DUSTFALL RATES AND TRACE METAL CONCENTRATIONS FOR THE HAMILTON, ONTARIO REGION

By

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ABSTRACT

The main objective of this research was to examine the effects of dry deposition or dustfall. The dustfall was collected in buckets lined with polyetholene and set out at four locations around the Hamilton Ontario region. The total dustfall collected decreased rapidly away from the industrial area. The dustfall was fractionated up into three approximate particle sizes, sand, silt and clay. The largest amount collected for each site was in the silt size, the sand was the second largest amount collected the clay was the lowest.

Trace metal concentrations were then determined for the dust using 12 metals, Al, Ba, Br, Ca, Cl, Co, Cu, I, Mn, Na, Ti, and V. Metal concentrations for Al, Ca and Mn where large and increaed towards the industrial area. Cu was another metal indicative of the industrial area. Within the industrial area, it became the most important of the small scale metals. As the distance away from the industrial area increased, the concentration of Cu dropped below detection.

Generally the greatest concentrations were found in the silt size material and the lowest was the clay size.

ACKNOWLEDGEMENTS

I wish to express my thanks to my advisor Dr. John Drake who provided me with the opportunity to collect the data for my thesis and the use his facilities for the analysis. I would like to thank Dr. Drake and Kim Irvine for their constant encouragement and guidance throughout the work. I would also wish to thank Annita Simson and Stephen Vermette for their help during the trace metal analysis using the Neutron Activation Analysis. For the opportunity to collect the dustfall in the industrial area, I would like to thank Mr. Al Kosten who permitted the gauges to be placed at the Petro Cananda bulk plant.

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CHAPTER ONE

1.1 Introduction

In recent years there has been a greater public awareness of atmospheric pollution in terms of both wet and dry deposition. However much of the publicity has been in terms of wet deposition such as acid or toxic rain, with very little dealing with the problems of dry deposition or dustfall. Therefore the main objective of this research is to determine the dustfall rates and their trace metal concentrations for the Hamilton Ontario region. With Hamilton being a large industrial city housing the two largest steel manufacturing plants in Canada the effects of the dustfall may be more pronounced than in other areas.

1.2 BACKGROUND INFORMATION

Dustfall is the removal of material from the atmosphere to a position 1mm above the surface (Cryer, 1986). For particles of sand, silt and clay size fractions, the movement through the atmosphere takes the form of saltation and suspension. Saltation is the movement of particles in a trajectory from one site to another. This occurs when the turbulent vertical components of wind have no significant effect on the trajectory of the particle (Tsoar and Pye, 1987). Suspension is the movement of particles for an infinite distance before being settled. For particles in suspension, deposition occurs through the processes of sedimentation and turbulent diffusion (Cryer, 1986). Sedimentation of the particles is affected by the particles settling velocity. The settling velocity for still air can be approximated by Stokes' Law (Green and Lane, 1964) to be:

$$U_f = KD^2 \qquad (1)$$

where : U_f is the settling velocity (cm s^{-1})

D is the grain diameter (cm)

$K = \rho_s g / 18 u$

where : ρ_s is grain density

g is the acceleration due to gravity

u is the dynamic viscosity of the air

Turbulent diffusion is the turbulent transfer of particles to the surface and is greatly influenced by the nature or roughness of the surface. The turbulence of the flow can be approximated by the momentum transfer from layer to layer due to fluctuations in velocity (Tsoar and Pye, 1987). The friction velocity (u_*) of the turbulent flow in the boundary layer is (Owen, 1960):

$$u_* = (v + \varepsilon) d\bar{U}/dz \qquad (2)$$

where : v is the kinematic velocity

ε is the turbulent exchage

$d\bar{U}/dz$ is the rate of shearing stress

The ratio of U_f/u_* can be used to determine the degree of suspension for the particles. That is the ratio of settling velocity to the friction velocity. The lower the ratio the greater the level of suspension. For example from Gillette (1977), a ratio less than 0.1 for particles less than 20 um have been known to remain in suspension for days, months or ever years. Particles greater than 20 um would remain in suspension for only a limited time and would therfore be considered a short-range contaminant (Junge, 1963). The larger particles would have higher U_f/u_* ratios and would be influenced by gravity. The nature of the surface mainly would have little effect on

the deposition of the particles. For particles less than 1 um the effects of gravity decrease sharply (Junge, 1963) and would therefore be an important component of long-range transport. These particles are unlikely to penetrate the boundary layer (Chamberlain, 1975) and therefore would not contribute much to the total amount to dustfall.

Dustfall over an area is highly dependent on characteristics of the surface, whether flat or rough, smooth or sticky. It has been found that a forest can remove as much as ten times the dustfall from the atmosphere that would fallout over a smooth water surface (Cryer, 1986). For this reason, the nature of the gauge used to collect the dustfall would be important. The collectors used have varied from open buckets to flat plates (Dasch and Cadle, 1985., Ibrahim et al.,1983). The dustfall in buckets or on plates may be deposited similar to that on natural surfaces, but there is a problem with blow-off. Wind may entrain the dust from the gauges where it may not entrain as much dust from the natural surfaces. Therefore the actual dustfall collected may be an under estimate of the actual deposition on the natural surface. For this study the gauges for collection will be buckets lined with polyetholene (Dasch and Cadle, 1985).

The effects of dustfall on an area has been mainly discussed in terms of how it has contributed to the overall problem of pollutant loading. The effects of dry dustfall is now generally accepted to be a significant contributor to urban pollution (Jeffries and Snyder, 1981). In dealing with the problem of modelling pollution, such as urban stormwater pollution, it is important to try to predict the input of particulate matter. To predict the rates of dustfall, it is

necessary to determine the relationships of the physical processes of depostion (Slinn, 1977). For this purpose, Slinn (1977) examined the processes of dry dustfall and has developed relationships to predict the deposition of particulate matter through dustfall and also scavenging during rain events. The study of urban stormwater pollution has lead to the inclusion of dustfall as a significant component (Boregowda, 1984; James and Boregowda, 1985). In these studies they were able to model the processes of the deposition of dustfall on impervious land surfaces and that there are similar processes for the deposition on pervious surfaces. The dustfall on the impervious and pervious land surfaces flow into the sewer systems during a rain event and they determined that this was an important component to stormwater pollution.

Dustfall rates for the Hamilton area were determined by Boregowda (1984) throuth both theoretical and observed methods. Boregowda (1984) produced a number of models in which he compared the observed and predicted values of dustfall. The model used in the rest of his analysis was a model which was sensitive to meteorological data (i.e. wind speed and direction). It was found that wind speed and direction had an influence on the amount of dustfall in the area. The relative error for this model was 25%, meaning that the model explained 75% of the variation between observed and predicted values. There was also a study done in Burlington (Ng and Marsalek, 1983) which studied the effects of wet and dry deposition on the urban runoff quality. The results showed that while rainwater is a major source of nitrogen, copper and zinc, dustfall was a major source of phosphorous and lead. This shows that dustfall can be just as

important as rainfall to the pollutant loading of an urban environment.

CHAPTER TWO

2.1 Study Site

The study site is the city and surrounding area of Hamilton Ontario. The city is located at the south western end of Lake Ontario (Figure 1a) and has a population of 306 640 (1980). The city is divided into an upper and lower area by the Niagara Escarpment causing an average difference in elevation of 102 m (Boregowda, 1984). The escarpment runs east-west through the city then northwards surrounding the southwestern shore of Lake Ontario. There are a number of valleys cut into the escarpment. The Dundas Valley is the most important valley located at the southwest of the city. The lower section of the city is divided up into three major areas. The main industrial area, the central business district and the remaining area is residential. The industrial core is found along the southern shore of Hamilton Harbour in the Burlington Bay. The central business district is located in the core of the city south of the industrial area.

The prevailing wind for this area is dominately from the west to southwest. For the most part this helps to direct the airborne pollutants from the city towards Lake Ontario. Therefore the northeast and east winds are the winds that will direct the pollutants over the city, rather than away from the city. The meteorological data to be needed for data analysis will be collected on the roof of the John Hodgins Engineering building on the campus of McMaster University and will also be available from the Hamilton Airport weather office. The presence of Lake Ontario to the north and northeast of the city may cause an effect due to lake breezes. During

FIGURE 1a: Study Site.

