

Particulate Data from the First Year of Monitoring in Phoenix: Part II. Organic Carbon and Elemental Composition

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ABSTRACT

The Phoenix monitoring site was established to gather additional information on particulate loadings that may more decisively elucidate a statistical association with mortality and morbidity in urban areas. This paper reviews the first year (February 1995-January 1996) of data on particulate composition, centering on the prevalence of elements and organic/elemental carbon. Typically fine mass samples are 40 percent organic carbon, 10 percent elemental carbon, and about 15 percent other elements. Carbon concentrations rise in the late fall and winter, coincident with low wind speeds that may allow automotive emissions to be trapped near the surface. At the same time, carbon rises as a proportion of the fine mass. There is some evidence of leaded gasoline use in Phoenix. Higher wind speeds in the spring and summer result in a greater proportion of crustal elements and sulfur. Comparisons of measurements from the DFPSS (cyclone) and VAPS (virtual impactor), indicate biases consistent with the notion that the cyclone is less efficient at effecting the 2.5 μ m size cut, allowing larger particles through to the fine mass filters.

INTRODUCTION

The Phoenix particulate monitoring instruments are located at National Air Monitoring Site 04-013-0019, about 6 km WNW of downtown, and about 2.5 km west of Interstate 17 and 2.5 km north of Interstate 10. The principal instruments that provide daily particulate measurements are the TEOM^R (Tapered Element Oscillating Microbalance, Rupprecht & Patashnick, Inc. Series 1400a) and a Dual Fine Particle Sequential Sampler (DFPSS). The TEOM records hourly fine mass (<2.5 μ m) and PM10 (<10 μ m), from which coarse mass (2.5-10 μ m) is derived by differencing. The TEOM measurements are converted to daily values as explained in Part I of this paper¹. The DFPSS collects fine particle samples on both a Teflon and a quartz filter; the filters are changed at 7:00 AM local time each day. The samples are collected on dual channels using identical URG (Carrboro NC) cyclones to effect the particle size cut at 2.5 μ m. The quartz filter is analyzed for organic and elemental carbon, while the Teflon filter is weighed for mass and then subjected to X-ray fluorescence analysis for 44 elements. Operating on a reduced schedule of about every third day, a Versatile Air Pollutant Sampler (VAPS) also takes daily fine particle samples on quartz and Teflon filters that are subsequently analyzed for carbon and other elements. In the VAPS, the 2.5 μ m size cut is effected by a virtual impactor.

CARBON MEASUREMENTS

In a pure helium atmosphere, quartz filters are heated to about 700 C in order to drive off volatile (organic) carbon compounds. The carbon is converted to methane and measured by flame ionization. The remaining sample is heated to 850 C in the presence of 2% oxygen to burn off the remaining

(elemental) carbon, which is measured in the same manner.

Time Series

Figure 1 gives a time series of elemental and organic carbon from the DFPSS for the first year. The measurements begin on February 18, 1995, terminate on December 18 (coincident with a partial shutdown of the Federal government), and were not resumed in January 1996. Both forms of carbon show increased concentrations in October-December, mirroring the increase in fine mass seen in Part I. This increase is likely due to low-wind meteorological conditions and may be a recurring seasonal event. Figure 2 shows the carbon as a percentage of the fine mass concentration, indicating a winter rise in the proportion of carbon in the fine fraction.

VAPS/DFPSS Carbon Comparisons

For the first year, the archive holds 260 measurements of carbon from the DFPSS and 94 measurements from the VAPS; the latter instrument ran only about every third day. The carbon concentrations were determined from the quartz filters of each instrument. In addition, the Teflon filters were used to determine total fine mass and were subsequently subjected to elemental analysis by X-ray fluorescence. There are 285 and 99 fine mass measurements for the DFPSS and VAPS, respectively. Note that actual sampling did not start until February 7, 1995 and that the government shutdown was responsible for loss of 37 days. Other causes for loss of data were more mundane, e.g. "no operator", "no filters". Where simultaneous measurements were taken on the DFPSS and VAPS, they may be compared as displayed in Table 1.

As already discussed in Part I of this paper, the VAPS fine mass is about 18% less than the DFPSS fine mass. Compared to the virtual impactor on the VAPS, the cyclone inlet on the DFPSS is believed to be less sharp in effecting a size cut at $2.5\mu\text{m}$, allowing more large particles to get through and giving a higher mass reading. There may also be excess loss of volatilizable material (carbon or H_2O) from the VAPS since that instrument was outside at ambient temperature, while the DFPSS was maintained in a shelter at 30°C .

