

Components of Lead in the Atmosphere of St. Louis, Missouri

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ABSTRACT

By means of multiple linear regression analysis of a suite of more than 10 000 concentration measurements, of 14 elements at 11 sampling stations every 2 h over the course of a week in July 1975, Pb was found to be correlated in time most strongly with Br, secondarily with Zn, and also with K and Fe. At one station some Pb variation was apparently independent of other elements. On this basis and on the basis of wind directional relationships among the elements, at least four different components of Pb in the St. Louis aerosol may be identified.

1. Introduction

Automotive emissions constitute an important source of lead present in aerosol particles in urban atmospheres. Because this component of lead is generally large, other non-automotive components of lead tend to be obscured and overlooked. However, with anticipated decrease in the use of leaded gasoline, non-automotive lead will become relatively more prominent in urban atmospheres. In this investigation we have used statistical techniques for identifying trace element associations as the basis for resolving non-automotive lead components. The study area was St. Louis and the network of measurement stations was that of the Regional Air Pollution Study (RAPS).

The present investigation adopts an approach which differs considerably from that used in material balance studies of urban aerosol composition. In these studies precise elemental analyses of urban aerosol samples have been utilized for testing models of the urban atmosphere for the mixing of emissions from their principal sources. These models for the most part have depended on prior knowledge of the sources and their relative elemental compositions. Winchester and Nifong (1971) used published industrial emission factors and estimated emission compositions and pollution source strengths in northwest Indiana to predict the urban aerosol composition in that region and to compare with average measured composition. Miller *et al.* (1972) and Gartrell and Friedlander (1975) have proposed to model the measured aerosol composition as a linear combination of measured source compositions and to calculate the percentage contribution of each to the whole by finding the best material balance fit to the data. This approach has been extended by Gatz (1975), and recently Kowalczyk *et al.* (1977) have demonstrated

that direct measurement of multi-element composition of emissions from the major sources in Washington, D.C., can lead to a satisfactory average material balance for some 30 trace elements and their source coefficients in this city.

A statistical approach has been taken by Hopke *et al.* (1976) to interpret the average elemental composition of the Boston aerosol in terms of groups of associated elements determined by factor and cluster analysis. Cluster analysis has also been used by Dams *et al.* (1971) to interpret aerosol composition measurements in northwest Indiana. These studies did not require separate determinations of source compositions but instead through element associations suggested principal source types.

In the present investigation the aerosol composition data base available (Pilotte, 1977) included precision analyses for 11–14 elements every 2 h for up to a week at each of 11 sampling points in the St. Louis area. Thus, the set of over 10 000 measured concentrations was considerably larger than available for the previous studies. The temporal precision of this data set permits the development of detailed pollution models, hitherto possible only for gaseous pollutants where time variability data were available (Shir and Shieh, 1974). Our approach, which does not depend on prior knowledge of pollution source compositions or strengths, may reveal anomalies in elemental association patterns throughout the city which call for further investigation of possible sources. Therefore, the approach starts from ambient aerosol composition, which is relatively simply and inexpensively measured, rather than from emissions inventories of the presumed major sources. On the basis of statistical associations of the elements in the ambient atmosphere, certain source areas may be identified and selected for detailed inventories.

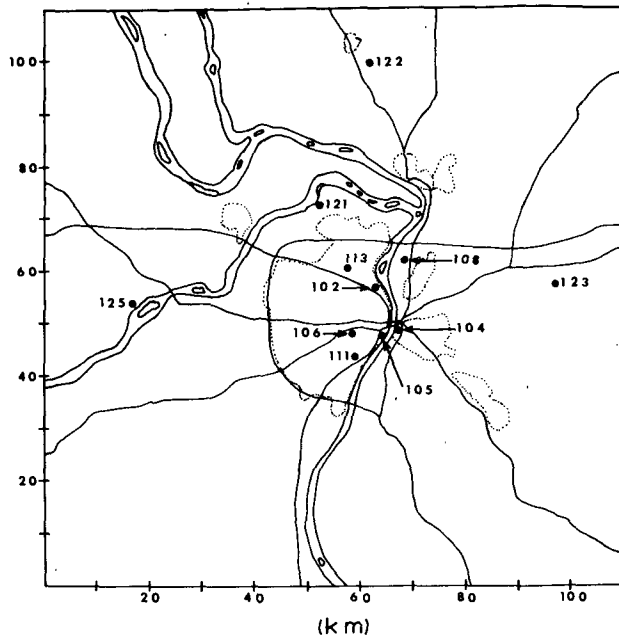


FIG. 1. Locations of the 11 stations of the Regional Air Pollution Study at which samples were collected for this study.

Consequently, the approach may be more flexibly applied to any urban area for assessing the importance of various sources of pollutants, in contrast to the material balance approach where detailed source compositions must be determined at the outset.