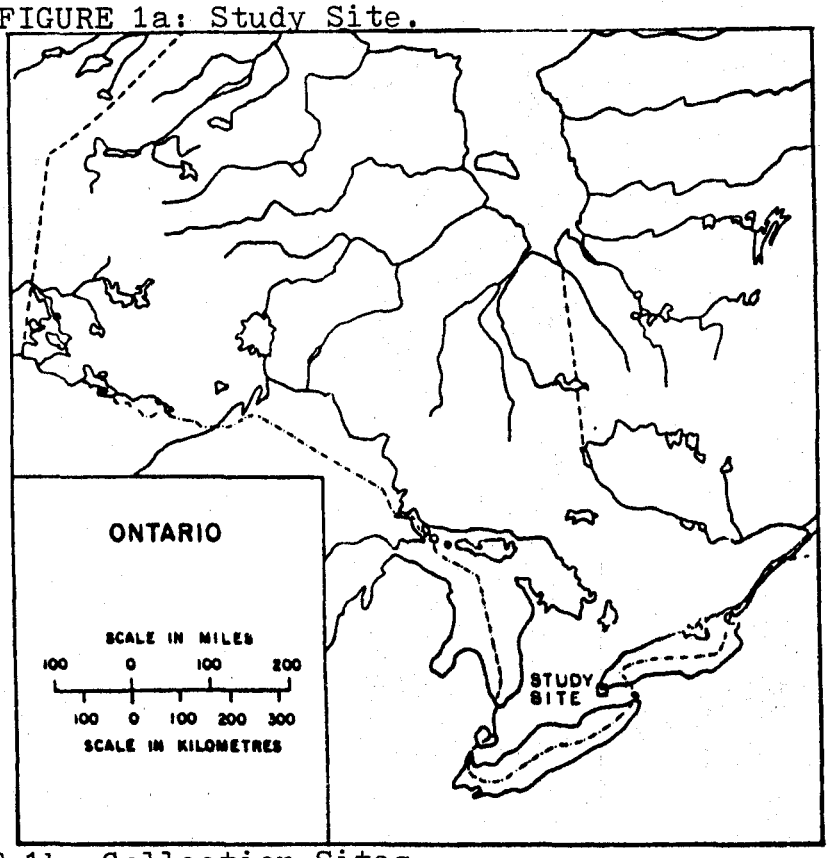
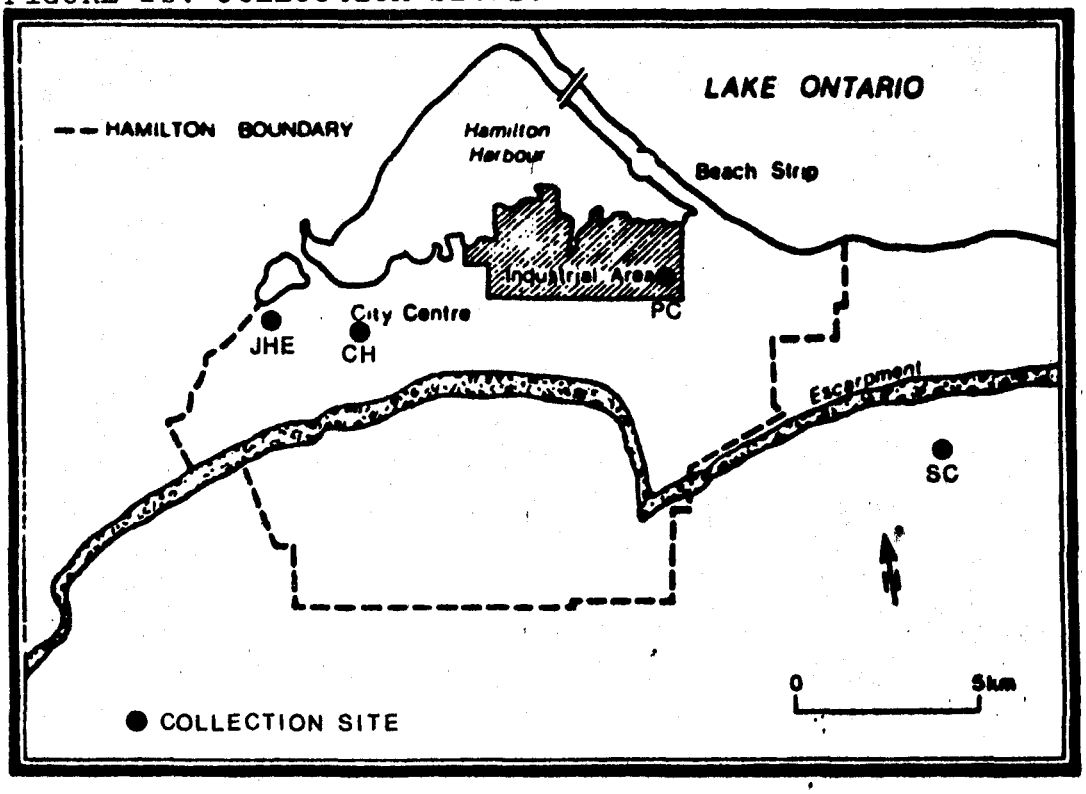


FIGURE 1b: Collection Sites.



the summer there can be a large temperature differential between the city and the lake. The result of this has resulted in a higher frequency of northeast and easterly winds from March to September (Boregowda and James, 1982). The frequency was also found to be higher during the day compared to night (Farharg, 1982) for the lower part of the city. Another meteorologic feature of the area is the tendency for atmospheric inversions (Rouse et al., 1972). The inversions tend to put an atmospheric cap or ceiling on the height the industrial output can diffuse, thus keeping the output closer to the surface inducing an increase in the dustfall rates.

2.2 Methodology

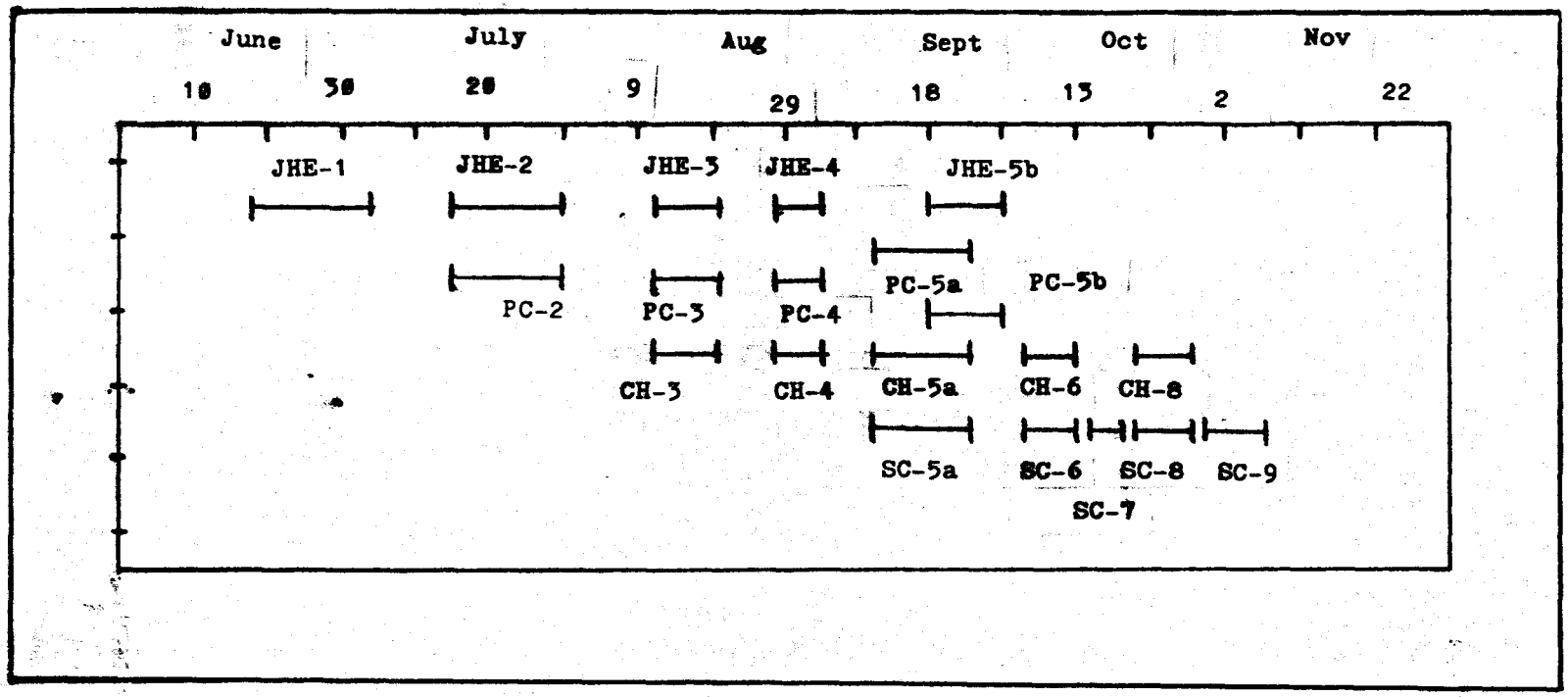
2.2.1 Sample Collection

The dustfall was collected at four sites throughout the city (Figure 1b) representing four major areas of the region. One site will be on the roof of the John Hodgins Engineering (JHE) building on the campus of McMaster University. This will represent the western fringe of the city in a mainly residential area. The second site will be on the roof of the City Hall (CH) building in the core of the city in the central business district. A third site will be in the industrial core of the city on the top of a storage tank at a Petro Canada (PC) bulk plant. The fourth site will be in a rural area in Stoney Creek (SC) approximately 4.5 km southeast of the city above the escarpment. This site will be used to help determine, if possible the average background level of dustfall received by the city by long-range transport. The dustfall was collected in gauges made of buckets lined with polyetholene (Dasch and Cadle,1985). The buckets were set out at the four sites around the city.