Because carbon is strongly associated with automotive exhaust and tends to be in the fine fraction, principally submicron, one may expect that the VAPS and DFPSS carbon values would be the same. However, a bias, albeit smaller, persists. The VAPS carbon is about 7% less than the DFPSS carbon (rows 2 and 3). A possible explanation is that some carbon is associated with the larger particles that are passed through the cyclone. Alternatively, there may be a bias between the instruments due to miscalculation of flow rates, or a bias due to volatilization.

Referring to Table 1, the ratios of mass, OC and EC from the each instrument (rows 1, 2, and 3) are all significantly different from zero. The ratios of carbon from the two instruments (rows 2 and 3) are not significantly different from each other, but they are different from the mass ratio (row 1). Finally, the ratios of carbon to mass for each instrument (rows 4 and 5, rows 6 and 7) merely reflect the preceding ratios. Typically, the fine mass is 40% organic carbon and 10% elemental carbon.

Correlation between Fractions

As seen in Table 2, organic and elemental carbon concentrations have quite high correlations with fine mass (0.94 and 0.86, respectively). On the other hand, the correlation between fine mass and coarse mass is only 0.68. This tends to be high when compared to cities in the eastern U.S.,² which is indicative of the arid region. The average ratio of coarse mass to fine mass in Phoenix is 3.2, compared to ranges of 0.33 to 1 in eastern cities³. If the PM-10 association with mortality is primarily due to fine mass, the effect may be discernable in Phoenix but with less ease than in other locations where correlations between FM and CM are lower. However, 88% of the variability of organic carbon can be explained by fine mass; the parameters are collinear and may be difficult or impossible to separate as explanatory variables.

ELEMENTAL MEASUREMENTS

The Teflon filters from the DFPSS and the VAPS are analyzed for elements by X-ray fluorescence. In the first year, two different X-ray analyzers were used, a Kevex EDX-771 and a machine custom built by Lawrence Berkeley Laboratory (LBL). Both analyzers are energy dispersive spectrometers. The Kevex was operated until July 29, 1996, and the LBL machine was operated for the remainder of the year.

Prevalent Elements

Although there are 44 elements, listed in the data base, considerably fewer are reported in any quantity. For each element, the data base lists an error term representing a 1σ confidence level, determined by propagating uncertainties from parameters used in the concentration calculations. Any reported value which does not exceed three times the error term is set to missing in the analysis presented here. For the DFPSS, 234 filters were analyzed for elements. Table 3 summarizes the elements that are reported most frequently at detectable levels. Because the Kevex can analyze for Na and Mg, while the LBL machine cannot, those two elements appear at relatively large concentrations up to the end of July 1995, but they are missing thereafter. Thus, Na and Mg are reported only 105 times, and yet account for the majority of the mass in the second group of Table 3. Typically the mass of the XRF-identified elements would be 15% of the fine mass.

For the 11 elements reported most often, Table 4 shows the mean ratios of the VAPS value to the DFPSS value. The results have been grouped by resulting mean ratio and show a distinct separation of crustal and non-crustal components. The ratios for the crustal components are even lower than those for fine mass (Table 1), indicating that the larger particles that pass through the DFPSS cyclone are disproportionately crustal, as expected.

The other elements show ratios closer to, but still less than, 1. A possible explanation is that these elements are in trace amounts in crustal particles either naturally or by contamination in the atmosphere. This effect parallels that seen for carbon.

The Pb and Br may indicate use of leaded fuels in Phoenix, with gasoline from Mexico a likely source. Typically, bromine and chlorine are introduced in the fuel to scavenge lead from the engine. Lead is principally emitted as $PbBrCl$, a compound where the weight ratio of Pb/Br would be 2.59, in line with observations⁴. Figure 3 shows a scatter plot of Pb versus Br; the slope of a simple linear regression is 2.75 ± 0.16 , and the mean ratio for those points where $Br > 6 \text{ ng/m}^3$ is 2.45 ± 0.17 . The concentrations of lead in Phoenix are only about 1 percent⁵ of those found in 1975.

The association of crustal elements can be seen in Table 5 which shows the correlations between the concentrations, *as percentage of fine mass*, of various elements. As the proportion of crustal mass tends to rise, the proportion of other mass tends to fall. Therefore, crustal elements have positive correlations with each other and negative correlations with non-crustals. Results of this kind of correlation analysis differs from that where actual concentrations are used. Because the stability of the atmosphere plays a large role in the concentrations of pollutants, concentrations tend to rise and fall in unison, and virtually every pollutant concentration will have significant positive correlation with every other.