In this investigation we have chosen to model the variation in concentration between elements with time, taking advantage of our short 2 h resolution instead of depending on the longer 12–24 h resolution generally available in earlier material balance studies. By this method we are able to describe the observed elemental data in terms of related components, each of which may represent a significant pollution source. Moreover, the existence of a sporadic or unexpected source is less easily overlooked than if only long-term average aerosol composition measurements were made. Inter-element correlations are determined in order to determine those elements which behave similarly either as a result of meteorological factors or as a result of similar emission rates. In addition, correlations between elemental concentrations and the coefficient of light scattering, b_{scat} , may be an indicator of total particle concentrations especially in the fine particle size range (Schuetzle *et al.*, 1976; Patterson and Wagman, 1976). Finally, we use stagewise multiple-linear regression analysis (Draper and Smith, 1966) as a means of explaining the observed variability of one element in terms of the other elements present at a site. This method, coupled with wind direction information, inter-element correlations, and some knowledge of likely element associations in principal pollution sources, are all used to identify related aerosol constituents and their local sources. Because the composition data used have short time

resolution, both long-term average and fluctuations over short intervals can be evaluated. Although the health effects importance of the former is recognized (U.S. Environmental Protection Agency, 1975; Schroeder, 1971), the possible importance of the latter may now be examined by the type of analysis presented in this study.

2. Experiment

The analysis of data in the present investigation is based on a week-long record of elemental concentrations at 11 RAPS stations collected on $0.4 \mu\text{m}$ Nuclepore 2 h time steps by time sequence filter “streaker” samplers (Nelson, 1977). Elemental analysis was performed using proton induced x-ray emission, PIXE (Johansson *et al.*, 1975). A full description of data analysis procedures is given by Pilotte (1977) and a summary of concentration data by Pilotte *et al.* (1976). The locations of the 11 RAPS stations at which the measurements were made are indicated in Fig. 1. Eight of the stations were within the greater St. Louis metropolitan area, and three were in outlying rural areas. In Fig. 2 the times over which the measurements were made at each station during July 1975 are shown. At most stations 81 2 h time steps extending over seven days were analyzed, but at several stations data only for shorter time periods were obtained.

The sampler utilizes the smooth back of Nuclepore filter and a sucking orifice which slides while drawing air at 0.8 l min^{-1} through a $2 \text{ mm} \times 5 \text{ mm}$ rectangular area, producing a time-dependent streak along the length of the filter. This streak is analyzed stepwise utilizing a $2 \text{ mm} \times 5 \text{ mm}$ collimated beam of 5 MeV protons which excite the characteristic x-rays of elements in the sample, x-ray detection by a Si(Li) detector system and multi-channel analyzer, and individual element resolution by computer. The proton bombardment procedure is automated so that the filter

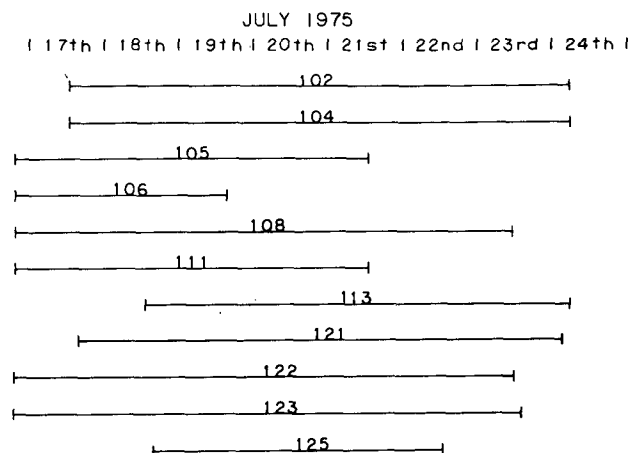


FIG. 2. Times of streaker sampling at each of the sites shown in Fig. 1.

TABLE 1. Mean concentrations of elements correlated with lead by multiple regression analysis.*

Station	n	Elements						
		Pb	Br	Zn	Fe	K	Ti	V
102	81	442±287 (81)	65±51 (81)	73±96 (80)	568±411 (81)	171±98 (81)	178±335 (68)	25±5 (10)
104	81	640±436 (81)	86±69 (79)	914±1060 (49)	1033±557 (81)	211±128 (81)	83±65 (77)	21±10 (8)
105	58	464±330 (58)	58±58 (58)	86±126 (58)	780±536 (58)	266±188 (58)	222±316 (58)	20±1 (3)
106	35	628±428 (35)	93±66 (35)	31±32 (31)	478±471 (35)	156±97 (35)	156±97 (35)	54±26 (2)
108	81	504±844 (81)	40±21 (81)	76±102 (74)	565±468 (81)	219±147 (81)	219±147 (81)	22 (1)
111	58	478±336 (58)	69±62 (58)	55±59 (58)	1104±1016 (58)	193±95 (58)	725±1022 (52)	40±33 (22)
113	68	540±361 (68)	91±55 (68)	46±48 (65)	517±402 (68)	182±100 (68)	85±132 (53)	15±4 (6)
121	76	381±501 (76)	40±44 (75)	104±217 (73)	329±215 (76)	143±87 (76)	86±179 (54)	22±12 (4)
122	81	133±142 (76)	14±8 (46)	92±144 (54)	289±204 (81)	144±67 (80)	33±35 (72)	— (0)
123	82	115±108 (81)	18±13 (60)	33±129 (41)	148±78 (82)	211±658 (76)	17±12 (69)	— (0)
125	47	82±63 (47)	13±6 (33)	13±19 (22)	205±110 (47)	126±47 (47)	36±32 (39)	— (0)
DL _{av.}		16	17	10	15	27	14	18

