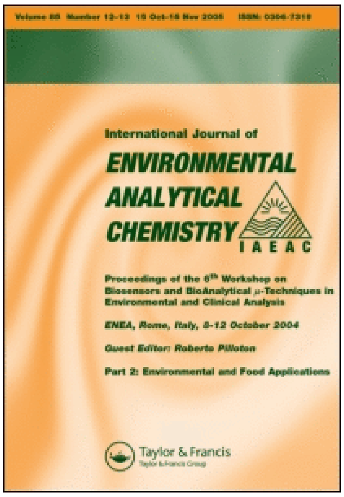

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Particle Size Determination of Trace Elements in Urban Air†

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KEY WORDS: Particle size distribution, trace metals in air, atomic absorption, anodic stripping voltammetry

Airborne urban particulate matter was collected and fractionated according to size by cascade impactors. The elements zinc, cadmium, copper and lead on each size fraction were analyzed by anodic stripping voltammetry. The elements aluminum, iron, manganese, calcium and magnesium were analyzed by atomic absorption spectrophotometry. The data showed three different classes of particle size distribution for these nine elements. Lead and cadmium belonged to the first class with more than 70% of the total collected element associated with particles having aerodynamic diameters below 0.5 micron. The calculated average mass median equivalent diameter (MMD) of cadmium and lead was approx. 0.1 micron. In the second class about 60% of the elements Zn, Cu, Mg and Fe was associated with particles smaller than 0.5 micron. The average MMD's for these elements were between 0.3 and 0.4 micron. For the elements Al, Ca and Mn about 50% of the metal was associated with particles smaller than 0.5 micron and the MMD's were between 0.5 and 0.6 micron. Examination of elemental ratios (using Al as a reference element) showed that Pb and Cd were about 1000 times more concentrated in atmospheric particulate matter than in average crustal material and that in general the Pb/Al and Cd/Al ratios are inversely proportional to particle size. The Zn/Al and Cu/Al ratios of atmospheric particles were more or less independent of particle size and approx. 20 times higher than these same ratios in average crustal material. The ratios Fe/Al, Mn/Al, Ca/Al and Mg/Al in all sizes of particulate matter were essentially identical to the same ratios in average crustal material.

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INTRODUCTION

In recent years, increasing attention has been paid not only to the atmospheric concentration of various constituents but also to the particle size distribution of materials in the atmosphere. Different sized atmospheric particles can play drastically different roles in factors such as visibility reduction,[1] lung penetration and retention,[2] and weather initiating processes.[3] Recent data from a number of investigators have described the chemical composition of atmospheric particulate matter as a function of particle size in a number of urban, near-urban and clean atmospheres.[4-15] From these data it is quite evident that the concentration of elements and compounds in atmospheric particulate matter can change drastically with changing particle size. Certainly data such as these can be important in understanding the chemical composition of the atmosphere and the effect of various atmospheric components on health, visibility and meterological processes. Additionally, the chemical composition of particulate matter as a function of particle size could be an important method of identifying sources and sinks of various atmospheric constituents.

Previous work in this laboratory with high-volume particulate samples had indicated that various trace metals in atmospheric particulate matter may have different types of sources. The atmospheric concentration of the elements Pb, Cd, Zn and Cu were found to be higher than would be predicted if these elements had as a source the weathering of crustal material. On the other hand, the atmospheric concentrations of the elements Ca, Al, Fe, Mg and Mn appeared from elemental ratios to have a source of continental origin. This work was designed to obtain particle size distributions of these nine elements in the local atmosphere and to determine if particle size data would provide a useful means of source identification and the chemical "fingerprinting" of sources.

