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FINE AND COARSE AEROSOL COMPOSITION IN AN URBAN SETTING: A CASE STUDY IN BEIJING, CHINA

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Abstract—Components of the near-ground urban aerosol in Beijing, China, which are derived from natural and pollution sources, have been identified by means of PIXE analysis of particle size fractionated samples and relationships among the concentrations of 18 elements. Samples were collected in city center and outlying suburban and rural locations on five days in July and December 1980. The particle size distributions of most elements were bimodal, with a gradual progression from mainly coarse mode Ca, Ti and Al to mainly fine mode S, As, and Br. Pb, Zn and Cu occurred mainly in fine particles and were apparently pollutants derived from the combustion of coal and other fuels, but not gasoline. Fine particle Cr, Mn and Fe concentrations were especially high on one July day and may have derived from a pulse of industrial air pollution. Si concentrations were singularly high in ultra-fine particles as if from the condensation of high temperature vapors from coal combustion. Coarse particles in the city center were apparently from local surface dust raised by vehicle traffic, and they were enriched in Pb, Zn and Cu compared to a rural location, suggesting a significant degree of city soil contamination by fine pollution aerosol fallout over time.

Key word index: Aerosol composition, China, urban air pollution, particulate matter, heavy metals.

INTRODUCTION

Human populations are exposed to heavy metals and other elements in airborne particulate matter, in soils, water and food, and in other materials which come into contact with man. In urban areas certain heavy metals often occur with abundances considerably above their natural levels, owing to anthropogenic processes which increase the rates of mobilization of these elements from their natural states to the environment. These increased concentrations present a human health risk. Whether the immediate pathways to man are directly from inhalation of polluted air, from ingestion, or by other means, the overall sequence of transport links between the pollution sources of heavy metals and a human receptor generally includes an atmospheric route as an important part. Consequently, the measurement of heavy metal concentrations in airborne suspended particulate matter is of practical public health interest (cf. U.S. EPA, 1982).

Mobilization to the atmosphere may occur by the combustion of fossil fuels and those industrial processes which discharge exhaust fumes from chimneys (Bertine and Goldberg, 1971), and transport of the resulting metal pollution through the atmosphere may extend far beyond the urban source area, even to remote regions (Murozumi *et al.*, 1969). Of special interest is contamination of the Arctic atmosphere by fine particulate pollutants from populated temperature latitude regions of Europe, Asia and North America (Rahn and McCaffrey, 1980). In principle, the source regions of greatest importance may be determined by a combination of characterizing trace element signatures and calculating air trajectories, and in practice some success has been achieved (Rahn, 1981). Detailed characterization of trace element composition within urban areas of China may add further precision to this determination.

In urban areas atmospheric particles smaller than about 10 micrometers (μm) diameter may occur in stable aerosol suspension, and a broad distinction may be made between 'coarse' particles larger than about 1 or 2 μm and 'fine' particles below that size. Fine particles may be further subdivided into an ultra-fine 'nuclei mode' below about 0.1 μm and an 'accumulation mode' above that size (Whitby, 1978). Coarse particles may be raised as dust, sea spray, or other dispersion products, whereas fine particles are often the result of vapor conversion to liquid or solid material by the cooling of initially high temperature fumes or by chemical reactions of gases within the atmosphere. By measuring heavy metal concentrations separately in coarse and fine particle size ranges, clues may be obtained concerning which of these possibilities may be the immediate source processes for releasing the metals to the atmosphere.

For determining whether pollution or natural sources are ultimately dominant in human exposures we may need additional evidence, for example from comparisons of the measured concentrations with the expected relative elemental compositions from these aerosol sources. In addition, the identification of major sources which contribute to aerosol composition at a receptor site may be aided by statistical analysis of

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ambient air measurements, such as in 'receptor modelling' (Cooper and Watson, 1980), or by relating the concentrations at different measurement sites with plume trajectories or with proximity to the sources. Some of the approaches we have taken previously in this laboratory for primary source identification, based principally on statistical analysis of ambient aerosol concentration measurements, have been reviewed elsewhere (Winchester, 1983b, 1984).

Suspended particulate matter in urban areas generally contains primary emissions from combustion, industrial processes, and other activities, secondary products from the conversion of pollution sulfur, nitrogen and other gaseous compounds to aerosol particle form, and additional re-entrained or 'fugitive' dust from the ground, such as from road traffic, which may already have become contaminated by deposition of air or water pollutants. Human exposures to airborne heavy metals, then, are not limited to primary air pollutants or their secondary conversion products, generally of fine particle size, but may also be due to re-entrainment of generally coarse particle dust from soil which may be contaminated. In the current study we have addressed the question of how to distinguish the primary aerosol emissions of metal pollutants from the pollution components present in soil dust which becomes re-entrained by vehicular traffic in a city center.

Our approach is based on street level sampling at sites which differ in degree of dustiness due to local traffic intensity but which may not differ in degree of impact by fine particle urban air pollution. Particle size selective aerosol sampling with elemental analysis by proton induced X-ray emission (PIXE) is used. The measurements were made in Beijing, China, where primary emissions of aerosol heavy metals are generally from chimneys and the taller stacks of combustion and industrial units which may allow fine particles to be distributed widely. Direct vehicular emissions of aerosol lead in China are minimal owing to lower lead concentration in gasoline and lower per capita motor fuel consumption than in many other countries (Jiang *et al.*, 1984). These features of the Beijing environment simplify the problem of distinguishing primary fine particle from coarse re-entrained dust pollution by lead and other heavy metals. However, the distinction may as well be valid in other more complex urban environments, making a study conducted in Beijing of general interest (Bi *et al.*, 1984).

