&EPA
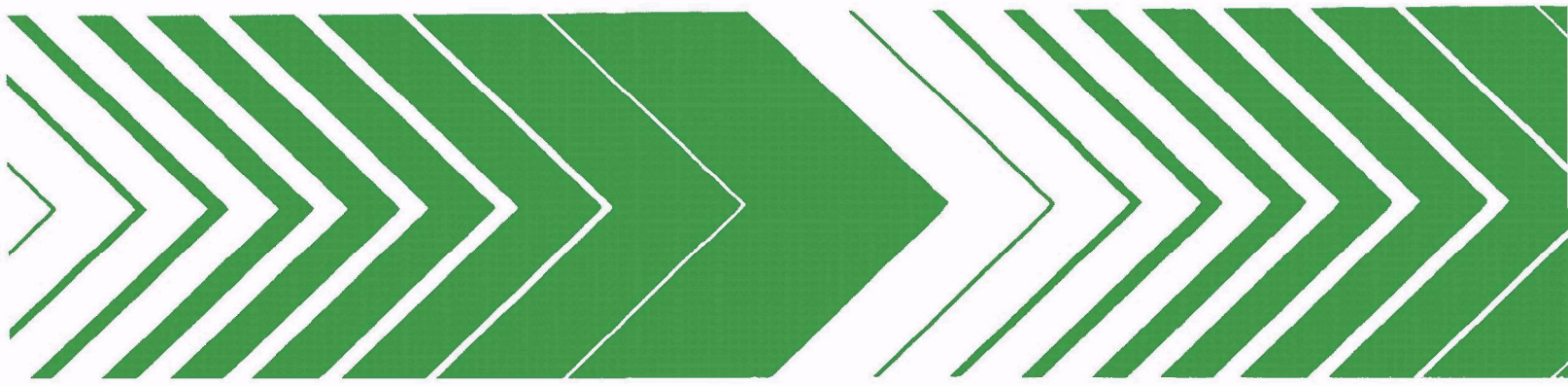
Sources and Transport of Trace Metals in Urban Aerosols

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SOURCES AND TRANSPORT OF TRACE
METALS IN URBAN AEROSOLS

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ABSTRACT

A methodology was developed, tested, and applied to the identification of trace element aerosol sources and trace element aerosol transport phenomena. The method uses lightweight and portable field sampling equipment and results in the acquisition of large data sets suitable for statistical analysis and the testing of aerosol transport models. Aerosol sampling in the ambient atmosphere was accomplished through a combination of time-sequenced filter collections with hourly resolution, and fractionated aerosol collections with 0.25 μm resolution. Elemental analysis was performed with particle induced X-ray emission, a sensitive and rapid method.

Aerosol characterization studies were focussed on St. Louis, Missouri, during the Regional Air Pollution Study. Trace element pollutants were distinguished from their natural components on the basis of particle size distributions. Statistical analysis of time-sequenced concentration measurements revealed four distinct pollution sources for lead. A related analysis demonstrated that meteorological factors controlling the transport of titanium aerosol across the city could be identified.

Extensions of the methodology were applied to (1) determination of trace element pollutant deposition in the human respiratory tract through direct sampling of exhaled breath, (2) the indoor environment by comparison of time variability in elemental concentrations with those measured outdoors, and (3) nonurban continental and marine atmospheres.

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SECTION 1

INTRODUCTION

The suspended particulate matter of urban atmospheres contains substantial quantities of trace metals together with sulfates, organic matter, and other non-metallic constituents. Trace metals, of course, occur naturally since all of them are constituents of naturally occurring dust which originates from materials at the earth's surface. However, urban activities, including the combustion of fuels, industrial processes, and the motions of vehicular traffic which tend to raise surface dust, are activities which tend to increase the concentrations of certain trace metals in the atmosphere above their natural levels.

Some trace metals play an active role in the metabolism of man and other living things, and some metals, when present to excess, may be toxic to man. Trace metals may also play an active role in the chemistry of the atmosphere, for example by acting as catalytic substrates for chemical reactions that convert gaseous into particulate material. Such may be the case for some metal oxides which may accelerate the conversion of sulfur dioxide to sulfates or may facilitate the condensation of organic vapors into small liquid droplets.

For these reasons a thorough investigation of the contents of trace metals in urban atmospheres is needed for setting optimum air pollution control strategies. Such an investigation should seek to find ways to identify the sources of individual trace metal constituents of the particulate matter and the factors which determine the extent of transport of these metals from their sources to other atmospheric locations and eventual removal from the atmosphere.

The atmosphere in most cities contains particulate matter derived from a multiplicity of sources. Seldom does one find an element which is derived predominantly from one source type, but rather any trace metal may enter the atmosphere from a number of different processes and types of human activity. Therefore it is not a straightforward task to identify the sources of trace metals by measuring their concentrations in the atmosphere. Indeed, it is also not straightforward to determine unambiguously whether the measured trace metal concentrations in the urban atmosphere are higher than their natural levels.

Consequently special measurement techniques should be devised for the study of trace metals in urban atmospheres which will help to identify sources and how trace metals are transported through the atmosphere.

New methods of investigation are needed for the collection of samples of atmospheric particulate matter, for their chemical analysis so that individual trace metal concentrations may be determined, and for the study of the concentration data, for example using methods of statistics or meteorology so that source and transport information may be obtained. In addition, it is important to gain some understanding of whether the concentrations observed and the characteristics of the particles containing the trace metals are such as to present a potential health risk to man, for example to his respiratory tract. Finally, a study of trace metals in urban atmospheres is not complete without some parallel investigation of clean air, air which has not been contaminated to the degree found in urban areas. Such a study is important, both to provide an estimate of the composition of the natural atmosphere, and thus by comparison the degree to which the urban atmosphere has been contaminated, and also to determine if urban atmospheric materials can be transported to cleaner areas sufficiently to modify the atmosphere of non-urban or marine areas by long range transport of air pollution.

In this report we shall review briefly the advances we have made at Florida State University in the methods of investigation of trace metals in urban aerosols; the characteristics of aerosol particles in the city of St. Louis, Missouri (in many ways a typical U.S. city); the clues that these characteristics provide for determining the sources of trace metals; the relationships between aerosol properties and the exposure presented to the human respiratory tract upon inhalation; and finally aerosol properties in cleaner air from which we may evaluate the extent of long range transport of pollutants outward from the urban areas.

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SECTION 2

CONCLUSIONS

1. The method of proton induced X-ray emission analysis, PIXE, is extremely precise and sensitive for the measurements of trace metal concentrations in atmospheric aerosol samples. It has been successfully calibrated and intercompared with other analytical methods for absolute accuracy of the order of 10%.

2. The PIXE method permits the use of small portable aerosol sampling equipment which can be economically deployed over networks on the urban scale. The small area of the analyzed portion of a sample permits use of miniature vacuum pumps with modest electrical power requirements. Thus, large scale aerosol sampling programs may be carried out with greater versatility and lower costs than if larger field sampling equipment were required.

3. Particle size distribution measurements can be made by sampling particle size fractions with cascade impactors. Impactors compatible with the PIXE method provide 6 particle size fractions, <0.25 μm, 0.25-0.5 μm, 0.5-1 μm, 1-2 μm, 2-4 μm and >4 μm aerodynamic diameter. The size range below about 4 μm, which comprises most of the particle mass for several trace metals of pollution importance, includes the respirable size range over which it is important to determine the distribution of elemental composition. Not only is this information desirable from a health effects standpoint, but it also assists in the identification of different pollution source processes for atmospheric trace metals.

4. Measurements of the time variability of aerosol trace metal concentrations with hourly time resolution can be made conveniently with the continuous time sequence "streaker" filter sampler. This time resolution is matched to the scale of important variability in the atmospheric motions that control the transport of aerosols over the urban dimensions. With time variability information transport models may be tested, and specific pollutants may be identified as useful transport tracers.

5. In St. Louis, trace metals from low temperature pollution sources may occur primarily in particles larger than 1 μm aerodynamic diameter; whereas high temperature sources

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preferentially emit submicrometer particles to the atmosphere. For example, automotive lead aerosol particles are significantly smaller than those of smelter lead aerosol. Industrial iron aerosol appears to have a larger component of submicrometer particles than iron derived from soil or other dust.

6. A local titanium pollution source in St. Louis causes elevated titanium concentrations throughout the St. Louis urban area. The concentrations show variations which are strongly dependent on wind direction, variability in mean wind direction, wind speed, atmospheric temperature gradient, land and water differences, and the occurrence of precipitation. The time variability pattern of titanium observed at different measurement stations has been used to evaluate quantitatively the importance of these factors in governing the titanium transport. In principle other trace elements and their associations may also be used as tracers to test transport mechanisms from stack emissions in the urban area in a manner similar to that demonstrated for titanium.

7. The association of lead with other trace metals in the St. Louis atmosphere has been analyzed statistically to demonstrate the existence of four different pollution components of atmospheric lead. These are the automotive component with a strong bromine correlation, a zinc related component possiby from smelter emissions, a crustal element related component possibly from fly ash, and an independent component possibly from secondary lead smelting, showing no other elemental association.

8. The high sensitivity of the PIXE method permits the sampling of exhaled human breath aerosol in normally polluted atmospheres by means of cascade impactors. Comparison of breath with ambient aerosol particle size fractions has enabled us to estimate the efficiency of particle deposition in the human respiratory tract as well as a humidification response on inhalation. The fact that a minimum deposition efficiency is observed for particles in the range 0.25-0.5 µm or possibly smaller points to the importance of particle size resolution in this range when evaluating potential health effects of pollution aerosols.

9. Streakers and cascade impactors have been used for monitoring lead, sulfur, and other elements along a heavily travelled roadway. Particle size of lead aerosol is found to be significantly greater for aged air parcels compared to air from the traffic lanes, an observation of importance to estimating human respiratory deposition of lead. Aged air is also characterized by a lower Br/Pb ratio than that of fresh automotive aerosol, suggesting bromine loss from the particles during atmospheric transport.

10. Indoor air pollution has been monitored directly with the streaker sampler and compared with outdoor concentrations. A detailed study of the correspondence in time variability patterns for certain residential atmospheres has established that lead and sulfur generally penetrate indoors from the outdoor urban atmosphere but that potassium has significant indoor sources. Some evidence has also been obtained indicating that a portion of the lead observed indoors may be due to recirculated contaminated household dust.

11. Measurements in nonurban continental and marine atmospheres have been made to evaluate the natural atmospheric concentrations with which the urban atmosphere may be compared. It is noteworthy that at Bermuda, more than 1000 kilometers from the eastern U.S. seaboard, fine particle sulfur aerosol was found to be many times above its level at highly remote sites in the Southern Hemisphere and indicates substantial long-range transport of pollution out over the Atlantic from the North American continent.

SECTION 3

TRACE METAL IDENTIFICATION TECHNIQUES

The measurement of trace metals in urban air particulate matter requires highly sensitive detection methods in order to measure the small quantities of each metal that may occur in samples collected over short periods of times. Furthermore, valuable clues concerning the sources of trace metals may be obtained by examining the distribution of concentration over different particle size ranges. Since sampling devices for short sampling intervals and for particle size selection gather only small amounts of suspended particulate matter, a high degree of sensitivity is required for a suitable elemental analysis technique.

The method of particle induced X-ray emission, using protons accelerated by a Van de Graaff accelerator up to 5 MeV, provides sensitivity for accurate measurements of many of the important trace metals in urban atmospheres down to a nanogram or less of each metal. Furthermore, this method is best used to analyze samples of very small dimensions, a few mm^2 or less, and those samples which are collected conveniently by time sequence and particle size fractionating devices. This method, known as PIXE, is the method of choice for obtaining the atmospheric chemical information described here.

PIXE PRINCIPLES

In principle, PIXE involves the bombardment of a sample for a minute or so in the vacuum chamber of a particle accelerator so as to generate X-rays characteristic of each element in the sample. These X-rays are detected by a solid state lithium drifted silicon detector, Si(Li). Electrical pulses from the detector are transformed electronically into signals recorded on a magnetic tape. After a few hundred analyses have been performed and recorded on the magnetic tape, the tape records of X-ray spectra of the individual samples are resolved into the concentrations of the individual elements by a digital computer. Most of the techniques for aerosol sampling, PIXE analysis and computer X-ray spectrum resolution which have been used in the work reported here have been developed especially for the purposes of this study of trace metals in urban aerosol particulate matter.

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Plate 1

Table I. Results of Analysis of Thin Homogeneous Standard Samples

Element (compound)	Amount given, μg	PIXE results Found, μg	Number of determinations	% Std dev per determination
Cl (NaCl)	6.8	5.6	3	5.2
Cl (KCl)	6.3	6.6	7	6.7
K (KCl)	7.0	7.1	7	6.5
Ca (CaF)	3.7	3.6	5	9.8
Ti metal	10.2	8.9	3	9.0
Cr metal	7.2	7.1	5	1.0
Fe metal	11.5	13.7	5	3.1
Cu (CuS)	7.9	8.1	14	7.1
Ga (GaP)	4.6	4.6	2	7.8
Br (CsBr)	3.1	3.0	3	3.0
Cs (CsBr)	5.2	5.5	3	6.0

Table II. Results from an Interlaboratory Comparison Study

	Sample on Millipore filter Amount given, ng[a]	Sample on Millipore filter Amount found[b] / Amount given	Sample on Whatman 41 filter Amount given, ng[a]	Sample on Whatman 41 filter Amount found[b] / Amount given
K	2040	1.032	943	0.981
V	374	1.071	233	1.069
Mn	1649	1.022	693	0.915
Fe	1916	1.093	1269	0.988
Cu	300	1.110	202	1.151
As	356	1.154	244	1.120
Pb	813	1.064	558	1.083
Mean		1.078		1.044

[a] Given amount of each element within area of proton beam striking sample. [b] Ratio of PIXE result to given amount for 2 to 4 replicate determinations. The standard deviation for a single determination by PIXE is approximately 15%.

Table III. Comparison between Heterogeneous and Homogeneous Samples

	Heterogeneous foil (~1 mm² piece)	Homogeneous foil
Zr-foil	5.66 ± 0.53 mg/cm²	5.01 ± 0.35 mg/cm²
Fe in Al-foil	21.3 ± 2.0 μg/cm²	23.3 ± 1.7 μg/cm²
Zn in Al-foil	1.02 ± 0.15 μg/cm²	0. 80 ± 0.10 μg/cm²
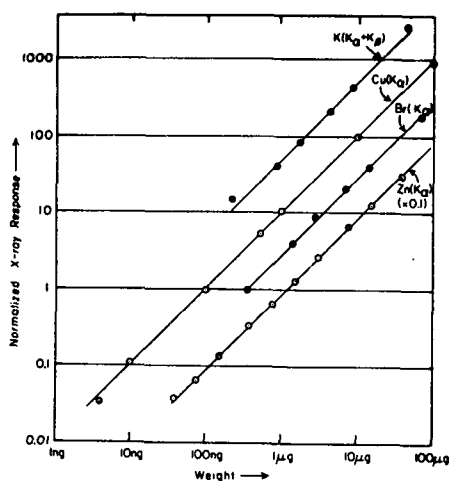
Figure 5. Results from linearity tests
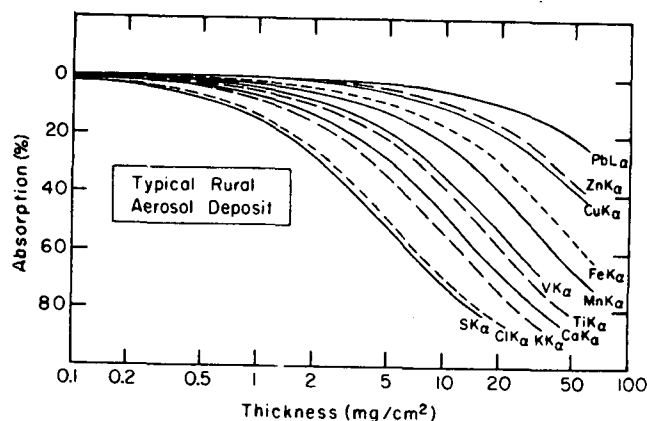
Figure 6. X-Ray attenuation in a homogeneous sample as a function of sample thickness

Source: A-2
Thomas B. Johansson, Rene E. Van Grieken, J. William Nelson, and John W. Winchester, Elemental trace analysis of small samples by proton induced X-ray emission, Anal. Chem., 47, 855-860, 1975.

In the development of the PIXE method a considerable amount of testing has been carried out to assure accuracy and reliability of the method. For example, Plate 1 shows in three tables that standard samples can be analyzed to an accuracy of 1 - 10% on an absolute basis. An interlaboratory comparison of PIXE method with the results obtained using other analytical methods at other institutions (Camp et al., 1974, 1975) shows an overall agreement for several trace metals of better than 10% on the average. We likewise have verified that the PIXE method is capable of analysis of a very small spot of sample as well as an evenly distributed wide area sample. This advantage is of special significance because it permits the analysis of individual particle size fractions collected by cascade impactors of the single orifice type which are described further below. This impactor collects samples as circular deposits of approximately 1 mm^2 diameter and requires the analysis of the entire sample spot. In the PIXE method the proton beam strikes a larger area which completely contains the spot and measures each trace metal contained within it.

Also shown in Plate 1, Figure 5, is a demonstration that the PIXE method permits a linear response of X-ray signal over at least a factor of 10,000 in amount of sample irradiated by the proton beam. A potential limitation to linearity is samples which are very thick and attentuate X-rays as they leave the sample after their proton induction. In Plate 1, Figure 6, a calculated absorption of X-rays in the sample shows that samples thinner than about 1 mg/cm^2 should give less than about 10% absorption for X-rays as soft as those for sulfur. More energetic X-rays are absorbed to a lesser extent so that lead X-ray attentuation reaches 10% only for thicknesses substantially greater than 10 mg/cm^2. Samples collected by the time sequence and particle size fractionation devices described below produce sample deposits thinner than these values for convenient sampling times in urban atmospheres.

For specialized applications of PIXE to the analysis of iron or other materials composed primarily of heavy elements, additional sources of error should be considered in the determination of trace elements with atomic number lower than that of the matrix, although these appear not to be serious in general for atmospheric particulate matter. Plate 2 illustrates the effect known as "enhancement," In the bombardment of a sample composed principally of iron, for example, considerable amounts of iron X-rays are generated. These X-rays may be critically absorbed by the trace metals also present in the sample and cause a secondary generation of their characteristic X-rays. Therefore the trace metal X-rays detected will be those not only due to the proton induction but also the secondary X-ray induction. As a result, a signal enhancement occurs which will cause an erroneously high analysis unless enhancement is corrected for. As indicated in

Plate 2

TABLE 1

Enhancement in % from the Fe K_α and Fe K_β X-rays on K_α X-rays from different elements. Calculated for 2.5 MeV protons in a 100% iron sample.

Z	Element	Exciting X-ray	
		Fe K_α	Fe K_β
25	Mn	0	7.8
24	Cr	41	4.7
23	V	24	2.8
22	Ti	14	1.6
21	Sc	8.6	0.95
20	Ca	4.9	0.54
19	K	2.7	0.30
17	Cl	0.83	0.09

TABLE 2

Analysis of NBS low alloy steel SRM 1261 (95.6% Fe), with 5 MeV protons.

Element	Concentration (%)		
	No enhancement correction	With enhancement correction	NBS value
Mn	0.80	0.71	0.66
Cr	1.24	0.71	0.69
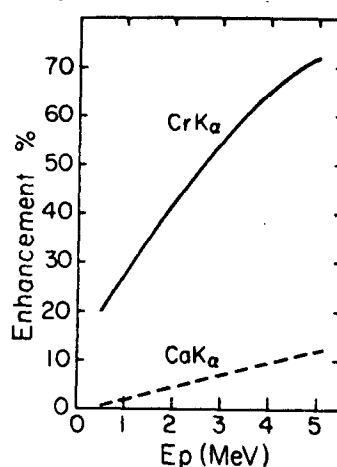
Fig. 2. Enhancement from Fe K_α X-rays on Cr K_α and Ca K_α X-rays as a function of proton energy in a 100% iron sample.

Source: A-4
Mats. S. Ahlberg, Enhancement in PIXE analysis, Nuclear Instruments and Methods, 142, 61-65, 1977.

Table 1 of Plate 2 the enhancement of chromium X-rays in an iron sample may be more than 40%. In a typical steel sample analyzed without enhancement correction the chromium analysis was found to be high, but if the enhancement correction is made, the analysis is in good agreement with the standard value. As seen in Figure 2, Plate 2, the enhancement problem becomes more severe at higher proton energies but is less severe for elements of considerably lower atomic number than the matrix, such as calcium in comparison with the matrix element, iron.

In aerosol analysis most major elements are of lower atomic number than the trace elements measured by PIXE. For example, more than half of the total particulate mass typically found in urban atmospheres is composed of the elements C, H, O, N, S, with additional Na, Mg, Al and Si, all of these being elements of atomic number lower than the trace metals whose concentrations are discussed further in this report. Even for the extreme case of measuring trace amounts of sulfur in pure rock salt, NaCl, calculations show that enhancement of sulfur X-rays is not a source of significant analytical error.