SAMPLING AND ANALYSIS PROCEDURE

Samples of particulate matter were collected according to size with a six-stage cascade impactor (CI-6, Sciotech Corporation, Columbus, Ohio). The sampling equipment was located on the roof (~10 m above the ground) of the Biological Sciences Building on the University of Arizona campus in Tucson, Arizona. The impactor used for this work permitted the collection of particles in seven different size ranges. The first stage of the impactor collects 16 micron diameter particles of unit density with an efficiency of 50%. The diameter of particles which are collected with 50% efficiency (D_{50}) decreases by a factor of 2 on each succeeding stage. Thus D_{50} for stages 2, 3, 4, 5, and 6 is 8, 4, 2, 1, and 0.5 micron, respectively, for spherical particles of unit density. In addition to the six collection stages, a back-up filter (Type EH, Millipore Filter Corporation, Bedford, Mass.) which collects all particles smaller than

0.5 micron was placed after the last impactor stage. Details about the impactor used in the work and collection efficiencies of these impactors are given elsewhere.[10,16] The normal method of collecting samples with the impactor used in this work is to impact the particles on glass slides. However, a slight modification of this collection procedure was used in this investigation. Samples were collected on Millipore filters (Type EA 03700 WP) which were placed on the glass collecting slides. The filters were used for two reasons. First, the filters provided a means of quantitatively transferring and dissolving the collected sample. Second, the filters were used to minimize bounce off of particles, which may be significant for samples collected from air of very low relative humidity.[17,18] Use of the filters does have the disadvantage of increasing the analytical blanks.

A procedure using the combination of atomic absorption spectrophotometry and anodic stripping voltammetry (ASV) was developed for the analysis of nine elements (Pb, Cd, Zn, Cu, Ca, Fe, Mg, Mn and Al) in size separated particles. ASV was used since the elements Pb and Cd were not sufficiently concentrated in the larger particles to permit analysis by conventional atomic absorption spectrophotometry. After collection of a sample, the Millipore filter and sample were placed in a Teflon cup and treated with 0.1 ml of 0.1 M K_2SO_4. (K_2SO_4 is used to facilitate sample ashing[19] and to act as an ionization buffer for the AA analysis.) The organic filter was destroyed with a low-temperature plasma asher (LTA-5, Trapelo Corporation, Waltham, Mass.). After ashing, 2 ml of 1:1 HF-HNO_3 was added to the cup and the cup was then sealed in a Teflon acid digestion bomb (PARR Instrument Company, Moline, Ill.) and heated to 120°C for 1 hr. This procedure permitted complete dissolution of the sample. The obtained sample was evaporated to dryness and the residue was dissolved in 5 ml of 2N HNO_3. To 1 ml of this solution 1 ml of 2,000 ppm La^{+3} was added and the elements Al, Fe, Mg, Ca and Mn were determined by conventional atomic absorption spectrophotometry using a Varian AA-5 atomic absorption spectrophotometer (Varian Techtron, Downey, Calif.). The remaining sample was evaporated to dryness and dissolved in 15 ml of 0.1 M KNO_3 for the determination of Pb, Cd, Zn and Cu by ASV. Cu and Zn were analyzed by ASV since these elements could be determined simultaneously with the lead and cadmium. The ASV was performed with a hanging drop mercury electrode and a PAR Model 174 Polarographic Analyzer (Princeton Applied Research Corp., Princeton, N.J.). Details of the ASV procedure are given elsewhere.[19] A flow chart of the analytical procedure is presented in Figure 1. Total blanks (filter-reagent) were determined using the same procedure It was found that the filter blanks for each element showed relatively large variability (i e., the standard deviation of the blank approximated the average of 12 determinations) It was, therefore, necessary to analyze a large number of blank filters (12) and subtract the average blank for each element from the metal concentration measured on the particle size samples. Thus, the analytical uncertainties for each sample result primarily from the uncertainty of the blank correction. For the largest particles (i.e., stages 1 and 2) the uncertainty of the blank correction was generally greater than 10% and as much as 30% of the weight of metal found in the sample. For all other impactor stages and the back-up filters this uncertainty was less than 10%.