The buckets were set out and exposed to the atmosphere for a total of five dry days, or a total of 120 hours. The term 'dry' or 'dry period' will be defined as the time period when there is no measurable precipitation. In the case of the occurrence of dew overnight, no attempt was made to separate this from the dry dustfall. However during times when there was fog the gauges were be covered, as they were when there was a rain event. Therefore the collection of dustfall over 120 hours is of 120 hours of dry weather. Since only one site was accessible at all times and the other three sites were only accessible during business hours, the gauges could not be open in times of threatening weather. When there was a substantial chance of rain overnight or on weekends the gauges had to be closed. Otherwise they might get contaminated from rainfall due to the inaccessibility of the gauges. Therefore the time period when the gauges were set out and brought in to the lab may be longer than 120 hours or five days.

The collection of the dustfall was completed over a period of 6 months, June to November 1986. The difficulties involved in having some sites accessible only during business hours as mentioned above and having the sites covering such a large area, not all the sites could be monitored at the same time periods. The collection of five samples from each site was completed in nine separate time periods over the six months (Table 1). For the first event at each site, the gauges were analyzed separately. For the JHE site, there were six gauges set out over a large area of the roof. This was to test the spatial variability of the dustfall. For the other three sites, two gauges were used to analyze variability. Before the dustfall could be

Table 1 : Time Periods of Collection.



analyzed, it had to be standardized to a standard time period of collection. Since it was difficult to collect the dustfall for the ideal 120 hours, a correction must be made. For all samples collected from the gauges, the dustfall values were standardized to a standard of 120 hours before the dustfall rates were calculated.

2.2.2 Lab Analysis

After the 120 hours of collection, the buckets were covered and brought into the lab for filtering. The dust was rinsed off the polyetholene with distilled deionized water into a clean acid washed plastic beaker. This solution was then filtered through a 'Millipore' type filtering system to extract the dust from the water. To determine the particle size distribution, the pore sizes used were 62 um (the division between sand and silt), 5 um (the approximate division between silt and clay) and .45 um (the division between clay and dissolved solids). The dust left on the filters will represent the amount of dustfall deposited over the time of collection.

The dustfall values were then converted from grams of dust per gauge over five days ($g\ gauge^{-1}\ 5\ days^{-1}$) to dustfall rates of milligrams per metre squared per day ($mg\ m^{-2}\ day^{-1}$). After the dustfall rates were determined the dustfall and filters were analyzed for trace metals.

The process used for the analysis is known as Instrumental Neutron Activation Analysis (INAA) available at the Nuclear Research Building on the campus of McMaster University. The determination of trace metal concentrations from filters through Instrumental Neutron Activation Analysis (INAA) was found to be successful by Hamilton and Chatt (1982). For the analysis, the filters must be placed in a

carrier to be sent to the reactor. The carrier is placed in a pneumatic tube where it is transported to the core for irradiation. The sample is then returned through the pneumatic tube where it is removed from the carrier and placed in front of a detector which counts the gamma-rays emitted from the sample. The values recorded for each metal species must then be entered into a computer program which converts the counts into concentrations. A more detailed examination of the process of INAA and its applications have been summarized by Salmon and Cawse (1983) and by Hamilton and Chatt (1982).

To reduce the effect of the polyetholene and filtering on the trace metal analysis, blank filters were run through the INAA process. The process of removing the dust from the gauges was performed with the polyetholene lined gauges before they were set out. The blank filters were then analyzed for trace metal concentrations. The concentrations would then represent the contaminants picked up from the filters, polyetholene and the lab during the filtering process. Therefore the concentrations from the dustfall must first be corrected for the contaminants from the sample collection and analysis.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Dustfall Rates

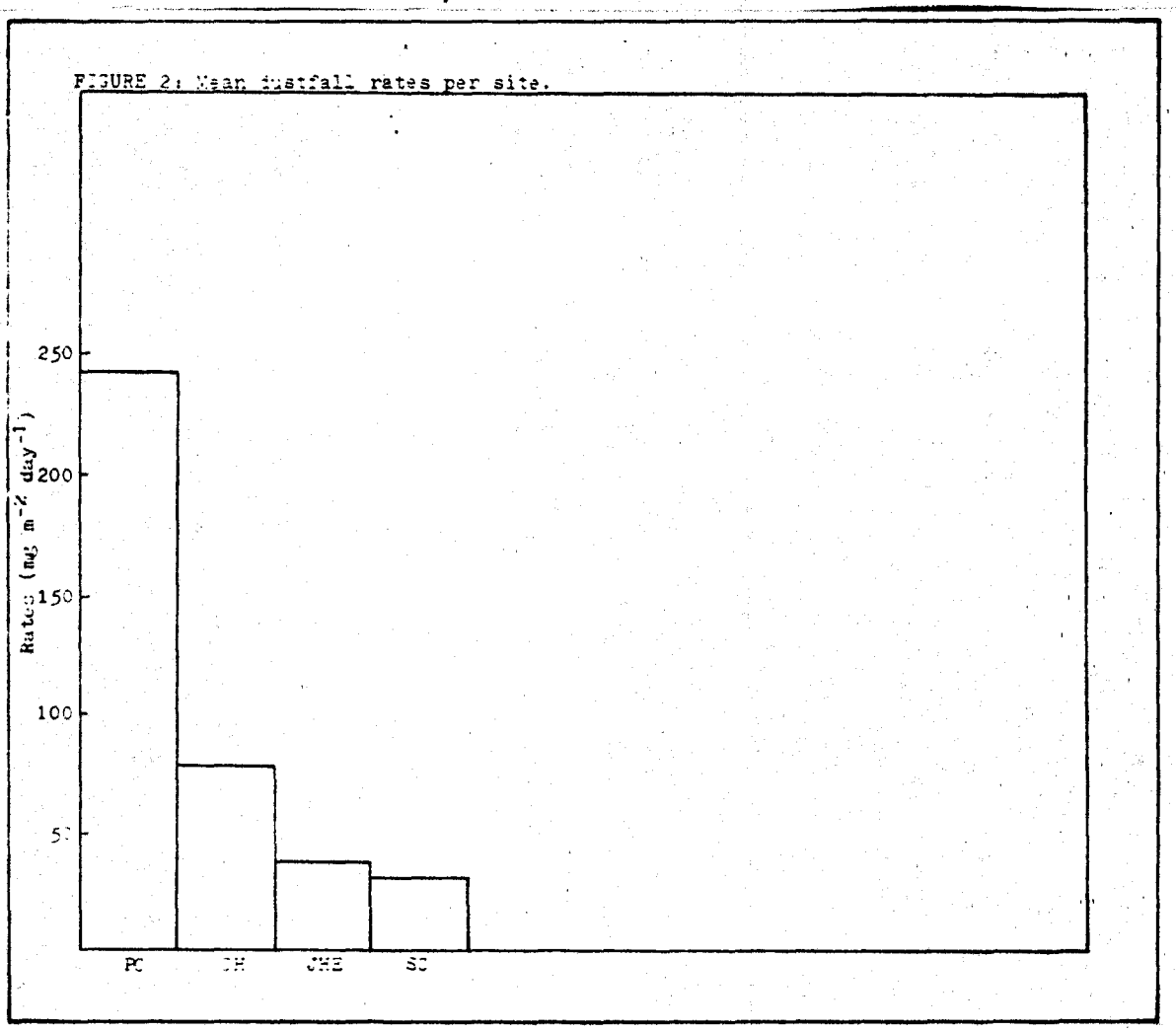
The dustfall rates for each site are in table 2. The rates determined from each event were compared for a temperal variation and tested statistically by the use of a simple linear regression test. The tests were performed on a statistical package known as Minitab. The test outputs and statistical inferences are shown in Appendix A, sections A1.1 - A1.4. The linear regressions were performed in order to examine the slope of the regression line. The slope represents the temperal variation of a site. If the slope is not significantly different from zero, then there is no significant variation with time. The results illustrate that there is no significant temperal variation for the CH and SC sites. However there is a significant temperal variation for JHE and PC. The dustfall rates decrease with time for the JHE and PC sites.

The dustfall rates from each site were compared for spatial variation in the city. For this the rates were entered into Minitab and an analysis of variance was performed. The results (Appendix A, section A2.1 - A2.3) show that the mean dustfall rates for each for each site are significantly different as shown in Figure 2. In performing the one way analysis of variance, all the rates were used in the test. The rates represent all different time periods over the summer and fall. The results of the analysis show that the greatest amount of dustfall falls in the industrial area at the PC site. The mean dustfall rate was 241.7 mg m^{-2} day^{-1}. The analysis was repeated for the remaining three sites to see if the PC site was a large

TABLE 2: Dustfall rates.