PIXE SPECTRUM RESOLUTION

A crucial part of the PIXE analytical procedure, and one without which the method would not succeed, is the translation of the accumulated electronic signals from the Si(Li) X-ray detector into a list of elemental concentrations in the sample. This feat is accomplished by the unraveling of the X-ray spectrum, consisting of a number of X-ray counts recorded in each of 600 or more individual energy channels, into the contribution from each elemental constituent of the sample. Plate 3, Figure 2 shows a typical X-ray spectrum for an aerosol sample collected on a filter. The three parts of the figure show the effect of interposing a thin absorbing material in front of the Si(Li) detector window causing some of the X-rays, especially those of lowest energy (lowest channel number), to be absorbed. In both cases individual elements present in the sample account for peaks in the spectrum, but a thin Mylar plastic absorber skews the entire spectrum in the low energy end so that the elements Al, Si, and S are completely suppressed. In samples where these elements may be so abundant that their X-rays are intense enough to limit the permissible bombardment intensity of the sample by the proton beam (because of limitations on the speed of electronic circuitry), and thus lengthen the total analysis time required to detect the heaviest elements in the sample, this technique of using an X-ray absorber is useful. By suppressing these troublesome light elements, a more intensive proton bombardment is permitted, and shorter analysis time is required for accurate measurement of heavier metals, for example lead.
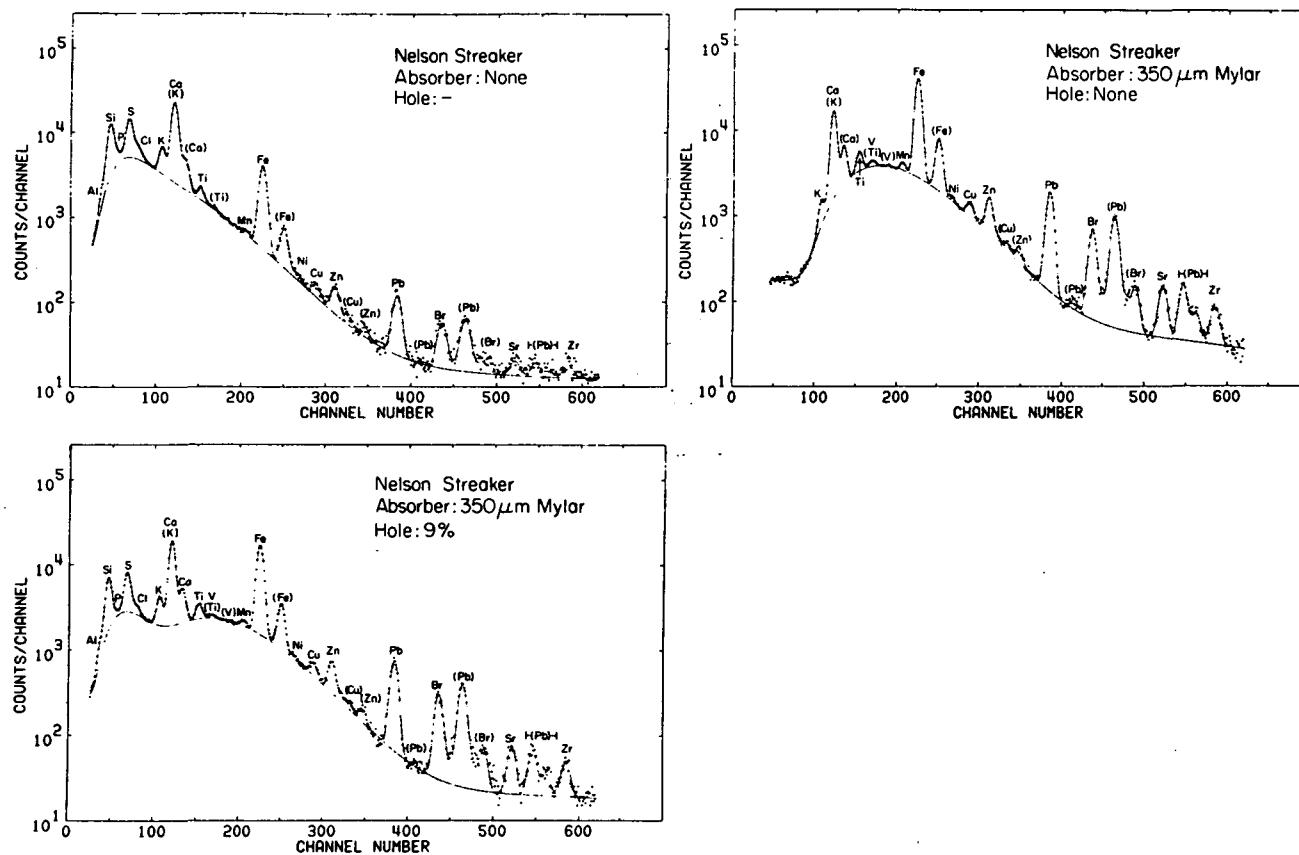
Fig. 2. Fits to proton induced X-ray emission spectra obtained from bombarding an aerosol sample obtained with the Nelson Streaker. For quantitative comparison see table 1.

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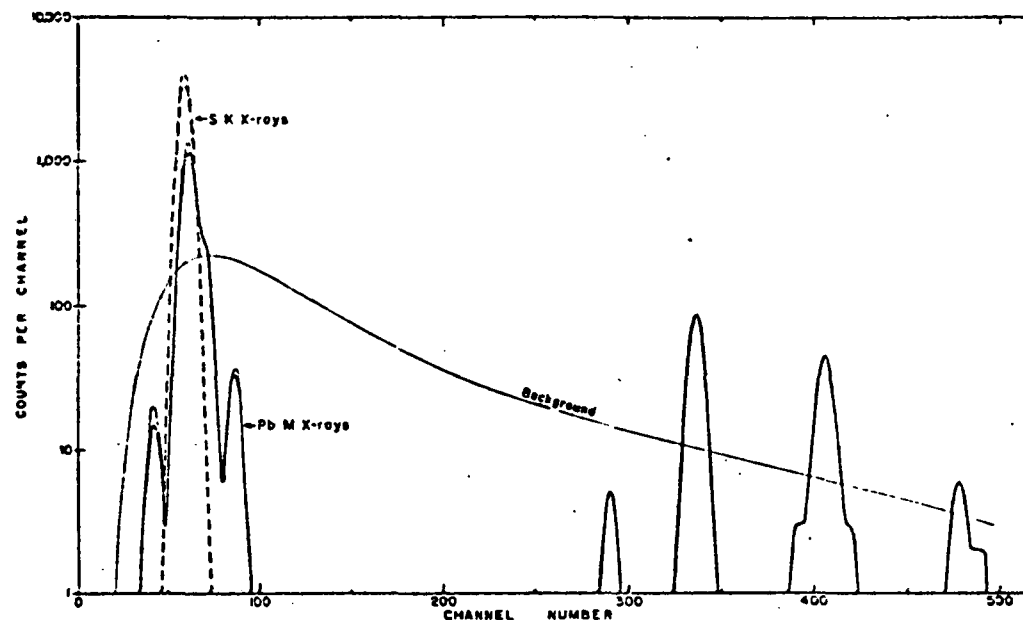
Figure 4. Display of relative contributions of S, Pb, and background
X-ray components for equal masses of S and Pb in typical
streaker sample subjected to routine PIXE analysis. Calcu-
lations with (———) and without (-----) self-absorption
corrections and a relative background position for Nucle-
pore filters are shown as separate components.

Source: A-18.
K.R. Akselsson, K.A. Hardy, G.G. Desaedeleer, J.W. Winchester, W.W. Berg, T.B. Vander
Wood, and J.W. Nelson, X-ray techniques for aerosol sulfur baseline assessment along
an urban freeway, Advances in X-Ray Analysis, vol. 19, R.W. Gould, C.S. Barrett, J.B.
Newkirk, and C.O. Ruud, eds., pp. 415-425, Kendall Hunt, Dubuque, Iowa, 1976.

A more usual case in aerosol analysis is where both the
light and heavy elements must be determined, and therefore a
complete suppression of the light elements is not desired. In
that case the absorber is used as before but in a modified form,
such that a small hole is cut in the center of the absorber in
order to transmit without absorption a small fraction of the
unattenuated X-rays; for example the spectrum using a 9% hole
absorber is shown in Figure 2 of Plate 3. The light elements,
which are completely suppressed by the remaining 91% of the
absorber area, are seen as unattenuated X-ray peaks at 9%
of the original intensity. The heaviest elements are
effectively unattenuated by the thin absorber, as before. A
few elements of intermediate character, in this case K and Ca,
are partially attentuated by the absorber, but from calibration
measurements their overall transmissions may be calculated.
With this X-ray absorber the entire spectrum of elements from
Al to Pb and beyond may be measured in a single bombardment
lasting only a minute or so depending on sample size.

A practical case of potential X-ray interference between
elements is illustrated for the case of measuring sulfur in
the presence of lead. Along roadways where leaded gasoline is
burned the concentration of atmospheric lead may be highest
relative to sulfur in comparison with air anywhere in the urban
environment. The lead X-ray spectrum contains many peaks, both
in the higher energy region where the peaks are used for element
identification and in the low energy region of the most important
sulfur peaks. These low energy M X-rays of lead pose a potential
interference in the accurate resolution of sulfur from the
spectrum. The computer X-ray resolution procedure developed
for this research removes the interference by accurately
calculating the amount of lead present, estimating the low
energy lead X-ray component, and determining the net sulfur
X-ray present. Under normal circumstances the extent of lead
X-ray interference in sulfur determination does not exceed a few
percent, and even in a roadway situation the interference,
whereas perhaps ten times greater, is still accurately
measurable.

This example illustrates that the PIXE X-ray spectrum
resolution problem requires a detailed evaluation of all physical
relationships among the constituent elements in the sample. An
especially important part of the problem is the accurate deter-
mination of the X-ray background contributed by the sample mass
and the sample substrate, for example filter paper or particle
impaction surface. This background is produced by atomic
interactions during proton bombardment distinct from those which
produce the characteristic X-rays of the elements. In the light
element region of sulfur and neighboring elements the background
X-ray spectrum exhibits considerable curvature, and in the
case of the absorber with hole the curvature is of complex
shape. If the concentrations of light elements are relatively

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low, the estimation of their amounts above background requires an accurate measurement of the background. In the computer procedure we do not use separate measurements of substrate materials without sample, e.g. blank filters, nor direct measurement of the background since this would not include the mass effect of the sample itself in causing the background X-radiation. Instead, in our procedure the principal physical processes causing the background have been identified, and the background shape has been successfully modeled. Comparison with standard samples indicates that this modeling of the background permits accurate measurements of the important light elements. Thus the computer procedure for spectrum resolution requires only the data contained in the sample spectrum alone, and offers a great advantage in simplicity and speed of the computer data processing (normally about one minute per spectrum) and in overall accuracy.

SECTION 4

SAMPLING THE URBAN AEROSOL

A comprehensive investigation of trace metals in urban aerosols requires techniques for measuring their concentrations in air which will:

1. Provide a determination of trace metal distributions among particles of different size over the stable aerosol size range <0.25 μm to >4 μm aerodynamic diameter.

2. Provide an indication of the time variability of trace metal concentration on a time scale comparable to the 3-hour meteorological data provided by the National Weather Service.

3. Provide for the simultaneous measurement in each sample of several trace metals of air pollution interest so that inter-element correlations may be studied as indicators of sources and transport pathways.

4. Provide data sets of sufficient size for statistical methods of interpretation to be employed.

5. Permit the ready deployment of large numbers of aerosol sampling devices simultaneously over an urban area, with minimum restrictions on site selection due to electric power, mounting platforms, or other logistic requirements.

6. Permit reasonable speed and cost for carrying out both sampling and elemental analysis of aerosols collected in field programs.

These conditions require the development and validation of aerosol particle sampling devices and methods which have not previously been employed on a large scale in studies of trace metals in the urban atmosphere.

The measurement of elemental composition as a function of particle size is accomplished by sampling with a cascade impactor. Plate 4 is a schematic diagram of the impactor used in connection with PIXE analysis. The basic design is that of the Battelle 5-stage impactor (Mitchell and Pilcher, 1959) and requires a flow rate of 1 liter/minute. The impactor may be

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Plate 4

AIR FLOW - 1 liter/min

A

AEROSOL

LARGE JET

LARGE
PARTICLE

SMALL
PARTICLE

SMALL JET

SMALL
PARTICLE

MYLAR FILM
with
STICKY COATING

C

CASCADE IMPACTOR

OPERATED IN THE INVERTED POSITION

B

STAGE

0

1 — DISC SUPPORTS (3)

— DELRIN WASHER

2

3

4 — CRITICAL-FLOW
ORIFICE

5 — FILTER STAGE
(for 25mm, 0.4 μ
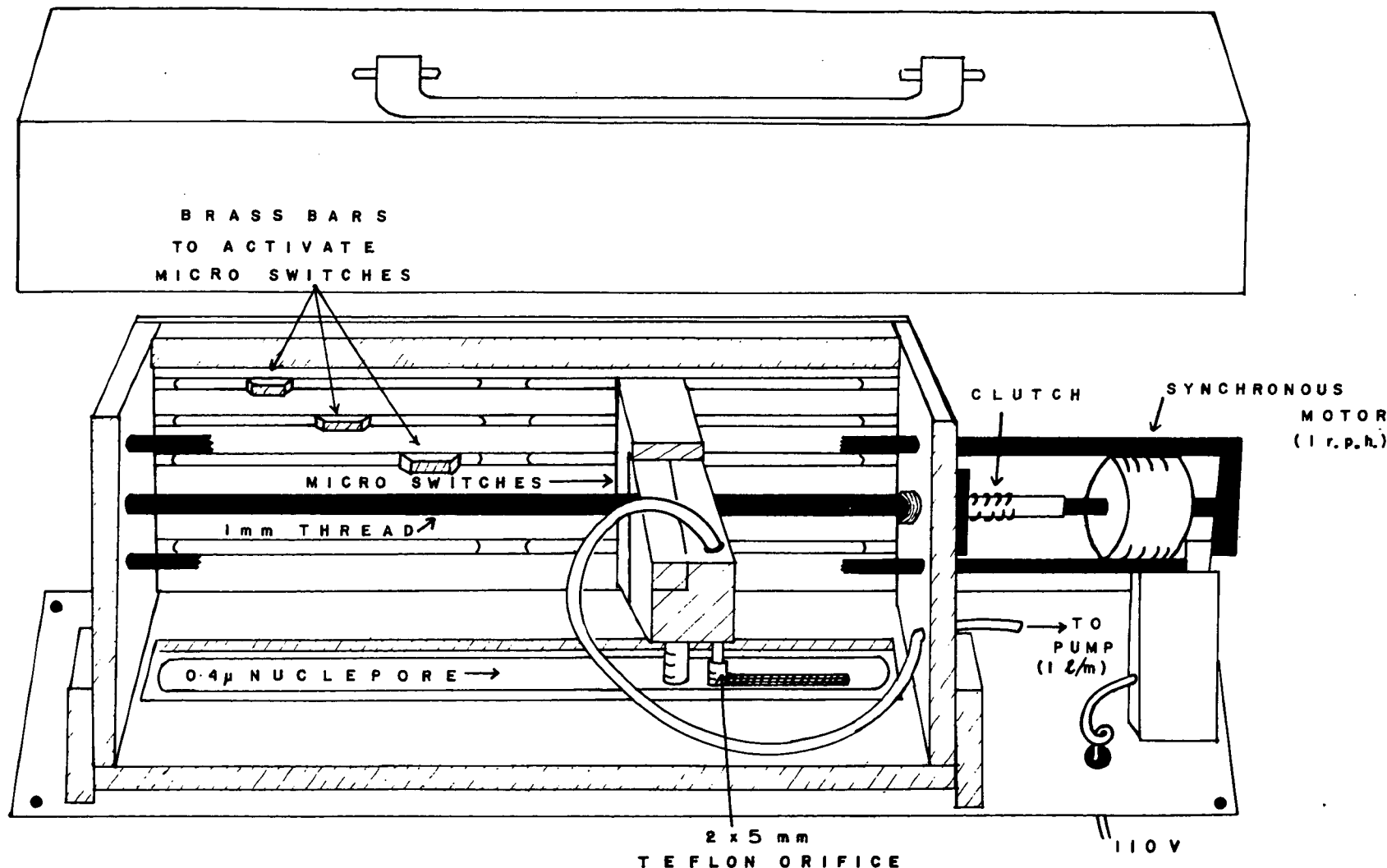Nuclepore)

6

TO VACUUM PUMP
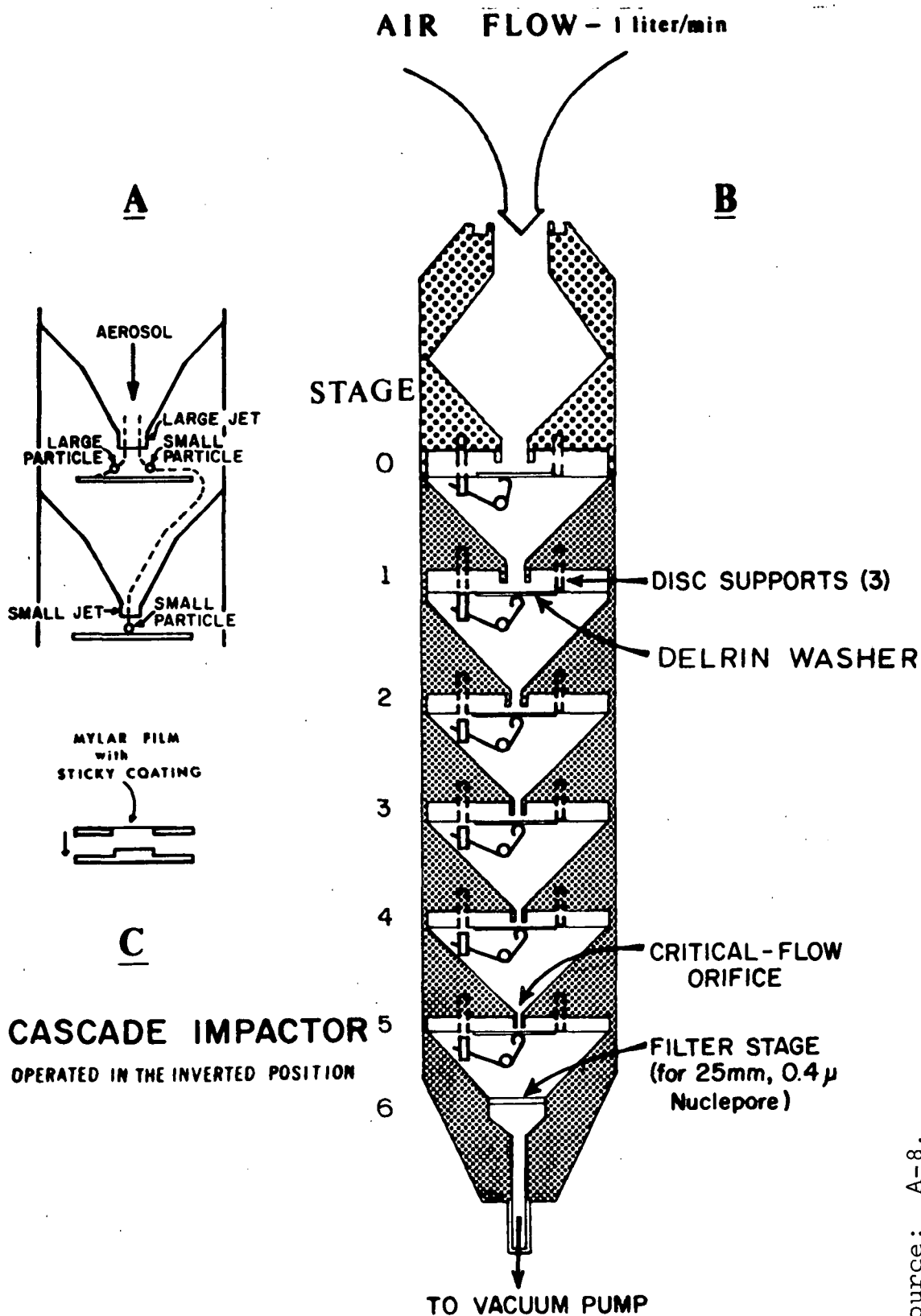
Source: A-8.
A.P. Woodard, Jr., B. Jensen, A.C.D. Leslie, J.W. Nelson, J.W. Winchester, R.J. Ferek, and P. Van Espen, Aerosol characterization by impactors and streaker sampling and PIXE analysis, in Proceeding of Symposium, Recent Advances in Air Pollutant Analysis, American Institute of Chemical Engineers, New York, (in press) 1977.

operated in any position so that air may be drawn vertically downward into the device from the top, or the impactor may be inverted face down so that air is drawn upward from below. The air is passed successively through a series of circular orifices of decreasing diameter which causes the linear flow rate of air to speed up as it goes through successive stages. Directly downstream of each orifice is an obstruction in the form of a sticky Mylar film backed by a solid support surface such that the largest particles passing through the orifices at each stage are caused to impact and stick to the Mylar surface. Smaller particles pass around the impaction surface but at the next stage, owing to increased air velocity, the largest of them will be collected by impaction. The impactor has been designed to give 50% collection efficiency for stages 0 through 5 of 8, 4, 2, 1, 0.5 and 0.25 µm aerodynamic diameter, so that the particle size range of the stages is the range of diameters between these values. Particles smaller than those collected by impaction stage 5 are collected by filter stage 6. The Nuclepore filter used is of small enough pore diameter to assure at least 60% collection of any particle size (Liu and Lee, 1976); calculations show that the minimum efficiency is in the range of the few hundredths of a micrometer diameter where diffusion and impaction mechanisms of particle uptake by the filter are comparable. Each sample is collected conveniently in a small area suitable for analysis by the proton beam in PIXE.

It should be emphasized that the particle size discrimination of the cascade impactor is effective for particles as small as 0.25 µm aerodynamic diameter. (Physical diameter differs from aerodynamic diameter if the density of the particles is different from 1 g/cm^3 and the shape of the particles is sufficiently different from spherical to cause shape-dependent air drag effects.) Cascade impactors may be designed to operate at higher flow rates but generally with the smallest size cut at larger diameters, e.g. 0.5 µm or greater. The work described in this report will demonstrate that the information obtained by small particle size resolution in the 0.25 µm range is extremely valuable for interpreting sources and transformations of trace elements in atmospheric particulate matter. Moreover, the response of the human respiratory tract to inhalation of fine particles varies significantly with particle diameter in the 0.25 µm region so that health effects can better be evaluated if particle size distribution and composition for particles this small can be determined.

The time variability of trace metal concentrations in the air can be obtained easily and automatically if sampling is carried out with a filter sampler whose exposed surface is changed continuously. In Plate 5a a diagram of a special sampler developed at Florida State University for this program is shown. This time sequence filter sampler consists of a single

BRASS BARS
TO ACTIVATE
MICRO SWITCHES

CLUTCH

SYNCHRONOUS
MOTOR
(1 r.p.h.)

