | Heindryckx, 1976 | Sept. 1971– Nov. 1973 | Gent, Belgium | Al,As,Br, Ca,Ce,Cl, Co,Cs,Cu, Hg,I,In,K, Mg,Mn,Na, Sb,Sc,Se, Sm,Ti,V,Zn |
| 84 | Huntzicker et al., 1975 | May, 1973; Feb. 1974 | Los Angeles, CA, freeway shoulder; Pasadena, CA | Pb |
| 85 | Kadowaki, 1979 | Mar. 1977; May 1978 | Nagoya, Japan | Al,Si |
| 86 | Khandekar et al., 1980 | Dec. 1977– Jan. 1979 | Bombay, India, average from three sites | Pb |
| 87 | Lawson and Winchester, 1978 | Apr. 1976 | Squaw Mountain, CO | Ca,Fe,K,Ti |
| 88 | Lawson and Winchester, 1979 | Summer 1977 | Zongo, Bolivia; Manaus, Brazil, dense tropical vegetation | Fe,K |
| 89 | Lee et al., 1968 | Sept. 1966 Feb. 1967 | Cincinnati, OH; Fairfax, OH | Cd,Cu,Cr, Fe,Pb |
| 90 | Lee et al., 1969 | Aug. 1965–Apr. 1966 | Fairfax, OH; Cincinnati, OH; Philadelphia, PA; Chicago, IL | Cd,Cl |
| 91 | Lee et al., 1972 | 1970 | Chicago, IL; Cincinnati, OH; Denver, CO; Philadelphia, PA; St. Louis, MO; Washington, D.C. | Cu,Fe,Mn, Ni,Pb,V,Zn |
| 92 | Lindberg and Harriss, 1983 | May–Oct. 1977 | E. Tennessee, Walker Branch Watershed | Cd,Pb,Zn |
| 93 | Lundgren, 1970 | Nov. 1968 | Los Angeles, CA | Fe,Pb |
| 94 | McDonald and Duncan, 1979 | Jun. 1975 | Glasgow, Scotland | Al,Cd,Cr, Cu,Fe,Mn, Ni,Pb,Zn |
| 95 | Maenhaut et al., 1983 | Apr.–Oct. 1979 | ITC zone—close to S. American continent; trade wind region—further from continent | Br,Ca,Cl, Fe,K,Mn,Si |
| 96 | Martens et al., 1973 | Jul. 1971 | San Francsico, CA | Br,Pb |
| 97 | Meinert and Winchester, 1977 | Oct.–Nov. 1973 | Hamilton Island, Bermuda | Ca,Fe,K,Zn |
| 98 | Nifong et al., 1972 | Jul. 1969– Feb. 1970 | Chicago, IL; Gary, IN | Al,Cu,Fe, Mn,Sb,Zn |
| 99 | Orsini et al., 1977 | Feb. 1974 | St. Louis, MO | Cl,K |
| 100 | Orsini et al., 1982 | Aug.–Sep. 1980 | Manaus, Brazil | Ca,Cl,Fe, K,Si |
| 101 | Paciga, 1976 | Summer 1973; winter 1973–1974 | Toronto, Canada, near battery recycling plant; U. of Toronto | Al,As,Br, Cl,Pb,Sb |
| 102 | Pacyna et al., 1984 | Mar.–Apr. 1983 | Ny-Alesund, Spitsbergen | Cr,Cu,Mn, Ni,Zn |
| 103 | Pattenden et al., 1974 | May–Aug. 1973 | Trebanos, England | Cu,Fe,Mn, Pb,Zn |
| 104 | Patterson and Wagman, 1977 | Sep.–Oct. 1970 | Secaucus, NJ | Fe,Mg,Pb, Zn |

*(Continued on next page)*

and hence gives a direct indication of the relative importance of man's activities on a global scale. Enrichment factors, on the other hand, provide an indication of the importance of crustal erosion at a particular sampling site[37]:

$$EF = \frac{X_{air}/Al_{air}}{X_{crust}/Al_{crust}} \quad (1)$$

where $X_{air}$ refers to the airborne concentration of any element $X$, $Al_{air}$ is the airborne concentration of Al, $X_{crust}$ is the average concentration of element $X$ in the earth's crust, and $Al_{crust}$ is the average concentration of Al in the earth's crust. Values of EF near unity suggest crustal weathering as the predominant source of element $X$, while much greater values of EF suggest other, noncrustal, sources. Difficulties in obtaining reliable estimates of source emissions and in interpreting crustal enrichment data[2] suggest that values of MF and EF can provide, at best, only rough indications of sources influencing airborne concentrations of a particular trace element.

Table II lists values of MF and EF from published literature surveys.[2,43] Also given for each element are values of the geometric mean and standard deviation of the airborne concentrations associated with the size distributions of Figure 1, as well as the range in concentrations. The trends in the Table II values are consistent with the preceding discussion: elements with small MMD and large MF have the greatest enrichments, suggesting noncrustal sources. The less volatile elements with larger MMD have crustal enrichments near unity, suggesting crustal erosion as the predominant source.

The standard deviations shown in Figure 1 must be interpreted with caution. Twenty-one of the elements have $N < 10$, indicating a very small data base. Even for those elements with $N > 10$, the data may not represent the wide range of environmental conditions likely to influence the size distributions.

Nevertheless, differences in the standard deviations for some of the elements are informative. Pb is a notable example of an element with relatively small standard deviations. On a global scale, nearly 70 percent of the total Pb emitted to the atmosphere in 1975 was derived from the combustion of leaded gasoline; most of the remaining 30 percent was emitted from the smelting of lead, iron, copper, and zinc.[44,45] These processes produce significant amounts of submicron particles,[46] resulting in similarity among the individual Pb distributions. Note that the shapes of the urban, nonurban continental, and marine distributions for Pb in Figure 2 are nearly identical.

**Table I.** *Continued.*

| Reference No. | Authors | Sampling dates | Sampling locations | Elements analyzed |
|---|---|---|---|---|
| 105 | Peden, 1977 | summer 1975 | Illinois, average from six locations | Cd,Mn,Pb |
| 106 | Ragaini et al., 1980 | Sept. 1973 | Los Angeles, CA | Al,Br,Cl,Na |
| 2 | Rahn, 1976 | Apr.–May 1972 | Liege, Belgium | Cd,Cu,Fe, Mn,Zn |
| 107 | Sadisivan, 1978 | May–Jun. 1973 | Arabian Sea | Br,Cl,Cr, Fe,I,Mn,Na, Sb,Sc,Zn |
| 108 | Sadisivan, 1981 | Nov.–Dec. 1976 | Trombay, Bombay, India | Co,Cr,Fe, Hg,Sb,Sc |
| 109 | Savoie and Prospero, 1982 | 1974 and 1981 | Miami, FL; Sal Island, Cape Verde Islands; Barbados, West Indies | Na |
| 110 | Tanaka et al., 1980 | Nov. 1978–Jan. 1979 | Tallahassee, FL | Pb |
| 111 | U.S. EPA, 1973, 1974 | Apr. 1973– Jan. 1974 | Kellogg, ID near Pb smelter | Cd |
| 112 | Wangen, 1981 | June 1977– Jan. 1978 | NW New Mexico | Al,As,Ba, Br,Ca,Ce, Cl,Co,Cr, Cu,Fe,Ga, Hf,I,In,K, Mn,Mg,Na, Sb,Sc,Se, Sr,Ta,Th, Ti,U,V, W,Zn |
| 5 | Wesolowski et al., 1980 | Jul.–Aug. 1972 | Berkeley, CA; San Jose, CA; Pasadena, CA; Fresno-Visalia, CA | Al,Br,Na,V |
| 113 | Winchester et al., 1979 | Apr. 1976 | Los Alamos, NM; 40 km w of St. Louis, MO; St. Louis, MO; Hubbard Brook, NH | Ca,Fe,K, Si,Zn |
| 114 | Winchester et al., 1981 | Mar. 1980 | Beijing, China | Ca,Cl,K |

Several of the elements showing large variability are also of interest. Ni and V show the greatest variability for very small and very large particles, with minimal variability in the mid-size ranges. Combustion of fuel oil, which produces primarily submicron particles, is a major anthropogenic source of both elements.[47,48] Also significant are emissions of these elements from crustal erosion,[48–50] which produces mostly large particles. A number of other anthropogenic and natural sources, producing a wide range of particle sizes, may also be significant. The resulting distributions for these elements represent averages of spectra which are primarily submicron at some sites and supermicron at others, depending on the relative influences of the various source categories.