Our study consisted of aerosol concentration measurements within and surrounding a large open courtyard in the former imperial palace, so that atmospheric composition in a public park could be compared with that in city streets, as well as that in locations more distant from the city center. Within the park local dust concentrations were expected to be comparatively low, whereas concentrations of widely dispersed air pollutants were expected to be similar to the other locations along the surrounding streets, thus providing a means of distinguishing locally generated from regional aerosol components. The samples were analyzed for elemental composition, from aluminum to lead in atomic weight, using particle induced X-ray emission (PIXE). On the basis of the elements characteristic of different aerosol sources and the variation of concentration with particle size a distinction between natural and pollution processes could be made. In some respects our urban setting resembled that of New York City where the finding of low air pollution concentrations in the parkland of central Manhattan, owing to the absence of pollution sources within it, has been dubbed the "Central Park Effect" (Davidson, 1967; Shieh *et al.*, 1970).

EXPERIMENTAL

Sampling as a function of particle size was performed during July and December 1980 using cascade impactors placed about two meters above the ground at the 7 sites listed in Table 1 which included a 5-site city center network in and around the Palace Museum, a west suburban site part way to a heavy industrial area, and a north rural site near the Ming Tombs. The geographic setting of the sites may be visualized by reference to a map of Beijing (Danforth, 1982). Based on direct observation during the sampling the center network sites are listed in apparent order of increasing dustiness due to vehicular traffic.

Samples were collected during dry weather in both July and December 1980 on the dates given in Table 2. Summer air flow

Table 1. Sampling sites in Beijing Central West, and North Areas, July and December 1980

Site*	Remarks
A Gugong	Palace Museum Courtyard, pedestrians only
B Zhongshan	Park near Gugong, pedestrians only
C Wangfujing	Street corner near busy Chang'an Avenue
D Jingshan	Busy street near Gugong north gate
E Qianmen	Traffic island in middle of major busy street
W Wukesong	Along Chang' an Avenue, 10 km west of central Beijing and 10 km east of Shijingshan iron and steel works
N Shisanling	At reservoir north of Ming Tombs, rural site 40 km north of central Beijing

* Central sites A–E are listed in increasing apparent order of dustiness due to traffic; see a city map (Danforth, 1982).

Table 2. Sampling conditions, Beijing 1980

Date, 1980*	Sites†	Temp. °C	r. h. (%)	Wind direction & speed, m s^{-1}	Skies and ground‡
29 July	A–E	27–32	49–71	S, 0–1.6	Part cloudy and dry
30 July	A–E	27–33	47–76	S, 0–1.2	Part cloudy and dry
23 Dec.	A, B, E	6	30–50	NW, 0.8–2.3	Clear and dry
25 Dec.	A, B, E	−0.3	63–77	NE, 1.2–4.6	Clear and dry
26 Dec.	W	−2.2	72	SW, 0.8	Clear and dry
29 Dec.	N	−10	50	NW, 0.3	Clear and dry

*Sampling times were 4.00 h starting at 0900 or 0930 on each day using cascade impactors operated at 1.5–2.5 m height, facing down, enclosed in wind decelerator devices; flow rates 0.6–0.9 ℓ min^{-1} in July and 0.44–0.66 ℓ min^{-1} in December.

† Samples were in duplicate at A in July and at W and N in December; total number of impactor samples $n = 12$ (July) and $n = 10$ (December).

‡ Partly cloudy conditions in July, although several days after last rainfall, so that ground was dry.

was generally from the south, although variable, whereas winter air flow was from the northwest, probably bringing cleaner air into the city during December than in July and also at higher wind speeds. Both of these air flow differences, direction and speed, may have led to lower primary pollutant concentrations at ground level during the winter sampling days, in spite of more coal burning within the city for space heating during cold weather. However, the concentrations of re-entrained surface dust particles were expected to be higher during winter owing to the prolonged drought typical of the cold months in northern China (Trewartha, 1981) and to the higher wind speeds on the December sampling days, except possibly for rural areas with good vegetative ground cover.

Cascade impactors were of the single orifice Battelle type, operated using Brailsford pumps and battery power, as reported earlier (Winchester *et al.*, 1981a). The impactor stages fractionated particles into factor-of-2 intervals of aerodynamic diameter, using 0.4 μm Nuclepore for stage 0 and paraffin or Vaseline coated Mylar for stage 1 and stages 2–6, respectively. No stage 7 was used. The size cuts between the stages for air flow of 1 liter per minute, in micrometers aerodynamic diameter (μmad), were: 0/1, 0.25; 1/2, 0.5; 2/3, 1; 3/4, 2; 4/5, 4; 5/6, 8. Under actual field conditions the air flow rates, in liters per minute, were 0.6–0.9 in July and 0.44–0.66 in December, causing particles to impact slightly further into the impactor than these nominal cutpoints. This bias is not important for the present interpretation which is based on a comparison of the concentrations of different elements relative to particle size.

PIXE analysis was carried out nondestructively at the Element Analysis Corporation, Tallahassee, FL, using a 3 MeV proton beam from a General Ionex Tandetron accelerator. X-ray spectra, recorded by a Si(Li) detector and computer, were resolved by the HEX program, corrected for mass absorption of X-rays in the samples, and reported as elemental concentrations in air using standardized procedures (EAC, 1982). Some of these procedures have been described elsewhere (Winchester, 1983a). The samples were also previously analyzed in the PIXE facility of the Institute of High Energy Physics, Chinese Academy of Sciences, Beijing. Average agreement between laboratories, for all samples and elements reported, was better than 5%, although with greater variation of individual data (Zhong *et al.*, 1984).

RESULTS

Concentrations of 18 elements, ranging from Al to Pb, were measured in seven particle size fractions from less than 0.25 to greater than 8 μmad. Tables A1–A4 in the Appendix list these concentrations as medians for the different sampling locations in July and in December. In the following discussion the data are examined in greater detail by distinguishing specific sites and dates where this may be to advantage.