MICRO SWITCHES →

1mm THREAD ↗

0·4μ NUCLEPORE →

TO
PUMP
(1 ℓ/m)

2 x 5 mm
TEFLON ORIFICE

110 V
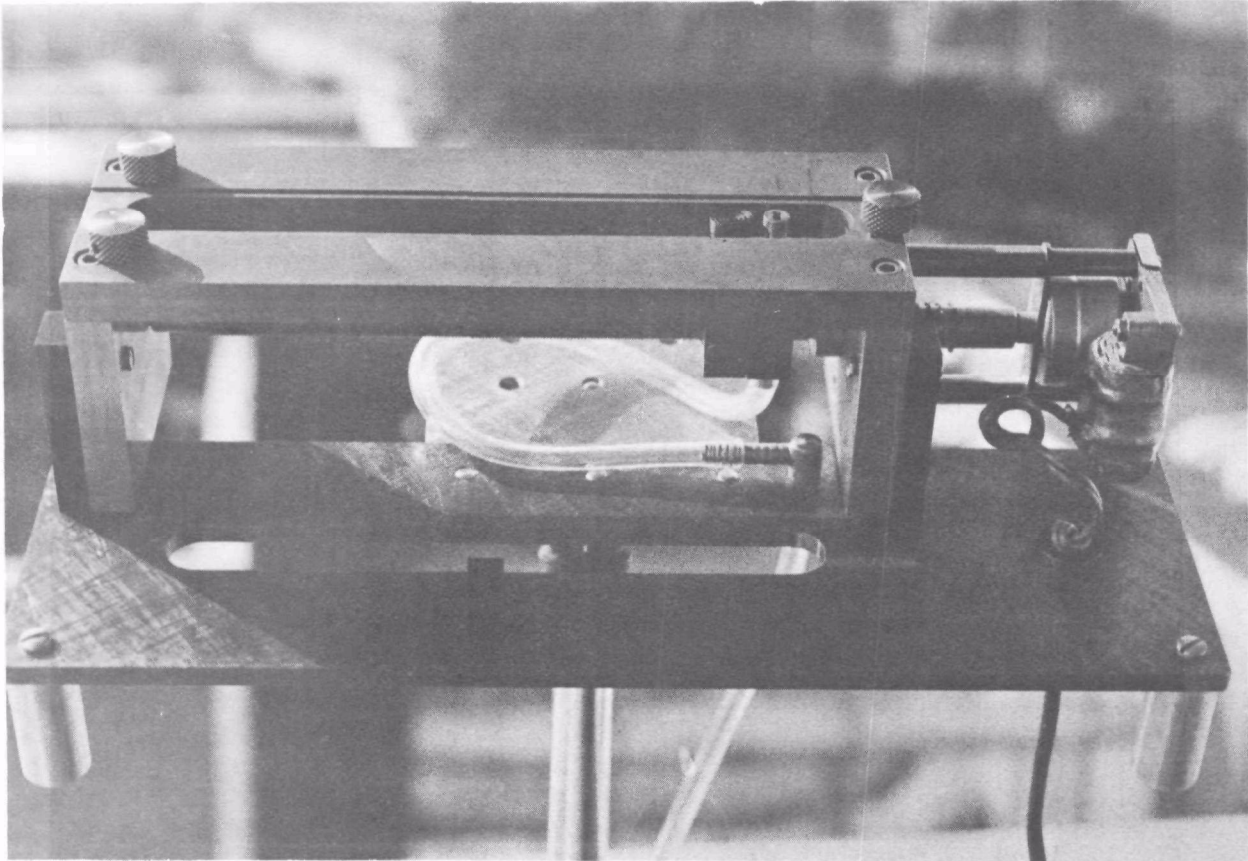
Figure 2.1 View of the continuous filter sampler. The 2- X 5- mm
air intake (upper right center) is driven to the left at a rate of
1 mm per hour by the synchronous motor. A Nuclepore filter strip is
placed over the intake to produce an 84- mm long strip sample in
one week.

Source: B-11.
J. William Nelson, Proton-induced aerosol analyses: methods and
samplers, in X-Ray Fluorescence Analysis of Environmental
Samples, Thomas G. Dzubay, editor, pp. 19-34, Ann Arbor Science
Publishers, 1977.

strip of Nuclepore filter stretched on a frame and mounted in a
device which causes a sucking orifice on Teflon or other smooth
plastic to be drawn gradually from one end of the filter to
the other. The sucking orifice is attached to a vacuum pump,
and as the orifice is drawn along the length of the filter, the
suction seals the orifice to the smooth back of the Nuclepore
while at the same time permitting air to be drawn through the
filter at a rate controlled by its porosity. The device is
designed to be driven by a clock motor connected to a precision
threaded screw so that 7 days (168 hours) is required for a full
transit along the length of the filter. In urban atmospheres
a feasible streak of aerosol particle deposit is produced over
the one week sampling period. Thus the sampler is known as a
"streaker." If desired the clock mechanism can be used to
control other sampling devices in a sampling program by means
of micro-switches which are attached to the moving orifice
mounting bracket. These micro-switches can be activated by
small brass bars mounted in positions as desired so as to close
electrical circuits at specific times. These circuits may be
used to automatically operate other samplers, for instance
cascade impactors, during the streaker sampling period.

The Nuclepore filter strip can be analyzed sequentially
by the proton beam in time steps corresponding to sampling time
intervals of two hours or less. In our accelerator bombard-
ment facility we carry out these stepwise bombardments semi-
automatically so that 90-100 separate bombardments, representing
a one-week streaker scan in 2-hour time steps plus blank
filter analyses, may be performed in as short a time as two
hours. Although individual samples may require longer PIXE
analysis times owing to low concentrations or other special
considerations, the procedure does permit rapid scans of
relatively large numbers of streaker samples so that data sets
of many hundreds of individually analyzed time steps over a
sampling network may be carried out. An illustration of the
streaker sampler used in this program is shown in Plate 5b.
The appearance of a typical streaker sample is shown in Plate 6
as it is being loaded into the vacuum chamber of the Van de
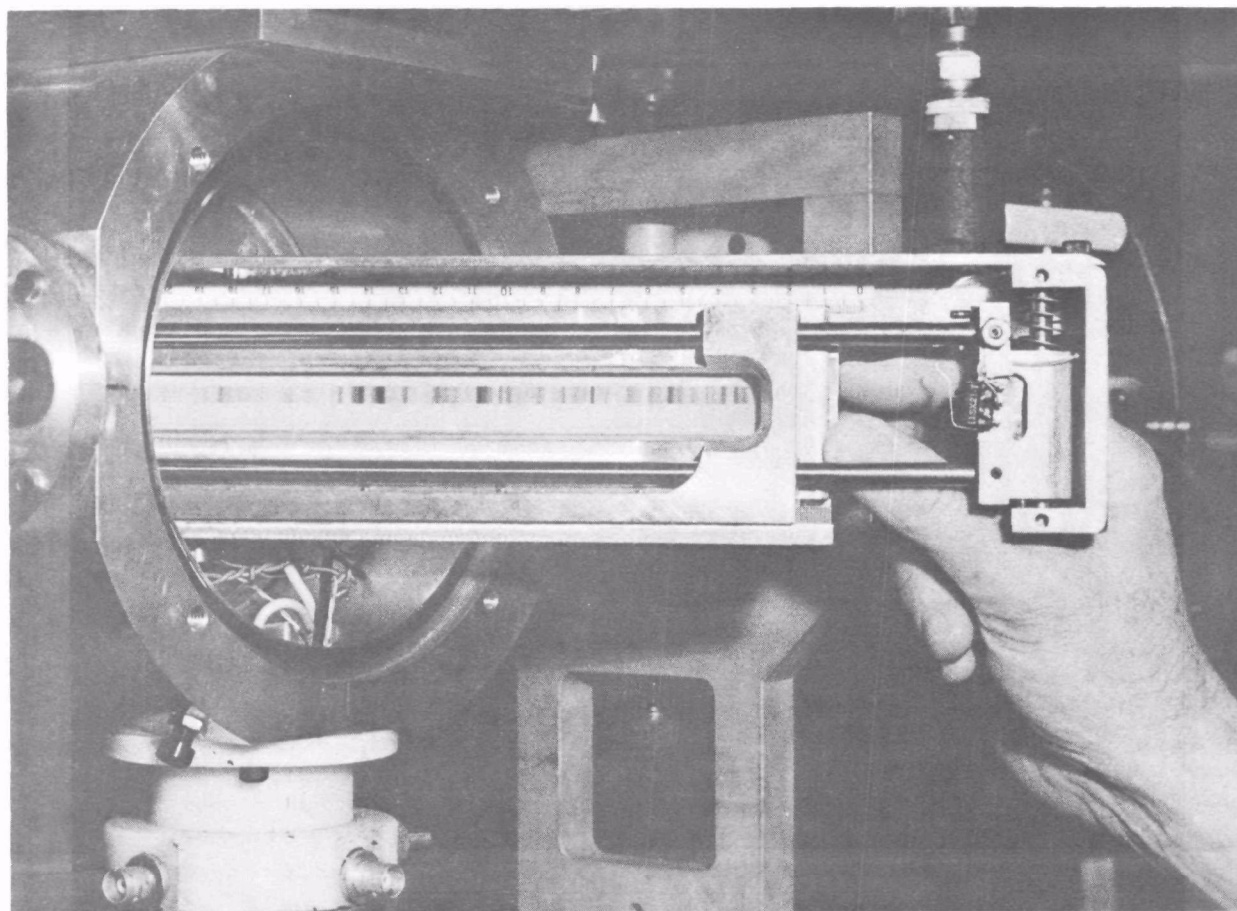Graaff accelerator for PIXE analysis.

Plate 6

Figure 2.4 A streaker sample being inserted into the sample holding chamber in preparation for proton bombardmemt.

SECTION 5

CLUES TO THE SOURCES OF TRACE METALS IN URBAN AEROSOLS

Direct measurement of concentrations of trace metals in the atmosphere of a city does not in itself demonstrate the presence of air pollution. Trace metals all occur naturally as well as the result of emissions from polluting processes. In order to demonstrate the presence of a pollution component we must make use of characteristics such as particle size distribution and time and location variability of the concentrations of individual trace metals. In addition, meteorological and statistical analysis of the concentration data needs to be carried out so that associations with measures of atmospheric transport dynamics and relationships among the various trace metals may be used as clues to the kinds and locations of pollution sources which may be present.

EVIDENCE FROM PARTICLE SIZE DISTRIBUTION

The city of St. Louis has been used as a case study area in this investigation, conducted during the Regional Air Pollution Study, RAPS. Plates 7 and 8 present the concentrations of a number of trace metals as a function of their particle size in St. Louis during August 1973. In these detailed plots most of the data points represent concentrations at an industrial area site "BH" (Broadway and Hurck Streets intersection) in the south of the city, and a central city site "HI" (Holiday Inn Downtown) during two meteorological episodes of about 2½ days each -- I during southerly air flow and II during generally northerly air flow. For comparison, additional data are shown for a north St. Louis site "WW" (Water Works), North Florida nonurban locations "NFL," and the marine atmosphere at Bermuda "BDA." For the element titanium, which has a large and distinct pollution source a short distance south of the BH site, individual samples for successive 12-hour periods beginning in the forenoon and evening of each day, August 16 to 21, 1973, are shown.

Titanium at the BH site appears to be principally derived from the pollution source when sampling was carried out during meteorological period I. During this time the generally southerly air flow transported pollution titanium over the BH sampling site and caused the concentrations to be generally in

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Source: A-13.
R. Akselsson, C. Orsini, D.L. Meinert, T.B. Johansson, R.E. Van
Grieken, H.C. Kaufmann, K.R. Chapman, J.W. Nelson, and J.W.
Winchester, Application of proton-induced X-ray emission
analysis to the St. Louis Regional Air Pollution Study, Advances
in X-Ray Analysis, vol. 18, W.L. Pickles, C.S. Barrett, J.B.
Newkirk, and C.O. Ruud, eds., pp. 588-597, Plenum Press, New
York, 1975.
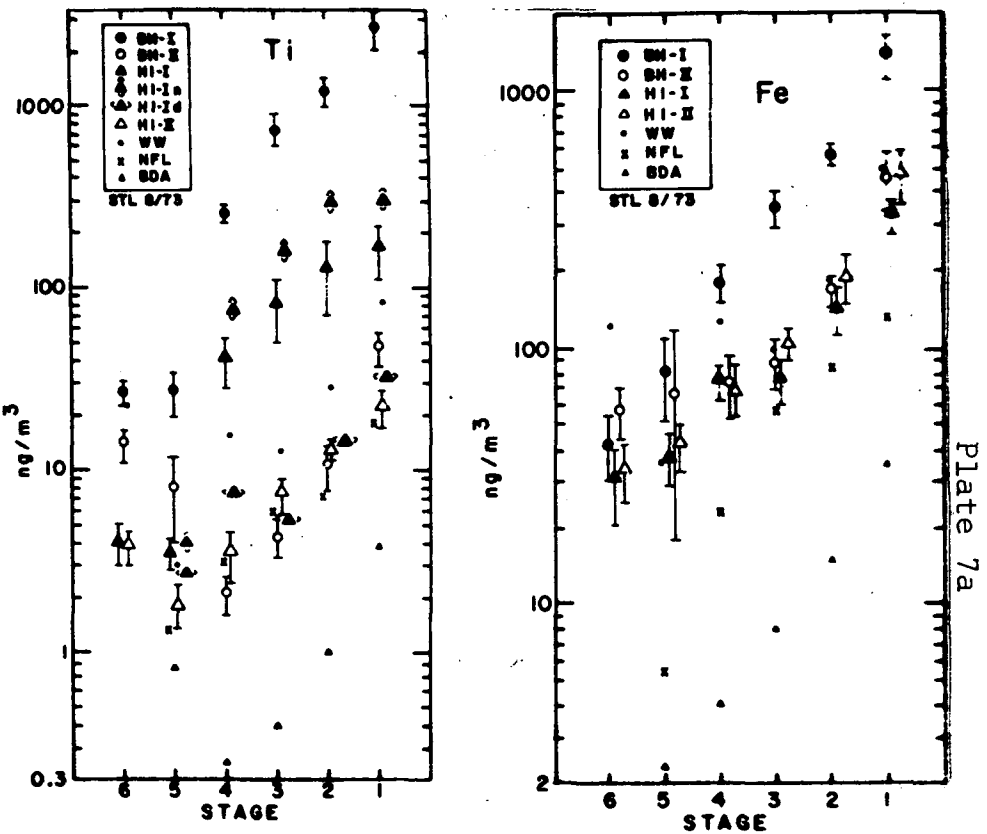
Fig. 2. Concentration of titanium and iron as a function of particle
size in St. Louis aerosol, 16-22 August 1973, at BH and HI sites.
Means of individual measurements for periods I and II are shown as
dotted lines for Ti at BH in the left diagram. Other diagrams show
means with standard deviations for periods I and II at BH and HI, with
HI n and d series means also plotted separately for Ti. Averages of
samples taken at locations WW, NFL, and BDA are also shown.

Plate 7a
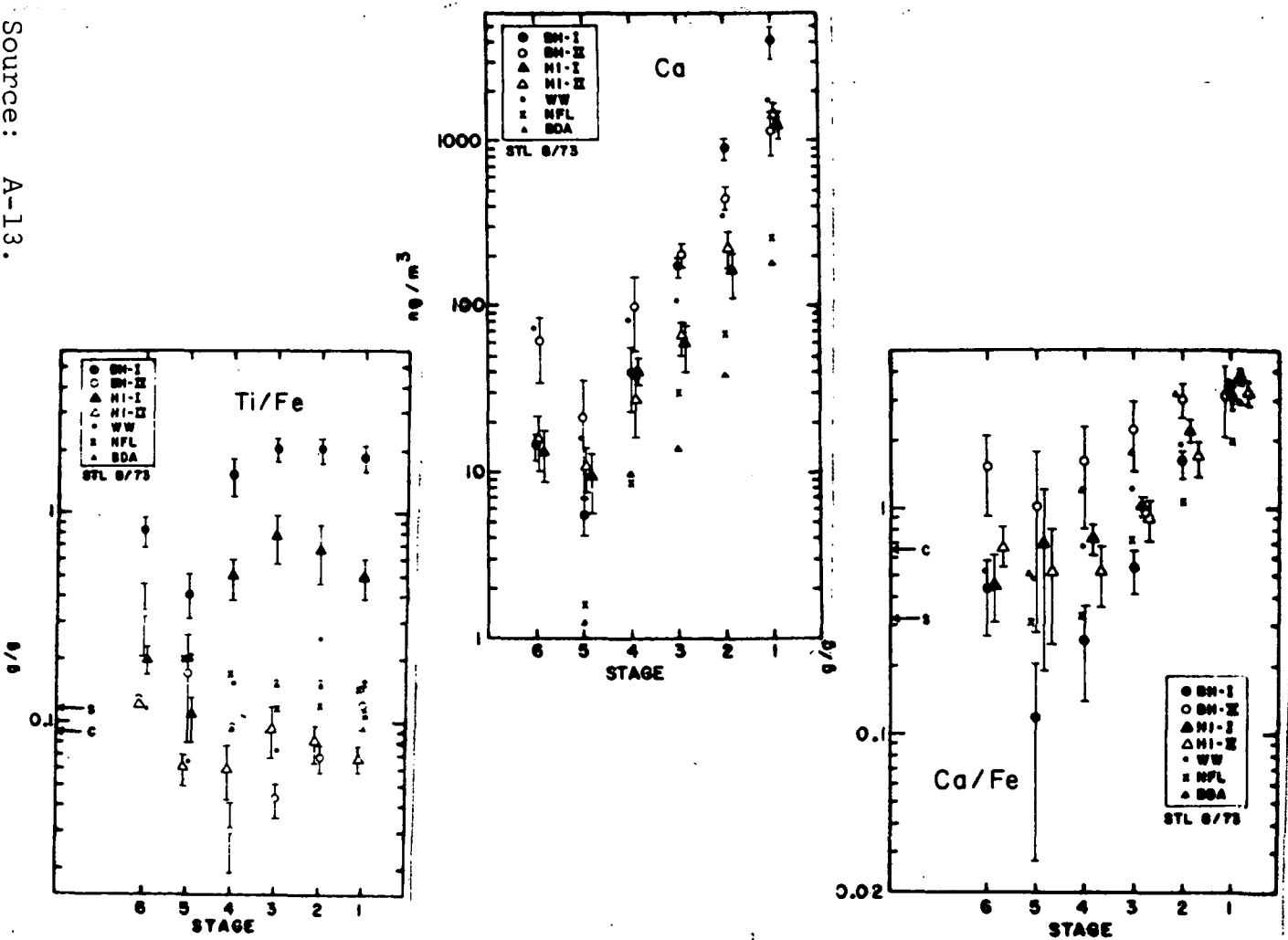
Fig. 3. Mean values for concentrations of calcium and weight ratios of titanium and calcium to iron as a function of particle size. Average composition of soil(s) and earth's crust(c) are shown for Ti/Fe and Ca/Fe. Upper limits to means are indicated by curved marks above points.

Source: A-13.
R. Akselsson, C. Orsini, D.L. Meinert, T.B. Johansson, R.E. Van Grieken, H.C. Kaufmann, K.R. Chapman, J.W. Nelson, and J.W. Winchester, Application of proton-induced X-ray emission analysis to the St. Louis Regional Air Pollution Study, Advances in X-Ray Analysis, vol. 18, W.L. Pickles, C.S. Barrett, J.B. Newkirk, and C.O. Ruud, eds., pp. 588-597, Plenum Press, New York, 1975.

24

Plate 7b

Plate 8a
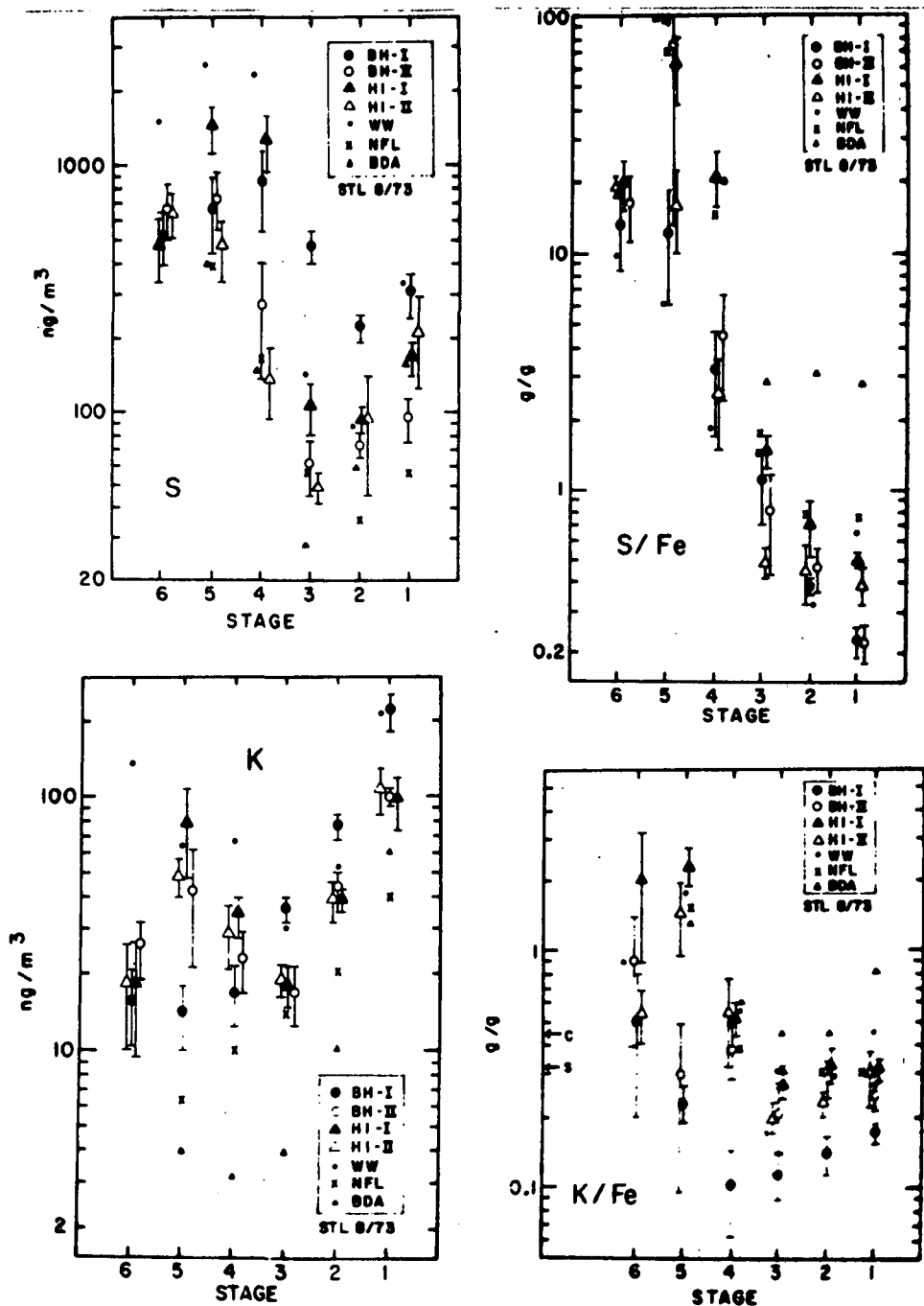
Fig. 4. Mean values for concentrations and weight ratios to iron of sulfur and potassium as a function of particle size.

Source: A-13.
R. Akselsson, C. Orsini, D.L. Meinert, T.B. Johansson, R.E. Van Grieken, H.C. Kaufmann, K.R. Chapman, J.W. Nelson, and J.W. Winchester, Application of proton-induced X-ray emission analysis to the St. Louis Regional Air Pollution Study, Advances in X-Ray Analysis, vol. 18, W.L. Pickles, C.S. Barrett, J.B. Newkirk, and C.O. Ruud, eds., pp. 588-597, Plenum Press, New York, 1975.