RELATIONSHIPS BETWEEN METEOROLOGY AND ELEMENTS

Air concentrations depend heavily on both meteorological factors and emissions, and the measurement at a fixed monitoring site is dependent on atmospheric mixing, ventilation, and wind direction relative to sources. The Phoenix site has its own hourly meteorological measurements including wind speed and wind direction. A daily wind vector was formed as the vector average of the hourly wind vectors. Recognizing that direction can be highly variable on a daily basis, an approximate flow direction was formed by assigning the daily vector wind direction to one of four 90 degree sectors centered on the compass points (1=N, 2=E, 3=S, 4=W). The daily wind speed was formed as an average of the hourly scalar wind speed (SWS). Figure 4 shows the daily wind direction sector and scalar wind speed for the

study period. By comparing to Figure 1, we note that the higher mass and carbon concentrations are linked to the period of low winds from the easterly direction. Under this scenario, we would expect diminished wind-blown dust and increased automotive emissions from I-17 and the downtown reaching the site. For much of the spring and summer the wind tends to be from the west and at higher speed, increasing wind-blown dust. During the warmer months, enhanced vertical mixing tends to bring elevated plumes (e.g. sulfur) to the surface.

Figure 5 gives time series of the elements lead, sulfur, and silicon, *all as a percentage of the fine mass*. These three elements likely are from disparate sources--automotive, smelter or power plant, and crustal dust--respectively. Reflecting both wind direction and speed, S and Si show higher summer components, while the Pb component rises in the winter when wind speeds are low and the local automotive sources are dominant. The pattern for Pb follows closely-associated carbon.

CONCLUSIONS

The first year of data collection has been a success. The data base holds entries from carbon analysis and X-ray fluorescence for, respectively, about 91 and 84 percent of the fine filter samples taken by the DFPSS. There were few gross outliers in any of the data.

Comparison of the concentrations of carbon and other elements between the DFPSS and VAPS indicated biases that could be explained by an expected, less-sharp fine particle cut of the cyclones used in the DFPSS. Only about 1/3 of the reported elements are found consistently above the 3σ error of the X-ray fluorescence determination.

With only one year of data, generalizations are unwise, but there appears to be a seasonal effect on particulate concentration and composition, with fine fraction mass and carbon reaching high levels in the winter when stagnate air flows result in trapping of automotive exhaust. The data set reveals some pronounced differences from eastern cities where PM/mortality associations have been demonstrated: the CM/FM ratio is high, there is a relatively high correlation between CM and FM, and the fine mass tends to peak in winter. Organic carbon and fine mass are strongly correlated, indicating that it may be difficult to ascertain their relative importance as explanatory variables in mortality studies.

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Table 1. Comparisons of carbon and fine masses between VAPS and DFPSS where FM=fine mass, EC=elemental carbon, OC=organic carbon.

	Comparison Ratio	Mean	S.D.	of N
		Mean		
1	VAPS FM/DFPSS FM	0.825	0.014	91
2	VAPS OC/DFPSS OC	0.927	0.013	91
3	VAPS EC/DFPSS EC	0.935	0.021	86
4	VAPS EC/VAPS FM	0.112	0.004	91
5	DFPSS EC/DFPSS FM	0.101	0.002	259
6	VAPS OC/VAPS FM	0.432	0.008	90
7	DFPSS OC/DFPSS FM	0.380	0.005	259

Table 2. Correlation matrix for fine mass, organic carbon, elemental carbon, and TEOM coarse mass.

	FM	OC	EC	CM
FM	1	0.94	0.86	0.68
OC		1	0.89	0.52
EC			1	0.51
CM				1

Table 3. Reported elemental values. Reported values are those in the data base that exceeded three times the calculated error for the element. Elements in bold type have a mean concentration exceeding 0.5% of the fine mass.