* Arithmetic mean concentrations (ng m⁻³) above blank levels, with standard deviations of the distributions of 2 h time step measurements; n represents number of time steps analyzed; in parentheses are number of values above detection limit (DL) which were averaged.

is advanced by a step-drive motor giving rapid sequential analysis of 90 time steps in a few hours. The present data base, consisting for the 11 RAPS stations of over 10 000 concentration measurements of 14 elements, is suitable for the application of statistical procedures of analysis in order to identify composition relationships which may be indicative of the components present in a mixed urban aerosol.

3. Results

In Tables 1 and 2 we present the mean elemental concentrations at each of the 11 stations over all of the time steps analyzed. Of the 14 elements, 11 (excluding Cl, Cr and Cu which were frequently at or below detection limits) were used in the multiple regression analysis described below. (The seven elements shown in Table 1 were those found by multiple-regression analysis to have significant associations with lead, and they are listed in approximate order of their appearance in the regression equations.)

It should be noted that in general S and Ca (Table 2) have the highest average abundances in the aerosol

samples, but neither is found in association with lead by multiple-regression analysis. Pb and Fe are next in overall average abundance followed by K, Ti, Zn and Br. Other elements have distinctly lower average concentrations. The standard deviations indicated for the distribution of measured concentrations about the arithmetic mean tends to be large in some cases and small in others, with the large values in general reflecting a pronounced time variability which is often directionally dependent.

Fig. 3 is an example of the time variations found at station 111 on Thursday, 16 July 1975. The station, located in a residential neighborhood near an industrial area in the southern part of the city of St. Louis, shows two prominent maxima for the 10 elements shown. A close examination of the positions of the maxima shows that they are not identical for all elements. Although the absolute time calibration for the steps may be uncertain by ±1 step (±2 h), the relative elemental concentrations found by PIXE analysis of a single time step are precisely determined. In step 8 (time 0745–0945) a maximum occurs for S, Ti, V, Mn, Fe and Br, but the maxima for K, Ca, Zn and Pb occur at step 9,

TABLE 2. Mean concentrations of other elements in the St. Louis aerosol.

Station	n	Elements						
		S	Cl	Ca	Cr	Mn	Ni	Cu
102	81	1438±807 (81)	30±17 (14)	1451±1185 (77)	24±18 (15)	32±32 (78)	83±146 (10)	63±103 (22)
104	81	2073±752 (81)	52±30 (10)	2272±1497 (81)	11±1 (5)	47±35 (79)	23±9 (2)	127±224 (42)
105	58	1933±938 (58)	35±21 (39)	1417±973 (58)	14 (1)	40±29 (32)	4±4 (24)	7±6 (49)
106	35	1346±608 (35)	22±17 (9)	761±446 (35)	34±14 (2)	47±79 (12)	9±11 (13)	5±6 (6)
108	81	1540±781 (81)	14±12 (34)	1035±858 (81)	46±27 (9)	28±19 (47)	6±8 (24)	46±44 (15)
111	58	1984±1050 (58)	14±12 (5)	1116±914 (58)	13±4 (3)	32±35 (58)	10 (1)	33±41 (7)
113	68	1730±941 (68)	21±12 (12)	1024±731 (68)	14±19 (15)	18±24 (56)	34±17 (16)	27±31 (9)
121	76	1827±1163 (76)	23±22 (23)	803±519 (76)	6±3 (14)	15±12 (67)	15±7 (4)	25±19 (20)
122	81	1764±1189 (81)	24±36 (23)	665±551 (80)	— (0)	23±19 (30)	16±15 (26)	18±12 (11)
123	82	1650±917 (82)	45±58 (78)	514±560 (82)	— (0)	27±29 (24)	9±3 (2)	— (0)
125	47	657±343 (47)	32±25 (2)	723±837 (45)	— (0)	15±10 (10)	17 (1)	50±65 (2)
DL _{av.}		66	50	30	15	13	13	12