Fig. 5. Mean values of concentrations and weight ratios to iron of zinc and lead as a function of particle size.

Source: A-13.
R. Akselsson, C. Orsini, D.L. Meinert, T.B. Johansson, R.E. Van Grieken, H.C. Kaufmann, K.R. Chapman, J.W. Nelson, and J.W. Winchester, Application of proton-induced X-ray emission analysis to the St. Louis Regional Air Pollution Study, Advances in X-Ray Analysis, vol. 18, W.L. Pickles, C.S. Barrett, J.B. Newkirk, and C.O. Ruud, eds., pp. 588-597, Plenum Press, New York, 1975.
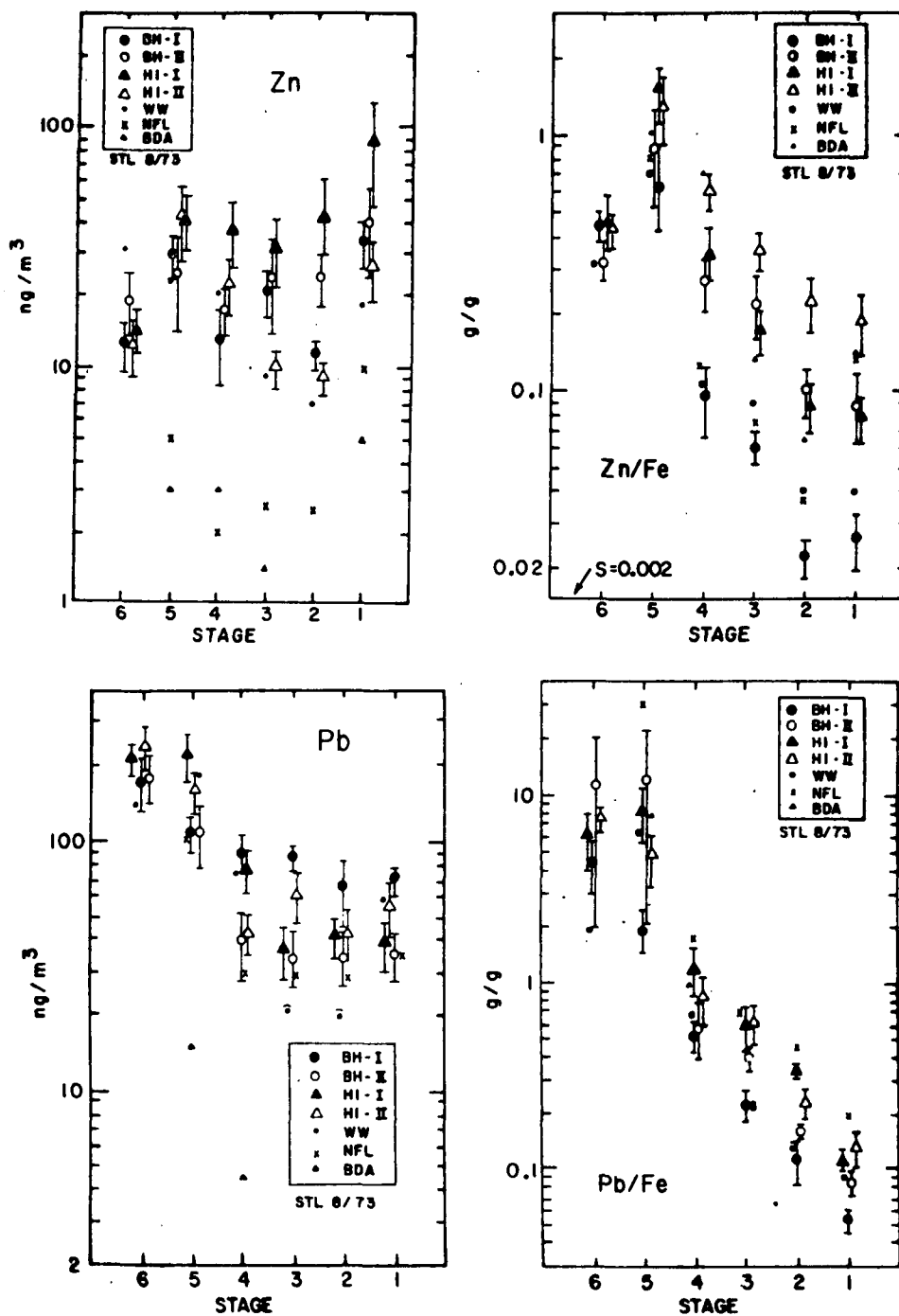
the range of 1,000 ng/m^3 or above. Particle sizes containing
most of the titanium were greater than 1 µm aerodynamic diameter,
i.e., impactor stages 3, 2, and 1. During meteorological period
II, generally northerly air flow, the titanium concentrations
decreased to 100 ng/m^3 or less and were principally found in
particles of diameter greater than 4 µm, impactor stage 1. The
latter values may represent a mixture of natural dust and other
pollution titanium, e.g. from fly ash, whereas the former repre-
sent primarily contributions from the unique titanium pollution
source. This source, which emitted TiO$_2$ particles from a paint
manufacturing process, apparently added smaller sized particles
to the atmosphere than did the other dust sources.

At the HI site it was found that the alternating 12-hour
sampling during meteorological period I showed more than 10
times higher concentrations during the AM ("n," night and
morning) than the PM samples ("d," afternoon and evening). The
former high concentrations we attribute to fumigation of an
overlying polluted layer during early morning break-up of an
atmospheric temperature inversion. This interesting case of
vertical pollution transport in the atmosphere of St. Louis is
discussed further below.

The particle size distribution of iron in the St. Louis
samples is shown in Plate 7. At the HI site concentrations are
not strictly dependent on wind direction as indicated by
similarity between meteorological periods I and II. During
period I at the BH site iron concentrations were higher, but
during period II they were similar to those found at HI. Iron
is known to be emitted by steel mills and other sources in the
urban area of St. Louis. No single unique source for iron is
identified as is the case for titanium. However, one of the
pollution sources may be locally very important in the south
St. Louis industrial region and account for the high BH values
during period I.

It is significant that iron in the smaller particle size
fractions, <1 µm diameter, stages 4, 5, and 6, is found at
relatively much higher concentrations than is found in the
North Florida aerosol, NFL, or the presumably terrestrially
derived iron at Bermuda, BDA. The coarse particle iron
concentrations in St. Louis are generally only somewhat higher
than in the relatively clean North Florida atmosphere; however,
the fine particle iron appears to be present in much greater
abundance. This result suggests that the impact of polluting
activities on the content of iron in the atmosphere of St. Louis
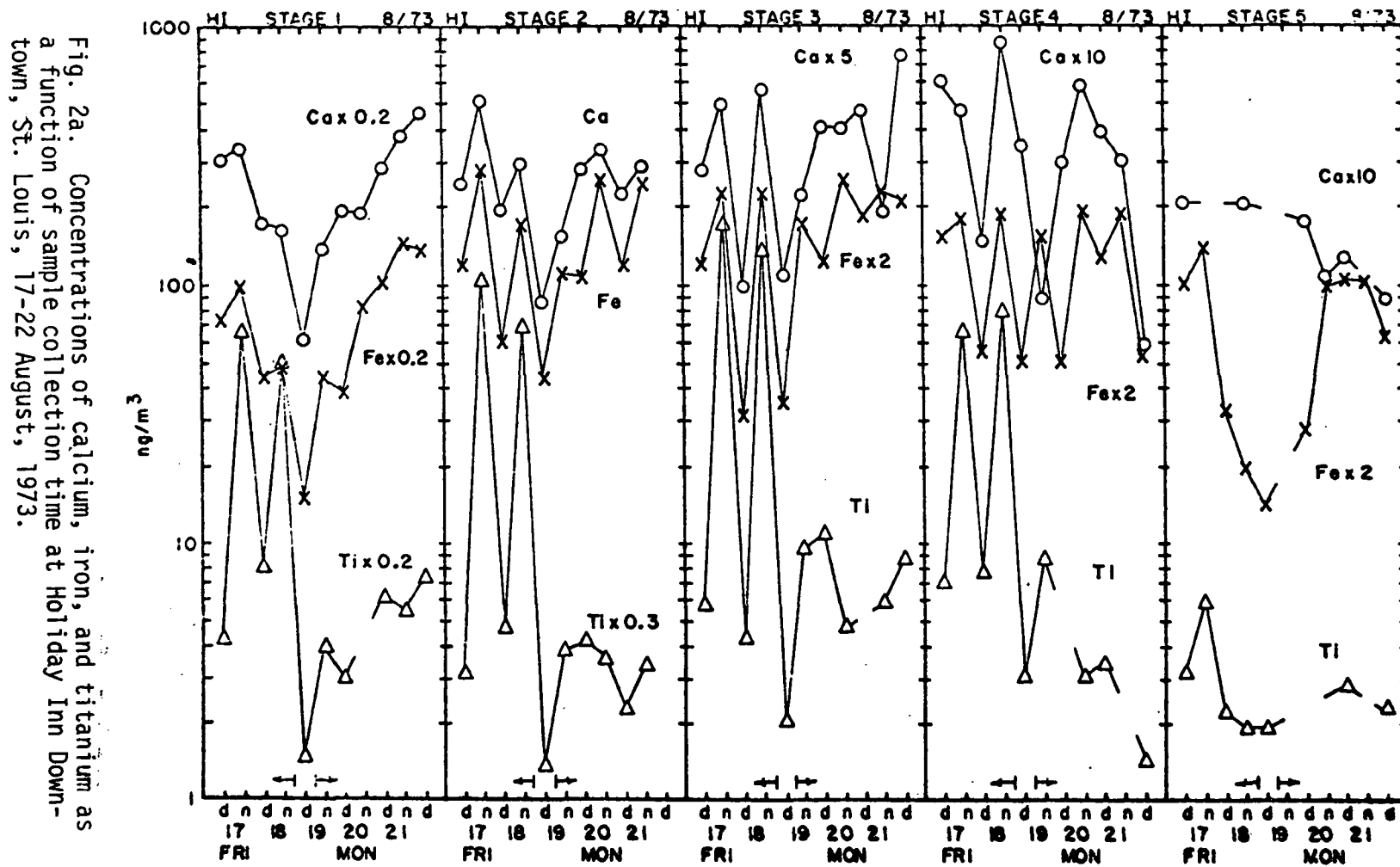is greatest in the sub-micrometer respirable size range.

Plate 7 includes a plot of the ratio Ti/Fe for the
different sampling locations and periods. In clean atmospheres,
as exemplified by North Florida and Bermuda, the ratio Ti/Fe
is very close to 0.1, the average composition of soil and the

earth's crust. During the northerly air flow period II in St. Louis, the ratio is significantly below this value suggesting the presence of additional iron, such as from steel mills, which does not contain relatively as much titanium as average earth crust materials. The depression of Ti/Fe below 0.1 is more pronounced for sub-micrometer particles than for larger sizes, in keeping with our observation earlier that the pollution impact on iron concentrations was greater for smaller particle sizes. Also shown in this figure are the very much higher Ti/Fe ratios, often in excess of unity, when the localized titanium pollution source made its greatest contribution. The particle size distribution of Ti/Fe indicates that the pollution titanium is present in larger particles on the average than is the case for pollution iron, although both elements' pollution contribution may be mainly in smaller particle sizes than that of soil dust.

In Plate 8 the particle size distributions of zinc and lead contrast significantly from those of iron. Both elements are enriched strongly above earth's crust values relative to iron, and zinc to a greater degree than is seen in North Florida, which suggests that pollution sources predominate over natural sources in St. Louis. Both elements are found to a much greater extent on smaller particle sizes in the sub-micrometer respirable range than is the case for iron. These results suggest the importance of pollution emissions at high temperatures, which may favor the formation of smaller particle sizes and more efficient transfer to the atmosphere through stack emission control devices than would be the case for more refractory and coarse particulate ash. Sulfur likewise shows a tendency to be found on smaller particle sizes, although a secondary mode of sulfur is found on coarse particles. The elements potassium and calcium contrast with each other, in that potassium appears to have a greater abundance in fine particles relative to coarse than is the case for iron, whereas the particle size distributions of calcium and iron are similar. These results suggest that some potassium may enter the atmosphere with combustion gases or fine particles formed from them, whereas calcium may be essentially nonvolatile even at high temperatures.

From these particle size distributions we have been able to formulate lines of further inquiry concerning possible sources of these trace metals in the atmosphere of St. Louis. The ideas presented for possible sources should be used as the basis for more detailed investigation and verification of the hypotheses stated.

Plate 9 is a more detailed presentation of the time variability of titanium and other elements at station HI mentioned above. We have plotted, as a function of time every 12 hours from August 17 to 22, 1973, the concentrations of

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Fig. 2a. Concentrations of calcium, iron, and titanium as a function of sample collection time at Holiday Inn Downtown, St. Louis, 17-22 August, 1973.

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Plate 9

Source: A-12.
John W. Winchester, Dennis L. Meinert, J. William Nelson, Thomas B. Johansson, Rene E.
Van Grieken, Celso Orsini, Henry C. Kaufmann, and Roland Akselsson, Trace metals in the
St. Louis aerosol, Proceedings of the Second International Conference on Nuclear
Methods in Environmental Research, July 29-31, 1974, University of Missouri, Columbia,
J.R. Vogt and W. Meyer, eds., USERDA CONF-740701, pp. 385-394, 1974.

titanium, iron and calcium for each individual particle size fraction collected by impactor stages 1 through 5. (Impactor stage 6, the particles smaller than 0.25 μm collected by a filter did not yield consistently measurable amounts of these elements and therefore is not plotted.) It is seen that the alternation of concentration for titanium for meteorological period I extends over a factor of 30 for stage 3, 1-2 μm particles, and nearly that much for larger and smaller sizes. For iron and calcium a similar, though not as drastic, alternation is seen.

The nature of the summer St. Louis atmosphere is such that stratified pollutant laden air layers could develop over the city at night. After sunrise these may mix with surface air as the result of ground heating and vertical turbulence. This may lead to a highly concentrated pollution layer, to dip suddenly downward over the sampling site, a process termed "fumigation," and increase the concentrations momentarily to very high levels. Apparently during meteorological period I night time emissions of titanium and certain other metallic pollutants were carried over the sampling site and caused the average concentration during the period "n" (midnight to noon) to become very high due to the influx toward the surface in the morning hours. Titanium therefore has proved to be a convenient "natural" tracer of air-pollution transport in the city.

METEOROLOGICAL ANALYSIS OF THE TITANIUM POLLUTION PLUME

The element titanium emitted as a fine particluate pollutant in the atmosphere of St. Louis is a useful tracer for pollution transport over the entire city. From a detailed analysis of the correlation between its concentrations at various sampling locations and measurements of average wind direction, directional variability, wind speed, vertical temperature gradient, and distance from the pollution source, a good understanding can be obtained concerning the factors which control transport of the titanium pollution plume. If this understanding is sufficiently detailed, the transport of any other aerosol pollutant generated in the city could be predicted.

Using the streaker sampler we have measured the time variability of titanium concentrations with a 2-hour time resolution at a number of locations around the city, utilizing the Regional Air Monitoring Stations of the Regional Air Pollution Study as sampling points. This time resolution is comparable to that of the meteorological parameters obtained at these stations.

Plate 10 shows as examples the trend of titanium concentration seen at two of the Regional Air Monitoring Stations. Station 105, located 11 kilometers to the NNE of the titanium pollution sources across the Mississippi River in Illinois, shows concentrations reaching almost 1,500 ng/m^3 although most of the time the concentrations are only a few tens of ng/m^3. At station 122 some 60 kilometers to the north in Illinois, the titanium fluctuations are also seen although the peak values are 10 times lower. At other stations similar fine structure to the titanium time variability is observed. The sharp maxima seen over short intervals of time are presumed to represent transport of the titanium pollution plume on the sampling site.

It would be useful to know if the plume transport can be understood in terms of routinely measured meteorological variables. If so, we could develop an ability to forecast pollution transport of any trace metal in plumes. Four stations were selected for a meteorological analysis of the time variability of titanium. These stations are arranged in a line generally running from the titanium source northward and at a distance of 5, 11, 21 and 35 kilometers for stations 111, 105, 113 and 121 respectively. Since the titanium pollutant is emitted from stacks which are about 35 m in altitude, whereas the samplers were placed at about 10 m height, both vertical and horizontal transport must occur for the titanium to reach the sampler.

The meteorological analysis employed consisted of first sectoring the concentrations measured over the one-week study period into groups according to the local wind direction observed at each sampling station. The sectoring scheme differed somewhat among the four stations so as to provide a suitable number of observations within each sector for the statistical analysis. These sectoring schemes are shown on Plate 11.

Treating the observations within each sector as individual subsets, it was generally found that concentrations were highest in the directly downwind sector (5 for stations 111 and 105 and 4 for stations 113 and 121). However, the concentrations were not uniformly high in these sectors and sometimes high concentrations were observed for the nearby wind direction sectors. Therefore interactions between the sectors and the meteorological measurements of standard deviation of wind direction (i.e., directional variability), wind speed, and the temperature differences between 30 m and 5 m (a measure of temperature gradient) were examined. In Plate 11 a summary of these correlations is presented. The sign, positive or negative, of the parameter b indicates qualitatively whether the correlation is direct or inverse.

31

Plate 10
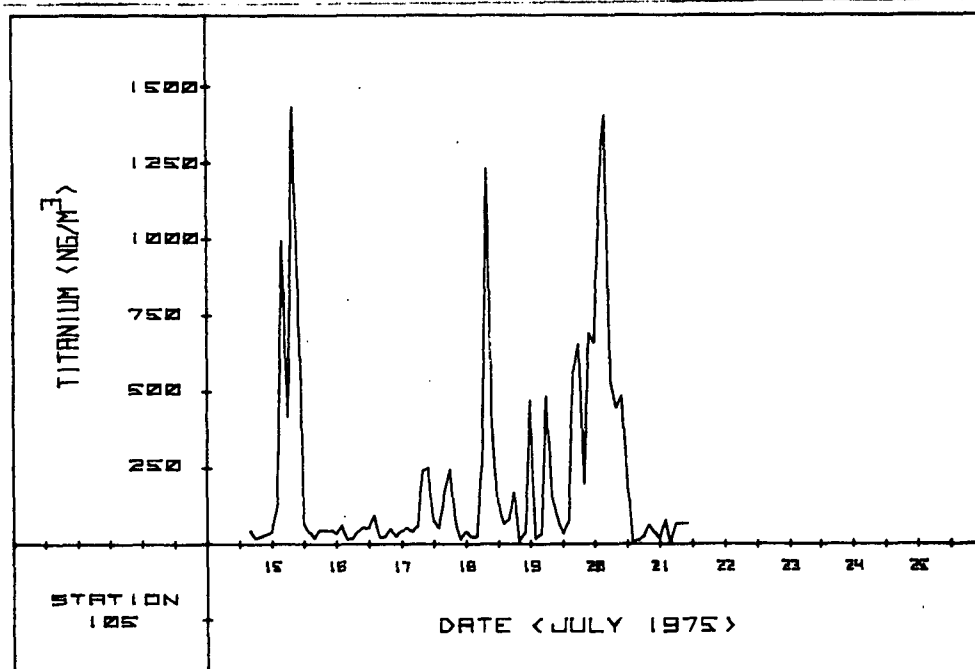
Fig. 6. Titanium versus time at station 105.
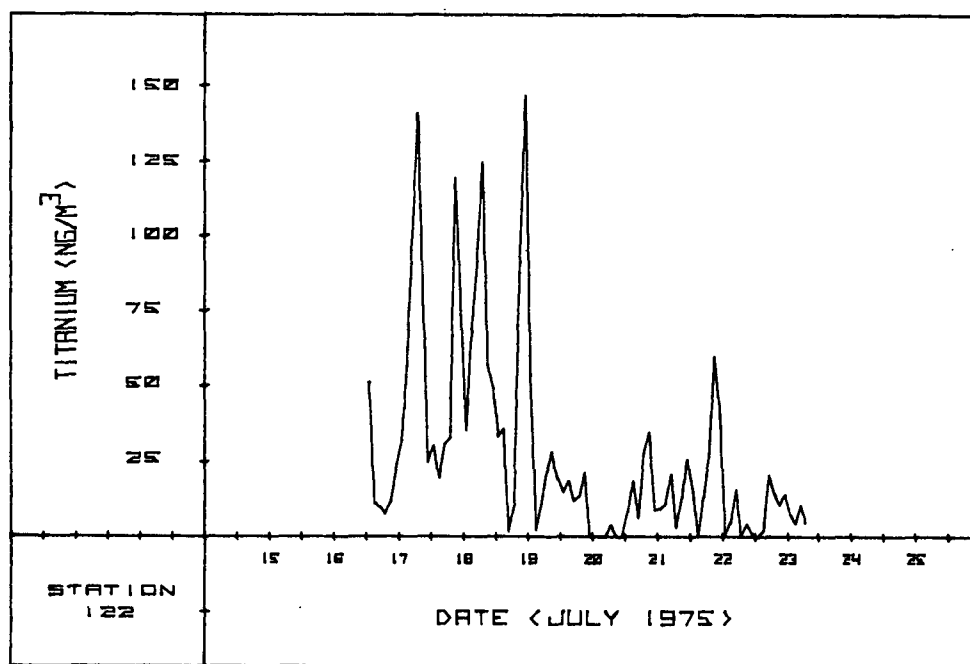
Fig. 9. Titanium versus time at station 122.

Source: D-2.
Scott Rheingrover, A Statistical Model for Titanium Pollution
Transport in the Atmosphere of St. Louis, M.S. Thesis, Dept. of
Meteorology, Florida State University, June 1977.

station III   **station I05**

station II3   **station I2I**

N
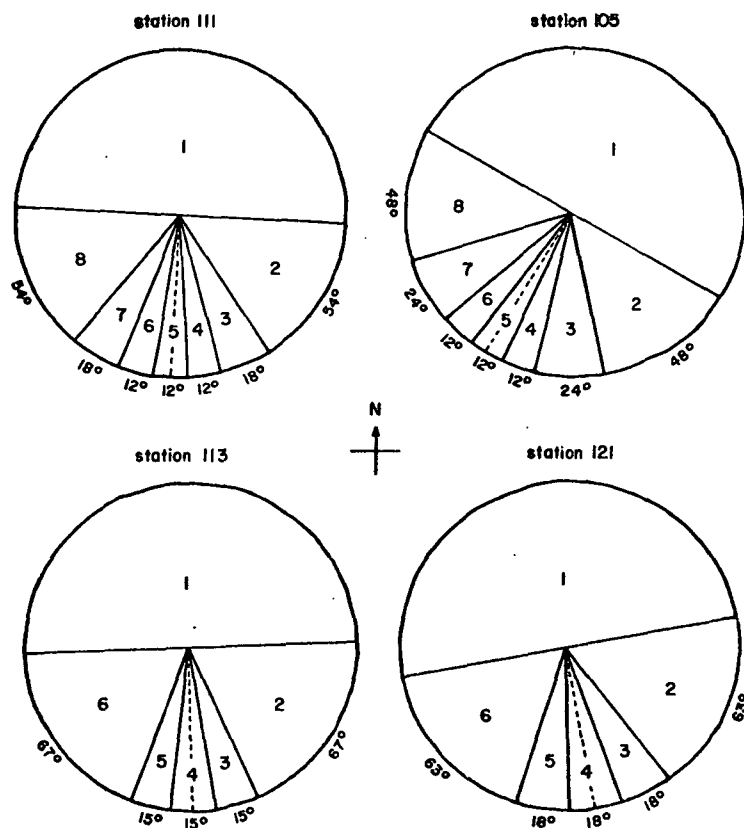
Fig. 10. Sectoring schemes for stations 111, 105, 113, and
121 with the theoretical source to station plume
centerline angle represented by the dashed line,
the sectors numbered clockwise starting with the
180 degree upwind sector numbered 1, and the degree
width of the remaining downwind sectors labled on
the perimeter.