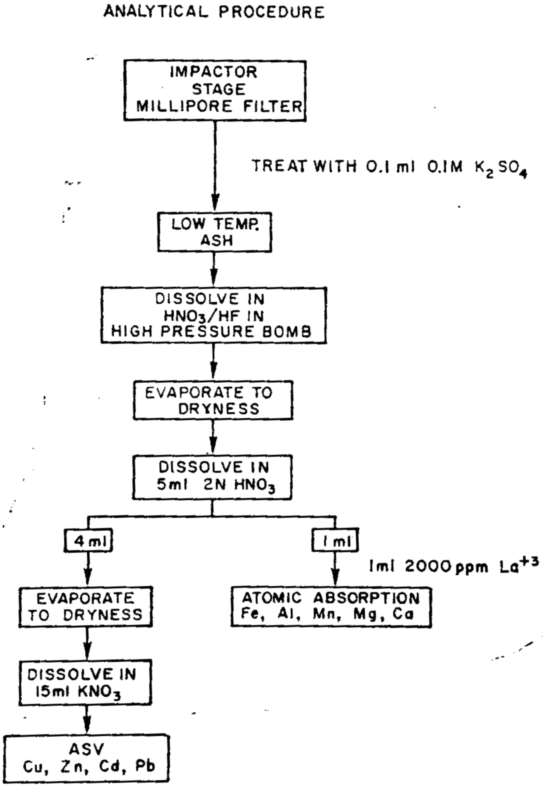

FIGURE 1 Flow chart of analytical procedure.

Ultra-pure nitric and hydrofluoric acids (Baker Ultrex and EM Suprapure) were used for the acid digestion of the ashed samples. All other reagents used were of analytical grade.

Eleven cascade impactor samples were collected between January and May, 1972. Each sample was collected for between 150–250 hr to ensure collection of enough material on each stage for analysis. These sampling periods provided samples containing between approx. 0.1 and 3 mg of particulate matter.

RESULTS AND DISCUSSION

A summary of the results obtained in this investigation is presented in Table I. Table I gives the date and time each sample was collected as well as the total atmospheric concentration of each element (i.e., the sum of all size fractions) and the mass median equivalent diameter (MMD) for each element in each sample. The total atmospheric concentrations for the nine elements are in good agreement with the atmospheric concentrations of these elements reported elsewhere.[6,14,20] Particle size distributions for each element were calculated as the cumulative per cent smaller than the 50% collection efficiency diameter for each impactor stage. Plotting the cumulative per cent less than a given diameter versus particle diameter allowed an estimation of the MMD for each element.[5] Since the last stage of the cascade impactor used in this work has a 50% collection efficiency for 0.5-micron diameter spherical particles of unit density, all values of MMD less than 0.5 micron required extrapolation of the distribution curve to the cumulative 50% value. Extrapolations were made as a linear extension of the distribution curve. Since it is not possible to know the actual shape of the distribution curve below a particle diameter of 0.5 micron, all values of the MMD less than 0.5 micron must be considered as somewhat uncertain and only an estimate of the actual MMD. Treatment of the data in this manner, however, does allow one to see the relative changes in the particle size distribution of a given element from one sampling period to another. Table I does show that rather larger changes in the apparent MMD for all elements studied in this investigation can occur from sample to sample even when relatively long sampling times are used. Almost certainly the shifts in particle size distributions evident in Table I result primarily from changes in meteorological conditions. This investigation did not include sufficient samples to allow a statistical evaluation of the effect of meteorological parameters upon elemental atmospheric concentration and the particle size distribution of the elements being studied.

Table II gives the average (and standard deviation) concentrations of each element, the average MMD for each element and the upper decile geometric deviation for each element. The average MMD was calculated from the average particle size distribution of each element as shown in Figures 2 and 3 for Cd and Al, respectively. From the MMD's in Table II it would appear that three classes of particle size distributions are apparent in the nine elements studied. Pb and Cd are concentrated on the smallest particles (~70% of each element associated with particles of diameters less than 0.5 micron) with an apparent MMD of about 0.1 micron. The elements Fe, Mg, Zn and Cu are