EVENT	RATE ($mg\ m^{-2}\ day^{-1}$)
JHE-1 #1	40.8
JHE-1 #2	34.5
JHE-1 #3	40.8
JHE-1 #4	43.9
JHE-1 #5	37.6
JHE-1 #6	40.8
JHE-2	37.6
JHE-3	32.9
JHE-4	34.5
JHE-5b	34.5
CH-3 #1	81.5
CH-3 #2	75.2
CH-4	78.4
CH-5a	83.1
CH-6	73.7
CH-8	75.2
PC-2 #1	250.8
PC-2 #2	247.7
PC-3	246.1
PC-4	241.4
PC-5a	230.4
PC-5b	233.6
SC-5a #1	28.2
SC-5a #2	31.4
SC-6	31.4
SC-7	28.2
SC-8	32.9
SC-9	31.4

FIGURE 2: Mean dustfall rates per site.



influence on the previous test. The result showed that there is still a significant difference between JHE, CH and SC. The next largest rate is 77.9 mg m^{-2} day^{-1} at the CH site. The rate dropped by two thirds from PC to CH. The analysis was again repeated for JHE and SC for a significant difference. The result was again a significant difference between JHE and SC. The drop is over one half to the third largest rate of 37.8 mg m^{-2} day^{-1} at JHE. The last site at SC had a rate of 30.6 mg m^{-2} day^{-1}. This is a much smaller drop in the rate indicating that the city effects are only beginning to be felt at JHE compared to SC.

The possible causes for the variation in the dustfall rates can be attributed to two main factors, geographical location and the effects of weather. The variation observed from site to site can be attributed to many factors one of which is geographical location (Figure 1b). As noted from the analysis of variance test the rates for each site are significantly different. Figure 2 illustrates that the dustfall rates increase towards the industrial core. Both SC and JHE are similar and are the lowest rates. SC is outside the city to the southeast and is the farthest from the industrial area. JHE is the next farthest site away from the industrial area and is to the southwest. The mean rates at the two sites are low indicating that they may not be affected much by the industrial area, however JHE is beginning to become affected. The CH site had the second highest dustfall rate and is also the second closest site to the industrial area. This site is close enough to the industrial area to be affected by the industrial output. The PC site was inside the industrial area

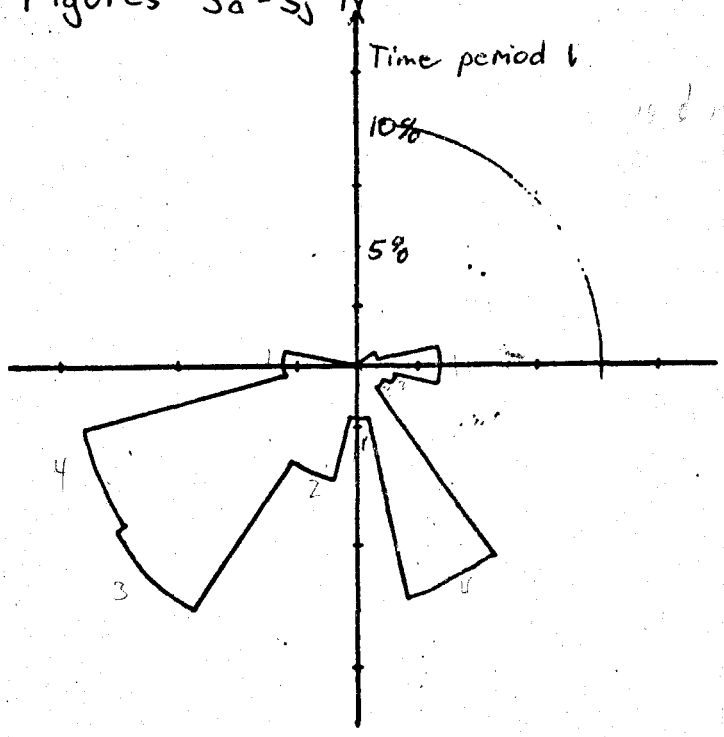
and by far had the largest dustfall rate. From this it can be seen that much of the particulate matter from the industrial output falls within the industrial area itself and out over a small surrounding area. The PC site is within the industrial area while CH appears to be within the small surrounding area. The site at JHE appears to be just on the fringe of the surrounding area and is not greatly affected be the industrial output. The SC site is well outside the surrounding area does not appear to be affected by the industries.

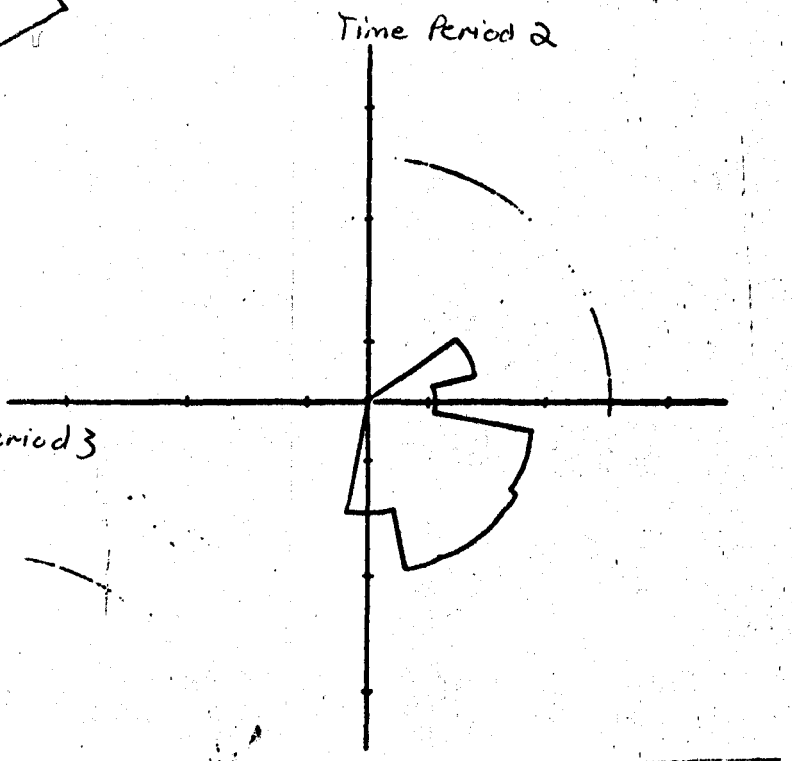
The wind direction and wind speed data collected at the JHE site. There is a reservation with using the data collected at one site and extrapolating it to the other sites. The data was collected within the urban layer and may not be representative of the wind throughout the city. The wind direction and wind speed was plotted on rose diagrams for each of the nine time periods (Figures 3a-3j). The diagrams display three main components to wind direction. The patterns are similar with the wind coming out of the WSW, SSE and ENE. The wind velocities were relatively low predominantly being less than 3 m s^{-1}. The combination of the similar pattern for wind direction, low wind velocity, the complicated urban surface and the low variance in the dustfall rates illustrates the wind had little effect on the dustfall while the gauges were open.

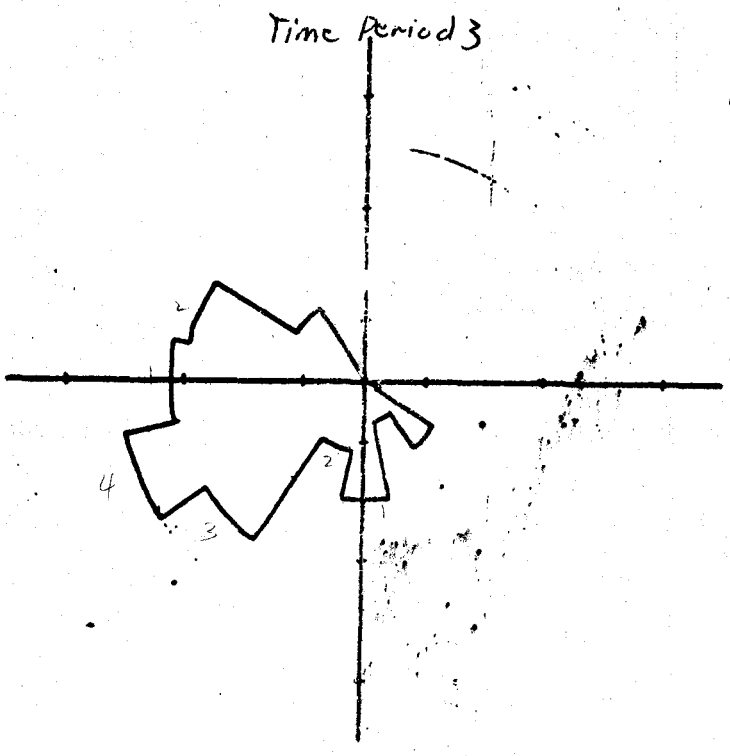
3.1.1 Fractionated Rates

The dustfall collected in the gauges was also analyzed for particle size distribution. Except for the first event for each site, the dust from the two gauges for each event were combined and fractionated. The dustfall rates were calculated for each of the sand, silt and clay size fractions. The individual rates for the particle