Number Reported	Elements	Average % of fine mass
N>220	S, Si, Fe, Ca, Al, K, Zn, Pb, Mn, Cu, Br	14.88
100<N<200	Na, Mg, Cl, P, Ti, Sr	1.45
N<100	all 27 other elements	0.10

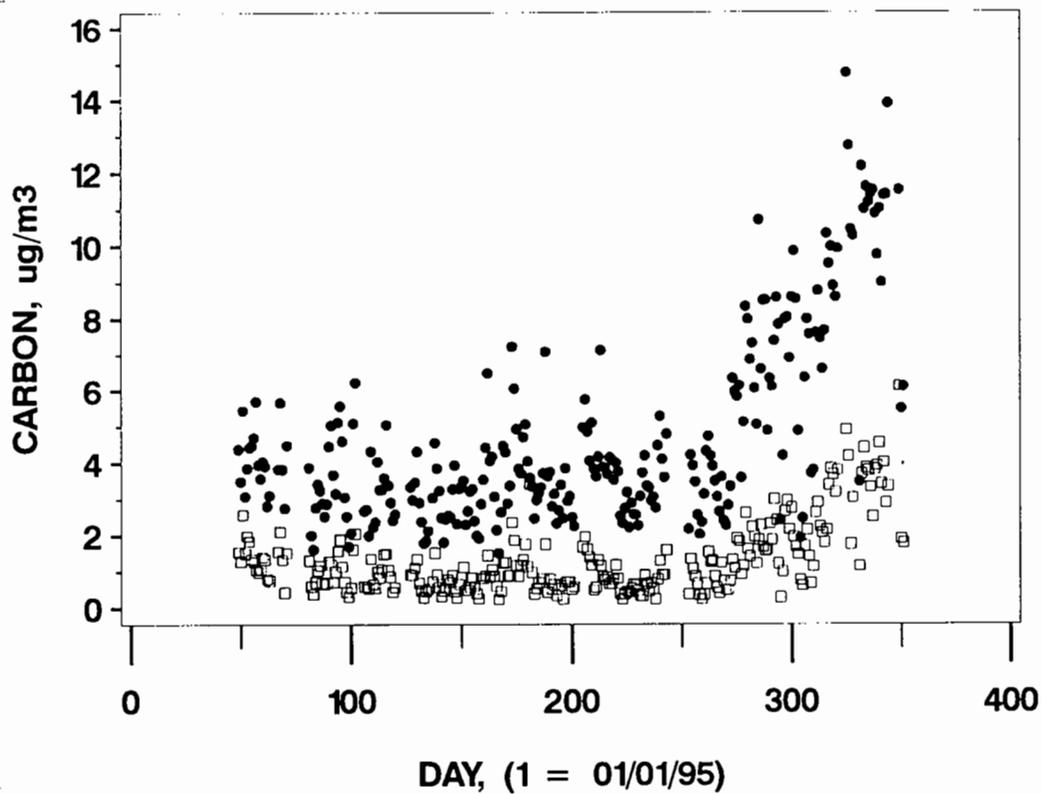


Figure 1. Time series of organic (●) and elemental (□) carbon concentrations ($\mu\text{g}/\text{m}^3$).