Tests of data quality

Six cascade impactors were employed, and some duplicate samples were taken for quality control, namely at Gugong Palace Museum on 29 and 30 July and at the west and north sites in December. An example of evidence for reproducibility of concentration measurements, data for Pb at Gugong, is presented in Fig. 1 (lower part). In many cases the agreement is within the few percent expected for PIXE

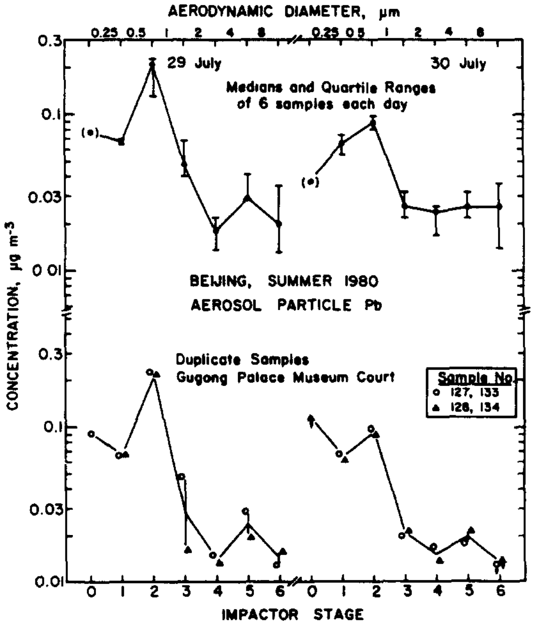

Fig. 1. Concentrations of Pb in Beijing city center on two summer days at sites A to E, as indicated in Tables 1 and 2. (*Upper*) Medians and ranges of the middle 4 of the 6 values (and medians of only 3 filter values) for each day. (*Lower*) Comparison of duplicate measurements at site A. The indicated aerodynamic diameters of the particles sampled by impactor stages 0–6 are approximate (see text).

analysis errors alone. Figure 1 also shows for each July day the quartile ranges around the medians of six samples from the five sampling sites. They are smaller than the range of variation of median concentration with particle size, so that the medians may be used as a basis for comparing sample subsets of different sites, times, and elements. In the remaining figures, for simplicity, we do not plot the quartile ranges or agreement between duplicates, since the results of Fig. 1 are generally representative.

Presence of fine and coarse modes of the elements

As indicated in Fig. 1, Pb occurs mainly in a submicrometer or fine particle size range, but coarser particles contain 10% or more of the total Pb concentration. It also appears that the distribution of Pb concentration with particle size may be represented by two superimposed modes, a fine mode centered about 0.5–1 μmad and a less abundant coarse mode about 4–8 μmad. The two modes may have separate origins, e.g. combustion and surface dust, respectively, and the mixing ratio of the two modes must depend on the relative importance of their respective sources at any particular place and time.

Most of the 18 elements investigated in this study appear to exhibit bimodal distributions of concentration with particle size. For some the fine mode is dominant, e.g. S, Zn and Cu shown in Fig. 2 as well as Pb, for others the fine mode is prominent though less abundant than a coarse mode, e.g. K shown in Fig. 2, whereas for still others the fine mode is subtle and inferred from detailed comparisons of size distributions within this group of elements. Fig. 3 shows a comparison of predominantly coarse Ca, Fe and Si median concentrations for each of the July sampling days. Compared to Ca, both the Fe and the Si distributions are skewed toward smaller particle sizes so that their concentrations in the 0.25–2 μmad range appear to be enhanced. For Fe this is especially true on the second day. In addition, on both days Si has very high concentrations in ultra-fine particles smaller than 0.25 μmad, far greater than the stage 0 filter blank level of 0.1 $\mu g\ m^{-3}$. The fine modes of these elements are examined further below after we consider some details within the coarse mode.

Winter and summer coarse mode comparison

For elements exhibiting mainly a coarse mode the concentrations in both fine and coarse particle size ranges, up to 8 μmad, during winter were similar to those in summer, while in the coarsest particles, above 8 μmad, the Beijing city concentrations were substantially higher in winter. Figure 4 illustrates this finding for Ca. The relative amounts of Ca contained in the fraction sampled by impactor stage 6 at both the center and west industrial locations during December were much higher than during July, suggesting the presence of very coarse particle dust from dry winter soils under windy conditions. On the other hand, at the north rural site, where surface vegetation was generally present, these coarsest particles are much less abundant, although the finer particles are only somewhat lower in

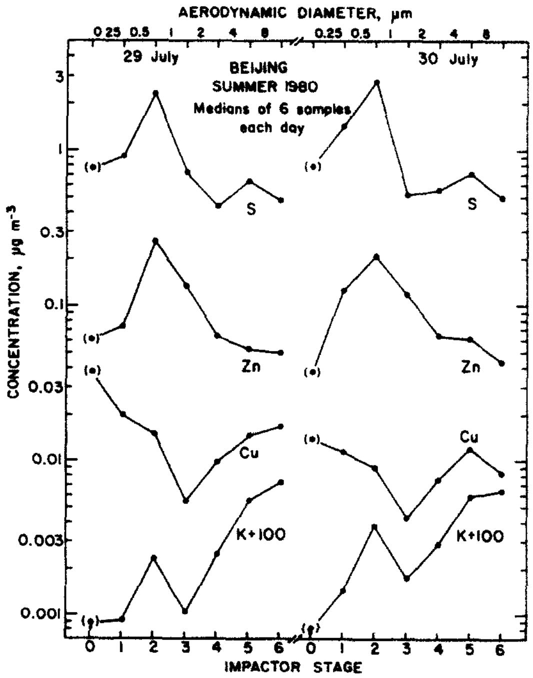

Fig. 2. Comparison of median particle size distributions of S, Zn, Cu and K, representative of elements having prominent fine mode concentrations, in the same samples as in Fig. 1.