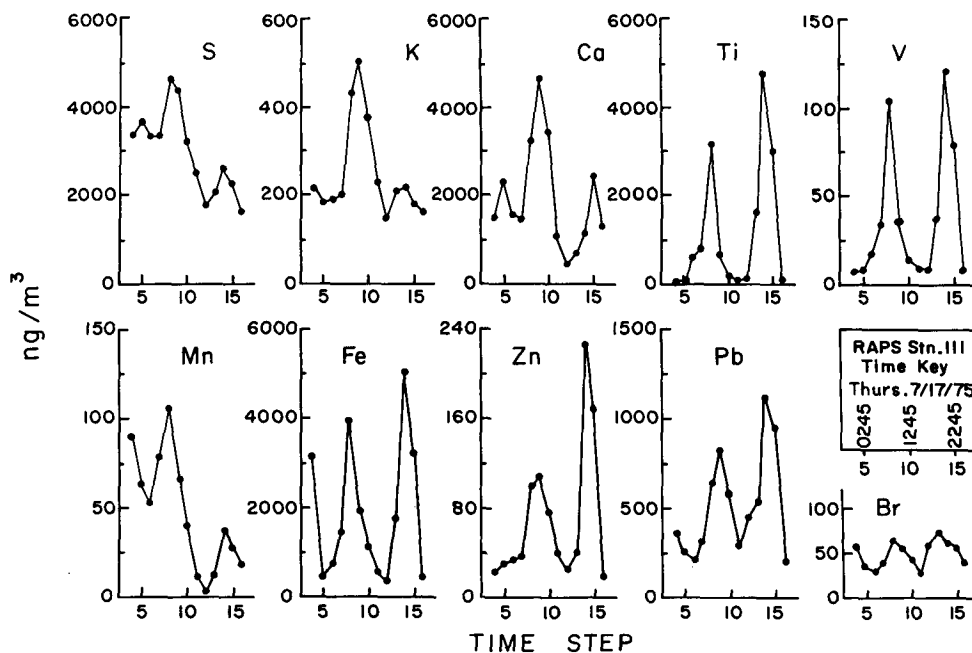


FIG. 3. Example of time variations in elemental concentrations found in southern St. Louis.

2 h later. A second maximum occurs at step 14 (time 1945–2145) for S, K, Ti, V, Mn, Fe, Zn and Pb but at step 15 for Ca and step 13 for Br. Apparently complex atmospheric processes regulate the transport of these elements from their sources to the sampling site. It is particularly noteworthy that Pb is not completely correlated in time with Br, suggesting that if Br is derived mainly from combustion of the ethyl fluid in gasoline then Pb may have both automotive and other pollution sources. The data analysis below will explore Br–Pb relationships in further detail.

Fig. 4 illustrates the time variation of Pb, Br and the ratio Br/Pb at stations 104 and 105 for 2.5 days. Since Pb and Br are both present in gasoline, they are generally regarded as indicative of automotive emissions. However, Fig. 4 reveals instances in which a change in the Pb concentration occurs without a corresponding change in the Br concentration. If we assume that Br is solely from automobile exhaust, then a non-automotive source for Pb is suggested. The anomalous behavior of Pb suggests the presence of additional non-automotive components of Pb in the aerosol. Evidence for such components is presented in the analysis below.

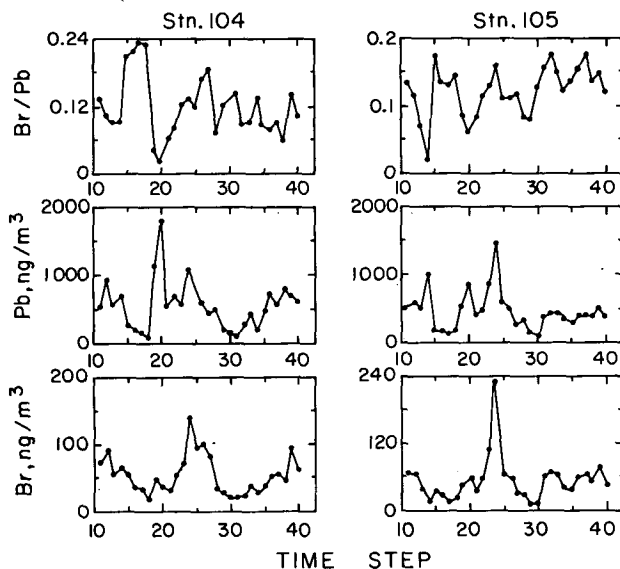


FIG. 4. Time variations of Pb, Br and Br/Pb found at two stations centrally located in the St. Louis area.

As a first step in statistically evaluating associations of other elements with Pb, pair correlation coefficients (shown in Table 3) were calculated. Br is strongly correlated with Pb at all 11 measurement stations, but several other elements as well as carbon monoxide are also in general strongly correlated. The correlations may reflect, not only elemental associations in aerosol sources, but also associations of urban aerosol constituents during meteorological transport, mixing and removal processes. Therefore, strong pairwise correlations are not necessarily indicative of associations in sources. Moreover, many of these elements and CO as well may have multiple sources in the St. Louis area.

Another correlation of interest is between elemental concentrations and optical density of the air as measured by the light scattering parameter b_{scat} . This correlation is quite good for S, consistent with other reports (Charlson, 1976, private communication) although not for Ca. We note some degree of correlation in Table 4 between b_{scat} and Fe or K, but in general the correlation with Pb is poor. The good S correlation may be the

TABLE 3. Pair correlation coefficients (n, r, P)* of lead with other elements and carbon monoxide.