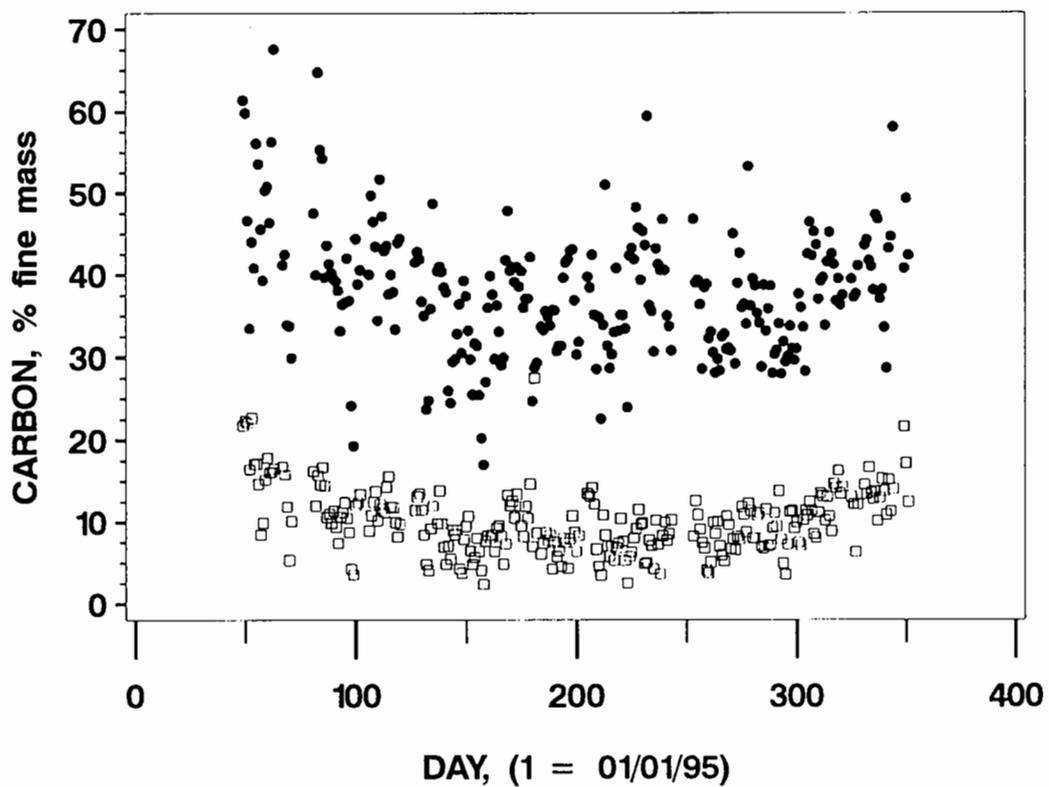


Figure 2. Time series of organic (●) and elemental (□) carbon concentrations as a percentage of the fine mass.

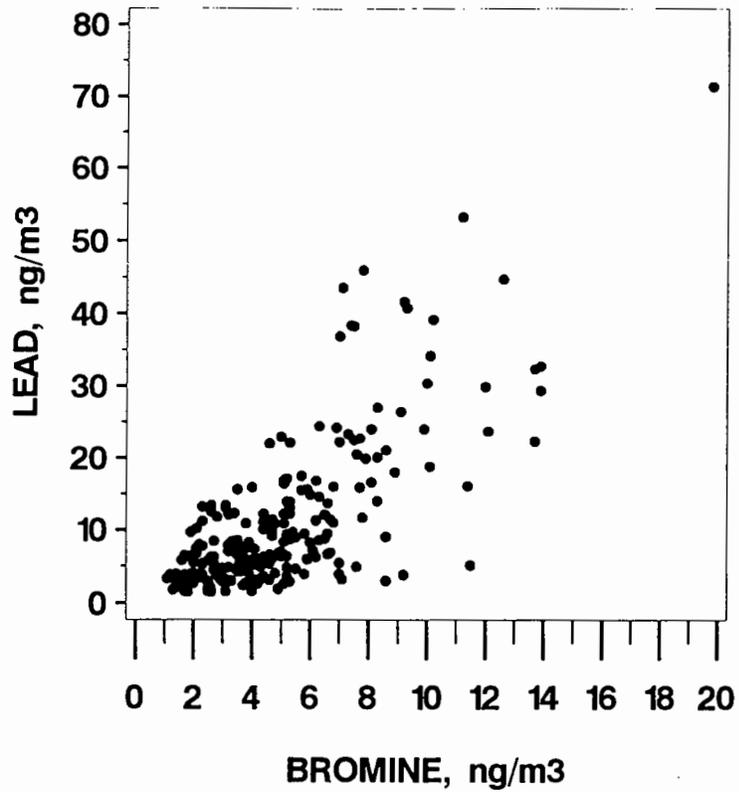


Figure 3. Lead versus bromine concentrations (ng/m³) measured by X-ray fluorescence.