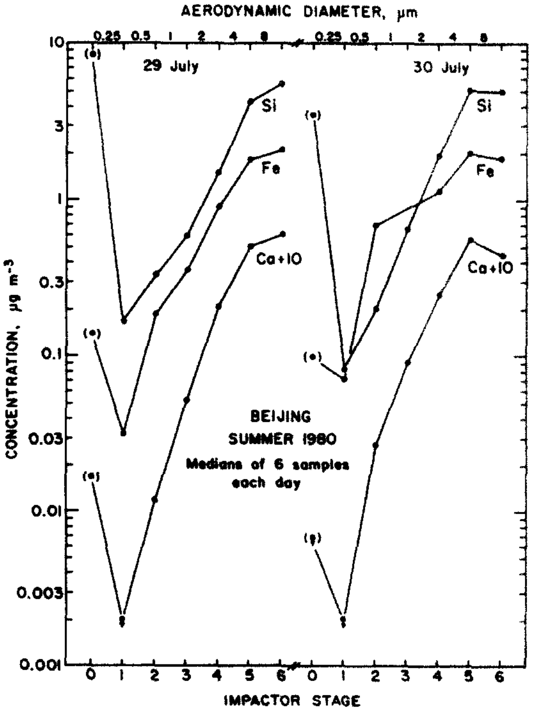

Fig. 3. Comparison of median particle size distributions of Si, Fe and Ca, representative of elements occurring mainly in a coarse mode, in the same samples as in Figs 1 and 2.

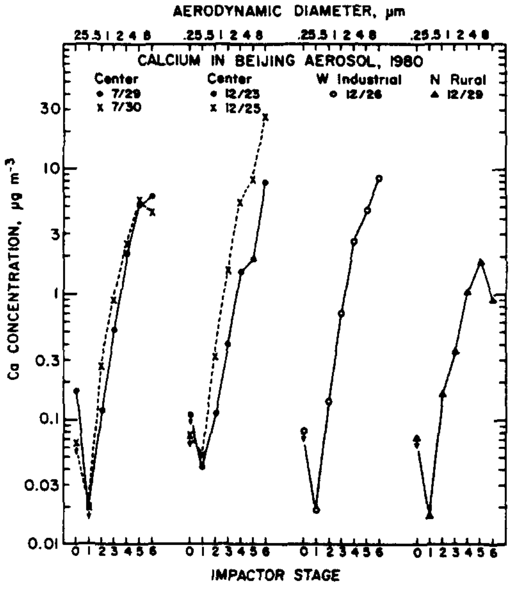

Fig. 4. Comparison of particle size distributions of Ca at the city center, west industrial, and north rural sites. Plotted points are medians of 6, 6, 3, 3, 2 and 2 samples for each subset, respectively, as indicated in Table 2.

concentration. For mainly coarse mode elements, then, the regional concentrations appear not to depend strongly on local surface conditions or seasonal differences, except for the very coarsest particles above 8 µmad. This conclusion is consistent with the data presented in Tables A3 and A4 for all the elements. Even concentrations during spring dust storms we have found to be enhanced mainly in the coarsest particle sizes (Wang *et al.*, 1982).

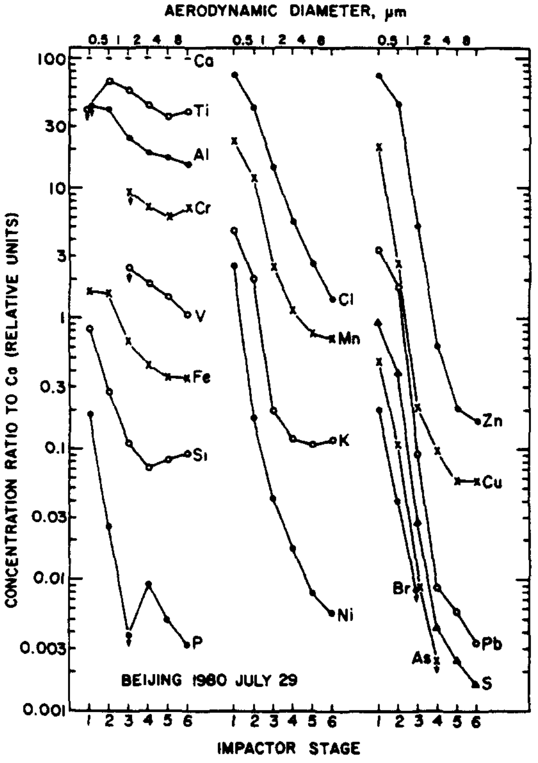

Fig. 5. Median concentrations normalized to Ca for sites A–E on one July day for 18 elements arranged in order of apparent increasing steepness of the particle size distribution trends, indicating increasing relative abundance of a fine mode. The concentration ratio scale is relative, but actual weight ratios can be obtained by multiplying the plotted ratios by the following factors: 50 (S); 10 (Si, P); 1 (Fe, K, Pb, As, Br); 0.1 (Ni); 0.05 (Zn, Cu); 0.02 (Al, Cl); 0.01 (Ca, V, Mn); 0.001 (Ti); 0.0002 (Cr).

Ordering of elements by relative fine mode prominence

For any element the distribution of concentration with particle size may, to a first approximation, be the result of the mixing of separate fine and coarse modes, each caused by distinct processes of aerosol formation. In an urban setting, such as Beijing, these processes may be either pollution or natural. By inspection of the median size distributions, we find that Ca appears to lie at one extreme of a monotonic progression, and S near the other extreme, of increasing mixing ratios of fine to coarse modes. This gradual change from mainly coarse to mainly fine can be seen by normalizing all distributions to that of the coarse end member, Ca. This has been done for the 29 July 1980, sampling day in Beijing center, shown in Fig. 5. For all the elements plotted there is a virtually monotonic decrease in normalized concentrations from fine to coarse particle size. The elements have been ordered in apparent increasing steepness of the decrease, from Ti and Al, which exhibit only slight enhancement of fine particle concentrations relative to Ca, to As and Br, which were detected only in submicrometer particles. This progression of the elements from coarse to fine suggests a progression of their increasing source strengths for fine mode aerosol, relative to the coarse particle sources, such as by combustion and other polluting processes in Beijing, as well as by natural processes for fine aerosol formation. A similar ordering of elements has been observed in the emissions from coal-fired power plants (Annegarn *et al.*, 1983).