Station	Elements										
	Br	Zn	Fe	K	Ti	V	S	Ca	Mn	Ni	CO**
102	0.89	0.39	0.40	0.29	0.35	0.69	0.01	0.14	0.19	0.34	0.23
	81 <.01	80 <.01	81 <0.1	81 1	68 0.5	10 3	81 93	77 22	78 11	10 34	70 6
104	0.78	0.46	0.58	0.32	0.29	0.53	0.12	0.53	0.60	—	0.54
	79 <0.1	49 0.1	81 <0.1	81 0.5	77 1	8 18	81 29	81 <0.1	79 <0.1	—	50 <0.1
105	0.87	0.44	0.40	0.29	0.32	1.0	0.29	0.55	0.05	0.01	0.73
	58 <0.1	58 0.1	58 0.2	58 3	58 2	3 0.7	58 3	58 <0.1	32 80	24 95	58 <0.1
106	0.96	0.21	0.24	0.05	0.14	—	0.40	0.53	0.30	0.33	-0.26
	35 <0.1	31 26	35 17	35 77	25 51	—	35 2	35 0.1	12 34	13 27	35 13
108	0.85	0.49	0.48	0.36	0.36	—	-0.10	0.16	0.47	0.02	0.57
	81 <0.1	74 <0.1	81 <0.1	81 0.1	79 0.2	—	81 38	81 15	47 0.1	24 91	81 <0.1
111	0.84	0.23	0.25	0.28	0.12	0.60	0.34	0.39	0.10	—	0.67
	58 <0.1	58 8	58 6	58 3	52 39	22 0.4	58 1	58 0.3	58 45	—	58 <0.1
113	0.95	0.31	0.45	0.30	0.41	-0.06	0.30	0.51	0.46	-0.05	0.76
	68 <0.1	65 1	68 <0.1	68 1	53 0.3	6 92	68 2	68 <0.1	56 <0.1	16 85	64 <0.1
121	0.86	0.42	0.28	0.07	0.46	0.44	0.26	0.28	0	0.83	0.63
	75 <0.1	73 <0.1	76 2	75 54	54 0.1	4 56	76 3	76 2	67 99	4 17	75 <0.1
122	0.65	0.55	0.51	0.45	0.41	—	0.52	0.33	0.33	0.33	0.80
	46 <0.1	53 <0.1	76 <0.1	76 <0.1	69 <0.1	—	76 <0.1	76 0.4	30 7	25 11	76 <0.1
123	0.90	0.42	0.47	0.17	0.18	—	0.17	0.43	-0.07	—	0.42
	60 <0.1	41 0.7	81 <0.1	75 15	68 15	—	81 13	81 <0.1	24 75	—	43 0.3
125	0.78	0.16	0.39	0.33	0.27	—	0.48	0.25	0.66	—	0.43
	33 0.1	22 46	47 0.7	47 2	39 10	—	47 0.1	45 9	10 4	—	47 0.5

* Indicated are the correlation coefficient r the number of values n , and the percent probability P of no correlation.
 ** Carbon monoxide concentrations were obtained from the RAPS network.

result of combined effects of total elemental concentration in the atmosphere, high for both S and Ca, and its distribution with particle size, skewed toward small particle sizes for S but toward large for Ca. The abundance in the submicrometer optically active size range and chemical properties such as hygroscopicity, which may enhance light scattering, are especially important. Although particle size distributions were not measured

for the elemental constituents of the aerosol in this study, previously measured size distributions in St. Louis (Akselsson *et al.*, 1975; Orsini *et al.*, 1977) may be representative. Some of these are shown in Figs. 5 and 6. The Pb size distribution is also shown for Los Angeles where automotive sources are predominant (Desaedeleer *et al.*, 1977). Both S and Pb are found to be more abundant in particles with aerodynamic

TABLE 4. Pair correlation coefficients n, r, P of b_{scat} with each element.**

Station	Pb	Br	Zn	Fe	K	Ti	V	S	Ca	Mn	Ni
102	0.04	-0.19	0.66	0.26	0.78	0.06	0.06	0.32	0.13	-0.26	—
	16 88	16 48	16 0.5	16 33	16 <0.1	16 82	4 94	16 23	16 63	16 33	—
105	-0.18	-0.18	0.15	0.26	0.58	0.14	0.51	0.63	0.35	0.08	—
	58 18	58 18	58 27	58 5	58 <0.1	58 30	3 66	58 <0.1	58 0.7	32 67	—
106	-0.14	-0.19	-0.07	0.02	0.09	0.13	—	-0.24	-0.31	0.16	—
	35 42	35 27	31 71	35 91	35 61	25 54	—	35 17	35 7	12 62	—
108	0.41	0.33	0.24	0.53	0.53	0.18	—	0.50	0.38	0.18	—
	81 <0.1	81 0.3	74 4	81 <0.1	81 <0.1	79 11	—	81 <0.1	81 0.1	47 23	—
111	-0.02	-0.04	0.47	0.36	0.13	0.13	0.16	0.76	0.12	0.44	—
	42 90	42 80	42 0.2	42 2	42 42	39 43	20 50	42 <0.1	42 46	42 0.4	—
113	0.27	0.14	0.38	0.11	0.25	0.06	-0.80	0.53	0.26	0.03	—
	51 6	51 33	48 0.8	51 44	51 8	37 72	5 10	51 <0.1	51 7	43 85	—
121	0.47	0.30	0.29	0.43	0.28	0.48	—	0.80	0.14	0.20	—
	59 <0.1	58 2	56 3	59 <0.1	59 3	38 0.2	—	59 <0.1	59 29	51 16	—
122	0.20	0	0.18	0.42	0.42	0.10	—	0.71	0.20	0.42	—
	76 9	46 99	54 20	81 <0.1	30 2	72 41	—	81 <0.1	80 8	30 2	—
123	0.22	-0.13	-0.04	-0.10	0.30	0.14	—	0.18	0	0.46	—
	52 12	38 44	28 84	53 48	48 4	44 37	—	53 20	53 99	19 5	—
125	0.29	0.09	0.57	0.49	0.45	0.09	—	0.82	-0.04	0.47	—
	47 5	33 62	22 0.6	47 <0.1	47 0.2	39 59	—	47 <0.1	45 79	10 17	—