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Plate 11

TABLE IX. Final form of the Interaction Dummy
Variable Multiple Regression Model

Station 111			Station 105		
Variable	b	sig	Variable	b	sig
SECTOR3	+1.86	.000	SECTOR3	+1.96	.000
S3BYSPD	-0.45	.006	S3BYSTD	-0.05	.008
SECTOR4	+4.54	.001	S3BYGRAD	-0.77	.002
S4BYSPD	-0.85	.014	SECTOR4	+5.06	.009
S4BYGRAD	-0.75	.105	S4BYSPD	-0.35	.089
SECTOR5	+2.12	.000	S4BYSTD	-0.05	.035
S5BYSTD	-0.03	.055	S4BYGRAD	-1.70	.023
SECTOR6	+4.70	.023	SECTOR5	+0.99	.000
S6BYSTD	+0.06	.111	SECTOR7	+1.43	.052
S6BYGRAD	-2.39	.046	S7BYSPD	-0.25	.150
S7BYSTD	+0.05	.000	Constant	+1.69	.000
Constant	+1.55	.000			

$$R^2 = .721 \qquad\qquad R^2 = .487$$

Station 113			Station 121		
Variable	b	sig	Variable	b	sig
SECTOR3	+1.46	.001	S4BYSPD	+0.18	.000
S3BYSPD	-0.12	.111	S4BYSTD	-0.06	.000
SECTOR4	+56.73	.012	S4BYGRAD	+0.85	.000
S4BYSPD	-3.48	.009	SECTOR5	-1.04	.075
S4BYSTD	-0.08	.001	S5BYSPD	+0.26	.006
S4BYGRAD	-20.96	.017	S5BYGRAD	+0.40	.069
Constant	+1.64	.000	Constant	+1.55	.000

$$R^2 = .797 \qquad\qquad R^2 = .903$$

The calculations indicate that variability in wind direction is associated with higher concentrations of titanium in sectors adjacent to the directly downwind sector, implying horizontal dispersion during plume travel. However, the reverse is found for the directly downwind sector, suggesting plume dilution during variable winds which reduces concentrations. Higher wind speeds tend to be associated with lower concentrations at nearby stations suggesting turbulent mixing, but at more distant stations wind speed is associated with higher concentrations suggesting the importance of less time available for particle settling en route. The temperature gradient information indicates that vertical mixing downward enhances concentration at nearby stations but enhances removal and lowers concentrations by the time the plume reaches more distant stations. The overall variability accounted for by the statistical analysis is 70-90% for three of the stations but is less for station 105. This station is separated from the titanium source by the waters of the Mississippi River, compared with the other stations where plume transport occurs only over land. The perturbing effect of the water thus could account for greater variability observed for station 105 than is seen for the other three stations. However, the overall degree of variability at the four stations accounted for by this analysis is impressive.

In Plate 12 a schematic diagram is presented for the apparent plume movements for both vertical and horizontal directions for the four stations downwind of the titanium source. The diagram, which has been constructed purely on the basis of the statistical analysis, is in good agreement with conventional ideas concerning plume transport. The titanium "natural" tracer is thus a means of quantifying the description of a plume as it is transported over a complex urban area. The quantitative calibration of a plume model may permit prediction of the transport of any plume carrying pollutants across the city.

LEAD, A MULTIPLE SOURCE POLLUTANT IN ST. LOUIS

Conventional wisdom says that urban lead is predominantly derived from the combustion of leaded gasoline. The attention given to this idea by air pollution investigators has tended to obscure the fact that lead in the urban atmosphere may be derived from other pollution sources as well. In the city of St. Louis other potential lead aerosol sources include the smelting of ores, the combustion of fuels, and metallurgical refining processes. The contributions of these sources to the overall atmospheric inventory of lead in St. Louis must be determined before we can accurately predict the adequacy of different emission control strategies on air quality.

Plate 12

$$\frac{\Delta T + 2}{\Delta Z} \text{ SMALL}$$

$$\frac{\Delta T + 2}{\Delta Z} \text{ LARGE}$$
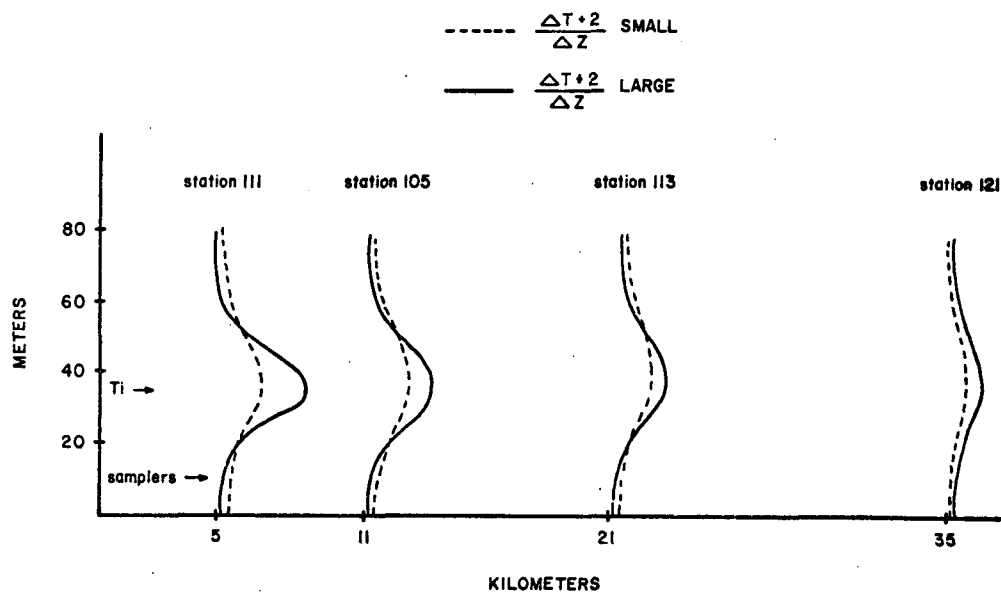
Fig. 18. Vertical (XZ) plume concentration profiles suggested by the $\frac{\Delta T+2}{\Delta Z}$ associations. (Adapted from Strom, 1976)

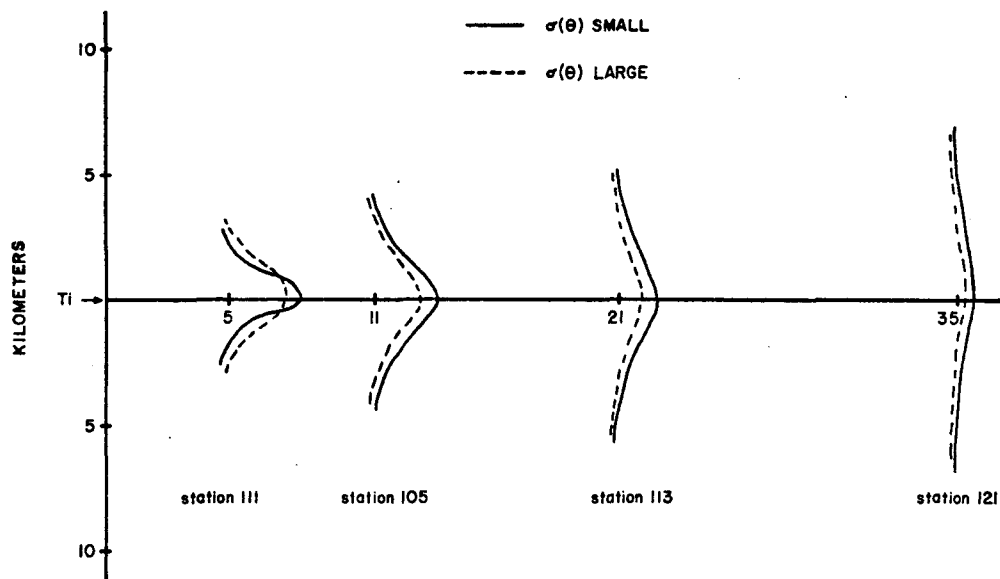$\sigma(\theta)$ SMALL

$\sigma(\theta)$ LARGE

Fig. 17. Horizontal (XY) plume concentration profiles suggested by the $\sigma(\theta)$ associations.

Source: D-2.
Scott Rheingrover, A Statistical Model for Titanium Pollution Transport in the Atmosphere of St. Louis, M.S. Thesis, Dept. of Meteorology, Florida State University, June 1977.

The time sequence filter sampler has a capability for collecting a large enough number of samples at many sites around the city so that a data set of sufficient size for statistical analysis may be assembled in a reasonable length of time. To test the possibility of resolving lead into its different components, a weeklong record of lead concentration was obtained with 2-hour time resolution for 11 of the Regional Air Monitoring Stations within and immediately outside the city. In general 10 or more elements could be detected in each of the time step samples, opening the possibility of using correlations with other elements as the basis for identifying different sources of lead.

Plate 13 shows a detail of the time trends observed for a one-day period, Thursday, July 17, 1975, at station 111 in an industrial section of St. Louis. During this day all elements were found to exhibit large concentration fluctuations, although not at precisely the same times. Thus iron and zinc show a maximum at time step 14 but calcium shows a maximum at step 15, two hours later. Of special interest is lead which shows a step 14 maximum. Bromine, with which automotive lead is invariabily associated, shows a maximum at step 13, two hours earlier than the maximum for lead. Similarly the earlier maximum of lead at step 9, corresponding to a zinc maximum at step 9, does not correspond to the maximum of iron at step 8 or that of bromine, also at step 8. Unless automotive lead and bromine can become decoupled in the atmosphere to such an extent as to cause these time shifts, the data suggest that lead has other sources as well as automotive.

A multiple linear regression analysis of lead has been carried out to examine the extent of correlation with other elements, in which each of the elements of the data set is taken in turn as independent variables. A summary of the results is shown in Plate 14. At all stations in the 11 station network, bromine is the element most highly correlated with lead. Its coefficient of about 5 is in keeping with the ratio of bromine/lead of about 0.2 often seen in urban environments. However, the regression analysis continues by examining the correlation between residual lead, i.e., the difference between the lead measured in each time step sample and the smooth regression curve through all of the data, and each of the other elements. At 7 of the stations zinc is seen to be a significantly correlated element with this residual lead. The coefficients suggest that the zinc-related lead is about 1/10 as abundant as the apparently automotive bromine-related lead. The zinc-related lead could be derived from the smelting of lead zinc ores.

As the regression analysis is continued, residuals of lead over and above the first two smooth regression relationships exhibit frequent correlations with other elements, including

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37

ng/m³

TIME STEP
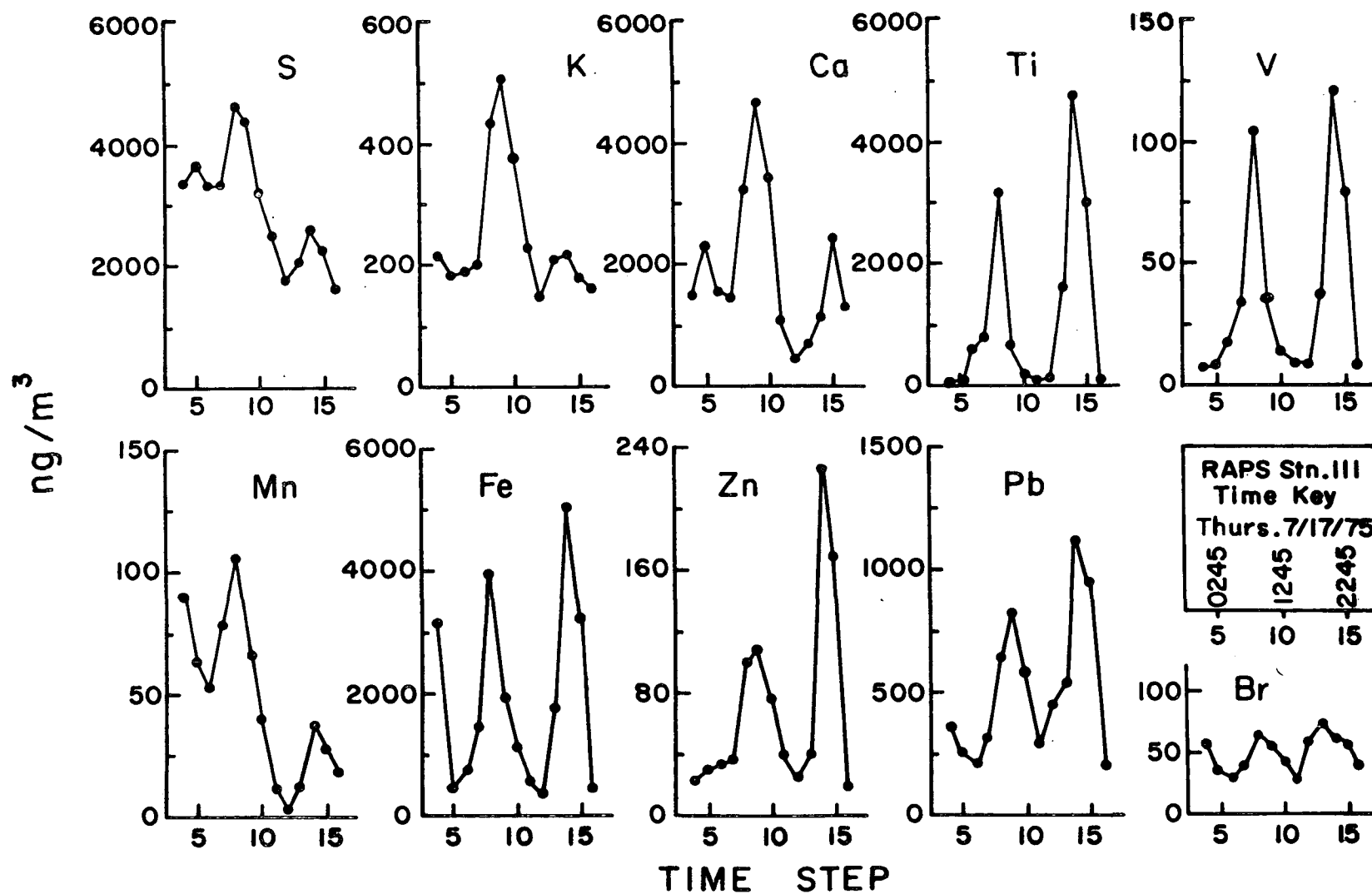
Source: A-16.
James O. Pilotte, John. W. Winchester, and J. William Nelson, Components of lead in the atmosphere of St. Louis, Missouri, J. Applied Meteorology, 17, 627-635, 1978.

TABLE 5. Multiple Linear Regression Analysis of Lead.*

Station	Pb av ng/m^3	Pb	a_1x_1	a_2x_2	a_3x_3	Int	ΔR_1^2	ΔR_2^2	ΔR_3^2	R^2
102	442	287	5.52 Br	0.64 Zn	–	41.28	0.978	0.003	–	0.981
104	640	436	5.35 Br	0.32 Zn	0.40 K	-64.48	0.862	0.055	0.034	0.951
105	464	330	4.76 Br	1.09 Zn	–	91.76	0.692	0.189	–	0.881
106	628	428	6.40 Br	–	–	9.45	0.987	–	–	0.987
108	504	844	8.04 Br	–	–	-35.03	0.107	–	–	0.107
108** (31-81)	307	223	7.59 Br	0.72 Zn	1.33 Ti	-57.44	0.481	0.260	0.146	0.887
111	478	336	4.37 Br	2.34 Zn	2.48 V	-18.09	0.658	0.241	0.092	0.991
113	540	361	6.15 Br	0.41 Zn	0.14 Fe	113.27	0.878	0.028	0.074	0.980
121	381	501	7.22 Br	0.67 Zn	0.67 Fe	191.24	0.441	0.074	0.250	0.765
122	133	142	11.79 Br	0.84 K	–	-86.72	0.917	0.032	–	0.949
123	115	108	7.69 Br	–	–	-16.64	1.000	–	–	1.000
125	82	63	6.51 Br	–	–	-12.92	0.9555	–	–	0.955

*The columns list station number, arithmetic mean Pb concentration over all time steps, standard deviation of the distribution of measured concentrations around the mean, first, second, and third independent variables in the regression equation with their coefficients, zero intercept on Pb coordinate, and contributions of first, second, and third independent variables to overall R^2 given in last column.

**Anomaly of time steps 1-30 excluded.

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Plate 14

potassium and iron, which may be typical of fly ash or other earth crust materials. Such a correlation may be expected if combustion of coal is a significant contributor of lead to the St. Louis atmosphere.

Station 108 is anomalous in showing little correlation with any element other than bromine, and in fact the bromine correlation is poor. During the first 30 time steps (60 hours), lead concentrations were singularly high, although concentrations of other elements were not especially high. When the regression analysis was repeated for the following steps only, a regression result similar to many of the other stations was obtained. The anomalously high lead concentrations were subsequently found to be due to emissions from a secondary lead smelter which did not carry other associated elements into the atmosphere. Thus a new fourth atmospheric lead component in St. Louis was identified at this station.

Examining the values of R^2 in the last column and the partial ΔR^2 values of the first, second and third regression results in the previous columns shows that on the whole a very high degree of variability in lead is accounted for. In the most nonurban stations the bromine correlation is found to account for nearly all of the variability. In such nonurban areas automotive emissions predominate over industrial sources of lead. In contrast, in the more urban locations the bromine correlation usually accounts for less of the overall variability of lead, and additional elemental correlations are found in general to account for most of the rest. Even for station 108 this is true during times when the secondary lead smelter emissions did not blow toward the sampling site.

By carrying out a multiple linear regression analysis a trace element fingerprinting of the lead from different sources has been obtained. If this result is compared with the transport modeling result of the titanium plume study described above, we see that it may also be possible to trace the transport of lead plumes across the city. Thus the complexity of the atmospheric trace metal content of the city of St. Louis may be unraveled and understood by judicious choice of sampling methods and data analysis techniques.

SECTION 6

AEROSOL PROPERTIES AND HUMAN RESPIRATORY EXPOSURE

Much of the interest in trace metals contained in the
suspended particulate matter of the urban atmosphere stems from
the potential for transfer of toxic materials to the human
respiratory tract. We have already stressed the importance
of particle size as providing clues about the sources of
airborne trace metal pollutants in the city. The particle
size is also critically important in regulating the transfer
of trace metals to different parts of the human respiratory
tract.

RESPIRATORY RESPONSE IN AEROSOL INHALATION

When aerosol particles are inhaled, two distinct responses
may occur: the first is the effect of the high humidity of
the respiratory tract on the incoming particles, possibly
causing a sudden particle size increase if the inhaled air
is initially dry and if the particles themselves are
hygroscopic. The second is the deposition of incoming aerosol
particles in different parts of the respiratory tract, with
an efficiency which depends on particle size after humidifica-
tion. The largest particles tend to be removed from the
inhaled air by impaction in the nasal passages and the ciliated
regions of the upper respiratory tract. However, particles
smaller than about 1 μm diameter may bypass these regions
and enter the pulmonary region. There they may be deposited
on the lung walls, but some particles are not deposited
and may be exhaled again. Particles that are substantially
smaller than 0.25 μm are deposited by their Brownian diffusion
to the walls of the pulmonary sacs and retained in the lung;
the efficiency of deposition by diffusion increases with
decreasing particle size. Therefore viewing the lung as
a whole the largest particles and the smallest particles
may be scavenged from the inhaled air in the upper and the
lower regions, respectively, by these two mechanisms, but
intermediate sized particles, in the region of a few tenths
of a micrometer diameter, may be retained by the lung to
a lesser extent and exhaled with the next breath. Thus
the efficiency of particle deposition in the respiratory
tract exhibits a minimum in the 0.5 μm size range. To determine
the position of the minimum experimentally for a specific aerosol

type requires that the effect of humidification be clearly distinguished from the effect of deposition so that the effective size of the particles within the lung can be determined.

The PIXE technique is sufficiently sensitive so that a human being breathing normally polluted air for a matter of minutes into a cascade impactor can exhale enough trace metal to be collected by the impactor stages and be detected by PIXE. This makes it practical to measure simultaneously the concentrations of trace metals in particle size fractions collected by identical cascade impactors sampling the ambient atmosphere and the exhaled human breath. The ambient atmosphere should preferably be brought to a high relative humidity corresponding to that in the lung before the sampling.

On Plate 15 the results of an experiment are shown comparing the particle size distributions of 8 elements in welding fume aerosol sampled in the unhumidified inhaled air and the humidified exhaled air. The prominent feature is a twofold increase in average particle diameter owing to the humidification effect. In addition, careful numerical analysis of 9 similar tests shows that particle deposition in the respiratory tract also occurred to the extent of 20 to 50% depending on the element. The lower part of Plate 15 shows the results of another of the 9 tests, this being an anomalous run in which the particle size shift was not observed. The anomaly is probably associated with a slight temperature difference between the exhaled breath temperature and that at which the cascade impactor was maintained, which would cause a difference in relative humidity in the sampling device and possible dehydration of exhaled particles. This result emphasizes the necessity of exact humidity and temperature control during the sampling of exhaled human breath.

Plate 16 illustrates the sampling arrangement used for experiments of this kind. Cascade impactors inside a heated area are maintained such that there is no humidity change during the passage of exhaled breath through them. Outside the heated area the ambient aerosol impactors may be used without humidity adjustment if the ambient humidity is high; otherwise prehumidification of the incoming airstream is required.