Insight into the variations in the distributions for Na and Al is provided by Figure 2. The urban area distributions have the most mass associated with large particles, while nonurban conti-

nental and marine spectra show progressively smaller sizes. It is likely that urban activities such as construction and industrial emissions produce large particles containing Na, Al, and a variety of other elements. Nonurban continental sites are probably influenced most by soil erosion, with mass distributions that peak in the range 5–10 $\mu$m according to Figure 2. Finally, the marine distributions for these two elements show peaks at 1–5 $\mu$m. As with many of the elements in Figure 1, the widely varying spectra for Na and Al are the result of averaging over a number of dissimilar distributions.

As examples of the utility of the trace element size distributions, the data summarized in this paper have been used to perform two types of calculations. In the first set of calculations, the fractional deposition in each compartment of the human respiratory tract has been estimated for several potentially toxic elements. In the second set, the overall dry deposition velocity for a

natural grass surface under specific meteorological conditions has been estimated for each of the 38 elements. Both sets of estimates have been derived using the data of Figure 1 with various size-dependent models, using methods established previously.[51]

For the compartments of the human respiratory tract, the overall deposition fraction is:

$$F = \sum_{i=1}^{n} f_i \, \Delta C_i \Big/ \sum_{i=1}^{n} \Delta C_i \qquad (2)$$

where $f_i$ is the mass deposition fraction in a compartment of the lung corresponding to size range $i$, and $\Delta C_i$ is the airborne mass concentration in that size range. The mass median diameter for each size interval has been used to determine $f_i$. Values of $F$ thus calculated represent the total mass of an element deposited in a specific compartment of the respiratory system, divided by the total mass of metal inhaled.

Values of $f_i$ have been taken from recent lung deposition studies[52–54] summarized by the U.S. Environmental Protection Agency.[42] Data are available for the extrathoracic (ET), tracheobronchial (TB), and pulmonary (P) regions. Because of wide variations in data for the pulmonary region, high and low deposition estimates were established using two curves which envelop the data. All of the data pertain to mouth breathing at respiration rates of 7.5—30 liters per minute. Tidal volumes are generally in the range 1.0–1.5 liters. The curves for $f_i$ constructed by the EPA are shown in Figure 3.

Values of $F$ for the ET, TB and P compartments have been calculated for Pb, Hg, Se, Cd, Sb, Ni, As, Cr, Zn, and V. Some concern about potential toxicity at concentrations found in the ambient atmosphere has been expressed for each of these elements.[55–58] Calculations for Al and Fe, elements which are associated with larger particles than the elements listed above, are included for comparison. The values of $F$ have been calculated for each original distribution, then averaged across all of the distributions for an element to give the results shown in Table III.

Total deposition fractions for the elements increase with MMD, reflecting greater deposition efficiencies for larger particles in the ET and TB regions. Deposition in the P region is remarkably consistent across all of the elements. Al and Pb, for example, have the highest and lowest total deposition fractions, respectively, yet virtually identical pulmonary deposition characteristics. The amount of mass in the size range 1–5 $\mu$m, which has the greatest pulmonary deposition efficiency, is about the same for all of these elements.

The results shown in Table III differ from previous estimates of lung deposi-

**Table II.** Parameters associated with the size distribution data averaged in Figure 1. Elements are arranged in order of increasing MMD. Values of EF$_{crust}$ are overall geometric means for urban, rural, and remote areas from Rahn[2]; values of MF are from Galloway et al.[43]

| Element | Range of $C_T$ ng/m³ | Geometric mean $C_T$ ng/m³ | Geometric standard deviation | MMD μm | EF$_{crust}$ | MF |
|---|---|---|---|---|---|---|
| W | 0.29–0.80 | 0.48 | 2.0 | 0.43 | 19 | |
| Pb | 0.11–14000 | 310 | 11 | 0.55 | 1500 | 340 |
| Hg | 0.08–81 | 1.9 | 31 | 0.61 | 560 | 280 |
| Se | 0.12–8.6 | 1.1 | 9.4 | 0.68 | 3100 | 34 |
| Cd | 0.05–1000 | 3.7 | 10 | 0.84 | 1900 | 19 |
| Sb | 0.003–680 | 2.3 | 22 | 0.86 | 1400 | 39 |
| Br | 2.1–6500 | 94 | 5.7 | 0.89 | 1900 | |
| Ni | 1.5–630 | 33 | 5.7 | 0.98 | 32 | 3.5 |
| I | 0.28–9.3 | 2.0 | 2.7 | 1.03 | 510 | |
| As | 0.27–290 | 4.3 | 2.8 | 1.11 | 310 | 28 |
| Cr | 0.74–130 | 6.4 | 4.1 | 1.11 | 8.1 | 1.6 |
| Zn | 1.8–2800 | 68 | 7.9 | 1.13 | 260 | 23 |
| Cu | 0.03–400 | 24 | 8.8 | 1.29 | 100 | 14 |
| V | 0.05–1200 | 4.7 | 6.2 | 1.44 | 14 | 3.2 |
| U | 0.21–0.92 | 0.44 | 2.8 | 1.56 | 2.9 | |
| In | 0.01–0.07 | 0.03 | 4.0 | 1.75 | 90 | |
| Ta | 0.0004–1.5 | 0.08 | 30 | 1.77 | 1.1 | |
| Cs | 0.0007–0.41 | 0.04 | 10 | 1.89 | 12 | |
| Mn | 0.07–290 | 20 | 3.2 | 2.06 | 3.9 | 0.52 |
| Eu | 0.0009–0.02 | 0.0031 | 5.8 | 2.59 | 2.7 | |
| Co | 0.002–4.8 | 0.77 | 7.2 | 2.63 | 3.5 | 0.63 |
| Th | 0.0009–4.2 | 0.07 | 11 | 2.73 | 1.8 | |
| Sm | 0.03–0.35 | 0.12 | 4.0 | 2.76 | 2.1 | |
| Cl | 110–13000 | 610 | 10 | 3.04 | 740 | |
| Ba | 0.5–250 | 19 | 10 | 3.31 | 5.5 | |
| Fe | 2.7–6100 | 430 | 4.3 | 3.42 | 2.1 | |
| K | 19–4000 | 180 | 3.0 | 3.76 | 2.0 | |
| Na | 250–12000 | 1100 | 4.0 | 3.78 | 4.4 | |
| Si | 21–5300 | 680 | 6.2 | 3.90 | 0.79 | |
| Sc | 0.008–2.3 | 0.25 | 3.4 | 4.39 | 1.2 | |
| Al | 2.3–5000 | 530 | 8.7 | 4.54 | 1.0 | |
| Ca | 14–9200 | 330 | 3.8 | 4.64 | 2.8 | |
| Ce | 0.008–22 | 6.4 | 2.9 | 5.10 | 2.6 | |
| Ga | 0.80–6.9 | 2.4 | 4.6 | 6.00 | 2.5 | |
| Mg | 340–8100 | 980 | 4.2 | 6.34 | 2.4 | |
| Ti | 3.9–800 | 42 | 4.0 | 6.52 | 1.4 | |
| Hf | 0.0007–3.6 | 0.10 | 29 | 7.65 | 2.0 | |
| Sr | 16–100 | 40 | 3.7 | 11.9 | 1.5 | |