TABLE IA

Summary of data for cascade impactor samples

Sample	Times and dates collected	Cd		Cu		Pb		Zn	
		Total (μg/m^3)	MMD	Total (μg/m^3)	MMD	Total (μg/m^3)	MMD	Total (μg/m^3)	MMD
1	1526 12/30/71 – 1000 1/10/72	0.0065	0.19	0.055	0.76	0.46	0.31	0.21	0.51
2	1032 1/10/72 – 1635 1/18/72	0.0082	0.15	0.047	0.09	0.91	0.11	0.16	0.39
3	0935 1/19/72 – 0950 1/26/72	0.010	0.21	0.060	0.72	0.98	0.32	0.14	0.79
4	1014 1/26/72 – 1600 2/3/72	0.0027	0.31	0.025	0.09	0.68	0.06	0.063	0.37
5	1600 2/3/72 – 0900 2/9/72	0.0043	0.11	0.082	0.18	0.67	0.03	0.075	0.25
6	1700 2/11/72 – 1450 2/23/72	—	—	0.021	0.22	0.52	0.04	0.066	0.32
7	0830 3/22/72 – 1500 3/27/72	0.0062	0.05	0.025	0.59	0.45	0.11	0.047	0.03
8	1600 3/27/72 – 1336 4/4/72	0.0044	<0.01	0.046	0.07	0.46	0.12	0.036	<0.01
9	1410 4/4/72 – 1455 4/13/72	—	—	0.042	0.78	0.34	0.04	0.040	0.23
10	1325 4/25/72 – 1340 5/5/72	0.0047	0.07	0.015	0.16	0.24	0.12	0.019	0.28
11	1630 5/5/72 – 1515 5/15/72	0.0016	0.30	—	—	0.22	0.20	0.024	0.59

TABLE IB

Summary of data for cascade impactor samples

Sample	Al		Ca		Fe		Mg		Mn	
	Total ($\mu g/m^3$)	MMD	Total ($\mu g/m^3$)	MMD	Total ($\mu g/m^3$)	MMD	Total ($\mu g/m^3$)	MMD	Total ($\mu g/m^3$)	MMD
7	1.4	0.63	1.5	0.35	0.67	0.52	0.34	0.42	0.014	0.83
8	3.1	0.01	1.2	0.41	0.45	0.54	0.27	0.43	0.015	0.32
9	1.4	2.5	1.2	0.66	1.1	<0.01	0.27	0.41	0.019	0.14
10	1.5	0.17	1.8	0.38	0.87	0.25	0.40	0.11	0.016	0.35
11	1.6	1.1	1.9	0.79	0.82	0.83	0.35	0.30	0.020	0.81

concentrated on slightly larger particles (about 60% of each element associated with particles of diameters less than 0.5 micron diameter) with apparent MMD's between 0.3 and 0.4 micron. The elements Al, Mn and Ca are the least concentrated on smaller particles (~50% of each element associated with particles of diameters less than 0.5 micron) and apparent MMD's between 0.5 and 0.6 micron. Figure 4 shows the average particle size distribution of these three groups of elements. The curves in Figure 4 are extrapolated to the cumulative 50% value of particle diameter. Figures 2 and 3 show the distribution curves for the elements Cd and Al. Included on Figures 2 and 3 are the ranges of cumulative per cent values for each particle size. Figures 2 and 3 are representative of the curves obtained for all nine elements.

Table II gives the upper decile geometric deviation ($d = D_{90\%}/D_{50\%}$) which is a measure of the dispersion of the particle size distribution for a given element. The d values in Table II are all relatively large,[6,15] indicating a rather broad range of particle sizes for each element. Considering the relatively long sampling times and meteorological changes which occurred during the sampling period, the broad range of particle sizes for each element is to be expected. In addition to the sampling time, one would expect large upper decile geometric deviations if any of the elements measured in this investigation had more than one source (e.g., a natural erosion and a man-made source). Additional data using much shortened sampling times would be required to comment further upon this possibility.

TABLE II

Average concentration and size distribution of various elements in airborne particulate matter

Element	MMD[a] (Microns)	d[b]	Av. conc. ± S.D. ($\mu g/m^3$)
Cd	0.11	22.7	0.0054 ± 0.0025
Pb	0.12	14.1	0.54 ± 0.25
Fe	0.31	21.4	0.78 ± 0.24
Mg	0.32	22.3	0.33 ± 0.054
Zn	0.32	13.8	0.080 ± 0.062
Cu	0.35	23.4	0.042 ± 0.021
Mn	0.50	13.1	0.017 ± 0.0025
Al	0.55	15.9	1.8 ± 0.74
Ca	0.56	12.7	1.5 ± 0.35

[a] MMD = Mass Median Equivalent Diameter

[b] $d = D_{90\%}/D_{50\%}$. The Upper Decile Geometric Deviation

From the particle size data alone it might be tempting to suggest three different classes of elements, with the elements within each class having the