* Indicated are the correlation coefficient r the number of values n and the percent probability P of no correlation.
 ** The b_{scat} data were obtained from the RAPS network. No data were available for station 104.

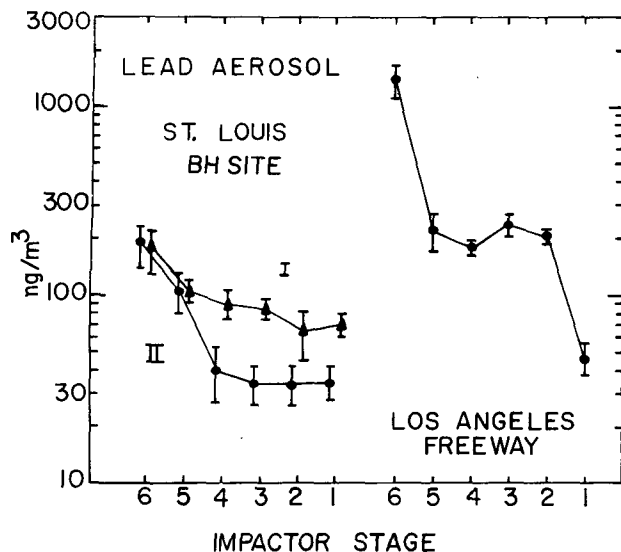


FIG. 5. Particle size distributions of Pb measured in St. Louis at a site near and south of RAPS station 111 during southerly air flow (I) and north to easterly flow (II), 16-18 and 19-21 August 1973, respectively. Each point is a mean and σ_{mean} of five 12 h samples. Industrial emissions were relatively greater during I than II. Also shown is a Los Angeles Pb size distribution, the mean of four simultaneous 2 h samples immediately downwind of a freeway on 12 September 1974. The Pb concentration ratio of 0.5-4 μm (stages 2, 3 and 4) to <0.5 μm particles (stages 5 and 6) at the St. Louis site during II (0.4) approximated that observed in Los Angeles.

diameter <1 μm , whereas Ca and other elements derived from dispersion sources are found in greater abundance in the >1 μm size range.

4. Multiple regression analysis

The factors which govern the associations of trace elements with Pb are undoubtedly complex. Although some suggestions of these factors may be seen in the patterns of time variability and pair correlations, this evidence by itself is not sufficient to identify the components of Pb which may be present in addition to the automotive component. Therefore, we have undertaken a multiple linear regression analysis of Pb as the dependent variable in a regression equation and have examined 10 other elements as independent variables. Table 5 presents the results of the analysis and is discussed below.

In applying the regression procedure to the set of elemental concentration data, a stagewise procedure (Draper and Smith, 1966) was selected. It has the advantage of accurately selecting the major independent variables of the regression, it can accommodate data sets of varying size as indicated by n in Tables 1 and 2, and the method can be adapted for use on a small computer. The numerical values of the regression coefficients calculated are in satisfactory agreement with values obtained using the SPSS multiple regression analysis routine (Nie *et al.*, 1970) for samples where

the unequal data set size limitation of SPSS was not a problem. Details of the stagewise procedure are given by Pilotte (1977).

In Table 5 it is indicated that the average Pb concentration at the urban sites lies in the range 380 to 640 ng m^{-3} , a rather small range, and at the three non-urban sites it is about 100 ng m^{-3} . The multiple-regression analysis finds Br to be the most significant independent variable in all cases, and its contribution to the overall value of R^2 , with one exception, lies between 44% and 100%. The exception, station 108, will be discussed further below.

Zn is found as the second most important independent variable in the regression equations for six urban stations and at station 108 as well for the latter portion of the time record. A rough indication of the quantitative importance of the Pb which is related to Zn, in addition to the Pb related to Br, can be obtained by noting the average Zn concentrations listed in Table 1. Multiplying these values with the regression coefficients suggests that Zn-related Pb is quantitatively smaller than Br-related Pb, though at some stations may average 10% or more.