tion by Natusch and Wallace.[59] These investigators used a model developed by the Task Group on Lung Dynamics[60] with lognormal distributions fit to particle size data to estimate deposition fractions. The fractions for Pb in the ET, TB, and P compartments were estimated as 0.17, 0.06, and 0.32, respectively, and for Fe as 0.48, 0.07 and 0.22. The estimates primarily reflect differences between the curves of Figure 3 and the Task Group model; the latter predicts greater deposition efficiencies for submicron particles in the pulmonary region, smaller efficiencies over most sizes in the tracheobronchial region, and greater efficiencies for supermicron particles in the extrathora-

cic region. The Pb and Fe size distribution data used by Natusch and Wallace were not significantly different from the average Pb and Fe distributions reported in the present study.

For estimating dry deposition velocities, the relevant equation is:

$$V_d = \sum_{i=1}^{n} v_{di}\, \Delta C_i / \sum_{i=1}^{n} \Delta C_i \quad (3)$$

Values of $v_{di}$ have been taken from the model of Davidson et al.[61] for deposition to a field of *Dactylus glomerata* (L) (orchard grass). The model uses equations of particle transport by diffusion, interception, impaction and sedimentation with data for the geometry of the vegetation and windfield characteristics above and within the canopy. The final curve of $v_{di}$ versus particle diameter for *Dactylus glomerata* is shown in Figure 4. For comparison, curves representing the models of Sehmel and Hodgson[62] and Slinn[63] are also shown in the figure.

For each element, the average and standard deviation of the deposition velocities calculated for each of the individual distributions is given in Table IV. Average values range from 0.48 cm s⁻¹ for Se (MMD = 0.68 μm) to 4.4 cm s⁻¹ for Sr (MMD = 11.9 μm), and increase roughly with increasing MMD for all of the elements. Variations in MMD do not completely explain the differences in deposition velocity, however, because $V_d$ is more sensitive to the fraction of large particles in a distribution than to overall MMD. Results of these calculations must be considered with caution since dry deposition velocity increases rapidly with particle size, while the distributions of Figure 1 are highly uncertain in the uppermost size ranges. In addition, the curves of Figure 4 are rough estimates which have not been verified experimentally.[61] When the size distributions are used with the deposition velocity curves of Sehmel and Hodgson[62] and of Slinn,[63] the resulting average deposition velocities are 0.23 and 0.37 cm s⁻¹ respectively for Pb, and 0.75 and 1.5 cm

**Table III.** Fraction of inhaled mass deposited in the pulmonary, tracheobronchial, and extrathoracic compartments of the human respiratory tract, based on the size distributions of Figure 1 and the deposition curves of Figure 3. High and low estimates of pulmonary compartment deposition are given. Values shown are arithmetic averages and standard deviations.

| Element | N | Pulmonary (low) | Pulmonary (high) | Tracheo-bronchial | Extra-thoracic | Total (low) | Total (high) |
|---|---|---|---|---|---|---|---|
| Pb | 41 | 0.11 ± 0.01 | 0.26 ± 0.03 | 0.07 ± 0.03 | 0.11 ± 0.07 | 0.29 ± 0.08 | 0.44 ± 0.08 |
| Hg | 5 | 0.11 ± 0.02 | 0.27 ± 0.04 | 0.09 ± 0.05 | 0.11 ± 0.09 | 0.31 ± 0.10 | 0.47 ± 0.10 |
| Se | 8 | 0.12 ± 0.03 | 0.28 ± 0.06 | 0.08 ± 0.03 | 0.10 ± 0.05 | 0.30 ± 0.07 | 0.46 ± 0.08 |
| Cd | 17 | 0.11 ± 0.03 | 0.27 ± 0.06 | 0.09 ± 0.03 | 0.18 ± 0.15 | 0.38 ± 0.15 | 0.54 ± 0.16 |
| Sb | 12 | 0.11 ± 0.02 | 0.29 ± 0.06 | 0.09 ± 0.03 | 0.14 ± 0.11 | 0.35 ± 0.12 | 0.52 ± 0.13 |
| Ni | 11 | 0.12 ± 0.03 | 0.27 ± 0.03 | 0.10 ± 0.04 | 0.14 ± 0.08 | 0.36 ± 0.10 | 0.50 ± 0.10 |
| As | 10 | 0.10 ± 0.02 | 0.26 ± 0.05 | 0.10 ± 0.04 | 0.20 ± 0.17 | 0.40 ± 0.18 | 0.56 ± 0.18 |
| Cr | 10 | 0.11 ± 0.03 | 0.28 ± 0.05 | 0.10 ± 0.06 | 0.18 ± 0.12 | 0.39 ± 0.13 | 0.56 ± 0.14 |
| Zn | 39 | 0.12 ± 0.03 | 0.27 ± 0.06 | 0.09 ± 0.02 | 0.18 ± 0.14 | 0.39 ± 0.15 | 0.54 ± 0.16 |
| V | 15 | 0.10 ± 0.03 | 0.25 ± 0.06 | 0.11 ± 0.05 | 0.23 ± 0.18 | 0.44 ± 0.19 | 0.59 ± 0.19 |
| Fe | 44 | 0.12 ± 0.04 | 0.28 ± 0.08 | 0.15 ± 0.04 | 0.34 ± 0.16 | 0.61 ± 0.17 | 0.76 ± 0.18 |
| Al | 21 | 0.10 ± 0.04 | 0.27 ± 0.08 | 0.15 ± 0.06 | 0.38 ± 0.20 | 0.63 ± 0.21 | 0.80 ± 0.22 |
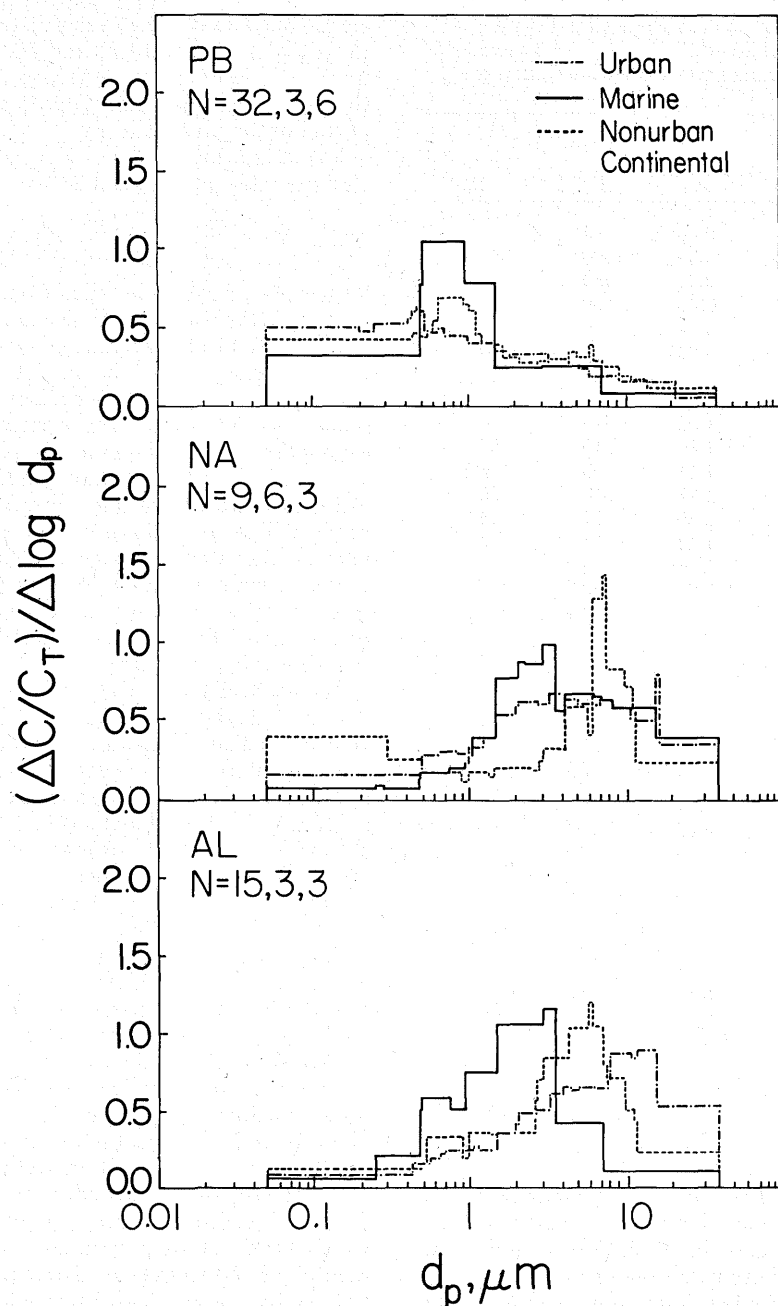
**Figure. 2.** Mass size distributions for Pb, Na and Al averaged according to sampling site category. The number of distributions averaged in the urban, marine, and nonurban continental categories, respectively, is indicated.