Plate 16 shows the results of the sampling of automotive lead aerosol under conditions of high outdoor humidity (during rain). The lead concentration data, as well as data from a similar chalk dust experiment, can be used to calculate the concentration ratio exhaled/ambient. This ratio is a measure of the fractional deposition on inhalation for each particle size range. Minimum deposition is clearly seen for impactor

Plate 15
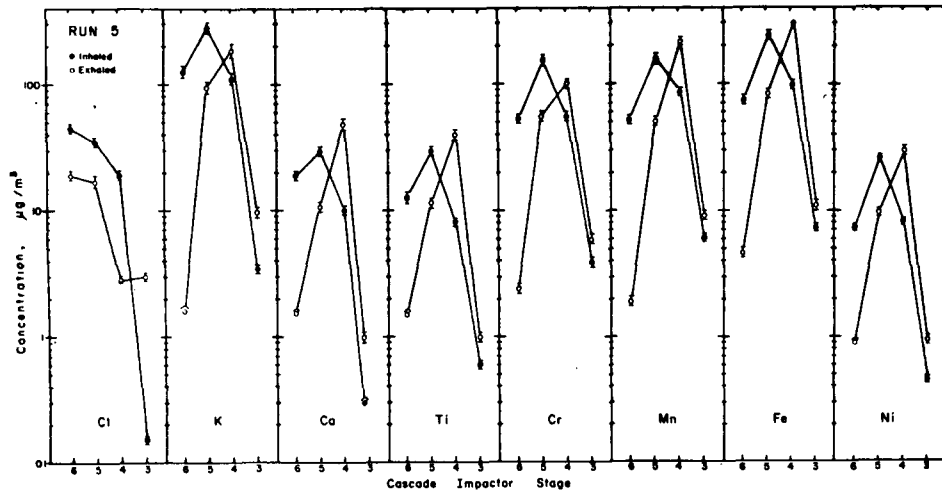
Fig.6(a). Particle size distributions of trace elements
in inhaled and exhaled air for Run 5. Metallic
elements generally show a shift toward larger particle
sizes in exhaled air.

Fig.6(b). Particle size distributions of trace elements
in inhaled and exhaled air for Run 8. No systematic
shift toward larger sizes is found, and exhaled
concentrations are generally lower than inhaled.
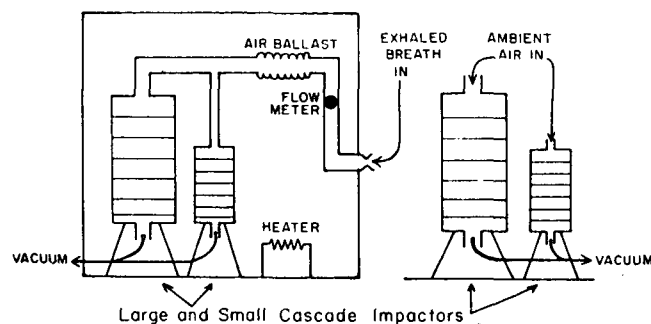
Figure 1. Diagram for simultaneous sampling of exhaled and ambient aerosols, showing air ballast arrangement for constant sampling flow rate, temperature regulator for humidity control, and flow meter for breathing rate regulation

Figure 2. Concentrations as a function of particle size for separate automotive exhaust and chalk dust experiments

Small cascade impactors (1 l./min air flow) were used for all data points except for Pb, Br, Cl on stages 4 and 3 where large impactor data (12 L/min air flow) were used. Exhaled air (O) deficit below ambient air (X) represents particle loss during breathing. Analytical errors of relative concentrations are less than the sizes of the plotted points

Plate 16

Figure 3. Concentration ratios as a function of particle size for simultaneous exhaled and ambient samples

Solid points are for separate automotive exhaust and chalk dust experiments; open points are for a mixed experiment. Pb, Cl, Br data for stages 6 and 5 by small impactor, stages 4 and 3 by large impactor; Ca data by small impactor except where marked by *. Error bars represent absolute standard deviations in the ratios

stages 5 and 4 encompassing the diameter range 0.25-1 μm, a result which is in close agreement with model calculations and experiments with synthetic aerosols. The beauty of being able to measure this curve directly as described here is that it can easily be accomplished while breathing ordinary polluted air. Possible differences between different polluting elements can be examined, and a variety of human respiratory parameters as well as environmental parameters can be tested for actual atmospheric aerosol pollutants.

THE FATE OF LEAD AEROSOL ALONG A ROADWAY

Along a roadway lead aerosol is generated primarily by automobiles which burn leaded gasoline. As we saw for the city of St. Louis, most of the automotive lead is found in the very smallest particles, typically smaller than 0.25 μm aerodynamic diameter. The studies of lead inhalation described in the previous paragraphs indicate that particles of this size are more likely to be deposited in the lower respiratory tract than particles somewhat larger in size. By comparing measurements of the particle size distribution of lead with those of the efficiency of deposition during inhalation we may estimate, as a function of particle size, the overall deposition of lead which occurs in the atmosphere as it enters the respiratory tract.

In Plate 17 are presented the results of measurements at three locations along a heavily traveled roadway in the city of Los Angeles. During the typical afternoon crosswinds blowing in that region, Site A was upwind and Sites C and D were immediately downwind of the traffic lanes. The overall appearance of the particle size distributions at the upwind and downwind sites are similar. However, close examination shows that the two downwind sites have a measurably higher relative concentration of <0.25 μm diameter lead than is found at the upwind site. For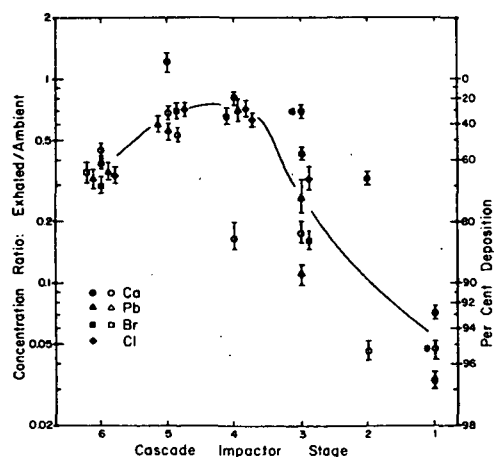 the downwind sites the aging time is shorter between emission from the exhaust pipes of the nearby automobiles and sampling at the sites a few meters away. On the other hand, lead at the upwind site is more likely to be due to the general lead aerosol in the city which has aged for a much longer time between its automotive sources and sampling at the site.

These results may be used together with the measured deposition efficiency curve described previously to estimate an overall lead fraction deposited in the respiratory tract. At downwind sites C and D fifty percent more of the stage 6 (particle size class 6) lead is deposited in thr respiratory tract than for the upwind Site A. Differences also exist for the larger particle size classes. Thus the total concentration of lead in the atmosphere is only approximately indicative of

Plate 17

KEY
■ SITE A
● SITE C
▲ SITE D

Fraction of Lead in Air

Lead Fraction Deposited

Particle Size Class

Lead Fraction Deposited

Sample   Site
Deposition   A   C
Pulmonary   o   ●
Tracheobronch.   Δ   ▲
Nasopharyng.   □   ■

Particle Size Class

Fig. 3. Predicted deposition efficiencies for lead aerosol at 35 m upwind (A) and 8 m downwind (C) sites along a Los Angeles freeway, using particle size distributions for lead at the two sites measured by PIXE and published deposition curves for three regions of the human respiratory tract.

Fig. 2. (a) Particle size distribution of lead aerosol, normalized to 1 μg Pb m^{-3}, at the upwind site (site A) and downwind sites (sites C and D).

(b) Fraction of the atmospheric lead at the upwind and downwind site deposited into the respiratory tract as a function of particle size.

Source: B-20.
Georges G. Desaedeleer, John W. Winchester, and K. Roland Akselsson, Monitoring aerosol elemental composition in particle size fractions for predicting human respiratory uptake, Nuclear Instruments and Methods, 142, 97-99, 1977.

the amount of deposition one can expect in the respiratory tract, since deposition must also depend upon particle size, and this will depend upon aging time in the atmosphere.

, Plate 17 also shows the results of combining the measured particle size distribution of lead at two of the sampling locations, A and C, with the theoretical predictions for deposition in three different regions of the respiratory tract: pulmonary, tracheo-bronchial, and naso-pharyngeal (Task Group on Lung Dynamics, 1966). These theoretical curves have not been verified by experimental methods for lead such as described above but are assumed to be reasonably good predictions. The results show that particles of size classes 1 and 2 (>2 μm diameter) are most likely to be deposited in the naso-pharyngeal region whereas particles of size class 6 (<0.25 μm) are most likely to be deposited in the pulmonary region. A much smaller fraction of these smallest particles are deposited in the tracheo-bronchial region. Therefore the particle size of the lead in the atmosphere determines not only the overall efficiency of deposition in the human respiratory tract but the site of the deposition as well.

Another feature of the lead aerosol along a roadway which can be used as an indicator of lead aerosol aging time, and therefore be of interest in the prediction of respiratory deposition, is the content of bromine relative to lead in the aerosol. Plate 18 shows the time variation in concentration of lead and in the bromine/lead ratio, every two hours from Friday until Monday, September 13-16, 1974, at Site A along the same Los Angeles freeway discussed previously. At this site, which was upwind during afternoon hours, the concentration of lead on a 24-hour basis exhibited a diurnal variation. In the afternoon "upwind" condition the lead concentrations were very low and represented lead, not just from the freeway, but mostly from other parts of the city. In the morning and night times a crosswind in the opposite direction developed, and Site A became "downwind." At these times the lead concentration reached values more than ten times higher, representing primarily relatively young lead aerosol generated along the freeway. The bromine to lead ratio also exhibited a diurnal fluctuation. If bromine and lead were equally stable 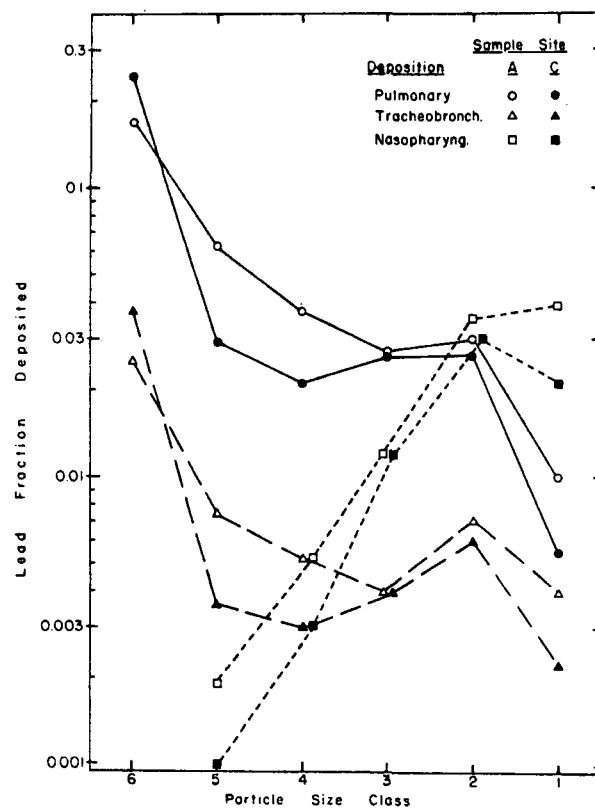elemental constituents of the aerosol particles generated by automotive emissions, the ratio should be invariant with time and total lead concentration. However, during the times when lead concentrations were highest, and therefore the lead aerosol aging time was shortest, the bromine content per unit of lead is seen to be highest. At other times, when the lead aerosol had been more aged, the bromine content relative to the lead was much less, suggesting that bromine is released from the aerosol during aging.

Plate 18
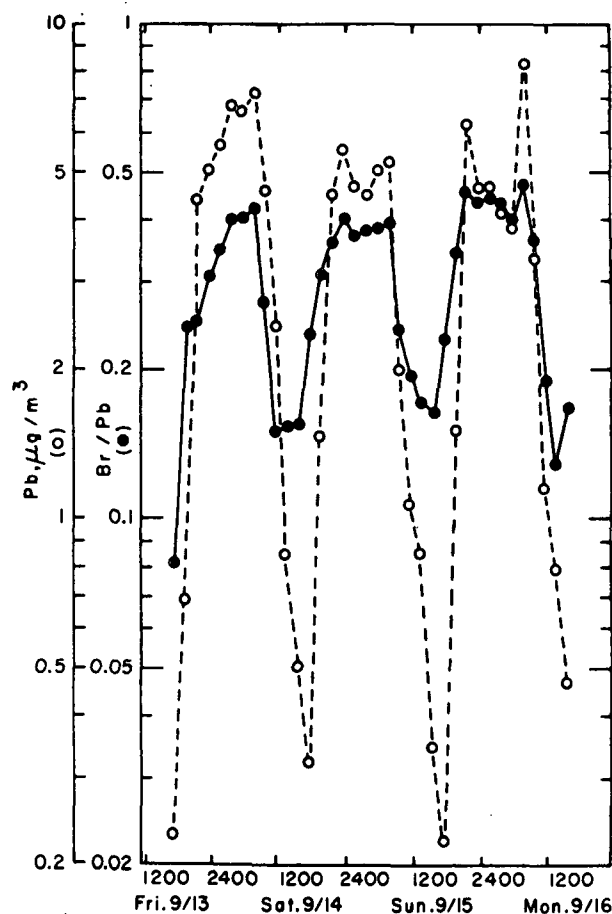
Fig. 1. Time-dependent Pb concentration and Br/Pb weight ratio relationships in the Los Angeles aerosol, freeway site A, 1974.

TABLE I

Lead and Bromine Concentrations in Cascade Impactor Particle Size Fractions*

	Pb, ng/m³			Pb, % mass			Br, ng/m³			Br, % mass			Br/Pb		
	A	C	D	A	C	D	A	C	D	A	C	D	A	C	D
Total	253	2185	2207				91	791	707					0.36	0.36
Stage 6	139	1395	1243	46.2	63.9	56.3	37.8	510	454	41.5	64.4	64.1	0.27	0.36	0.36
5	41.6	157	280	13.8	7.2	12.7	11.9	30.5	48.7	13.1	3.8	6.9	0.29	0.19	0.17
4	33.2	179	177	11.0	8.2	8.0	<9.2	51.9	38.3	<10.1	6.6	5.4	<0.28	0.29	0.22
3	28.9	221	246	9.6	10.1	11.2	8.6	92.7	77.1	9.5	11.7	10.9	0.30	0.42	0.31
2	<28	199	199	<9.5	9.1	9.0	10.5	82.1	64.3	11.5	10.4	9.1	>0.37	0.41	0.32
1	<28	<34.5	61.6	<9.5	<1.6	2.8	7.4	23.9	25.3	8.1	3.0	3.6	>0.26	>0.69	0.41

*Aerodynamic diameters, μm, for stages: >4(1), 4-2(2), 2-1(3), 1-0.5(4), 0.5-0.25(5), <0.25(6, filter). % mass for each stage relative to sum of stages. Samples collected at Los Angeles freeway sites A (upwind); C, D (downwind), 1530-1730 Thursday, 12 September 1974.

Source: A-17.
G.G. Desaedeleer, J.W. Winchester, R. Akselsson, and K.A. Hardy, Bromine and lead relationships with particle size and time along an urban freeway, Trans. Am. Nucl. Soc., 21, Suppl.3, 36-37,1975.

These results are consistent with the suggestion already made that, during times when Site A was upwind with air flow from the sampling site to the roadway, the measured lead was of significantly older age. This lead also had significantly lower relative concentration of finest particle lead. The aging process then results both in the liberation of bromine to the atmosphere as a gas and also the coagulation of finest particles into larger sizes. The aging of particles and the increasing of their average particle size is of direct bearing on estimating the efficiency and location of lead deposition in the respiratory tract. The bromine content relative to lead provides a useful indicator of the extent of aging that has occurred.

LEAD AEROSOL IN THE INDOOR RESIDENTIAL ATMOSPHERE

Lead aerosol from automotive emissions is seemingly ubiquitous and occurs both near and far from automobile traffic lanes. Whereas there may be other sources of lead in an urban atmosphere, automotive lead aerosol, even in the city of St. Louis where smelting and other industrial activities are carried out intensively, is still the major constituent of lead. It is of some interest to know to what extent the lead aerosol in the indoor residential atmosphere is automotively derived and how rapidly the air exchanges between indoors and outdoors to bring lead from the outdoor atmosphere to the indoor environment. In other words, does the house act as a barrier and cleanse the incoming air of lead? Or, is there an indoor source of lead, distinct from automotive, which should be taken into account when estimating average human exposures over a normal day of human activity?

Plate 19 summarizes the results of measurements by streaker samplers made simultaneously indoors and outdoors in a residential neighborhood in Denver, Colorado. During the one week of sampling that was carried out a meteorological change by chance occurred outdoors which provides us with the opportunity of estimating whether indoor sources of lead may exist. On the left hand side of Plate 19 the outdoor concentrations of lead, bromine, and the bromine/lead ratio are presented. During the first and last days of the week, lead concentrations outdoors were at values probably typical for the city. The same was also true for bromine and the bromine/lead ratio. During the middle of the week, however, a several day period was encountered when lead levels at this particular sampling site dropped to very low values. The same was true for bromine, but, owing to the inability to detect bromine much of the time, the bromine/lead ratio was usually indeterminant.

At an indoor location the lead concentrations during the initial and final periods of the week were similar to those

Plate 19
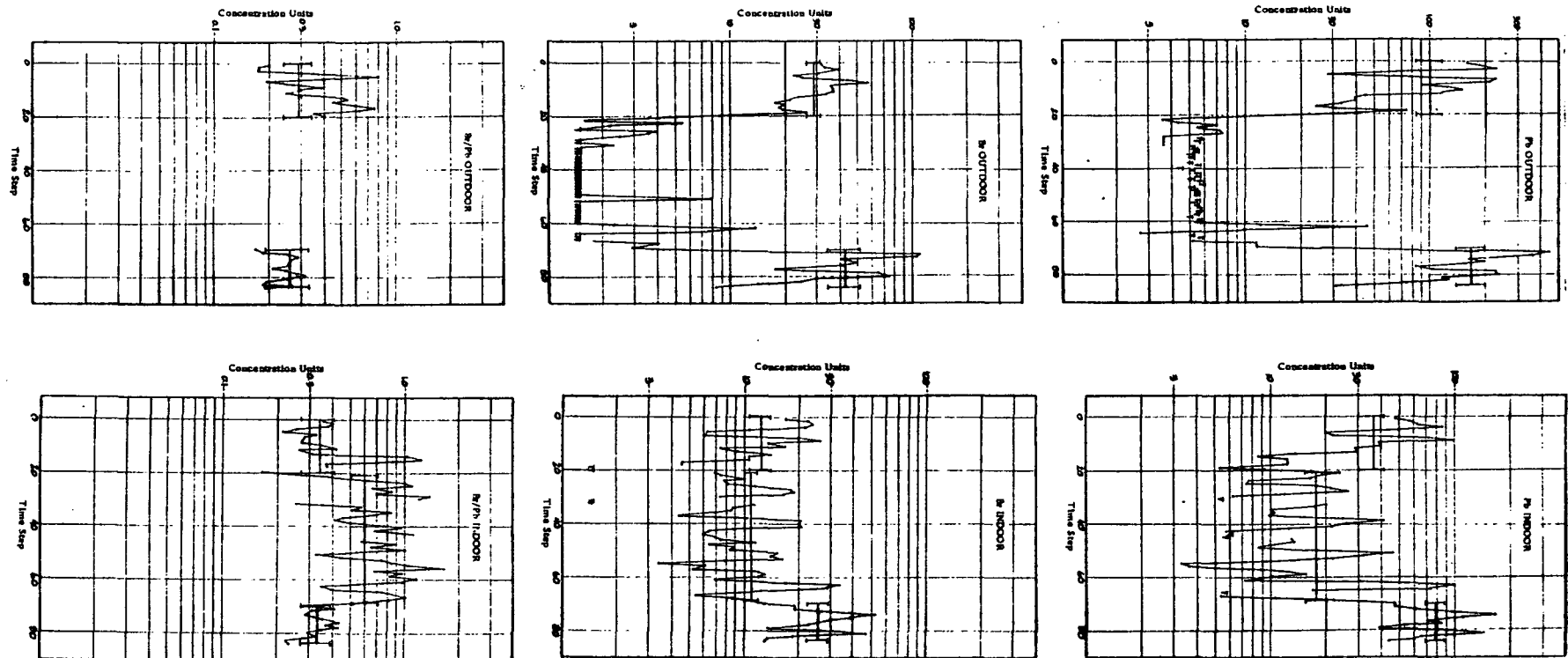
Figure 3. Time variation of Pb and Br concentrations (in relative units) and Br/Pb ratio in Denver single-family dwelling. Time steps represent 2-hour sampling intervals, starting and ending at 1600 hours October 5-12, 1976. Mean values $\overline{Pb}$, $\overline{Br}$, and $\overline{Br/Pb}$ for each of three time periods are indicated by horizontal bars, with their standard deviations as vertical bars.

Source: A-23.
D.J. Moschandreas, W. J. Courtney, J.O. Pilotte, J.W. Winchester, H.C. Kaufmann, J.W. Nelson, and R.M. Burton, Indoor and outdoor sources of particulate air pollution in a residential environment, in proceeding, Fourth Joint Conference on Sensing of Environmental Pollutants, 1977.

measured outdoors (actually somewhat lower) and the bromine/lead ratios were also similar. During the middle part of the week, however, when lead outdoors was scarcely detectable, indoor lead concentrations were significantly higher. Although lower than the indoor concentrations during the initial and final parts of the week, they were sufficiently higher than the simultaneous measurements outdoors to suggest that an indoor source of lead existed in this house. The bromine also was only somewhat lower during the middle of the week than early and late in the week, in contrast with outdoors when the bromine level was much less, and the indoor bromine/lead ratio was actually greater during this period than that measured either outdoors or indoors during the beginning and end of the week.

These results suggest that lead aerosol during normal times infiltrates into the house with only a small degree of particle removal so that the indoor lead concentration is similar to that outdoors. However, during the middle of the week the outdoor lead was so low that a secondary indoor lead source, characterized by a somewhat higher than average bromine/lead ratio, prevailed. This source may be secondary entrained dust from furnishings in the house which had become inoculated with, one may assume, automotive lead over many years of occupancy of the house. Normally, this component of lead is a small fraction of the total concentration of lead in the indoor atmosphere. By chance, however, we encountered a time when, because of special meteorological circumstances, the secondary indoor source became dominant and could be discerned. Consequently the indoor living environment can not be assumed to have a simple relationship with the outdoor atmosphere. Some pollutants may be infiltrated from outdoors and some may be generated from within. In the case of lead in the Denver house, apparently both source processes are operative.