At a few stations, K, Fe, Ti and V appear to be next in importance in the regression equations for Pb. Their associations with Pb are independent of those for Zn and Br, and therefore still another component of Pb is suggested. The case of station 108 appears to be unique in that the regression equation shows no element other than Br significantly correlated with Pb. However, the regression equation shows a poor overall fit, as indicated

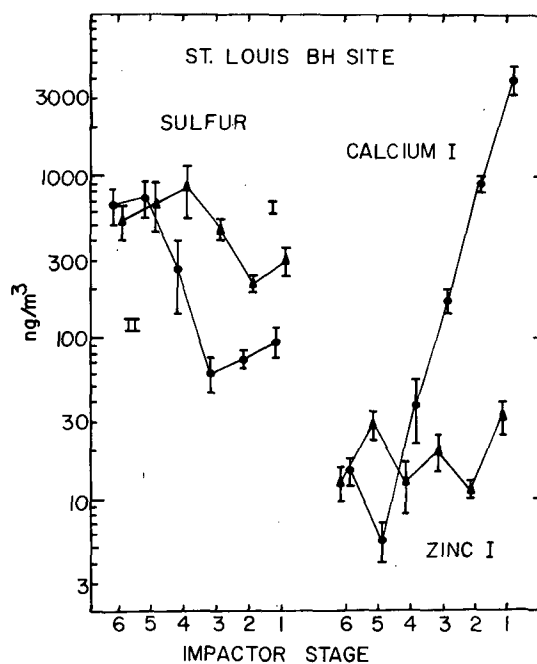


FIG. 6. Particle size distributions of S, Ca and Zn during southerly flow (I) and of S during north to easterly flow (II) for the same samples as in Fig. 5.

TABLE 5. Multiple linear regression analysis of lead.*

Station	Pb (av) (ng m ⁻³)	σ Pb	a_1x_1	a_2x_2	a_3x_3	Intercept	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	0.955	—	—	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.

by $R^2 \sim 10\%$, suggesting the presence of substantial amounts of non Br-related Pb. We remarked earlier that anomalously high Pb concentrations were observed in the first 30 time steps, but Br appeared at typical levels. A new regression equation was calculated using only the data after this episode, and a better overall R^2 fit was obtained. Apparently a component of Pb is present which is especially prominent during the first 30 time steps but which is not correlated with Br or with the other elements measured in this investigation.

The regression results in Table 5 were obtained by pooling all measurements without regard to wind direction. At the six stations where Zn appeared as a prominent second independent variable, we have also calculated a linear regression between the measured Br/Pb ratio and the Zn/Pb ratio for discrete 10° wind direction sectors, assuming the importance of a third independent variable to be relatively small. From the slope and intercept of the regression we can estimate the Br/Pb ratio of the Br-related Pb component and the Zn/Pb ratio for the component of Pb-related to Zn. The Br/Pb value (0.2) as an average for the six stations is in approximate agreement with the reciprocal of the first regression coefficients in Table 5. The Zn/Pb ratio, averaging about 1.4 over the six stations, is in the range of the reciprocals of the second regression coefficients of Table 5. Therefore, this procedure, which gives greater weight to observations in wind directions when Zn-related Pb is most prominent (although ignores contributions of other Pb components), is consistent with the multiple regression analysis of all data pooled without regard to wind direction.

In summary, stagewise multiple linear regression analysis suggests that Pb in the St. Louis area contains four components, the most prominent of which is Br-related, but with the others being related to Zn, to K,

to Fe, and to other elements, and at station 108 apparently not to any other element in our data set.

5. Discussion

The further definition of Pb components is greatly assisted by examining the variation of concentration with mean wind direction at each sampling site. A complete graphical presentation of each element at each site is given as wind rose diagrams by Pilotte (1977). We present in Table 6 a synopsis of Pb, Br, Zn and Ti concentrations measured at stations 108 and 104 in each of thirty six 10° sectors. Out of the total of 81 time step measurements made at each station the climatology over the week was such that at least a few measurements were made in nearly all of the sectors. However, the most frequent wind direction was south-westerly, and observations in sectors 22-24 were three times more frequent on the average than those in other wind direction sectors.

At station 108 exceptionally high concentrations of Pb were measured when air flow was from the south-southwest, but similar anomalies of Br and Zn are not apparent. Therefore, consistent with the regression analysis results (Table 5) there is substantial Pb detected at station 108 which is not associated with Br or Zn, and its source apparently lies south-southwest of the sampling station. A survey of listings of pollution sources in the area reveals secondary Pb smelting operations in this general direction at 2-3 km distance. Emissions of Pb from such operations are not expected to be associated with other trace elements measured in this study. The apparent similarity of Ti and Pb wind directional dependence, which represents partially overlapping plumes from different sources, is discussed further below.

TABLE 6. Mean concentrations for Pb, Br, Zn and Ti at stations 108 and 104 in each of the thirty-six 10° wind sectors.