peak in the range of 0.5–1 $\mu$m and a smaller peak at 3–5 $\mu$m. Elements with larger mass median diameter generally have a single peak, with relatively little mass below 1 $\mu$m.

Some of the elements show surprising uniformity among the original distributions; Pb, with emissions on a global scale dominated by anthropogenic combustion activities, is the most notable example. Elements influenced by a multiplicity of source categories show greater variability.

As an example of the utility of the size distributions, the data for several elements which are potentially toxic have been used to estimate fractional deposition in the human respiratory system. In addition, velocities of dry deposition onto a wild grass canopy have been calculated for all of the elements. The results indicate that fractional deposition in the pulmonary compartment of the lung is nearly identical for a wide variety of trace elements, although deposition in the tracheobronchial and extrathoracic compartments is greater for elements with larger mass median diameter. Velocities of dry deposition onto the grass canopy are also greater for elements with larger mass median diameter. It is important to note, however, that the actual distributions of the mass of the elements, as well as their MMDs, affect the calculations of deposition fractions in the respiratory tract and the calculations of dry deposition velocities.

### Acknowledgments

$s^{-1}$ respectively for Al. These values illustrate the dependence of estimated deposition velocities on the choice of model, as well as on characteristics of the size distribution used as input data.

### Summary

Particle size distributions for 38 trace elements reported in the literature have been reviewed. Represented in this collection of data are the results of field sampling programs conducted in urban, rural, and remote areas.

Previous research has shown that volatile elements, which have anthropogenic and natural combustion processes as predominant sources, are generally associated with submicron particles. Less volatile elements are associated with larger particles, produced by soil erosion, dispersion of sea salt, and other mechanical processes. The average size distribution data reported here are consistent with these findings: elements with small mass median diameters have greater mobilization factors and crustal enrichment factors than elements associated primarily with larger particles.

Many of the elements with mass median diameter less than 2 $\mu$m have bimodal distributions, with a dominant

### References

1. R. E. Lee, Jr., D. J. von Lehmden, "Trace metal pollution in the environment," *JAPCA* **23**: 853 (1973).
2. K. A. Rahn, "The Chemical Composition of the Atmospheric Aerosol," technical report, Graduate School of Oceanography, University of Rhode Island, 1976.
3. C. I. Davidson, "The deposition of trace metal-containing particles in the Los Angeles area," *Powder Technol.* **18**: 117 (1977)
4. J. B. Wedding, A. R. McFarland, J. E. Cermak, "Large particle collection characteristics of ambient aerosol samplers," *Environ. Sci. Technol.* **11**: 387 (1977).
5. J. J. Wesolowski, A. E. Alcocer, B. R. Appel, "The Validation of the Lund-
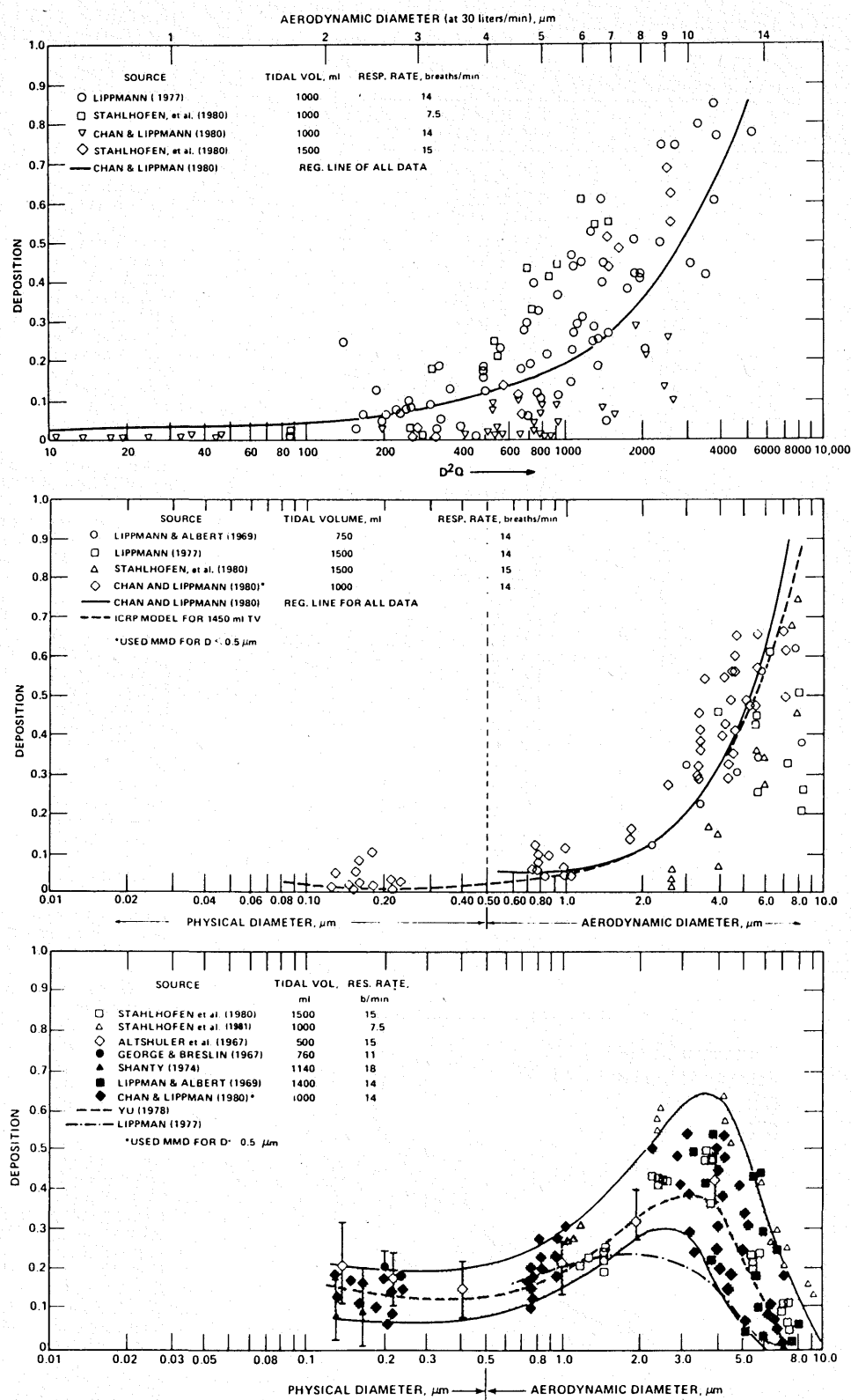
**Figure. 3.** Deposition of monodisperse aerosols in the (a) extrathoracic, (b) tracheobronchial and (c) pulmonary regions of the human respiratory tract. The scale on the abscissa in Figure 3(a) is $D^2Q$, where D is particle diameter in $\mu$m and Q is average inspiratory flow rate in liters/min. All of the curves pertain to mouth breathing except the dash-dot line in Figure 3(c), which was derived for nose breathing[115-121] (from U.S. EPA[42]).