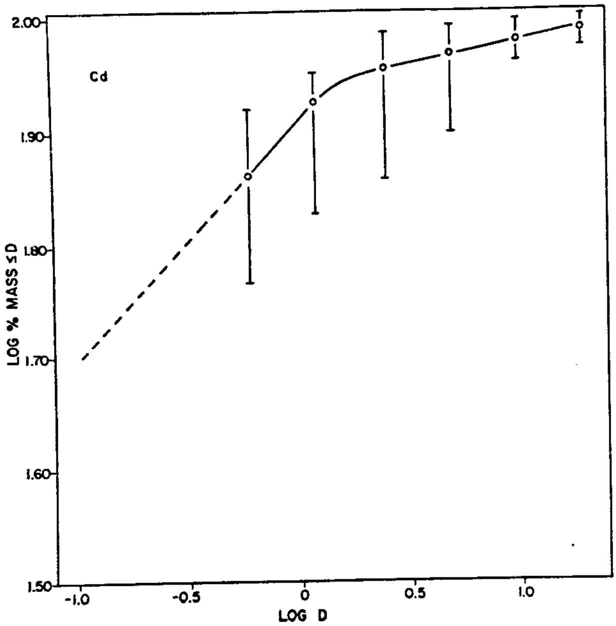

FIGURE 2 Average size distribution curve for Cd.

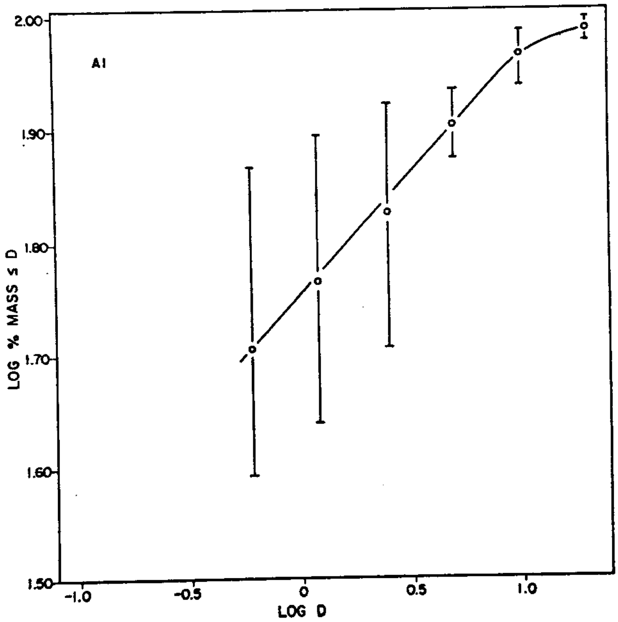

FIGURE 3 Average particle size distribution curve for Al.

same or similar types of sources. However, particle size distributions alone do not provide sufficient information to warrant such conclusions. The variability of the particle size distribution for each element plus the requirement of extrapolation of the distribution curves presents rather large uncertainties as to how much meaning can be extracted from the limited amount of data presented here. Examination of elemental ratios provides an additional means of assessing the meaning of the data obtained in this investigation. Calculations of elemental ratios using aluminum as a reference element were made and two interesting observations were apparent from these data. First, it is possible to compare atmospheric ratios with the same ratios of suspected

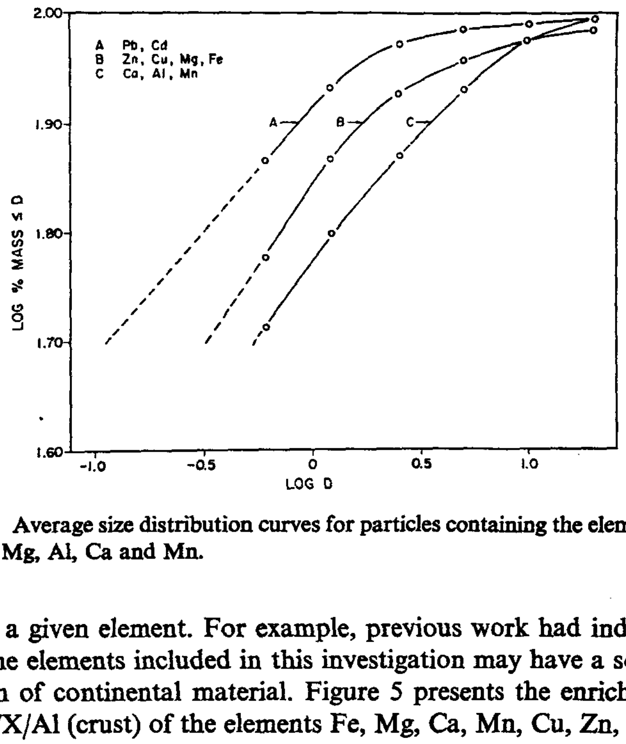

FIGURE 4 Average size distribution curves for particles containing the elements Pb, Cd, Fe, Zn, Cu, Mg, Al, Ca and Mn.