Figures 3a-3j







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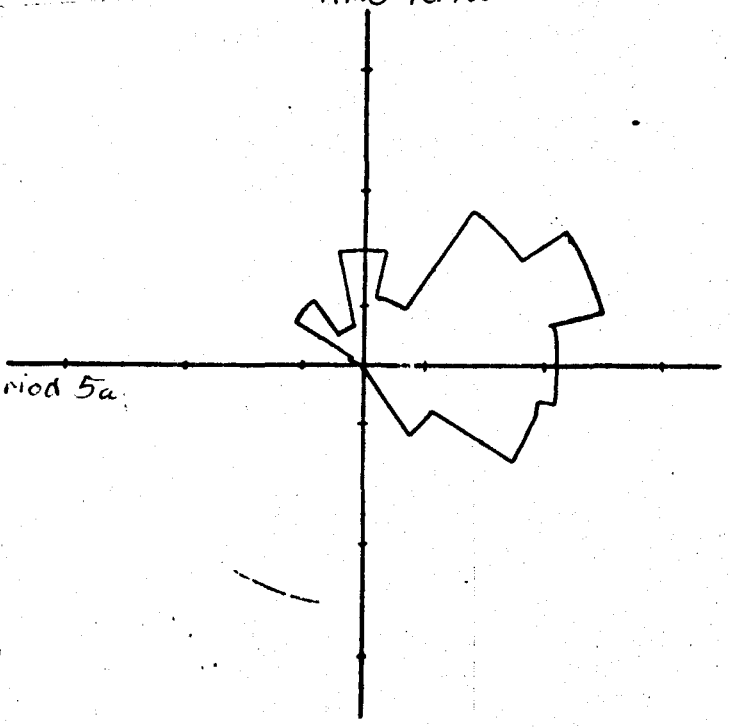
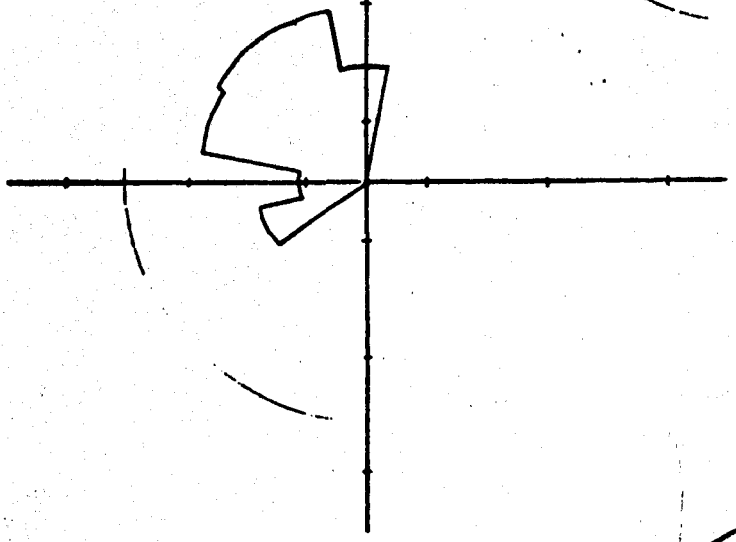
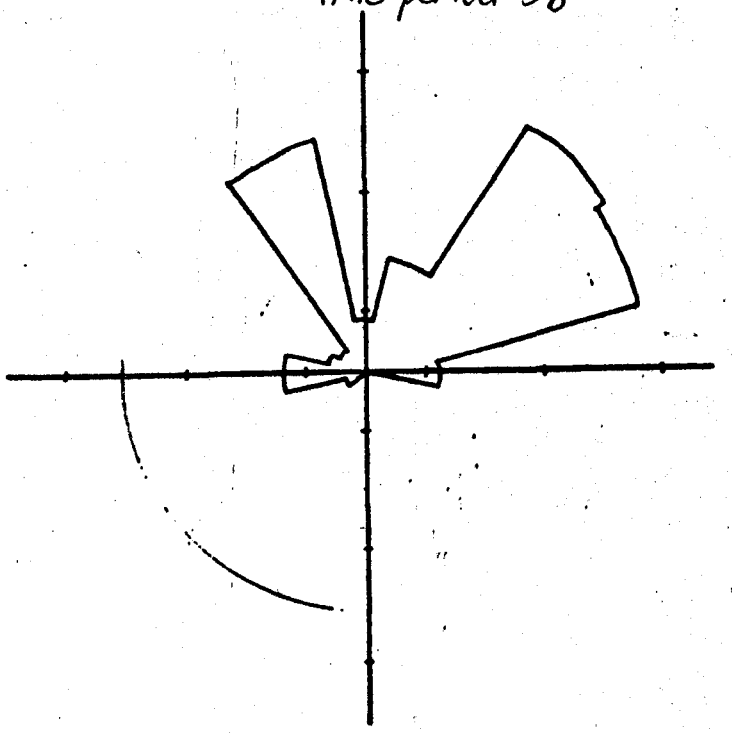


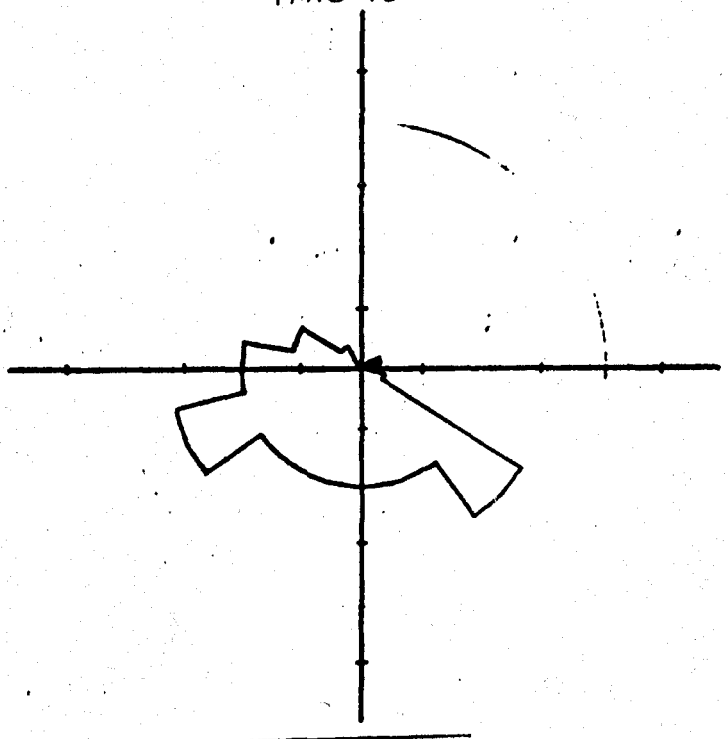
Time Period 5a



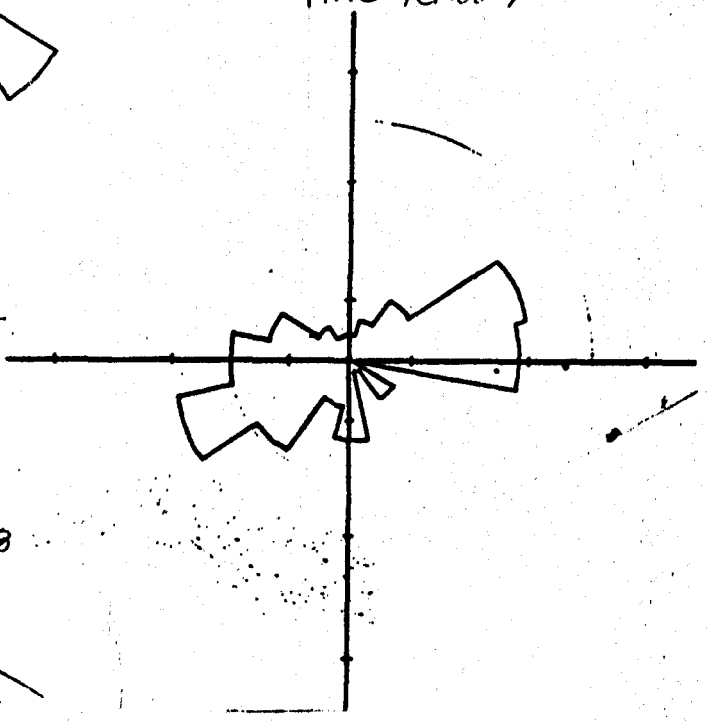
Time period 5b



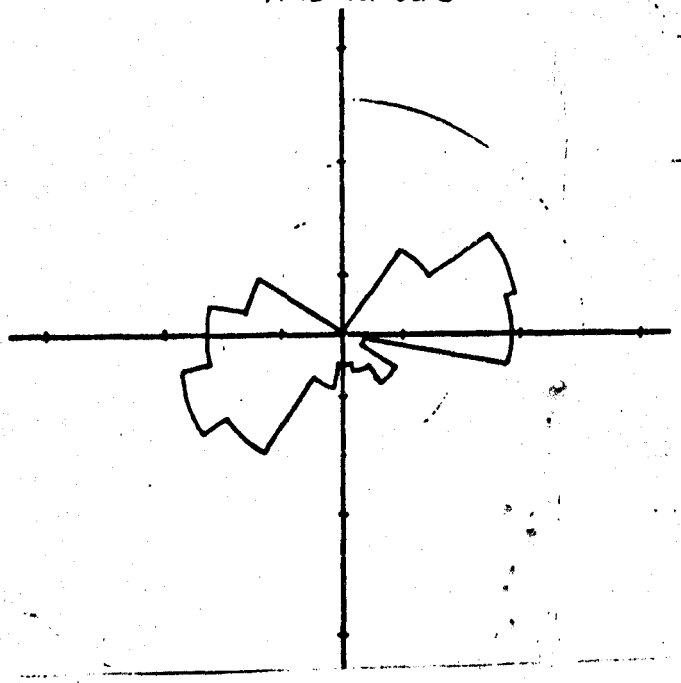
Time Period 6



Time Period 7



Time Period 8



sizes for each event are in table 3 and illustrated in Figures 4a-4d.