gren Impactor," in *The Character and Origins of Smog Aerosols*, Advances in Environmental Science and Technology, v. 9, John Wiley and Sons, New York, 1980, pp. 125–145.

6. B. Y. H. Liu, D. Y. H. Pui, "Aerosol sampling inlets and inhalable particles," *Atmos. Environ.* **15:** 589 (1981).

7. A. R. McFarland, J. T. Wedding, J. E. Cermak, "Wind tunnel evaluation of a modified Andersen impactor and an all weather sampler inlet," *Atmos. Environ.* **11:** 535 (1977).

8. K. M. Cushing, J. D. McCain, W. B. Smith, "Experimental determination of sizing parameters and wall losses of five source-test cascade impactors," *Environ. Sci. Technol.* **13:** 726 (1979).

9. L. G. Felix, J. D. McCain, "Errors in Recovered Particle Size Distributions Caused by Impactor Sampling with Bent Nozzles," paper 81-7.4, 74th Annual Meeting, Air Pollution Control Association, Philadelphia, PA, June 1981.

10. T. L. Chan, D. R. Lawson, "Characteristics of cascade impactors in size de-

**Table IV.** Dry deposition velocity for a field of *Dactylus glomerata* (L), based on the size distributions of Figure 1 and the appropriate deposition curve in Figure 4. Values shown are arithmetic averages and standard deviations.

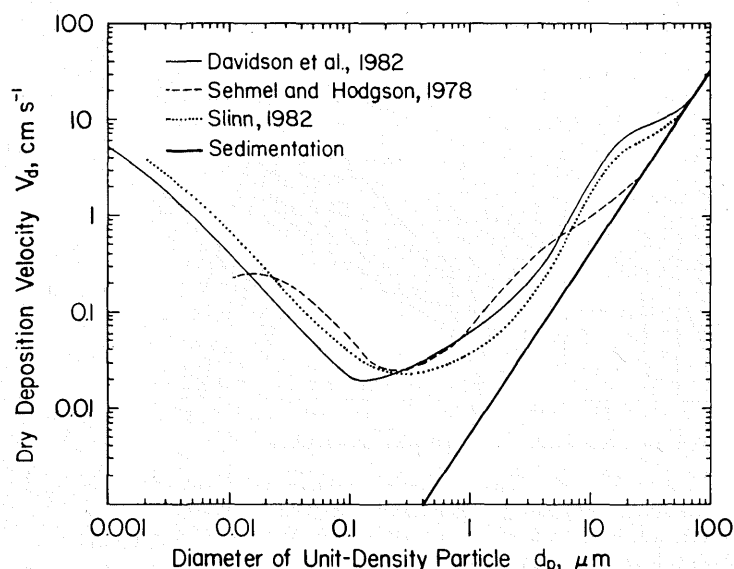| Element | $N$ | Dry deposition velocity (cm/s) |
|---------|-----|-------------------------------|
| W  | 2  | 1.5 ± 1.6 |
| Pb | 41 | 0.57 ± 0.46 |
| Hg | 5  | 0.64 ± 0.56 |
| Se | 8  | 0.48 ± 0.31 |
| Cd | 17 | 1.0 ± 0.9 |
| Sb | 12 | 0.81 ± 0.71 |
| Br | 21 | 0.88 ± 1.0 |
| Ni | 11 | 0.66 ± 0.53 |
| I  | 6  | 1.0 ± 0.5 |
| As | 10 | 1.2 ± 1.1 |
| Cr | 10 | 1.1 ± 0.78 |
| Zn | 39 | 1.0 ± 1.1 |
| Cu | 25 | 0.98 ± 0.80 |
| V  | 15 | 1.4 ± 1.3 |
| U  | 2  | 1.6 ± 1.0 |
| In | 4  | 1.2 ± 0.5 |
| Ta | 3  | 1.6 ± 1.0 |
| Cs | 4  | 1.0 ± 0.6 |
| Mn | 32 | 1.3 ± 0.9 |
| Eu | 2  | 0.98 ± 0.70 |
| Co | 9  | 1.7 ± 1.1 |
| Th | 5  | 1.7 ± 2.0 |
| Sm | 2  | 1.4 ± 0.3 |
| Cl | 21 | 1.8 ± 1.0 |
| Ba | 5  | 1.7 ± 0.9 |
| Fe | 44 | 1.8 ± 1.1 |
| K  | 24 | 2.0 ± 1.2 |
| Na | 18 | 2.0 ± 1.3 |
| Si | 7  | 2.0 ± 0.8 |
| Sc | 9  | 2.3 ± 1.6 |
| Al | 21 | 2.4 ± 1.4 |
| Ca | 20 | 2.2 ± 1.0 |
| Ce | 4  | 2.8 ± 2.3 |
| Ga | 2  | 2.8 ± 0.8 |
| Mg | 8  | 2.5 ± 1.5 |
| Ti | 6  | 2.8 ± 1.4 |
| Hf | 4  | 3.4 ± 2.6 |
| Sr | 2  | 4.4 ± 1.3 |



**Figure. 4.** Calculated dry deposition velocity as a function of particle diameter for several models. The solid curve represents a model of dry deposition to a canopy of *Dactylus glomerata* (L), (canopy height = 57 cm, friction velocity = 64 cm s$^{-1}$, roughness height = 5 cm, and zero plane displacement height = 14 cm.)[61] The dashed curve represents the model of Sehmel and Hodgson[62] based on wind tunnel data (friction velocity = 30 cm s$^{-1}$, roughness height = 3 cm). The deposition velocity curve of Slinn,[63] based on calculations for a Eucalyptus forest (canopy height = 27.4 m, friction velocity = 75 cm s$^{-1}$, roughness height = 1.86 m, zero plane displacement = 21.6 m) is shown as the dotted curve. The relationship between sedimentation velocity and particle diameter for unit-density particles is also shown.

termination of diesel particles," *Atmos. Environ.* **15:** 1237 (1981).

11. T. G. Dzubay, L. E. Hines, R. K. Stevens, "Particle bounce errors in cascade impactors," *Atmos. Environ.* **10:** 229 (1976).

12. D. R. Lawson, "Impaction surface coatings intercomparison and measurements with cascade impactors," *Atmos. Environ.* **14:** 195 (1980).

13. P. R. Walsh, K. A. Rahn, R. A. Duce, "Erroneous elemental mass-size functions from a high-volume cascade impactor," *Atmos. Environ.* **12:** 1793 (1978).