The progression of elements in Fig. 5 resembles the ordering of elements, X, in remote as well as polluted atmospheres, according to their enrichment factors (E.F.) of concentration (Rahn, 1976), defined by

$$\text{E.F.} = (X/R)_{\text{aerosol}}/(X/R)_{\text{reference}}.$$

Here R refers to a reference element used for normalizing concentrations, and 'reference' refers to a reference composition with which the aerosol composition is compared. It is frequently informative to select the earth's crust as a reference composition, e.g. the geochemical average of the major rock types (Mason, 1966; Mason and Moore, 1982), since soil dust from rock weathering is an important aerosol component, and we may wish to know for various trace elements whether that source is sufficient to account for the observed atmospheric concentrations. In this case the reference element R is frequently chosen to be Al, Fe, or another easily measured major soil constituent. Such reference elements occur mainly in coarse particle sizes, as expected if dust is their principal source.

Trace elements may have values of E.F. from near unity to many thousands. Those with high E.F. are referred to as 'anomalously enriched elements' (AEE), since their atmospheric concentrations cannot be explained by dispersion of soil dust alone. Additional sources must be important. In contrast to the major soil elements chosen as a reference in the E.F. equation above, the AEE generally occur in finer particle sizes, implying that their sources probably involve the transformation of vapors into particles, by either pollution or natural processes. The relationship found between E.F. and fineness of particle size indicates that the numerical values of E.F. at any measurement site must be determined by the mixing ratios of fine to coarse particle modes in the size distributions of the elements. Near the ground the E.F. value of an AEE may be depressed by accidental admixture of local dust, and high above the ground or on a glacier of continental dimensions the paucity of coarse dust particles should cause an increase in the E.F. value of an AEE. In general, however, there is an ordering of elements in their E.F. values, reported anywhere in the world, which resembles our ordering in Fig. 5 based on a single day of measurements in central Beijing. If pollution from coal combustion is a major source in this urban area, it may be asked whether combustion, anthropogenic or natural, is ultimately a major determinant for the anomalously enriched elements in remote regions, as we have suggested elsewhere (Winchester *et al.*, 1981b, c).

A fine aerosol excursion on 30 *July*

As noted above, Fig. 3 showed unusually high relative concentrations of submicrometer Fe at all five sites in Beijing center on 30 July 1980. Fine particle Mn and other elements were also found to be unusually high, but still other typically fine particle elements, e.g. Pb and Zn, were not unusually high. In order to identify more exactly those elements which were part of the 30 July excursion, the concentration ratios 30 July/29 July were computed for each element and particle size fraction median for the five sites and plotted in Fig. 6. If the ratios are greater than unity, concentrations were higher on 30 July.

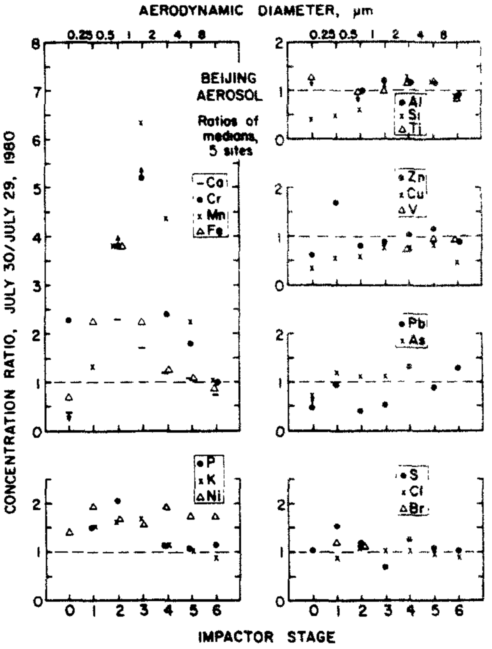

Fig. 6. Ratios of median concentrations at sites A–E, 30 July/29 July. The ratios are significantly greater than unity for the seven elements shown on the left, principally in fine to intermediate particle size fractions, whereas the ratios are approximately unity for the remaining 11 elements.

Generally three groups of elements can be identified in Fig. 6. The first consists of the major dust constituents Al, Si and Ti which have nearly equal median concentrations on the two days. The second consists of predominantly fine mode elements, presumably mainly of pollution origin in Beijing (Zn, Cu, Pb, Br, As and S) which also have similar median concentrations on the two days. V and Cl resemble the first and second groups, respectively. The third group, shown on the left side of Fig. 6, consists of elements with significantly higher 30 July concentrations in fine to intermediate size particles—for Ca, Cr, Mn and Fe by a factor of 2–6, and for P, K and Ni by at least 1.5 times. These elements occur generally in a coarse mode with varying admixture of a fine mode and are of intermediate character in Fig. 5. They are also among the expected emissions of some heavy industrial processes, such as the smelting of iron and the manufacture of steel, but not necessarily expected to be among the elements enriched in coal combustion emissions, as are the elements of the second group. The 30 July excursion of the third group of elements suggests an unusual industrial emission event, whereas the second group of elements may be more typical of the Beijing atmosphere.

Metal contamination of coarse dust

Human exposures to atmospheric heavy metals may be by contact with either fine or coarse particles, the fine probably representing primary emissions and the coarse at least in part representing re-entrained surface dust. The coarse particles, or the soil from which they are formed, of course, may have become contaminated by fallout of primary fine pollutants. Relative elemental composition is useful for the detection of pollution, but demonstration whether either fine or coarse particles actually contain contamination relative to the natural atmosphere cannot be made on the basis of enrichment factors E. F. alone. For mainly fine mode elements the E. F. relative to a major soil constituent is determined by the mixing ratio of fine and coarse modes and may be high in both natural and polluted atmospheres. When these same elements are found in coarse particles, the E. F. relative to geochemical average earth crust composition may only indicate a comparison of natural soil composition with that of average rock, since element fractionation may occur in weathering and the formation of soils. Instead, a comparison of elemental concentrations and their ratios of E.F. values in polluted and much cleaner regions should be used as an indication of pollution. For metals in fine aerosol particles, the comparison is straightforward, and high concentrations in an urban area compared to the countryside strongly suggest pollution. For metals in coarse particles, the comparison is not as straightforward but is possible for Beijing using the results of this study.