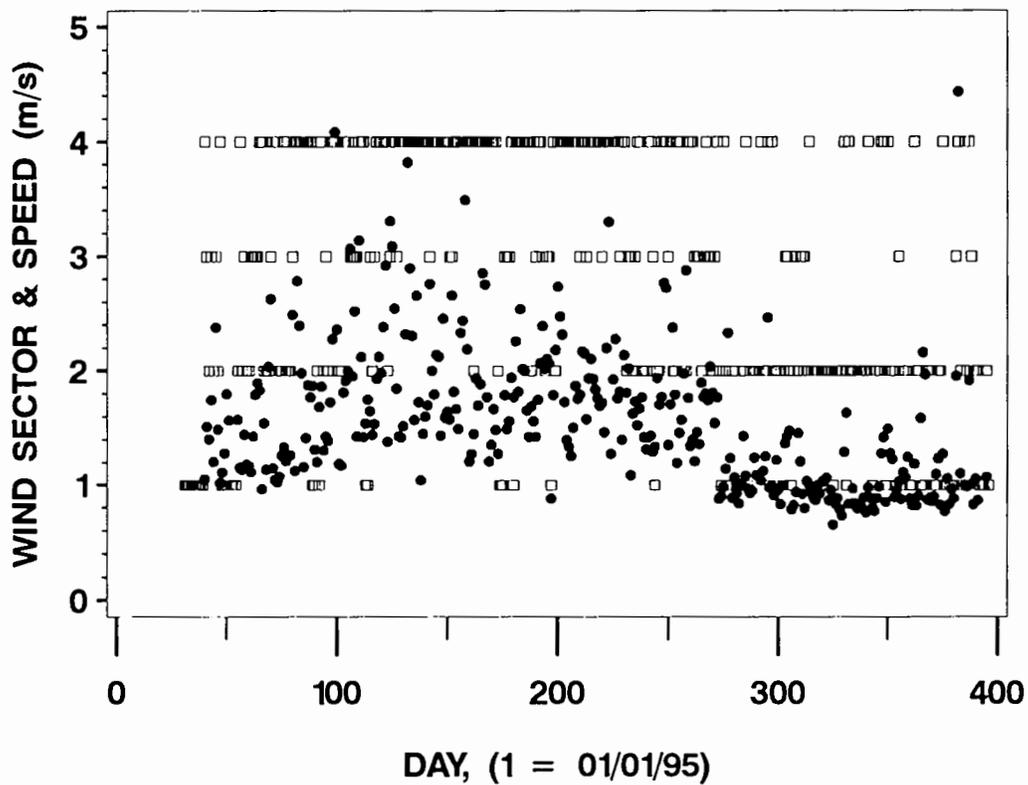


Figure 4. Time series of daily wind speed (●) and 90 degree wind direction sector (□), where 1=N, 2=E, 3=S and 4=W is the direction from which the wind blows.

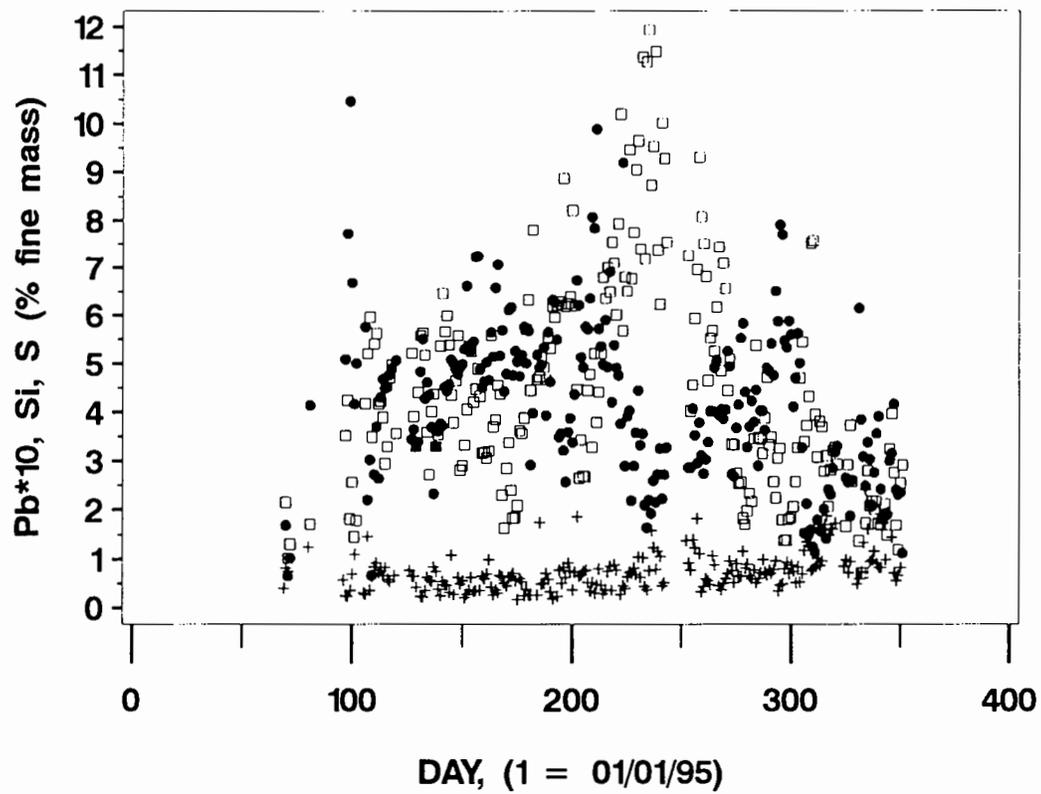


Figure 5. Time series of the concentrations of silicon (●), sulfur (□), and lead x 10 (+) expressed as a percentage of the fine mass concentration.

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