Sector	Station 108				Station 104			
	Pb	Br	Zn	Ti	Pb	Br	Zn	Ti
1	425	39	79	36	608	124	—	136
2	269	26	92	23	711	113	422	120
3	716	72	636	27	483	93	—	154
4	402	59	35	9	633	90	20	55
5	82	19	—	24	1395	239	41	58
6	308	31	56	42	—	—	—	—
7	663	74	199	25	—	—	—	—
8	—	—	—	—	1212	330	—	24
9	205	32	8	19	748	139	—	32
10	354	49	18	8	373	70	—	48
11	314	46	4	38	1044	209	67	48
12	—	—	—	—	—	—	—	—
13	—	—	—	—	390	72	26	45
14	295	44	22	23	540	99	—	31
15	359	56	45	29	187	43	—	44
16	304	43	59	26	—	—	—	—
17	476	56	128	69	124	30	5	28
18	353	43	163	62	254	47	56	39
19	1905	40	117	91	547	64	363	112
20	1230	43	177	308	199	32	150	41
21	2050	36	70	152	491	53	902	85
22	553	52	105	105	529	49	543	63
23	371	46	27	51	566	39	1516	127
24	227	33	14	62	956	51	1642	91
25	—	—	—	—	716	74	944	115
26	140	21	15	36	804	132	840	68
27	339	46	8	38	1487	69	3552	149
28	—	—	—	—	1079	65	2482	191
29	—	—	—	—	—	—	—	—
30	132	16	6	65	—	—	—	—
31	133	20	4	9	411	59	361	95
32	226	29	7	22	1286	251	143	47
33	360	43	23	17	538	73	172	62
34	146	22	—	16	—	—	—	—
35	46	10	37	38	1096	183	—	52
36	216	32	49	14	—	—	—	—

The results for four elements at station 104 (Table 6) show some relationships between Pb, Zn and Br, although they are not as easy to identify by scanning the data as in the case of station 108. Of the four elements Zn shows the most prominent wind directional dependence, ranging from a few ng m^{-3} to over 3000 ng m^{-3} . For Br and Pb the wind directional dependence is much less marked. However, in the 270° and 280° wind sectors when Zn has its highest values, Pb also exhibits maxima. Other Pb maxima at 50°, 80°, 110°, 320° and 350° appear to be associated with maxima in Br. Ti maxima are generally found in different wind direction sectors from either Pb or Zn. The strength of Pb associations with Br and with Zn, dependent on wind direction, may be indicative of the relative contributions from different sources of Pb. However, the multiple linear regression analysis approach in this investigation, which utilizes measurements over time periods short enough so that excessive time averaging during sampling does not occur, has been critically important in singling out element associations which

warrant further study. Without first obtaining the regression results, it would be time consuming and inefficient to scan data, such as in Table 6 for station 104, for all the elements in search of such relationships. At other stations, where the relationships with wind direction are more subtle, the advantage of the multiple-regression analysis as the initial step is even greater.

Several lines of evidence, as presented in this study, tend to reinforce the concept that Pb in St. Louis is the result of mixing from a complex of sources which have characteristic trace element associations with Pb. The evidence suggests that at least four different components must be present: 1) a Br-related presumably automotive Pb; 2) a Zn-related presumably industrial Pb emitted into the atmosphere from a small number of relatively localized sources; 3) a Pb not associated with any other trace elements, detected at station 108 only; and 4) Pb related to K, Fe and other elements which may be derived from still additional sources.

The regression procedure, when applied to a sufficiently large data set of measurements made with suitable climatology, can identify elemental associations characteristic of sources, as distinguished from accidental associations by the overlapping of plumes from different sources. In practice, plume overlap is seldom complete over many days of observations, such as in this study. And the regression procedure applied to time-dependent concentration data is sensitive to incomplete mixing of plumes which reach a sampling site from similar directions. This is illustrated in the Ti and Pb data from station 108 (Table 6). A prominent Ti maximum occurs in sector 20 but Pb maxima occur in sectors 19 and 21 with a shallow minimum in sector 20. In the first 30 time steps, when both Ti and Pb exhibit strong time variations and some of their highest concentrations, the Ti-Pb pair is not significantly correlated, consistent with this. The multiple-regression analysis of Pb for all 81 time steps at station 108 did not find Ti to be a significant independent variable. (Regression analysis of steps 31-81 alone found Ti as a third independent variable, but its physical significance is less owing to the smaller data set chosen.) On the basis of other evidence, we understand a Ti pollution source to be located some 30 km south-southwest of station 108, whereas a Pb source appears to be located relatively nearby in approximately the same direction. The multiple regression procedure found Ti and Pb to be mutually independent, in spite of approximately overlapping plumes.

It should be pointed out that a wind direction dependence of elemental associations is only a crude indicator of atmospheric transport of related elements from their sources. Rheingrover (1977) has shown that pollution Ti, which has a strong and apparently unique source in St. Louis, is transported throughout the urban area such that its concentration at various sampling sites is a function depending not only on wind direction

from the source, but also on the standard deviation of the fluctuations in the wind from its mean direction, on the mean wind speed, on the vertical temperature gradient, which affects vertical mixing, and on particle removal by dry or wet deposition, especially over long transport distances. In our study of Pb in St. Louis, if the non-automotive Pb sources could be identified and are found to be stacks located at elevations substantially higher than the 10 m levels of the streaker samplers at the 11 RAPS stations, then the transport of Pb may be accounted for by a meteorological modeling approach similar to Rheingrover's. On the basis of his Ti transport model, we would anticipate that Pb transport from tall stack emissions would not be simply governed by wind direction at the sampling site alone, but the other parameters he found to be important must also be considered. A combination of meteorological modelling and the multiple regression analysis approach taken here for resolving the multiple components of Pb may be applicable to developing monitoring and air quality control strategies for pollution aerosols on an urban scale.

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