In the first place, the five sites in central Beijing, sampled simultaneously in July 1980, differed in degree of local dust concentration. Figure 7 displays the concentrations of the major elements Si, Fe and Ca and shows a progressive increase from site A to site E. All other coarse particle elemental concentrations showed similar monotonic increases, not only major elements such as Al, but trace elements as well. The trends of Zn, Pb and Cu are also shown in Fig. 7. These indicate that the coarse particle components of their atmospheric concentrations should be attributed to local surface dust, not to regionally distributed air pollution fallout.

Fine particle concentrations of the elements do not show the monotonic increases with increased local dustiness. Concentration trends of six of the elements are shown in Fig. 8, elements which may be pollutants directly associated with Beijing regional stack emissions. Although some differences between sites are found, there is no systematic trend of the type shown in Fig. 7. It is more reasonable to believe that the fine particle component was generally descending from the atmosphere to the ground, whereas the coarse particles were being re-entrained from the ground upward. If this process took place over a prolonged period, and if the fine particles were mainly of pollution origin, the soil may have become contaminated, and the re-entrained dust would contain relatively higher concentrations than similar dust in less polluted areas.

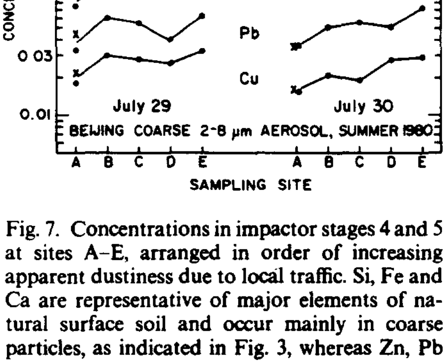

Fig. 7. Concentrations in impactor stages 4 and 5 at sites A–E, arranged in order of increasing apparent dustiness due to local traffic. Si, Fe and Ca are representative of major elements of natural surface soil and occur mainly in coarse particles, as indicated in Fig. 3, whereas Zn, Pb and Cu may be contaminants. The parallel trends of all six elements suggest that their coarse particle concentrations are due to the resuspension of surface dust.

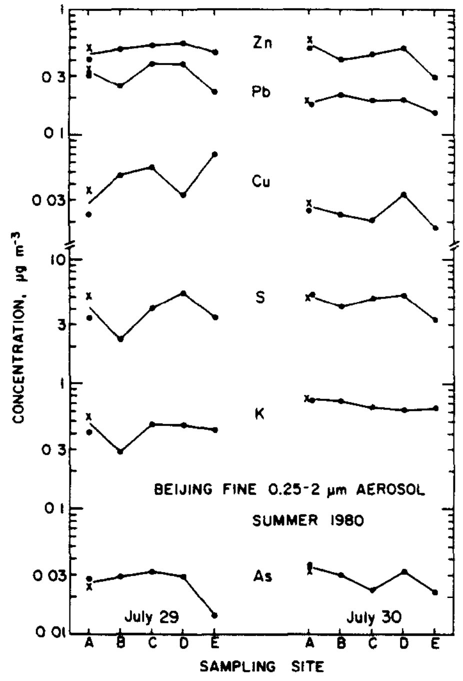

Fig. 8. Concentrations in impactor stages 1, 2 and 3 at sites A–E, plotted as in Fig. 7. Zn, Pb, Cu, S, and As are representative of several elements which occur mainly in these fine particle size fractions, as indicated in Fig. 5, and K has a prominent fine mode in addition to a coarse mode, as indicated in Fig. 2. The lack of systematic trends with site location suggest that the fine particle concentrations of these six elements are not related to resuspended surface dust.

This expectation can be tested by a second comparison, the relative elemental composition of coarse particles in the city center with that at the north rural site. Ratios to Al of median concentrations for each element in 4–8 μmad particles are shown in Table 3 for each sampling region and day. The elements fall mainly into two groups. The first group consists of nine elements where the Al-normalized concentrations are significantly greater in the city than to the north. The second group contains seven elements with similar city and north rural normalized concentrations. (Two elements were not detected in coarse particles and could not be compared.) The first group includes several heavy metals found abundantly in finer particle sizes (cf. Fig. 5) and may be attributed to pollution fallout to the soil. It also includes Ca which may reflect

Table 3. Coarse 4–8 μmad weight ratios to Al, 1980*

Element	Beijing City Center				West	North	Great	Earth
	7/29	7/30	12/23	12/25	12/26	12/29	Wall	Crust
				Elevated				
S	0.37	0.36	0.31	0.21	0.11	0.10	0.07	0.0032
Cl	0.16	0.13	0.14	0.06	0.03	0.02	0.04	0.0016
K	0.32	0.30	0.31	0.33	0.23	0.23	0.31	0.319
Ca	2.94	2.82	2.63	2.73	1.30	1.26	1.43	0.446
Mn %	2.23	4.40	2.14	2.04	1.50	1.66	1.64	1.17
Ni %	0.23	0.35	0.31	0.11	0.14	0.14	0.09	0.092
Cu %	0.85	0.61	0.63	0.40	0.23	<0.21	0.11	0.068
Zn %	3.05	3.10	2.78	1.47	1.08	1.03	0.43	0.086
Pb %	1.67	1.30	0.97	0.64	1.17	0.36	0.29	0.0160
				Not elevated				
Al	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Si	2.44	2.51	2.81	2.70	2.14	2.36	2.86	3.41
P	0.14	0.14	0.22	0.11	0.08	0.13	—	0.0129
Ti	0.10	0.11	0.15	0.11	0.10	0.09	0.06	0.054
V %	0.43	0.35	<0.83	0.27	0.56	0.34	0.26	0.166
Cr %	0.36	0.57	0.56	0.40	0.28	0.41	0.11	0.123
Fe	1.05	1.01	0.86	0.92	0.74	0.85	0.71	0.615
				Indeterminate				
As %	<0.34	<0.30	<0.69	<0.23	<0.22	<0.34	<0.01	0.0022
Br %	<0.40	<0.46	<1.40	<0.40	<0.14	<0.76	<0.01	0.0031