The rates for all the samples show some consistent similarities. In all cases except for SC-9, the rates are greatest in the silt fraction (5 um filter) and the lowest for the clay fraction (.45 um filter). The only exception to this rule is the SC-9 event where the sand and silt fraction (62 um and 5 um filters) both have the greatest dustfall rates but the rate for the clay fraction still has the least.

Within each site, the four events fractionated also show some trends. For each site, the rates for each fraction were similar. Figure 4a illustrates the rates for JHE which were similar through the four events with mean rates of 12.9, 16.5 and 5.5 mg m^{-2} day^{-1} for the 62 um, 5 um and .45 um filters. The mean rates for CH (Figure 4b) were 21.1, 45.9 and 10.6 mg m^{-2} day^{-1} for the 62 um, 5 um and .45 um filters with little variation. The PC and SC sites also showed the same trend with the mean rates 64.5, 163.8 and 9.8 mg m^{-2} day^{-1} for PC (Figure 4c) and 12.5, 15.3 and 4.0 mg m^{-2} day^{-1} for SC (Figure 4d).

The rates for each fraction are different for each site. The greatest variation between sites occur in the 5 um filter, or silt size fraction. The next greatest variation occurs in the 62 um filter and the .45 um filter does not vary much from site to site. The variation between the three fractions within each site increases as the total rate increases. For example, there is a greater variation between the three fractions for the PC site compared to the JHE site. As the toal dustfall rate decreases (from PC, CH, JHE to SC), the variation between the fractions decrease.

TABLE 3: Fractionated dustfall rates.

EVENT	FILTER SIZE	RATE ($mg\ m^{-2}\ day^{-1}$)
JHE-2	62 um	14.1
	5 um	17.2
	.45 um	6.3
JHE-3	62 um	12.5
	5 um	15.7
	.45 um	4.7
JHE-4	62 um	11.0
	5 um	17.2
	.45 um	6.3
JHE-5b	62 um	14.1
	5 um	15.7
	.45 um	4.7
MEAN	62 um	12.9
	5 um	16.5
	.45 um	5.5
CH-4	62 um	23.5
	5 um	47.0
	.45 um	7.8
CH-5a	62 um	21.9
	5 um	48.6
	.45 um	12.5
CH-6	62 um	17.2
	5 um	43.9
	.45 um	12.5
CH-8	62 um	21.9
	5 um	43.9
	.45 um	9.4
MEAN	62 um	21.1
	5 um	45.9
	.45 um	10.6

TABLE 3: Cont.

	62 um	73.7
PC-3	5 um	166.2
	.45 um	6.3
	62 um	63.7
PC-4	5 um	172.4
	.45 um	6.3
	62 um	59.6
PC-5a	5 um	155.2
	.45 um	15.7
	62 um	61.1
PC-5b	5 um	161.5
	.45 um	11.0
	62 um	64.5
MEAN	5 um	163.8
	.45 um	9.8
	62 um	12.5
SC-6	5 um	15.7
	.45 um	3.1
	62 um	11.0
SC-7	5 um	15.7
	.45 um	1.6
	62 um	12.5
SC-8	5 um	15.7
	.45 um	4.7
	62 um	14.1
SC-9	5 um	14.1
	.45 um	3.1
	62 um	12.5
MEAN	5 um	15.3
	.45 um	4.0