SECTION 7

AEROSOL TRANSPORT OUT OF THE URBAN SOURCE REGION

In studies of trace metals in the urban atmosphere it is
of considerable importance to have a general understanding of
the composition of cleaner air. A study of clean air serves
both to provide a baseline or reference for comparison of the
urban atmosphere, in order to determine to what degree the
urban atmmosphere has been polluted beyond natural levels,
and also to facilitate the detection of pollutants transported
outward from the urban region into cleaner areas. Two case
studies are of a special interest in the investigation of urban
trace metals in North American cities.

THE NORTH FLORIDA COASTAL ZONE

North Florida is a region containing small cities and
towns and large areas of forested land. Heavy industry is
virtually absent, and the quality of air is considered good.
Within the eastern United States, north Florida may have an
atmospheric composition closer to natural than any other
area. Furthermore, the coastal zone is a zone of interaction
of maritime and terrestrial influences and provides an
opportunity to compare the chemical relationships in these
two types of air.

As in the city of St. Louis, we have sought in Florida
to determine the relative trace metal composition of the
aerosol as a function of particle size. In Plates 20 and 21
trace element concentrations and their ratios, as determined
by cascade impactor sampling and PIXE analysis, are presented.
These several elements divide naturally into at least three
groups: elements associated primarily with soil dust; elements
which are anomalously enriched in the atmosphere, including
copper and zinc; and the element sulfur, a class by itself,
which may be largely due to gas-to-particle conversion into
sulfates. The soil dust elements iron, potassium, calcium,
titanium, and manganese are very nearly in the ratios in which
they occur in natural soils, and all of them occur
preferentially on particles greater than 1 μm aerodynamic
diameter (impactor stages 3, 2 and 1). This observation is
consistent with the dispersion nature of the soil dust
source, forming large particles preferentially to smaller

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Plate 20
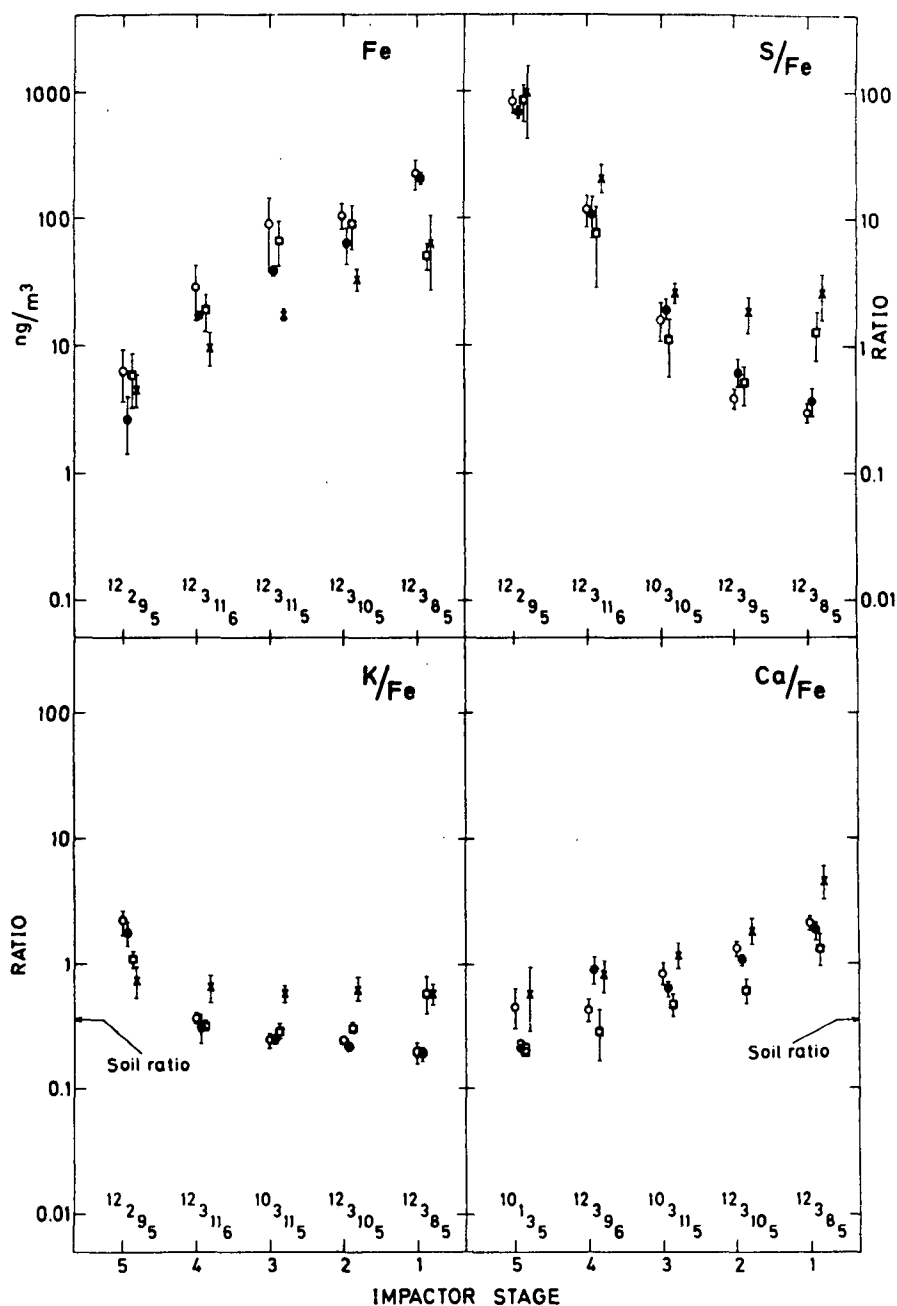
Fig. 3. Arithmetic mean values of Fe concentrations and of weight ratios for other elements to Fe plotted versus impactor stage number, equivalent to a logarithmic scale of aerodynamic particle diameter. The vertical bars represent one standard deviation of the mean of the data set. The numbers at the bottom of each graph show the number of nonzero values included in the averages. Where this number is less than the corresponding number of samples analyzed (Table I), the element was below detection limit in the remaining analyses. If the element was detected in more than half the number of analyses, a value has been plotted; otherwise, an upper limit value is indicated. Points for city site A are indicated by open circles, for city site B by closed circles, for the forest by open squares, and for the coast by crosses.

Source: B-25.
Thomas B. Johansson, Rene E. Van Grieken, and John W. Winchester, Elemental abundance variation with particle size in north Florida aerosols, J. Geophys. Res., 81, 1039-1046, 1976.

Plate 21
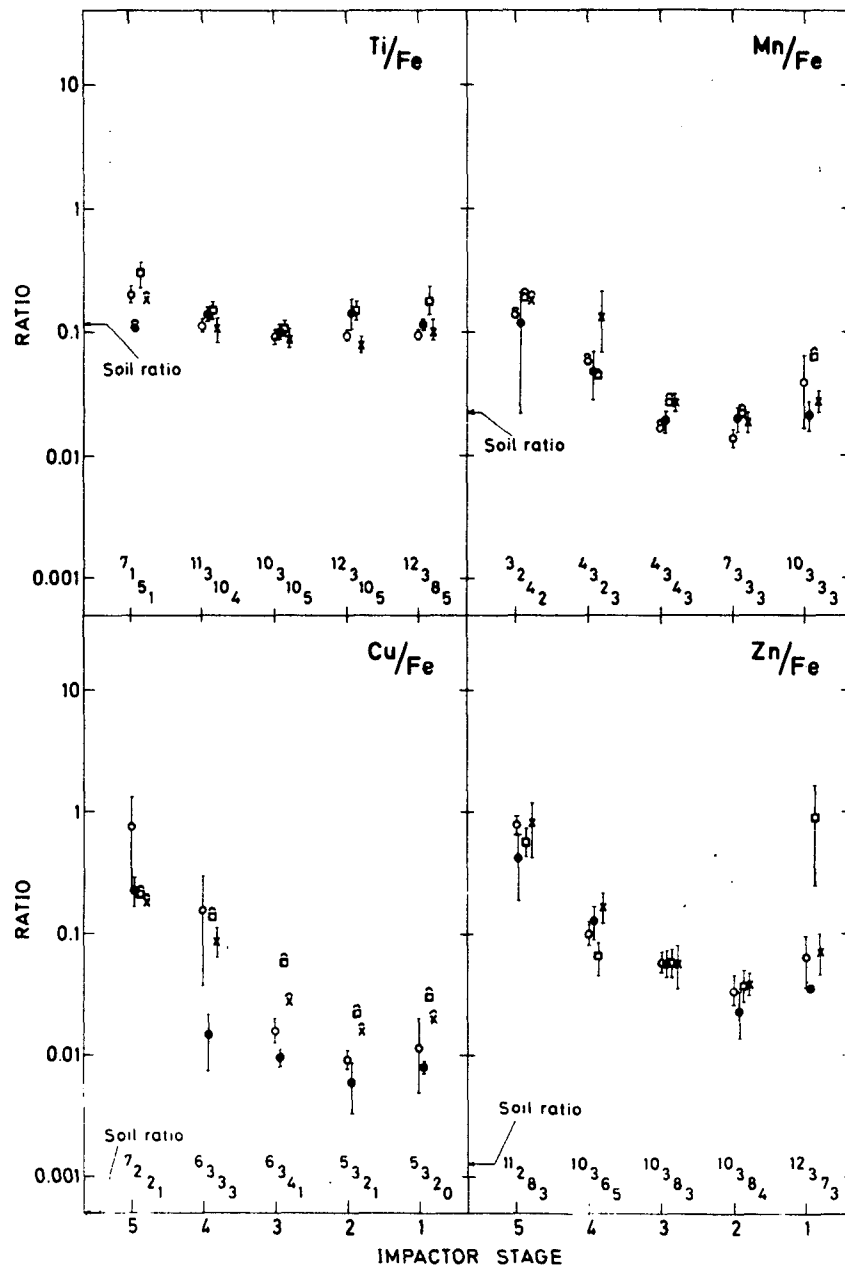
Fig. 3. (continued)

Source: B-25.
Thomas B. Johansson, Rene E. Van Grieken, and John W. Winchester, Elemental abundance variation with particle size in north Florida aerosols, J. Geophys. Res., 81, 1039-1046, 1976.

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ones by the mechanical action of wind on rock and soil material.

The elements copper and zinc have concentrations relative to iron significantly greater than the soil ratios. The ratios observed here are typical of those found elsewhere in clean atmospheres and may represent a natural state of the atmosphere in which certain elements are "anomalously enriched." In remote areas the anomalous enrichment is believed to be due to a natural process not associated with long range transport of air pollution. However, to detect one of these elements as a pollutant above the natural level is complicated by our lack of clear understanding of the cause of the natural anomalous enrichment in the first place. The important task of developing techniques for monitoring the long range transport of heavy metal air pollution has been begun by this study of the North Florida aerosol.

The element sulfur is in a class by itself. Present indications are that all of the eastern United States, including north Florida, is covered by a large cloud of air pollution derived sulfate. This sulfate migrates into the north Florida area and diminishes in concentration gradually during transport over longer distances. The particles are in general of very fine size resulting from the gas-to-particle conversion nature of the source process. Thus, as observed, the ratio of sulfur to iron increases strongly with decreasing particle size. Little evidence for local sources of sulfur are observed in the north Florida area when compared to the overwhelming amount of sulfate aerosol transported into the region.

In conclusion, we may say that the north Florida aerosol provides a useful reference of relatively clean air for comparison with more polluted urban atmospheres. However, at least sulfur is already a significant contaminant.

AIR POLLUTION PRESENT IN THE NORTH ATLANTIC MARINE ATMOSPHERE AT BERMUDA

As with the study of the north Florida aerosol, the particle size distribution of trace elements in the atmosphere of Bermuda provides a useful indicator of the presence of long range transport of air pollution. Bermuda lies some 1500 kilometers southeast of New York and its atmosphere is representative of much of that over the North Atlantic ocean far from the North American continent. Air pollution is not visibly present.

If the aerosol particles are carefully sampled as a function of particle size under a wide variety of wind direc- tions and weather conditions varying from stormy to calm, it

is possible by a regression procedure to resolve the ever-present sea spray component of the aerosol from that of aerosol particles of other sources. In an investigation of this possibility a series of ten cascade impactor samples collected over a period of three weeks in the fall of 1973 were analyzed using PIXE for their elemental composition as a function of particle size. Plate 22 presents a summary of the findings.

It was noted that under stormy conditions the large particle chlorine content of the samples collected was significantly higher than that of samples collected under calmer conditions. However, for other elemental constituents of the aerosol, that was not necessarily true. A resolution of two aerosol components was made, assuming one to be due to sea spray containing all of the measured large particle chlorine and the other consisting of tropospheric, ultimately terrestrial, components typified by iron, which was assumed to come solely from this source. By a graphical regression technique the ratios of each element to iron, the indicator of the tropospheric component, were determined for this component as a function of particle size. In this way the sea spray contribution to each of the elements was resolved. In Plate 22 are plotted the ratios of the tropospheric component of each element relative to iron as a function of particle size. As with north Florida, the sulfur to iron ratio decreased sharply with increasing particle size, suggesting that the sulfur may be derived primarily by gas-to-particle conversion in the atmosphere whereas the iron is a terrestrial dust component found predominantly in larger particle sizes.

The particle size trend of zinc showed similar features, owing to its being found primarily in smaller particle sizes than is typical of terrestrial dust. The origin of the zinc may be natural or pollution, but in any event is of a size distribution suggesting that its source process produces fine particles. One such source process may be the condensation of high temperature vapors, but other source processes could include biogenic evolution of zinc containing aerosol, such as from organic vapor condensation.

Calcium is found as a rule on larger particle sizes than is iron, and the Bermuda data in Plate 22 are typical of many areas including north Florida (cf. Plate 20). On the other hand potassium is found as a rule on smaller particle sizes than is iron (cf. Plate 20). Since the contribution of sea spray related aerosol production has been removed, we examine in Plate 22 only the net tropospheric or terrestrial component of these elements. The large particle size preference for calcium over iron may be due to the nature of the dispersion mechanism which generates calcium-bearing aerosol, such as the dispersion of calcite, from that of iron which may be derived from different clay mineralic constituents of soil. In the
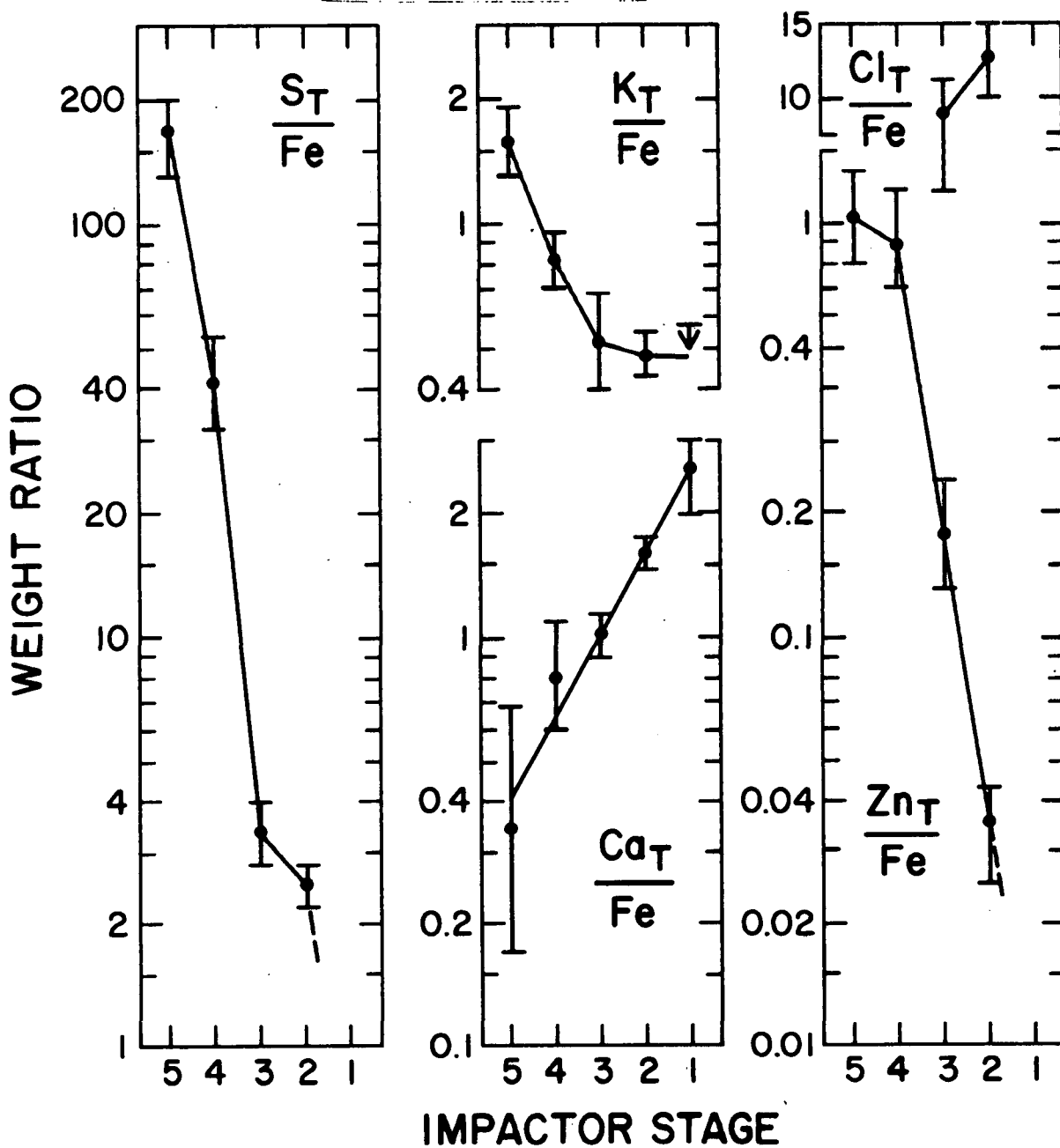
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Plate 22

case of potassium, the significant enrichment over iron in the smallest particle sizes is as yet an unexplained observation. A biogenic source of fine potassium containing aerosol is suggested.

Studies elsewhere in the world indicate that the sulfur content observed in fine particles in Bermuda is by no means typical of the marine atmosphere. Sulfur in the aerosol sampled at Bermuda is predominantly in the sub-micron particle sizes, not the coarse particles greater than 1 μm and typical of sea spray, and it now appears that the fine particle sulfur is mainly due to long range transport of air pollution from the continental areas 1000 km or more distant. The comparative study of urban with the maritime atmosphere suggests that particulate materials may be transported over considerable distances and contaminate atmospheres far from their sources. In the case of sulfur the strength of pollution sources is sufficiently great so that the pollution effect can be seen as far from the North American continent as Bermuda. Whether this is also true for trace metals has not yet been determined. However, by extending investigations of this kind we may gain a sharper understanding of the potential for the remote atmosphere to be contaminated with any air pollutant. Studies of apparently clean air serve as an important complement to studies of the urban atmosphere in understanding the impact of man's activities on the atmospheric environment as a whole.

REFERENCES

1. Camp, D.C., J.A. Cooper, and J.R. Rhodes. X-Ray Fluorescence Analysis -- Results of a First Round Inter-comparison Study. X-Ray Spectrometry, 3:47-50, 1974.

2. Camp, D.C., A.L. Van Lehn, J.R. Rhodes, and A.H. Pradzynski. Intercomparison of Trace Element Determinations in Simulated and Real Air Particulate Samples. X-Ray Spectrometry, 4:123-137, 1975.

3. Liu, B.Y.H. and K.W. Lee. Efficiency of Membrane and Nuclepore Filters for Submicrometer Aerosols. Environmental Science Technology, 10:345-350, 1976.

4. Mitchell, R.I. and J.M. Pilcher. Improved Cascade Impactor for Measuring Aerosol Particles Sizes. Industrial and Engineering Chemistry, 51:1039-1042, 1959.

5. Task Group on Lung Dynamics Committee II. Health Physics, 12:173-208, 1966.

LIST OF PUBLICATIONS AND REPORTS

A.   STUDIES WITH MAJOR EPA FUNDING SUPPORT

Elemental Analysis and Aerosol Sampling Techniques

Proton Induced X-Ray Emission, PIXE

A-1   J.W. Nelson, J.W. Winchester, and R. Akselsson,
Aerosol composition studies using accelerator proton
bombardment, Proc. 3rd Conf. on Appl. of Small
Accelerators, North Texas State Univ., Denton,
Texas, 21-23 October 1974, Vol. 1, The Use of
Small Accelerators in Research and Teaching,
J.L. Duggan and I.L. Morgan, eds., USERDA
CONF-741040- P1, pp. 139-147, 1974.

A-2   Thomas B. Johansson, Rene E. Van Grieken, J. William
Nelson, and John W. Winchester, Elemental trace
analysis of small samples by proton induced X-ray
emission, Anal. Chem., 47, 855-860, 1975.

A-3   M.S. Ahlberg and F.C. Adams, Experimental comparison
of photon and particle induced X-ray emission
analysis of air particulate matter, X-Ray
Spectrometry, 7, No. 2, 73-80, 1977.

Thick Target PIXE Analysis

A-4   Mats S. Ahlberg, Enhancement in PIXE analysis,
Nuclear Instruments and Methods, 142, 61-65, 1977.

A-5   Mats S. Ahlberg, Comparison of yield versus depth
for particle induced and photon induced X-ray
emission analysis, Nuclear Instruments and Methods,
146, 465-467, 1977.

A-6   Mats S. Ahlberg, Matrix effects in trace analysis
by proton induced X-ray emisiion, in Proceedings of
Fourth Conference on the Scientific and Industrial
Applications of Small Accelerators, IEEE, 76CH
1175-9 NPS, pp. 106-109, 1976.

59

Filter and Impactor Sampling of Aerosols

A-7   R.E. Van Grieken, T.B. Johansson, K.R. Akselsson,
       J.W. Winchester, J.W. Nelson, and K.R. Chapman,
       Geophysical applicability of aerosol size
       distribution measurements using cascade impactors
       and proton induced X-ray emission, Atmospheric
       Environment, 10, 571-576, 1976.

A-8   A.P. Woodard, Jr., B. Jensen, A.C.D. Leslie,
       J.W. Nelson, J.W. Winchester, R.J. Ferek, and
       P. Van Espen, Aerosol characterization by impactors
       and streaker sampling and PIXE analysis, in
       Proceedings of Symposium, Recent Advances in Air
       Pollutant Analysis, American Institute of Chemical
       Engineers, New York, (in press) 1977.

A-9   Walter W. Berg, A directional air sampling control
       system, Dept. of Oceanography, Florida State
       University, Tallahassee, FL 32306, July 1974
       (unpublished report).

Urban Aerosol Trace Metal Studies

Urban Aerosol Trace Metal Characterization

A-10   Thomas B. Johansson, Rene E. Van Grieken, and
       John W. Winchester, Interpretation of aerosol trace
       metal particle size distributions, Proceedings of
       the Second International Conference on Nuclear
       Methods in Environmental Research, July 29-31,
       1974, University of Missouri, Columbia, USERDA
       CONF-740701, pp. 356-365, 1974.