* Ratios of medians of impactor stage 5 concentrations for 2 to 6 samples each day, grouped by whether city center values are elevated over west and north values. % indicates element ratios × 100. Also shown are ratios for Great Wall at Badaling on 1 April 1980 (Winchester *et al.*, 1981a) and geochemical average earth crust composition (Mason, 1966; Mason and Moore, 1982).

dust from building materials in the city. The second group includes mainly coarse particle elements (cf. Fig. 5) which are expected to occur mainly in re-entrained dust. For the first group, the extent to which city center relative concentrations are elevated may be several-fold, although less than a factor of 10, and therefore suggests the accumulation of air pollution fallout over an extended period of time.

It is of interest that the ratio Pb/Al in coarse particles is up to 5-fold greater in the city center (29 July median for five sites) than the north site (on 29 December). In average earth crust this ratio is 100 times lower than in the city center, but we cannot attribute such a great difference mainly to pollution fallout. Instead, we may better assume that natural enrichment of Pb in soil aerosol compared to average earth crust rock may be as great as 20-fold, since the north rural site is not near major urban pollution sources. An additional 5-fold enhancement in the city may be caused by urban air pollution transfer to the ground. Subsequent pathways to man of this surface contamination may include the atmosphere by re-entrainment, water by leaching, or soil through plants grown for food.

DISCUSSION

The data base used in the present study consisted of 12 cascade impactor sets from two July days and 10 sets from three December days, each representing 4 h of sampling time and fractionation into seven particle size fractions. In all, 154 particle size fractions were analyzed by PIXE for 18 elements, representing 2772 individual concentration measurements. Each fraction required 4 min for PIXE analysis which provided a report of all elemental concentrations simultaneously, and the whole data set was obtained in about 12 h of PIXE analysis time. The data set could be searched for relationships among the different elemental concentrations, particle size distributions, locations, and sampling times. As described in the foregoing section, the relationships indicate that the urban aerosol is a complex mixture of components which derive from a number of different natural and pollution sources. Because the particle size fractionated samples were collected in locations which differed in the degree of impact by the different sources, these components could be recognized.

Most elements measured in the Beijing aerosol are bimodal in their particle size distributions, with a coarse mode apparently derived from surface soil as re-entrained fugitive dust, and a fine mode with certain elements originating in stack emissions from the combustion of coal and other fuels and with certain other elements intermittently emitted by industrial processes such as iron and steel manufacture. Some heavy metals typical of the fine mode are enriched in the coarse mode of the city center samples relative to a background site outside of the city, suggesting a significant degree of contamination of the ground surface in the city caused by deposition of fine combustion aerosol over an extended period of time.

Such contamination is of public health interest, since it may reach man by inhalation of resuspended dust, by ingestion of water contaminated by leaching, or by consumption of foods grown in contaminated soil. The approach taken in this study could be applied to cities in North America, Europe, or elsewhere to determine whether similar contamination also exists.

Both natural and pollution aerosol may be transported across national boundaries, and China may be both a source and a recipient country for international aerosol transport. It is now established that dust from China frequently crosses Japan and may reach Hawaii, especially during spring. It has also been found that pollution aerosol may be transported outside the borders of China, and it is possible that this, together with emissions from Europe and North America, contributes to Arctic haze. Such a possibility may be tested by careful scrutiny of elemental abundance ratios in fine aerosol particle size fractions, since the emissions of V and Pb are rather low in China owing to limited combustion of fuel oil and leaded gasoline, the concentrations of Zn seem to be high according to the present study, and other significant elemental differences may also be found to exist.

Coal combustion is an important cause of air pollution in Beijing, and in future years it may be of rising importance in air pollution of North America and Europe if the replacement of oil and gas by coal for industrial and electricity generating use proceeds as planned. It is likely that the Beijing aerosol fine mode contains a number of elements primarily derived from coal combustion, and the singular ultra-fine Si concentrations may also be of coal combustion origin. The observed concentrations of these elements provide an indication of the probable composition of past urban atmospheres in Western cities when 'coal was king' as well as possible future composition if emission controls are inadequate. International cooperation in atmospheric chemical investigations of cities in China can lead to findings of general interest to all countries.

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APPENDIX

Table A1. Median concentrations in fine particle size fractions, Beijing Center, 1980*

	Center July†				Center Dec.‡			
Element	(0)	1	2	3	(0)	1	2	3
				μg m^{-3}				
Al	<0.27	<0.02	0.10	0.28	<0.45	0.40	0.103	0.450
Si	6.0	0.12	0.26	0.63	8.0	0.46	0.28	0.94
P	<0.12	0.046	0.046	< 0.02	<0.2	0.035	0.023	0.054
S	0.78	1.16	2.54	0.62	1.27	0.34	0.31	0.15
Cl	0.16	0.03	0.10	0.16	0.21	0.007	0.032	0.062
K	<0.09	0.12	0.31	0.14	<0.13	0.047	0.050	0.142
Ca	0.12	<0.02	0.20	0.72	<0.01	0.052	0.193	0.96
Ti	<0.03	<0.008	<0.008	0.030	<0.05	0.004	0.013	0.051
Fe	0.12	0.05	0.44	0.57	0.12	0.03	0.09	0.37
				ng m^{-3}				
V	<21.	<1.3	<1.5	<1.5	<34.	<2.	<2.	<2.
Cr	24.	<0.9	<2.4	3.1	101.	<1.	<1.	<2.
Mn	<20.	5.5	3.4	4.8	< 23.	4.2	6.3	9.0
Ni	9.	7.6	2.9	2.8	14.	1.2	1.1	1.5
Cu	26.	15.9	12.1	4.9	18.	2.7	2.2	2.7
Zn	50.	100.	237.	127.	68.	50.	22.	5.7
As	<28.	10.0	13.4	4.8	<36.	<4.	<4.	<3.
Br	<100.	4.4	5.1	<4.4	§	<8.	<7.	<7.
Pb	57.	66.	150.	37.	47.	21	12.	<10.