14. V. A. Marple, B. Y. H. Liu, "Characteristics of laminar jet impactors," *Environ. Sci. Technol.* **8:** 648 (1974).

15. V. A. Marple, B. Y. H. Liu, K. T. Whitby, "Fluid mechanics of the laminar flow aerosol impactor," *J. Aerosol Sci.* **5:** 1 (1974).

16. C. C. Patterson, D. Settle, "The Reduction of Orders of Magnitude Errors in Lead Analyses of Biological Materials and Natural Waters by Evaluating and Controlling the Extent and Sources of Industrial Lead Contamination Introduced During Sample Collecting, Handling, and Analysis," in *Accuracy in Trace Analysis: Sampling, Sample Handling, and Analysis*, Proceedings of the 7th IMR Symposium, Oct. 1974, Gaithersburg, MD, National Bureau of Standards Special Publication 422, 1976, pp. 321–351.

17. A. Ng, C. Patterson, "Natural concentrations of lead in ancient Arctic and Antarctic ice," *Geochim. Cosmochim. Acta* **45:** 2109 (1981).

18. C. F. Boutron, C. C. Patterson, "The occurrence of lead in Antarctic recent snow, firn deposited over the last two centuries and prehistoric ice," *Geochim. Cosmochim. Acta* **47:** 1355 (1983).

19. E. J. Hoffman, G. L. Hoffman, R. A. Duce, "Contamination of Atmospheric Particulate Matter Collected at Remote Shipboard and Island Locations," in *Accuracy in Trace Analysis: Sampling, Sample Handling, and Analysis*, Proceedings of the 7th IMR Symposium, Oct. 1974, Gaithersburg, MD, National Bureau of Standards Special Publication 422, 1976, pp. 377–388.

20. M. Thompson, S. J. Walton, S. J. Wood, "Statistical appraisal of interference effects in the determination of trace elements by atomic-absorption spectrophotometry in applied geochemistry," *Analyst* **104:** 299 (1979).

21. G. J. Waughman, T. Brett, "Interference due to major elements during the estimation of trace heavy metals in natural materials by atomic absorption spectrophotometry," *Environ. Res.* **21:** 385 (1980).

22. W. H. Zoller, G. E. Gordon, "Instrumental neutron activation analysis of atmospheric pollutants utilizing Ge(le) γ-Ray detectors," *Anal. Chem.* **42:** 257 (1970).

23. T. G. Dzubay, R. K. Stevens, "Applications of X-Ray flourescence to particulate measurements," Second Joint Conference on Sensing of Environmental Pollutants, Instrument Society of America, Washington D.C., 1973.

24. T. B. Johansson, R. E. Van Grieken, J. W. Nelson, J. W. Winchester, "Elemental trace analysis of small samples by proton induced X-Ray emission," *Anal. Chem.* **47:** 855 (1975).

25. G. M. Hidy, "Characterization of Aerosols in California," final report, Air Resources Board Contract No. 358, Science Center, Rockwell International, 1974.

26. D. B. Johnson, "Ultragiant urban aerosol particles," *Science* **194**: 941 (1976).

27. D. F. S. Natusch, J. R. Wallace, "Determination of airborne particle size distributions: calculation of cross-sensitivity and discreteness effects in cascade impaction," *Atmos. Environ.* **10**: 315 (1976).

28. N. A. Esmen, "An Iterative Impactor Data Analysis Method," 51st Colloid and Interface Science Symposium, American Chemical Society, New York, NY, 1977.

29. O. G. Raabe, "A general method for fitting size distributions to multicomponent aerosol data using weighted least-squares," *Environ. Sci. Technol.* **12**: 1162 (1978).

30. D. A. Lundgren, "Determination of particulate composition, concentration and size distribution changes with time," *Atmos. Environ.* **5**: 645 (1971).

31. R. E. Lee, Jr., "The size of suspended particulate matter in air," *Science* **178**: 567 (1972).

32. K. T. Whitby, R. B. Husar, B. Y. H. Liu, "The aerosol size distribution of Los Angeles smog," *J. Colloid Interface Sci.* **39**: 177 (1972).

33. S. Kadowaki, "Size distribution of atmospheric total aerosols, sulfate, ammonium and nitrate particulates in the Nagoya area," *Atmos. Environ.* **10**: 39 (1976).

34. M. W. Wadley, S. Witz, W. Bope, R. D. MacPhee, "Size distribution measurements of particulate matter in Los Angeles and Anaheim using high-volume Andersen samplers," *JAPCA* **28**: 364 (1978).

35. R. L. Davison, D. F. S. Natusch, J. R. Wallace, C. A. Evans, Jr., "Trace elements in fly ash. Dependence of concentration on particle size," *Environ. Sci. Technol.* **8**: 1107 (1974).

36. R. E. Lee, Jr., H. L. Crist, A. E. Riley, K. E. McLeod, "Concentration and size of trace metal emissions from a power plant, a steel plant and a cotton gin," *Environ. Sci. Technol.* **9**: 643 (1975).

37. W. H. Zoller, E. S. Gladney, R. A. Duce, "Atmospheric concentrations and sources of trace metals at the South Pole," *Science* **183**: 198 (1974).

38. R. A. Duce, G. L. Hoffman, W. H. Zoller, "Atmospheric trace metals at remote northern and southern hemisphere sites: pollution or natural?" *Science* **187**: 59 (1975).

39. E. Patterson, D. Gillette, "Commonalities in measured size distributions for aerosols having a soil-derived component," *J. Geophys. Res.* **82**: 2074 (1977).

40. F. MacIntyre, "The top millimeter of the ocean," *Sci. Am.* **230**: 62 (1974).

41. R. A. Duce, G. L. Hoffman, B. J. Ray, I. S. Fletcher, G. T. Wallace, J. L. Fasching, S. R. Piotrowicz, P. R. Walsh, E. J. Hoffman, J. M. Miller, J. L. Heffter, "Trace Metals in the Marine Atmosphere: Sources and Fluxes," in H. L. Windom, R. A. Duce, eds., *Marine Pollutant Transfer*, D. C. Heath, Lexington, MA, 1976, pp. 77–119.

42. "Air Quality Criteria for Particulate Matter and Sulfur Oxides," v. II, p. 4-7 and v. III, pp. 11-22, 11-24, and 11-28, EPA 600/8-82-029a, U.S. Environmental Protection Agency, 1982.

43. J. N. Galloway, J. D. Thornton, S. A. Norton, H. L. Volchok, R. A. McLean, "Trace metals in atmospheric deposition: a review and assessment," *Atmos. Environ.* **16**: 1677 (1982).

44. J. O. Nriagu, "Lead in the Atmosphere," in J. O. Nriagu, ed., *The Biogeochemistry of Lead in the Environment*, v. 1, Elsevier, Amsterdam, 1978, pp. 137–183.

45. C. C. Patterson, "An Alternative Perspective—Lead Pollution in the Human Environment: Origin, Extent, and Significance," in *Lead in the Human Environment*, National Academy of Sciences, National Academy Press, Washington, D.C., 1980, pp. 265–349.

46. "Air Quality Criteria for Lead," v. II, external review draft, EPA 600/8-83-028B, U.S. Environmental Protection Agency, 1984, pp. 5-10,11.

47. R. Faoro, T. McMullen, "National Trends in Trace Metals in Ambient Air, 1965–1974," EPA450/1-17-003, U.S. Environmental Protection Agency, 1977.

48. J. A. Schmidt, A. W. Andren, "The Atmospheric Chemistry of Nickel," in J. O. Nriagu, ed., *Nickel in the Environment*, Wiley, New York, NY, 1980, pp. 93–135.