sources of a given element. For example, previous work had indicated that many of the elements included in this investigation may have a source from the erosion of continental material. Figure 5 presents the enrichment E = X/Al (air)/X/Al (crust) of the elements Fe, Mg, Ca, Mn, Cu, Zn, Pb and Cd in atmospheric particulate matter as compared to the relative concentration of these same elements in average crustal material.[21,22] In Figure 5, it is seen that the concentration of Fe, Mg, Ca and Mn in atmospheric particulate matter is about that expected from an erosion source if the aluminum in the atmosphere results from crustal erosion. The elements Zn and Cu appear to be enriched in the atmosphere, compared to average crustal material, by approximately a factor of 20. Pb and Cd are about 1000 times enriched in the atmosphere with respect to average crustal material.

Examination of the element/Al ratio of the elements Pb, Cd, Zn, Cu, Ca, Mn, Fe and Mg for different sized particles showed that the ratios Pb/Al and Cd/Al were higher than the same crustal ratios for particles of all sizes and these ratios increased with decreasing particle size. Figure 6 shows the changing Pb/Al ratio as a function of cascade impactor stage (i.e., particle size).

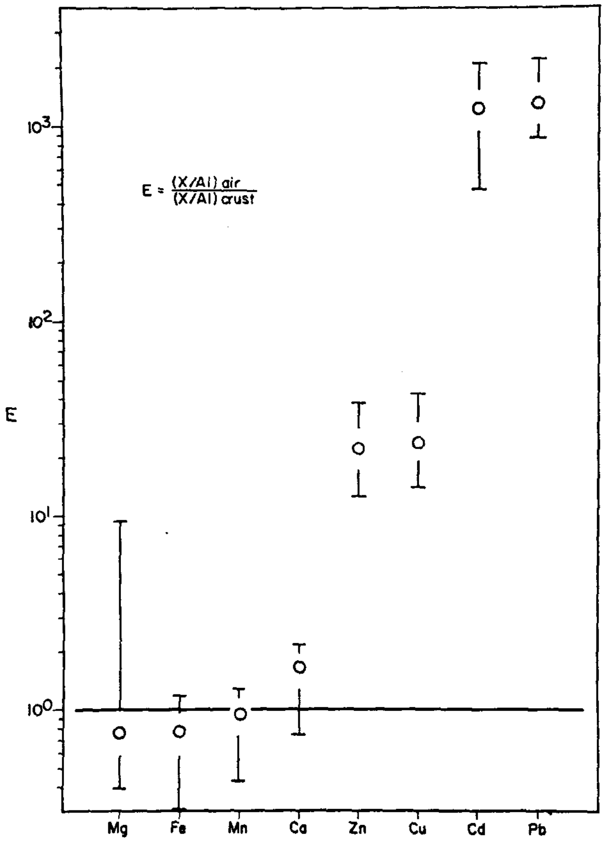

FIGURE 5 The enrichment of the elements Pb, Cd, Zn, Cu, Mg, Fe and Ca in atmospheric particulate matter with respect to average crustal material (Al reference element).

The ratios for impactor stages 1 and 2 must be viewed with some uncertainty. Impactor stage 1 collects particles of about 20 micron diameter and larger with 100% efficiency. Thus, any contamination resulting from activity around the impactor during start up and shut down would probably be caught on the first stage (for example, lint from clothing or larger particles in the area which may be stirred up by laboratory personnel as the impactor is being started up or turned off). Stages 1 and 2 collect the least amount of atmospheric material (i.e., the concentration of all elements show a minimum on either stage 1 or stage 2) and, therefore, analytical uncertainties resulting from the blank correction are greatest for stages 1 and 2 (from 10 to 30%). Thus, stage 1 and stage 2 data show the greatest variability for all elemental ratios and this is due in a large part to the analytical uncertainties of stages 1 and 2 data.