A-11   Kenneth A. Hardy, Roland Akselsson, John W. Nelson,
       and John W. Winchester, Elemental constituents of
       Miami aerosol as a function of particle size,
       Environmental Science and Technology, 10, 176-182,
       1976.

A-12   John W. Winchester, Dennis L. Meinert, J. William
       Nelson, Thomas B. Johansson, Rene E. Van Grieken,
       Celso Orsini, Henry C. Kaufmann, and Roland
       Akselsson, Trace metals in the St. Louis aerosol,
       Proceedings of the Second International Conference
       on Nuclear Methods in Environmental Research,
       July 29-31, 1974, University of Missouri, Columbia,
       J.R. Vogt and W. Meyer, eds., USERDA CONF-740701,
       pp. 385-394, 1974.

A-13   R. Akselsson, C. Orsini, D.L. Meinert,
        T.B. Johansson, R.E. Van Grieken, H.C. Kaufmann,
        K.R. Chapman, J.W. Nelson, and J.W. Winchester,
        Application of proton-induced X-ray emission
        analysis to the St. Louis Regional Air Pollution
        Study, Advances in X-Ray Analysis, vol. 18,
        W.L. Pickles, C.S. Barrett, J.B. Newkirk, and
        C.O. Ruud, eds., pp. 588-597, Plenum Press,
        New York, 1975.

A-14   Celso Q. Orsini, Henry C. Kaufmann, K. Roland
        Akselsson, John W. Winchester, and J. William
        Nelson, Variation of elemental composition with
        particle size in the St. Louis aerosol, Nuclear
        Instruments and Methods, 142, 91-96, 1977.

A-15   James O. Pilotte, J. William Nelson, and John W.
        Winchester, Application of multi-station time
        sequence aerosol sampling and proton induced X-ray
        emission analysis techniques to the St. Louis
        Regional Air Pollution Study for investigating
        sulfur-trace metal relationships, in Proceedings,
        ERDA X and Gamma-Ray Symposium, Ann Arbor, MI,
        pp. 161-163 (CONF 760539), 1976.

A-16   James O. Pilotte, John W. Winchester, and J. William
        Nelson, Components of lead in the atmosphere of
        St. Louis, Missouri, J. Applied Meteorology, 17,
        627-635, 1978.

A-17   G.G. Desaedeleer, J.W. Winchester, R. Akselsson,
        and K.A. Hardy, Bromine and lead relationships
        with particle size and time along an urban freeway,
        Trans. Am. Nucl. Soc., 21, Suppl. 3, 36-37, 1975.

A-18   K.R. Akselsson, K.A. Hardy, G.G. Desaedeleer,
        J.W. Winchester, W.W. Berg, T.B. Vander Wood, and
        J.W. Nelson, X-ray techniques for aerosol sulfur
        baseline assessment along an urban freeway,
        Advances in X-Ray Analysis, vol. 19, R.W. Gould,
        C.S. Barrett, J.B. Newkirk, and C.O. Ruud, eds.,
        pp. 415-425, Kendall Hunt, Dubuque, Iowa, 1976.

A-19   John W. Winchester, Georges G. Desaedeleer, and
        K. Roland Akselsson, Time variations in elemental
        composition of atmospheric particulate matter along
        a Los Angeles freeway, (to be published).

A-20   Georges G. Desaedeleer, K. Roland Akselsson, and
        John W. Winchester, Aerosol particle size relation-
        ships along a Los Angeles freeway, (to be published).

A-21   William J. Courtney, Scott Rheingrover, James
        Pilotte, Henry C. Kaufmann, Thomas A. Cahill, and
        John W. Nelson, Continuous observation of
        particulates during the General Motors Sulfate
        Dispersion Experiment, Journal of the Air Pollution
        Control Association, 28, 224-228, 1978.

A-22   G. Desaedeleer, J.W. Winchester, J.O. Pilotte,
        J.W. Nelson, and H.A. Moffitt, Proton induced X-ray
        emission analysis of roadway aerosol time sequence
        filter samples for pollution control strategy, in
        Measurement, Detection and Control of Environmental
        Pollutants, International Atomic Energy Agency,
        Vienna, pp. 233-244, 1976.

A-23   D.J. Moschandreas, W.J. Courtney, J.O. Pilotte,
        J.W. Winchester, H.C. Kaufmann, J.W. Nelson, and
        R.M. Burton, Indoor and outdoor sources of
        particulate air pollution in a residential environ-
        ment, in Proceedings, Fourth Joint Conference on
        Sensing of Environmental Pollutants, 1977.

A-24   D.J. Moschandreas, J.W. Winchester, J.W. Nelson, and
        R.M. Burton, Fine particle residential air pollu-
        tion, Atm. Environ., submitted, August 1978.

Human Aerosol Inhalation and Hair Studies

A-25   K. Roland Akselsson, Georges G. Desaedeleer,
        Thomas B. Johansson, and John W. Winchester,
        Particle size distribution and human respiratory
        deposition of trace metals in indoor work environ-
        ments, Annals of Occupational Hygiene, 19, 225-238,
        1976.

Marine Aerosol Studies

    Coastal Zone Aerosol and Trace Metal Transport

A-26   Jonathan Sheline, Roland Akselsson, and John W.
        Winchester, Trace element similarity groups in north
        Florida Spanish moss: evidence for direct uptake of
        aerosol particles, J. Geophys. Res., 81, 1047-1050,
        1976.

        Air-Water Interface Studies

A-27   Walter W. Berg, Jr., and John W. Winchester, Aerosol
        chemistry of the marine atmosphere, in Chemical
        Oceanography, 2nd edition, vol. 7, J.P. Riley and
        R. Chester, editors, Academic Press, New York,
        In press 1977. (87 pages + 5 tables + 11 figures).

62

B. STUDIES WITH CONTRIBUTING EPA FUNDING SUPPORT

Elemental Analysis and Aerosol Sampling Techniques

Proton Induced X-Ray Emission, PIXE

B-1   T.B. Johansson, J.W. Nelson, R.E. Van Grieken, and
       J.W. Winchester, Elemental analysis of aerosol size
       fractions by proton-induced x-ray emission, Trans.
       Am. Nucl. Soc., 17, 103, 1973.

Proton Elastic Scattering Analysis, PESA

B-2   J.W. Nelson, I. Williams, T.B. Johansson, R.E.
       Van Grieken, K.R. Chapman, and J.W. Winchester,
       Elemental analysis of aerosols using proton
       scattering, IEEE Trans., Nucl. Sci., vol. NS-21,
       618-621, Feb. 1974.

B-3   J. William Nelson and Dennis L. Meinert, Proton
       elastic scattering analysis - a complement to
       proton-induced X-ray emission analysis of
       aerosols, Advances in X-Ray Analysis, vol. 18,
       W.L. Pickles, C.S. Barrett, J.B. Newkirk, and
       C.O. Ruud, eds., pp. 598-605, Plenum Press, New
       York, 1975.

B-4   R. Akselsson, J.W. Nelson, and J.W. Winchester,
       Proton scattering for analysis of atmospheric
       particulate matter, Proceedings of Conference on
       Nuclear Cross Sections and Technology, National
       Bureau of Standards Special Publication 425,
       vol. 2, pp. 484-487, U.S. Depart. of Commerce,
       Oct. 1975. (Cf. abstract of paper FB-5, Bull. Am.
       Phys. Soc., Ser. II, 20, 155, 1975).

B-5   J.W. Nelson and W.J. Courtney, Light element
       analysis by proton scattering, Nuclear Instruments
       and Methods, 142, 127-132, 1977.

Computer Spectrum Resolution

B-6   H.C. Kaufmann and R. Akselsson, Non-linear least
       squares analysis of proton-induced X-ray emission
       data, Advances in X-Ray Analysis, vol. 18, W.L.
       Pickles, C.S. Barrett, J.B. Newkirk, and C.O. Ruud,
       eds., pp. 353-361, Plenum Press, New York, 1975.

B-7   Henry C. Kaufmann, K. Roland Akselsson, and
        William J. Courtney, REX: a computer program for
        PIXE spectrum resolution of aerosols, Advances in
        X-Ray Analysis, vol. 19, R.W. Gould, C.S. Barrett,
        J.B. Newkirk, and C.O. Ruud, eds., pp. 355-366,
        Kendall Hunt, Dubuque, Iowa, 1976.

B-8   Henry C. Kaufmann, K. Roland Akselsson, and
        William J. Courtney, REX - a computer programme
        for PIXE analysis, Nuclear Instruments and Methods,
        142, 251-257, 1977.

                Thick Target PIXE Analysis

B-9   R.E. Van Grieken, T.B. Johansson, J.W. Winchester,
        and A.L. Odom, Micro-determination of zirconium-
        hafnium ratios in zircons by proton induced X-ray
        emission, Z. Anal. Chem., 275, 343-348, 1975.

        Filter and Impactor Sampling of Aerosols

B-10   B. Jensen and J.W. Nelson, Novel aerosol sampling
        apparatus for elemental analysis, Proceedings of
        the Second International Conference on Nuclear
        Methods in Environmental Research, July 29-31,
        1974, University of Missouri, Columbia, USERDA
        CONF-740701, pp. 366-375, 1974.

B-11   J. William Nelson, Proton-induced aerosol analyses:
        methods and samplers, in X-Ray Fluorescence Analysis
        of Environmental Samples, Thomas G. Dzubay, editor,
        pp. 19-34, Ann Arbor Science Publishers, 1977.

B-12   W.J. Courtney, H.C. Kaufmann, and J.W. Nelson,
        Continuous time sequential analysis of air
        particulate matter with proton beams, in Proceedings
        of Fourth Conference on the Scientific and Indus-
        trial Applications of Small Accelerators, IEEE,
        76CH 1175-9 NPS, pp. 120-123, 1976.

B-13   J.W. Nelson, G.G. Desaedeleer, K.R. Akselsson,
        and J.W. Winchester, Automatic time sequence filter
        sampling of aerosols for rapid multi-element
        analysis by proton induced X-ray emission, Advances
        in X-Ray Analysis, vol. 19, R.W. Gould, C.S. Barrett,
        J.B. Newkirk, and C.O. Ruud, eds., pp. 403-413,
        Kendall Hunt, Dubuque, Iowa, 1976.

B-14   M.S. Ahlberg, A.C.D. Leslie, and J.W. Winchester, Environmental and occupational health analyses using proton induced X-ray emissions, in <u>Electron Microscopy and X-Ray Applications to Environmental and Occupational Health Analysis</u>, Philip A. Russell and Alan E. Hutchings, eds., Ann Arbor Science Publishers, 1978, pp. 41-46.

B-15   Ronald J. Ferek, Lawrence Wangen, and Thomas A. Cahill, Ambient air comparison tests of stacked filter units with virtual, multiday, and Battelle impactors (to be published).

Urban Aerosol Trace Metal Studies

    Statement of urban aerosol research objectives

B-16   John W. Winchester and Georges G. Desaedeleer, Applications of trace element analysis to studies of the atmospheric environment, in <u>Nondestructive Activation Analysis</u>, Saadia Amiel, Ed., Elsevier, Amsterdam, in press, 1977, (iii + 54 pages, 7 tables and 10 figures).

B-17   T.B. Johansson, R.E. Van Grieken, J.W. Winchester, and J. Bogen, Trace elements in atmospheric aerosol in the Heidelberg area, measured by instrumental neutron activation analysis (discussion), Atm. Environ., $\underline{8}$, 297-299, 1974.

    Human Aerosol Inhalation and Hair Studies

B-19   Georges G. Desaedeleer and John W. Winchester, Trace metal analysis of atmospheric aerosol particle size fractions in exhaled human breath, Environ. Sci. Technol., $\underline{9}$, 971-972, 1975.

B-19   A.C.D. Leslie, J.W. Winchester, F.W. Leysieffer, and M.S. Ahlberg, Prediction of health effects of pollution aerosols, in <u>Trace Substances in Environmental Health-X</u>, Delbert D. Hemphill, ed., University of Missouri, Columbia, pp. 497-504, 1976.

B-20   Georges G. Desaedeleer, John W. Winchester, and K. Roland Akselsson, Monitoring aerosol elemental composition in particle size fractions for predicting human respiratory uptake, Nuclear Instruments and Methods, $\underline{142}$, 97-99, 1977.

65

B-21   E.C. Henly, J.W. Nelson, and M.E. Kassouny, Single
        human hair root analysis by nuclear particle
        accelerator techniques, in Trace Substances in
        Environmental Health-X, D.D. Hemphill, eds.,
        University of Missouri, pp. 333-341, 1976.

B-22   E.C. Henly, M.E. Kassouny, and J.W. Nelson, Proton-
        induced X-ray emission analysis of single human
        hair roots, Science, 197, 277-278, July 15, 1977.

B-23   Mats S. Ahlberg, Harold J. Annegarn, Björn O.
        Dahlbäck, Alistair C.D. Leslie, and John W.
        Winchester, Particle size dependent aerosol
        deposition in the human respiratory tract, in Trace
        Substances in Environmental Health-XII, Delbert D.
        Hemphill, ed., University of Missouri, Columbia,
        in press, 1978.

Marine Aerosol Studies

Coastal Zone Aerosol and Trace Metal Transport

B-24   T.B. Johansson, R.E. Van Grieken, and J.W.
        Winchester, Marine influences on aerosol composition
        in the coastal zone, Journal de Recherches
        Atmospherique, 8, No. 3/4, 761-776, 1974.

B-25   Thomas B. Johansson, Rene E. Van Grieken, and
        John W. Winchester, Elemental abundance variation
        with particle size in north Florida aerosols,
        J. Geophys. Res., 81, 1039-1046, 1976.

B-26   J.W. Winchester, Approaches to evaluating dry
        deposition of atmospheric aerosol pollutants onto
        lake surfaces, Journal of Great Lakes Research, 2,
        Suppl. 1, 33-38, 1976.

B-27   John W. Winchester, Assessing air pollution
        particulate fallout potential for water pollution
        in Lake Michigan, in Proceedings of the Second
        Federal Conference of the Great Lakes, Argonne
        Natl. Lab., March 25-27, 1975, (issued August 1976),
        pp. 330-337.

Marine Aerosol Characterization

B-28   Dennis L. Meinert and John W. Winchester, Chemical
        relationships in the North Atlantic marine aerosol,
        J. Geophys. Res., 82, 1778-1782, 1977.

Air-Water Interface Studies

B-29   Walter W. Berg and John W. Winchester, Organic and
        inorganic gaseous chlorine concentrations in
        relation to the particle size distribution of
        chloride in the marine aerosol, in preprints of
        Symposium, the Non-Urban Tropospheric Composition,
        Am. Geophys. Union and Am. Meteorol. Soc., Miami,
        Nov. 10-12, 1976.

B-30   Walter W. Berg and John W. Winchester, Organic and
        inorganic gaseous chlorine concentrations in
        relation to the particle size distribution of
        chloride in the marine aerosol, J. Geophys. Res.,
        82, No. 37, 5945-5953, 1977.

C.   STUDIES RELATED TO EPA PROGRAM BUT WITHOUT EPA SUPPORT

Elemental Analysis and Aerosol Sampling Techniques

            Proton Induced X-Ray Emission, PIXE

C-1   T.B. Johansson, R. Akselsson, M. Ahlberg,
        G. Johansson, and K. Malmqvist, Analytical use of
        proton-induced X-ray emission, Trans. Am. Nucl.
        Soc., 21, Suppl. 3, 1975.

Urban Aerosol Trace Metal Studies

    Statement of urban aerosol research objectives

C-2   John W. Winchester, Trace metal associations in
        urban airborne particluates, Bull. Am. Meteorol.
        Soc., 54, 94-97, 1973.

C-3   John W. Winchester, Application of neutron
        activation analysis to the investigation of natural
        and pollution aerosols, J. Radioanalytical Chemistry,
        19, 311-317, 1974.

C-4   John W. Winchester, Natural and pollution sources of
        trace elements in atmospheric particulates, in
        Trace Contaminants in the Environment, Andre F.
        LeRoy, ed., Am. Inst. Chem., Eng. Symp. Ser. No. 149,
        pp. 16-18, 1975.

67

C-5   P.R. Harrison, K.A. Rahn, R. Dams, J.A. Robbins,
       and J.W. Winchester, Areawide trace metal distribu-
       tions in northwest Indiana aerosols, in Trace
       Contaminants in the Environment, Andre F. LeRoy,
       ed., Am. Inst. Chem. Eng. Symp. Ser. No. 149,
       pp. 19-25, 1975.

C-6   John W. Winchester, Atmospheric sciences and problems
       of society: atmospheric chemistry, Bull. Am.
       Meteorol. Soc., 57, 1447-1449, 1976.

C-7   John W. Winchester, Urban air pollution impacts
       on remote regions, in Earthcare: Global Protection
       of Natural Areas, E.A. Schofield, ed., Westview
       Press, Boulder, Colorado, 1977.

C-8   John W. Winchester, Current environmental threats
       to the atmosphere, in Earth Program Journal,
       14th Biennial Wilderness Conference, National
       Audubon Society and Sierra Club, New York,
       pp. 108-111, June 5-8, 1975.

    Urban Aerosol Trace Metal Characterization

C-9   G.G. Desaedeleer, J.W. Winchester, M. Demuynck,
       and R. Dams, One-year study of total suspended
       particulate matter at 14 locations in Belgium:
       discussion, Atmospheric Environment, 10, 563-564,
       1976.

Marine Aerosol Studies

    Coastal Zone Aerosol and Trace Metal Transport

C-10   D. Skibin, Raymond Staley and John W. Winchester,
       Comment on water pollution in Lake Michigan from
       pollution aerosol fallout, Water, Air, and Soil
       Pollution, 2, 405-407, 1973.

C-11   John W. Winchester, Sources, sinks, and budgets of
       atmospheric trace constituents, in Atmospheric
       Chemistry, Problems and Scope, Report of the
       Panel on Atmospheric Chemistry, Richard A. Craig,
       chairman, Committee on Atmospheric Sciences,
       National Academy of Sciences, Washington, D.C.,
       pp. 59-69, 1975.

C-12   James O. Pilotte, John W. Winchester, and Robert C.
       Glassen, Detection of heavy metal pollution in
       estuarine sediments, Water, Air, and Soil Pollution,
       9, No. 3, 363-368, 1977.

68

C-13   Robert C. Glassen and John W. Winchester, Review
        of application for site certification, Arvah B.
        Hopkins Generating Station, Tallahassee, Florida,
        Department of Oceanography and Florida Resources
        and Environmental Analysis Center, Florida State
        University, Tallahassee, November 1974.

C-14   Robert C. Glassen and John W. Winchester, Review
        of application for site certification, Caryville
        Steam Plant, Caryville, Florida, Department of
        Oceanography and Florida Resources and Environmental
        Analysis Center, Florida State University,
        Tallahassee, September 1975.

                Air-Water Interface Studies

C-15   John W. Winchester, Atmospheric Chemistry of
        Halogens, McGraw-Hill Encyclopedia of Science and
        Technology, 4th edition, in press.

C-16   Rene E. Van Grieken, Thomas B. Johansson, and
        John W. Winchester, Trace metal fractionation
        effects between sea water and aerosols from bubble
        bursting, Journal de Recherches Atmospheriques,
        8, No. 3/4, 611-621, 1974.

C-17   Rene E. Van Grieken, Thomas B. Johansson, John W.
        Winchester, Dennis L. Meinert, and Walter W. Berg,
        Jr., Laboratory tracer experiments on fractionation
        during bubble bursting, Technical Report 8-74,
        Department of Oceanography, Florida State University,
        Tallahassee, August 1974.

C-18   John W. Winchester, The ocean as a source of
        particulate matter, in Background Papers for a
        Workshop on the Tropospheric Transport of Pollutants
        to the Ocean, Miami, December 1975, Ocean Sciences
        Board, National Research Council (Issued May 1977),
        pp. 270-275.

C-19   John W. Winchester and Robert A. Duce, The air-water
        interface: particulate matter exchange across the
        air-water interface, in Fate of Pollutants in the
        Air and Water Environments, J.H. Suffet, ed.,
        Part 1, pp. 27-47, New York, Wiley, 1977.

D. THESES AND DISSERTATIONS

Urban Aerosol Trace Metal Studies

Urban Aerosol Trace Metal Characterization

D-1   James O. Pilotte, Aerosol composition relationships
        in time sequence samples of an urban atmosphere,
        M.S. Thesis, Department of Oceanography, Florida
        State University, June 1977.

D-2   Scott Rheingrover, A statistical model for titanium
        pollution transport in the atmosphere of St. Louis,
        M.S. Thesis, Department of Meteorology, Florida
        State University, June 1977.

Marine Aerosol Studies

Marine Aerosol Characterization

D-3   Dennis L. Meinert, Chemical relationships in the
        North Atlantic marine aerosol, M.S. Thesis, Depart-
        ment of Oceanography, Florida State University,
        June 1974.

D-4   Michael Darzi, Terrestrial influences on aerosol
        composition over the western North Atlantic Ocean,
        M.S. Thesis, Department of Oceanography, Florida
        State University, August 1977.

Air-Water Interface Studies

D-5   Walter W. Berg, Jr., Chlorine chemistry in the
        marine atmosphere, Ph.D. Dissertation, Department
        of Oceanography, Florida State University, August
        1976.

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16. ABSTRACT

A methodology was developed, tested, and applied to the identification of trace element aerosol sources and trace element aerosol transport phenomena. The method uses light weight and portable field sampling equipment, and results in the acquisition of large data sets suitable for statistical analysis and the testing of aerosol transport models. Aerosol sampling in the ambient atmosphere was accomplished through a combination of time-sequenced filter collections with hourly resolution, and fractionated aerosol collections with 0.25 μm resolution. Elemental analysis was performed with particle induced X-ray emission, a sensitive and rapid method.

Aerosol characterization studies were focussed on St. Louis, Missouri, during the Regional Air Pollution Study. Trace element pollutants were distinguished from their natural components on the basis of particle size distributions. Statistical analysis of time-sequenced concentration measurements revealed four distinct pollution sources for lead. A related analysis demonstrated that meteorological factors controlling the transport of titanium aerosol across the city could be identified. Extensions of the meteorology were applied to (1) the determination of trace element pollution deposition in the human respiratory tract through direct sampling of exhaled breath, (2) indoor environments, and (3) nonurban continental and marine atmospheres.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

* Air pollution   *˙Particle size distribu-
  Field tests   tion
  Sampling   * Sources
* Aerosols   * Identifying
  Urban areas   * Meteorology
* Metals
* Chemical analysis
	St. Louis, MO	13B
		14B
		07D
		05K
		07B
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