49. W. H. Zoller, G. E. Gordon, E. S. Gladney, A. G. Jones, "The Sources and Distribution of Vanadium in the Atmosphere," in *Trace Elements in the Environment*, Advances in Chemistry Series, American Chemical Society, 1973.

50. R. A. Duce, R. Arimoto, B. J. Ray, C. K. Unni, P. J. Harder, "Atmospheric trace elements at Enewetak Atoll: 1. Concentrations, sources, and temporal variability," *J. Geophys. Res.* **88**: 5321 (1983).

51. C. I. Davidson, J. F. Osborn, "The Sizes of Airborne Trace Metal-Containing Particles," in J. O. Nriagu, C. I. Davidson, eds., *Toxic Metals in the Atmosphere*, Wiley, New York, NY, 1986, in press.

52. M. Lippmann, "Regional Deposition of Particles in the Human Respiratory Tract," in D. H. K. Lee, H. L. Falk, S. D. Murphy, eds., *Handbook of Physiology*, Section 9: Reactions to Environmental Agents, American Physiological Society, Bethesda, MD, 1977.

53. T. L. Chan, M. Lippmann, "Experimental measurements and empirical modeling of the regional deposition of inhaled particles in humans," *Am. Ind. Hyg. Assoc. J.* **41**: 399 (1980).

54. W. Stahlhofen, J. Gebhart, J. Heyder, "Experimental determination of the regional deposition of aerosol particles in the human respiratory tract," *Am. Ind. Hyg. Assoc. J.* **41**: 385 (1980).

55. D. Purves, *Trace Element Contamination of the Environment*, Elsevier Scientific Publishing Co., Amsterdam, 1977.

56. F. J. Macciolli, T. H. Risby, *Determination of Toxic Metals and Metalloids in Ambient Air*, The Pennsylvania State University Press, University Park, PA 1978.

57. H. A. Waldron, ed., *Metals in the Environment*, Academic Press, London, 1980.

58. R. Harkov, "Toxic air pollutants—assessing their importance," *Sci. Total Environ.* **26**: 67 (1982).

59. D. F. S. Natusch, J. R. Wallace, "Urban aerosol toxicity: the influence of particle size," *Science* **186**: 695 (1974).

60. Task Group on Lung Dynamics, "Deposition and retention models for internal dosimetry of the human respiratory tract," *Health Physics* **12**: 173 (1966).

61. C. I. Davidson, J. M. Miller, M. A. Pleskow, "The influence of surface structure on predicted particle dry deposition to natural grass canopies," *Water, Air, Soil Pollut.* **18**: 25 (1982).

62. G. A. Sehmel, W. H. Hodgson, "A Model for Predicting Dry Deposition of Particles and Gases to Environmental Surfaces," Battelle Pacific Northwest Labs., Report PNL-SA-6721, 1978.

63. W. G. N. Slinn, "Predictions for particle deposition to vegetative canopies," *Atmos. Environ.* **16**: 1785 (1982).

64. M. O. Andreae, "Marine aerosol chemistry at Cape Grim, Tasmania, and Townsville, Queensland," *J. Geophys. Res.* **87**: 8857 (1982).

65. B. R. Appel, J. J. Wesolowski, A. Alcocer, S. Wall, S. Twiss, R. Giauque, R. Ragaini, R. Ralston, "Quality Assurance for the Chemistry of the Aerosol Characterization Experiment," in *The Character and Origins of Smog Aerosols*, Advances in Environmental Science and Technology, v. 9, John Wiley and Sons, New York, 1980, pp. 69–105.

66. W. W. Berg, J. W. Winchester, "Organic and inorganic gaseous chloride concentrations in relation to the particle size distribution of chloride in the marine aerosol," *J. Geophys. Res.* **82**: 5945 (1977).

67. D. M. Bernstein, K. A. Rahn, "N.Y. summer aerosol study: trace element concentration as a function of particle size," *Ann. N.Y. Acad. Sci.* **322**: 87 (1979).

68. L. C. S. Boueres, R. K. Patterson, "Aerosol emissions near a coal gasification plant in the Kosovo region, Yugoslavia," *Nuclear Instru. and Meth.* **181**: 353 (1981).

69. E. Caruso, G. M. Braga Marcazzan, P. Redealli, "PIXE investigation of element concentration and particle size distribution in Milan atmospheric aerosol," *Nuclear Instru. and Meth.* **181**: 425 (1981).

70. P. A. Cawse, "A Survey of Atmospheric Trace Elements in the U.K.," Report AERE-R7669, United Kingdom Atomic Energy Authority, Harwell, Oxfordshire, 1974.

71. J. Cholak, L. J. Schafer, D. Yeager, "The air transport of lead compounds present in automobile exhaust gases," *Am. Ind. Hyg. Assoc. J.* **29**: 562 (1968).

72. E. A. Crecelius, E. A. Lepel, J. C. Laul, L. A. Rancitelli, R. L. McKeever, "Background air particulate chemistry near Colstrip, Montana," *Environ. Sci. Technol.* **14**: 422 (1980).

73. R. H. Daines, H. Motto, D. M. Chilko, "Atmospheric lead: its relationship to traffic volume and proximity to highways," *Environ. Sci. Technol.* **4**: 318 (1970).

74. C. I. Davidson, W. D. Goold, M. A. Nasta, M. T. Reilly, "Airborne Size Distributions in an Industrial Section of Pittsburgh," paper 81-28.6, 74th Annual Meeting, Air Pollution Control Association, Philadelphia, PA, June 1981.

75. C. I. Davidson, T. C. Grimm, M. A. Nasta, "Airborne lead and other elements derived from local fires in the Himalayas," *Science* **214**: 1344 (1981).

76. C. I. Davidson, W. D. Goold, G. B. Wiersma, "Sources and Sinks of Airborne Trace Metals in the Olympic National Park Biosphere Reserve," Final Report to the U.S. Environmental Protection Agency, Contracts No. V-1441-NAEX and V-4196-NAET, Carnegie-Mellon University, Pittsburgh, PA, 1983.

77. C. I. Davidson, W. D. Goold, T. P. Mathison, G. B. Wiersma, K. W. Brown, M. T. Reilly, "Airborne trace elements in Great Smoky Mountains, Olympic and Glacier National Parks," *Environ. Sci. Technol.* **19**: 27 (1985).

78. R. A. Duce, B. J. Ray, G. L. Hoffman, P. R. Walsh, "Trace metal concentration as a function of particle size in marine aerosols from Bermuda," *Geophys. Res. Lett.* **3**: 339 (1976).

79. D. A. Gillete, J. W. Winchester, "A

study of the aging of lead aerosols - 1. Observations," *Atmos. Environ.* **6:** 443 (1972).

80. K. A. Hardy, R. Akselsson, J. W. Nelson, J. W. Winchester, "Elemental constituents of Miami aerosol as a function of particle size," *Environ. Sci. Technol.* **10:** 176 (1976).

81. P. R. Harrison, W. R. Matson, J. W. Winchester, "Time variations of lead, copper and cadmium concentrations in aerosols in Ann Arbor, Michigan," *Atmos. Environ.* **5:** 613 (1971).

82. R. M. Harrison, C. R. Williams, "Airborne cadmium, lead and zinc at rural and urban sites in north-west England," **16:** 2669 (1982).

83. R. Heindryckx, "Comparison of the mass-size functions of the elements in the aerosols of the Gent industrial district with data for other areas. Some physicochemical implications," *Atmos. Environ.* **10:** 65 (1976).

84. J. J. Huntzicker, S. K. Friedlander, C. I. Davidson, "Material balance for automobile-emitted lead in Los Angeles basin," *Environ. Sci. Technol.* **9:** 448 (1975).