The ratios Zn/Al, Cu/Al, Ca/Al, Mn/Al, Fe/Al and Mg/Al showed no regular variation with changing particle size. The ratios Fe/Al, Ca/Al, Mg/Al and Mn/Al showed very little change with changing particle size and were

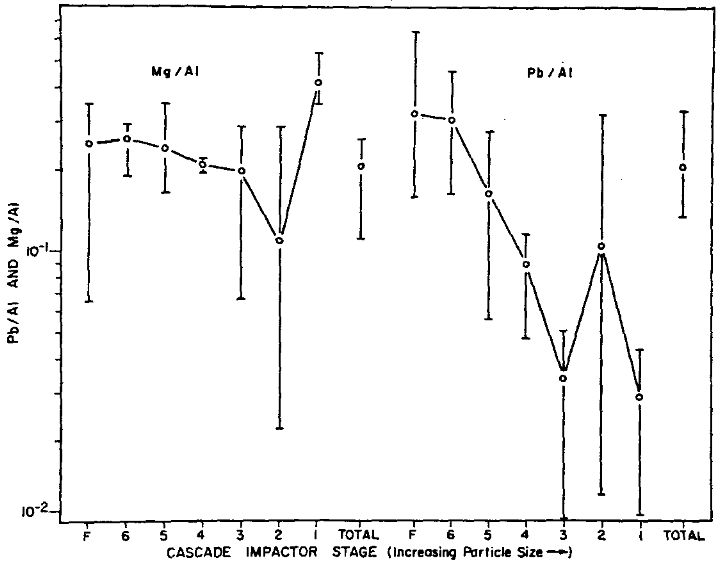

FIGURE 6 Change in Pb/Al and Mg/Al ratios with changing particle size.

essentially identical to crustal ratios. Figure 6 shows the average Mg/Al ratio (and the standard deviation) as a function of particle size. The Zn/Al and Cu/Al ratios of all different sized particles were higher than the crustal ratios for these elements. Rather large changes in the Zn/Al and Cu/Al ratios did occur for different sized particles (i.e., changes of more than a factor of 10); however, these changes were neither regular with changing particle size nor the same from sample to sample. The inconsistent ratios for Zn/Al and Cu/Al probably explain why Zn and Cu have particle size different from that of Al. Since the Mg/Al and Fe/Al ratios showed no variation with particle size it might be expected that the MMD's for Fe, Mg and Al would be similar. This apparent discrepancy is probably due in a large part to the limited number of samples and the necessity to extrapolate the distribution curves to obtain the MMD for each element. Additionally, if different sources are responsible for the particle size distribution of these elements in the atmosphere then small changes in the elemental concentrations of sources may be more easily seen in the size distribution curves than in the ratio values (the ratios include the uncertainties of two elements and the distribution curves include only the uncertainty and variability of a single element).

An important fact evident in these data is that an unusually high concentration of metals with an apparent crustal origin (i.e., Al, Fe, Mn, Ca and Mg) is associated with sub-micron particles. Tucson is a city of approx. 300,000 residents and is located in the Sonoran Desert area of southern Arizona. If these elements in the atmosphere had a source from the erosion of crustal material then it would be expected that the particle size distribution of these elements would be shifted more towards larger particles than was found in this work. From these preliminary data, it would appear that some process more energetic than natural erosion is introducing sub-micron particles into the local atmosphere. The source of these small "soil-like" particles is uncertain at the present time. It is possible that local metallurgical processes may contribute to the small particle population of aerosols found in the local atmosphere.[23] Additional data are required to assess the impact of various industrial processes on the aerosol population of the Tucson atmosphere.

These data, although of a preliminary nature, do indicate that particle size distribution for a number of elements should provide a useful method for identifying and "fingerprinting" the sources of atmospheric particulate matter. From the variability of these data, it is apparent that to accurately describe the particle size distribution of elements a large number of samples would be required, so that rigorous statistical data treatment could be performed. By properly using particle size data, elemental ratio data, and meteorological data, it should be possible to obtain significant information about the sources of elements present in the atmosphere. Additional investigations into these matters are being carried out in our laboratory.

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