FIGURE 4a: Fractionated Rates for JHE

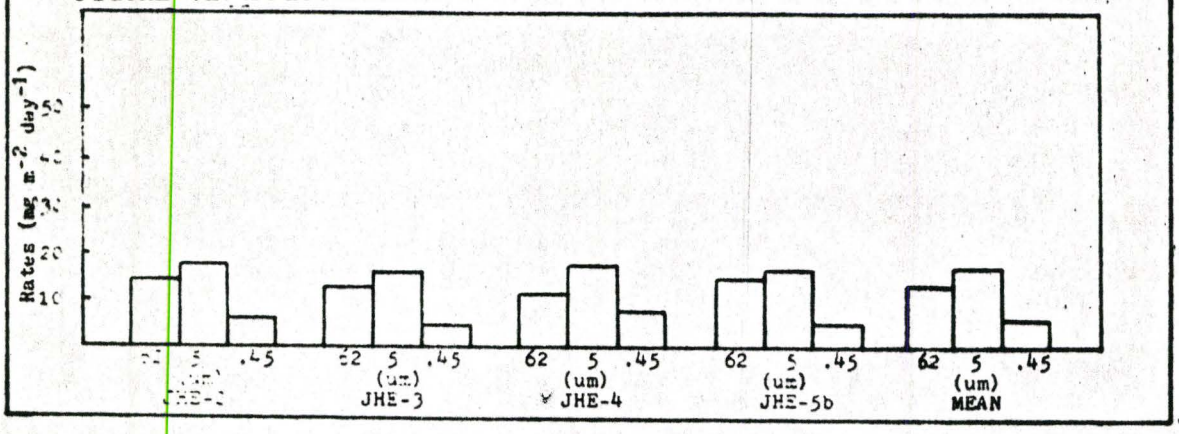


FIGURE 4b: Fractionated Rates for CH

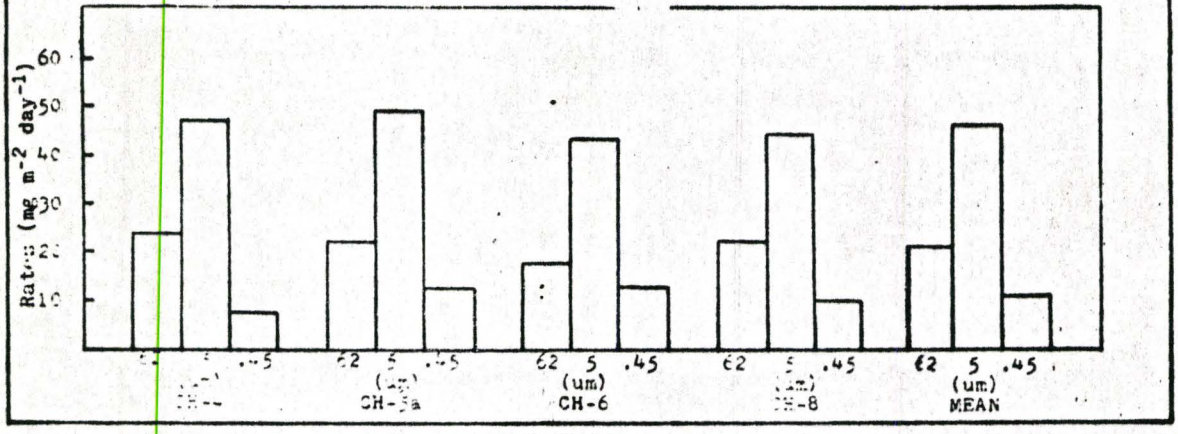


FIGURE 4d: Fractionated Rates for SC

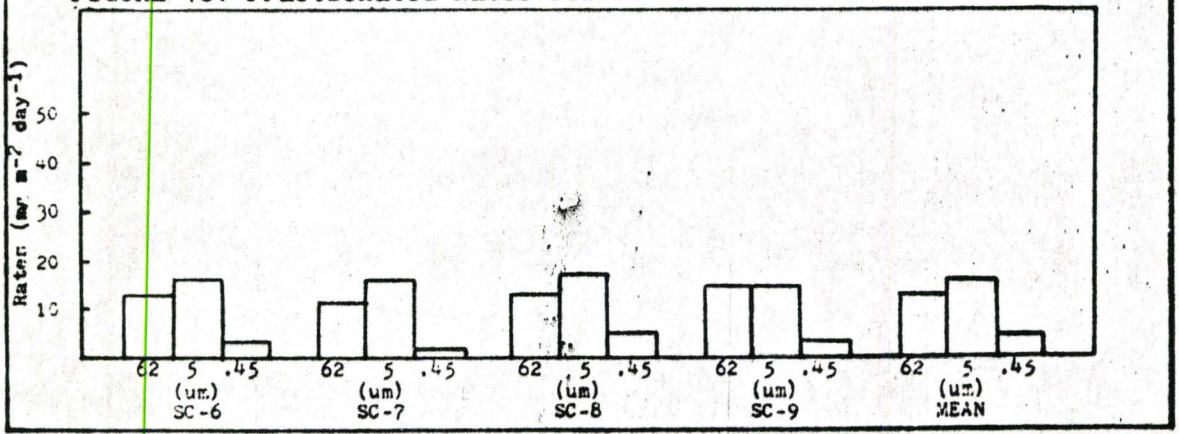
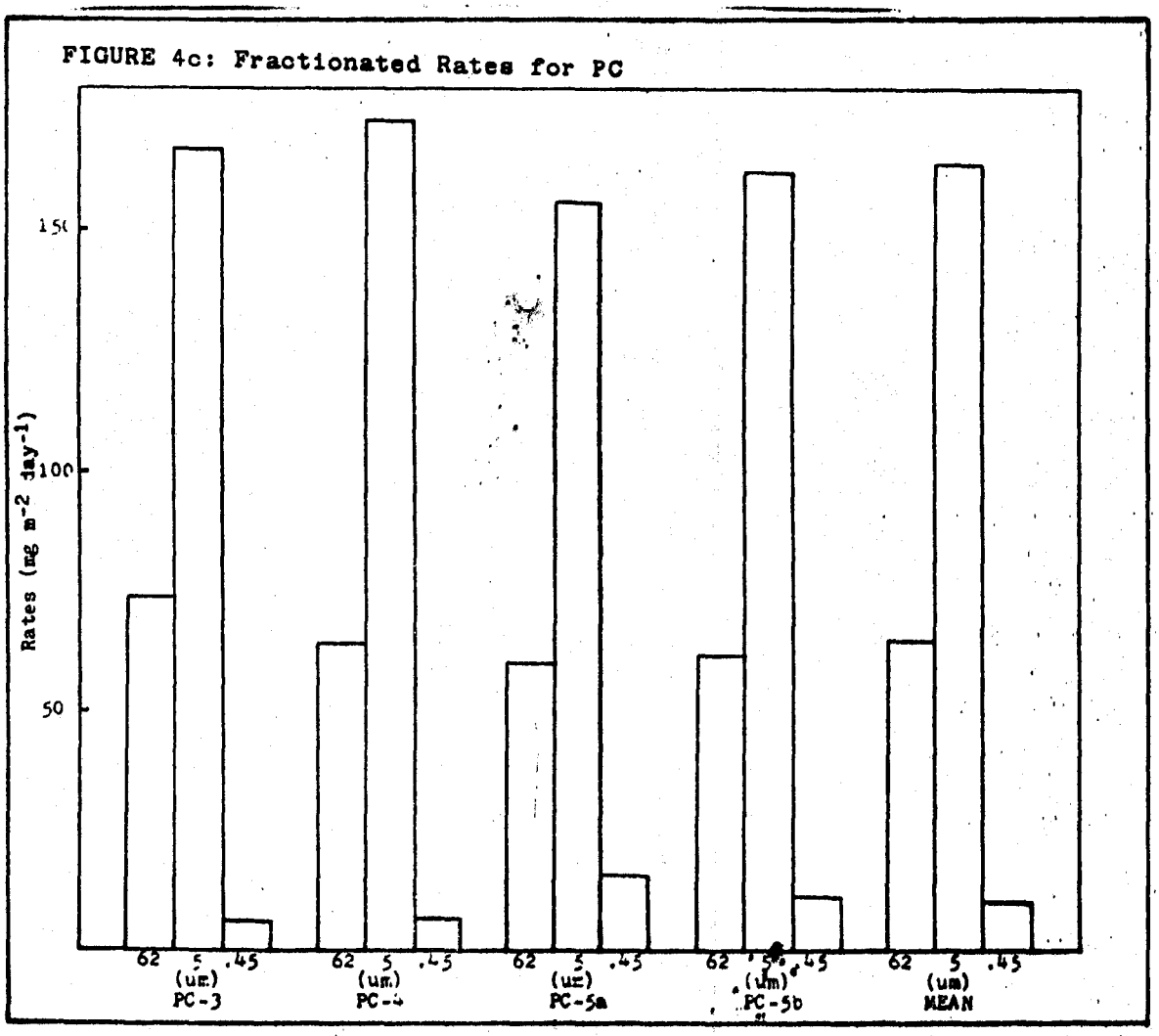


FIGURE 4c: Fractionated Rates for PC



The reason for the variation between the three fractions can be explained mainly by the effects of gravity. The larger particles are affected by gravity more than they are by the wind and would settle out in a short period of time. Particles greater than 10 um consist of dust, grit, fly ash and visible smoke (Oke, 1978) whose sources can be within an urban area. Particles of this size tend to settle out in a short time after release and the particles greater than 20 um are unlikely to travel mare than 30 km (Tsoar and Pye, 1987). These are considered to be a short-range transport of dustfall. Particles less than 10 um can remain in suspension for an unlimited period of time. These are long-range transport particles and may travel worldwide in suspension (Tsoar and Pye, 1987). It is suggested that particles less than 1 um will not contribute significantly to the overall dustfall rate (Chamberlain, 1975). The turbulent motion of the wind would have a greater effect since the effect of gravity decreases sharply (Junge, 1963) for particles of this size.

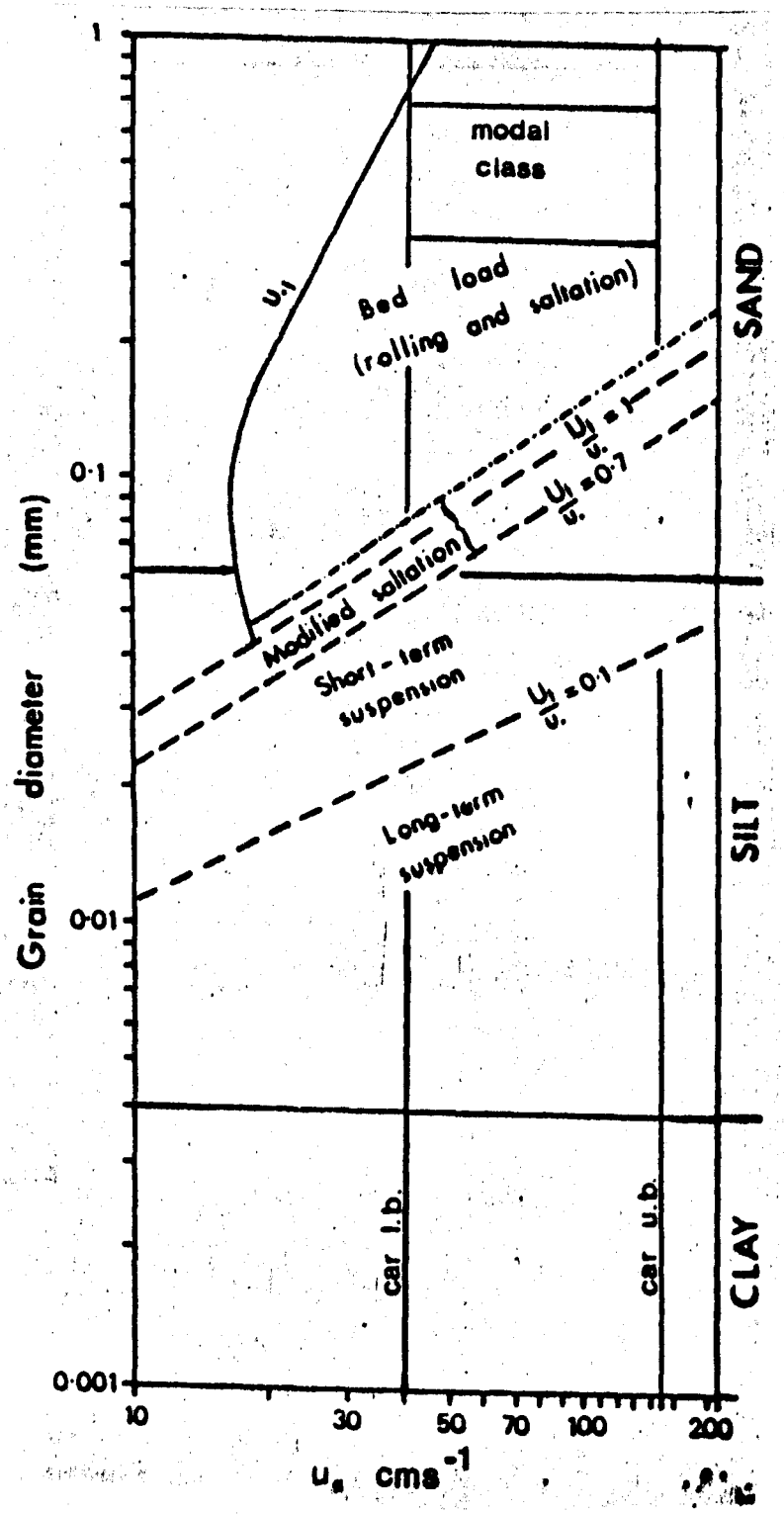
The nature of an urban environment can have a significant effect on the particle size distribution. The presence of irregular objects (i.e. buildings) and constant disturbance of the surface (i.e. traffic) can effect the deposition of dust particles. The buildings cause large differences in wind speed and direction and the turbulent motion of the wind. The buildings can shield areas from high winds that would normally flush an area of the fine dust particles. For this reason much of the fine particles (> 1 um) may not decend into the urban layer and deposit within the city. Another cause for variation due to the urban environment is the constant distrubance of

the surface . The traffic can cause the resuspension of dust from the roadways. Figure 5 (Vermette et al., 1987) illustrates the effect of a car passing by an area. The force exerted by the car on the dust resuspends the finer particles of silt and clay (5 um and .45 um filters). The U_f/u_* ratio (Equation (1)/(2)) is low enough (<Ø.1) to resuspend the particles. This could lead to an artificially enhanced deposit of silt and clay on the nearby areas. This may be a problem for the CH and PC sites. The CH site is in the city core where there is a great deal of traffic and the PC site is near a busy roadway used by cars and large trucks. Therefore this may result in an increase in the silt or clay fractions contributing to the overall dustfall rate.