85. S. Kadowaki, "Silicon and aluminum in urban aerosols for characterization of atmospheric soil particles in the Nagoya area," *Environ. Sci. Technol.* **13:** 1130 (1979).

86. R. N. Khandekar, D. N. Kelkar, K. G. Vohra, "Lead, cadmium, zinc, copper and iron in the atmosphere of greater Bombay," *Atmos. Environ.* **14:** 457 (1980).

87. D. R. Lawson, J. W. Winchester, "Sulfur crustal reference elements in nonurban aerosols from Squaw Mountain, Colorado," *Environ. Sci. Technol.* **12:** 716 (1978).

88. D. R. Lawson, J. W. Winchester, "Sulfur, potassium and phosphorus associations in aerosols from South American tropical rain forests," *J. Geophys. Res.* **84:** 3723 (1979).

89. R. E. Lee, Jr., R. K. Patterson, J. Wagman, "Particle-size distribution of metal components in urban air," *Environ. Sci. Technol.* **2:** 288 (1968).

90. R. E. Lee, Jr., R. K. Patterson, "Size determination of atmospheric phosphate, nitrate, chloride, and ammonium particulate in several urban areas," *Atmos. Environ.* **3:** 249 (1969).

91. R. E. Lee, Jr., S. S. Goranson, R. E. Enrione, G. B. Morgan, "National Air Surveillance Cascade Impactor Network. II: Size distribution measurements of trace metal components," *Environ. Sci. Technol.* **6:** 1025 (1972).

92. S. E. Lindberg, R. C. Harriss, "Water and acid soluble trace metals in atmospheric particles," *J. Geophys. Res.* **88:** 5091 (1983).

93. D. A. Lundgren, "Atmospheric aerosol composition and concentration as a function of particle size and of time," *JAPCA* **20:** 603 (1970).

94. C. McDonald, H. J. Duncan, "Particle size distribution of metals in the atmosphere of Glasgow, *Atmos. Environ.* **13:** 977 (1979).

95. W. Maenhaut, H. Raemdonck, A. Selen, R. van Grieken, J. W. Winchester, "Characterization of the atmospheric aerosol over the eastern equatorial Pacific," *J. Geophys. Res.* **88:** 5353 (1983).

96. C. S. Martens, J. J. Wesolowski, R. Kaifer, W. John, "Lead and bromine particle size distributions in the San Francisco Bay area," *Atmos. Environ.* **7:** 905 (1973).

97. D. L. Meinert, J. W. Winchester, "Chemical relationships in the North Atlantic marine aerosol," *J. Geophys. Res.* **82:** 1778 (1977).

98. G. D. Nifong, E. A. Boettner, J. W. Winchester, "Particle size distributions of trace elements in pollution aerosols," *Am. Ind. Hyg. Assoc. J.* **33:** 569 (1972).

99. C. Q. Orsini, H. C. Kaufmann, K. R. Akselsson, J. W. Winchester, J. W. Nelson, "Variation of elemental composition with particle size in the St. Louis aerosol," *Nuclear Instru. and Meth.* **142:** 91 (1977).

100. C. Q. Orsini, P. A. Netto, M. G. Tabacniks, "Preliminary data on atmospheric aerosol of the Amazon basin," *Atmos. Environ.* **16:** 2177 (1982).

101. J. J. Paciga, R. E. Jervis, "Multielement size characterization of urban aerosols," *Environ. Sci. Technol.* **10:** 1124 (1976).

102. J. M. Pacyna, V. Vitols, J. E. Hanssen, "Size-differentiated composition of the Arctic aerosol at Ny-Alesund, Spitsbergen," *Atmos. Environ.* **18:** 2447 (1984).

103. N. J. Pattenden, "Atmospheric Concentrations and Deposition Rates of Some Trace Elements Measured in the Swansea/Neath/Port Talbot Area," Report AERE-R7729, United Kingdom Atomic Energy Authority, Harwell, Oxfordshire, 1974.

104. R. K. Patterson, J. Wagman, "Mass and composition of an urban aerosol as a function of particle size for several visibility levels," *J. Aerosol Sci.* **8:** 269 (1977).

105. M. E. Peden, "Flameless Atomic Absorption Determinations of Cadmium, Lead and Manganese in Particle Size Fractionated Aerosols," in *Methods and Standards for Environmental Measurement*, Proceedings of the 8th IMR Symposium, Sept. 1976, Gaithersburg, MD, National Bureau of Standards Special Publication 464, 1977, pp. 367-377.

106. R. C. Ragaini, H. R. Ralston, D. Garvis, R. Kaifer, "Instrumental Neutron Activation Analysis Techniques for Measuring Trace Elements in California Aerosols," in *The Character and Origins of Smog Aerosols*, Advances in Environmental Science and Technology, v. 9, John Wiley and Sons, New York, 1980, pp. 169-196.

107. S. Sadisivan, "Trace elements in size separated aerosols over sea," *Atmos. Environ.* **12:** 1677 (1978).

108. S. Sadisivan, "Trace elements in size separated atmospheric pariculates at Trombay, Bombay, India," *Sci. Total Environ.* **20:** 109 (1981).

109. D. L. Savoie, J. M. Prospero, "Particle size distribution of nitrate and sulfate in the marine atmosphere," *Geophys. Res. Lett.* **9:** 1207 (1982).

110. S. Tanaka, M. Darzi, J. W. Winchester, "Short term effect of rainfall on elemental composition and size distribution of aerosols in north Florida," *Atmos. Environ.* **14:** 1421 (1980).

111. U.S. Environmental Protection Agency (1973, 1974) computer printouts of data supplied by G. G. Akland, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC.

112. L. E. Wangen, "Elemental composition of size-fractionated aerosols associated with a coal-fired power plant plume and background," *Environ. Sci. Technol.* **15:** 1080 (1981).

113. J. W. Winchester, R. J. Ferek, D. R. Lawson, J. O. Pilotte, M. H. Thiemens, L. E. Wangen, "Comparison of aerosol sulfur and crustal element concentrations in particle size fractions for continental U.S. locations," *Water, Air, Soil Pollut.* **12:** 431 (1979).

114. J. W. Winchester, M. Wang, L. Ren, W. Lu, H. C. Hansson, H. Lannefors, M. Darzi, A.C.D. Leslie, "Nonurban aerosol composition near Beijing, China," *Nuclear Instru. and Meth.* **181:** 391 (1981).

115. M. Lippmann, R. Albert, "The effect of particle size on the regional deposition of inhaled aerosols in the human respiratory tract," *Am. Ind. Hyg. Assoc. J.* **30:** 257 (1969).

116. International Commission on Radiological Protection, *Report of the Task Group on Reference Man*, Pergamon Press, Oxford, England, 1975.

117. W. Stahlhofen, J. Gebhart, J. Heyden, "Biological variability of regional deposition of aerosol particles in the human respiratory tract," *Am. Ind. Hyg. Assoc. J.* **42:** 348 (1981).

118. B. Altshuler, E. D. Palmes, N. Nelson, "Regional Aerosol Deposition in the Human Respiratory Tract," in C. N. Davies, ed., *Inhaled Particles and Vapours II*, Pergamon Press, Oxford, England, 1967, p. 323.

119. A. C. George, A. J. Breslin, "Deposition of natural radon daughters in human subjects," *Health Phys.* **13:** 345 (1967).

120. F. Shanty, "Deposition of Ultrafine Aerosols in the Respiratory Tract of Human Volunteers," Ph.D. thesis, The Johns Hopkins University, Baltimore, MD, 1974.

121. C. P. Yu, "A two component theory of aerosol deposition in human lung airways," *Bull. Math. Biol.* **40:** 693 (1978).

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