* Approximate aerodynamic diameter ranges of the impactor stages: Filter stage 0, <0.25; stage 1, 0.25–0.5; stage 2, 0.5–1; and stage 3, 1–2 μmad.

† Medians of 12 samples (except 6 filter stages) at 5 sites on 2 days.

‡ Medians of 10 samples (except 4 filter stages) at 3 sites on 2 days.

§ Br contamination of Nuclepore suspected, giving apparent concentration of 4330 ng m^{-3}.

Table A2. Median concentrations in fine particle size fractions, Beijing West and North Sites, 1980*

	West Dec.†				North Dec.†			
Element	(0)	1	2	3	(0)	1	2	3
				μgm^{-3}				
Al	<0.31	<0.003	0.073	0.740	<0.32	0.034	0.186	0.575
Si	5.0	0.44	0.29	1.40	4.80	0.11	0.34	1.08
P	<0.13	0.043	0.020	0.041	<0.14	0.020	0.021	0.043
S	0.61	0.54	0.57	0.18	0.92	0.18	0.43	0.13
Cl	<0.11	<0.007	0.039	0.059	<0.12	<0.006	0.100	0.034
K	<0.09	0.149	0.185	0.161	0.19	0.123	0.340	0.104
Ca	<0.07	0.019	0.137	0.71	<0.08	0.017	0.160	0.35
Ti	<0.04	0.002	0.016	0.087	<0.04	0.006	0.019	0.053
Fe	0.08	0.07	0.22	0.67	0.12	0.02	0.17	0.46
				ng m^{-3}				
V	<24.	<2.	<2.	2.9	<25.	<2.	<2.	<3
Cr	174	<1.	2.0	4.1	65.	<1.	<3.	6
Mn	<17.	7.0	16.5	17.0	<14.	3.8	13.0	8.9
Ni	15.	2.8	2.6	3.6	14.	0.8	2.0	2.4
Cu	<13.	4.4	3.6	3.4	16.	1.0	1.9	0.9
Zn	34.	87.	64.	14.	65.	19.	27.	2.2
As	<29.	6.8	6.2	4.8	<27.	3.4	3.0	<2.5
Br	‡	13.0	6.8	4.7	‡	<6.	<5.	<5.
Pb	97.	88.	61.	39	<80.	<10.	<10.	<9.

* See caption to Table A1.

† Average of 2 simultaneous samples.

‡ Br contamination of Nuclepore suspected, giving apparent concentrations of 3130 and 3370 ng m^{-3} at west and north sites, respectively.

Table A3. Median concentrations in coarse particle size fractions, Beijing Center, 1980*

	Center July†			Center Dec.‡		
Element	4	5	6	4	5	6
			μg m^{-3}			
Al	0.83	1.87	1.73	1.35	1.70	7.40
Si	1.72	4.64	5.25	3.37	4.27	20.2
P	0.20	0.26	0.21	0.29	0.33	0.57
S	0.50	0.68	0.49	0.33	0.33	1.26
Cl	0.23	0.26	0.17	0.11	0.14	0.50
K	0.27	0.58	0.68	0.44	0.48	2.45
Ca	2.28	5.38	5.27	3.35	3.78	16.5
Ti	0.092	0.20	0.22	0.17	0.19	0.87
Fe	1.04	1.92	1.98	1.22	1.43	7.0
			ng m^{-3}			
V	3.3	7.2	6.4	6.1	7.0	40.
Cr	5.1	8.4	8.6	6.3	7.2	34
Mn	63.	63.	44.	27.	32.	133.
Ni	5.3	5.5	4.7	3.	3.4	13.
Cu	8.8	13.5	12.6	6.2	5.9	31.
Zn	65.	58.	47.	33.	43.	82.
As	<5.	<6.	<5.	<8.	<8.	<10.
Br	<7.7	<8.0	<7.8	<15.	<15.	<20.
Pb	21.	28.	23.	20.	10.	62.

* Approximate aerodynamic diameter ranges of the impactor stages: Stage 4, 2–4; stage 5, 4–8; and stage 6 >8 μmad.

† Medians of same 12 samples as in Table A1.

‡ Medians of same 10 samples as in Table A1.

Table A4. Median concentrations in coarse particle size fractions, Beijing West and North Sites, 1980*

	West Dec.†			North Dec.†		
Element	4	5	6	4	5	6
			μg m^{-3}			
Al	2.22	3.60	5.27	1.15	1.45	0.35
Si	4.41	7.69	12.4	2.47	3.42	1.00
P	0.28	0.30	0.40	0.19	0.19	0.15
S	0.28	0.39	0.84	0.20	0.15	0.09
Cl	0.10	0.10	0.28	0.05	0.03	0.05
K	0.48	0.81	1.36	0.23	0.33	0.15
Ca	2.6	4.7	8.6	1.04	1.82	0.89
Ti	0.24	0.35	0.54	0.11	0.13	0.036
Fe	1.74	2.65	4.21	1.02	1.23	3.36
			ng m^{-3}			
V	7.7	19.	17.	6.	5.	<4.
Cr	5.7	10.	3.7	11.	6.	<3.
Mn	36.	54.	85.	17.	24.	18.
Ni	4.9	5.1	6.7	3.7	2.1	1.7
Cu	7.2	8.1	14.	2.8	<2.9	3.9
Zn	32.	39.	85.	15.	15.	17.
As	<7.	<8.	<7.	<9.	<5.	<5.
Br	8.1	4.5	9.5	<10.	<11.	<10.
Pb	44.	42.	35.	<15.	5.2	<12.

* See caption to Table A3.

† Average of the same 2 simultaneous samples as in Table A2.