The particles emitted from the city can disperse upwards through the turbulent motion caused by the city, over the city or over the lake depending on the wind direction. The city has a tendency for atmospheric inversions. The inversions would prevent the upward dispersal of the pollutants emitted from within the city. Therefore much of the particulate matter from within the city will be dispersed either over the city or over the lake.

The fine particles on the .45 um filter did not vary much from site to site. Dust of this size has an influence on a number of factors. The particles between 5 um and .45 um are fine enough to flow through the urban runoff sewer system without settling out. This has a influence on the storm water runoff quality since the pollutants associated with this fraction will affect the water quality. Larger particles greater than 5 um will settle out in the urban environment or storm sewer network and will not make it to the outflow. Therefore

Figure 5


1
0·1
0·01
0·001
Grain diameter (mm)
modal class
Bed load (rolling and saltation)
u*t
Modified saltation
Short-term suspension
Long-term suspension
u1/u* = 1
u1/u* = 0·7
u1/u* = 0·1
car l.b.
car u.b.
SAND
SILT
CLAY
10
30
50
70
100
200
u1 cms-1

it is the fine particles that are important and the depositional rates for these do not vary much over the city. Therefore the industrial atmospheric output does not seem to have an enhancing effect on the stormwater quality with respect to fine particulate matter.

The fine particles are also important in terms of the inhalation of dust. Particles less than 3 um (Pengelly, 1986) are not trapped in the nose by filters, but rather can flow through the nose and into the lungs. This can have an effect on the efficiency of the lungs and may be a contributing factor to the occurrence of lung disease. As noted, the fine paricles do not vary over the city. However, this is the deposition of the fine particles which may not be representative of the concentration of fines in the air. For this factor, an air sampler could have been used to determine the concentration of dust in the air. The presence of fine particles may increase towards the industrial area in relation to the deposition of dustfall, but not enough information is known to make an accurate deduction.

3.2 Trace Metals

The filters and dustfall were analyzed for trace metals in the nuclear reactor at McMaster University. The process used was INAA to find the concentrations for twelve trace elements (Al, Ba, Br, Ca, Cl, Co, Cu, I, Mn, Na, Ti and V). The metal concentrations were determined for all the events for each site, including the fractionated samples. The concentrations were multiplied by the loading for each sample to determine the mass loading of each metal. Tables B1.1 - B2.4, in Appendix B show the concentrations and loadings for all the samples for JHE, CH, PC, and SC respectively.

3.2.1 Concentrations

The concentrations were plotted on line graphs to help to identify trends. For the graphs the metals were divided into two groups. The metals were divided into a large and small scale group according to concentrations. The large scale metals are Al, Ca, Cl, Mn, Na and Ti and the small scale metals are Ba, Br, Co, Cu, I, and V. The series of graphs illustrating the trends in both the large and small scale metals are in appendix C1.1.

The large scale metals for JHE were plotted for each of the six samples from the first event, and for the three filters (62, 5 and

six gauges are similar with a few major peaks. The main peaks are Al (45000 - 70000 ppm), Ca (43000 - 96000 ppm) and a secondary high for Mn (11000 - 26000 ppm) and a low concentration for Cl (<5000 ppm) except for #1 (36000 ppm). The other four events show some similarity to this pattern, with some variation. The general trend shows high concentrations for Al, Ca and Mn while Cl is low. The 5 um and .45 um filters show low values for Al, also the .45 um does not register as high for Mn. The pattern for the three sizes show that generally the concentrations are highest for the 62 um and lowest for the .45 um filters. The exception to this pattern involves the 5 um filter. The 5 um is lowest for both Cl and Ti while highest for Mn.

The samples from CH for the first event (CH-3) show little variation from gauge to gauge. The main features are high concentrations for Ca (122000 - 144000 ppm) and Mn (71000 - 78000 ppm) and also a high level for Al(29000 - 35000 ppm). The main low value is for Cl. The remaining events were fractionated and the trends are

a high concentration for Ca and also high levels for Mn and TI. However the high for Ca generally only occurs in the 5 um filter and in the 62 and 5 um filters for Ti. The 5 um and 62 um filters had the highest levels while the .45 um was the lowest. However for this site the levels determined seem to be quite variable.

The first event for the PC site show a large variation in the metal concentrations. The large concentration for one gauge is only Ca (67000 ppm) but for the other gauge Al (26000 ppm), Ca (180000 ppm) and Mn (30000 ppm) displayed large values. For the remaining four events, the actual concentrations vary but the pattern remains consistent. The 5 um is usually the highest for Ca, Mn and Ti and the 62 um is usually the lowest. The main abnormality is the .45 um for PC-4. All the values are lower then expected from the other three events, and the concentration for Ca was below detection. This is not consistent with the other three events and because of the large difference it may have been caused by human error somewhere along the process of the analysis.

The SC site was very similar for the two gauges from the first event. The high levels were recorded for Al(62000 - 65000 ppm) and Ca (96000 ppm) while the low was for Cl (<1000 ppm). The same general pattern remains for the fractionated samples. The 5 um filter is highest in Al and Ca while the 62 um filter is lower but follows the same pattern. The .45 um filter is quite variable for Al and Ca. All three filters are quite similar and consistent for Cl, Mn, Na and Ti.

The small scale metal concentrations were also graphed to identify trends. The concentrations for JHE only display three metals

(Br, I and V) above detection. For the first event, the six gauges only show one variation. The metal I is above detection for four of the six gauges (600 - 1200 ppm). The other two metals are Br (240 - 490 ppm) and V (100 - 160 ppm). The pattern continued for the remaining four events with the concentrations higher for the .45 um filter except for V. The 5 um filter generally has the lowest concentration except for V.

The concentrations for CH are very similar for the first event with the same three metals as JHE, plus a large concentration for Cu. The same pattern is consistent for the remaining events with very little variation.

The concentrations for the PC site was variable for the two gauges that collected the first event. One of the gauges only detected Cu and V while the other detected Br, Cu, I and V. The Cu peak was by far the largest for both gauges (250 - 980 ppm). The remaining events displayed variation in the concentrations between the metals and between the filter sizes. The larger values were recorded for Ba, Br and Cu. The V concentration remained constant (<120 ppm) over time and between the filters.

The SC site was consistent for the first event with the larger metal concentration (210 - 560 ppm) for Ba. This remained the largest throughout the last four events. There were also low or nil concentrations for I, and Cu was below detection at all times.

3.2.2 Loadings

The concentration of each metal was multiplied by the dust deposited to determine the trace metal loadings. The loadings were combined for the 62 um and 5 um filters and will be considered the

bulk pollution loading. The .45 um filter will represent the fine particle pollution which is important in terms of human lungs and stormwater management.

The metals for each site are in Appendix B2.1 - B2.4 for JHE, CH, PC and SC. The loading for the first event for each site were not fractionated so that only a total loading was determined for the large and small scale metals. The large scale metal loadings show little variation for CH and SC. The large values for CH were Ca (3.43 mg), Mn (1.85 mg) and also Al (.74 - .84 mg). The large values for SC were Ca (.87 - .96 mg) and Al (.59 - .63 mg) and Cl (.01 mg) was the low value. The JHE values were variable but follow some trends. The metals Al and Ca were the largest values and Cl was the lowest except for one of the gauges. The PC site had large values for Al, Ca, Mn and Ti for one gauge. The values were variable with one gauge low for Mn and low for Ti compared to the other gauge. The remaining events follow some general patterns. For the large scale metals of the bulk pollution particles (62 um and 5 um filters) the patterns can be summarized in a few generalizations. The remaining events for each site showed similar patterns for metal loadings. The PC site shows a higher loading of the large scale trace metals than any other site except for Ti in CH-4 and CH-5. In all other cases the loading is highest in the industrial area due to the output from industries. The CH and JHE sites were very similar in the amount of loading of the metals. The loading for the SC site is also similar for the large scale metals. Therefore the industrial area seems to effect the PC site more than the other three sites. The other three sites are

either not effected by the industries in terms of trace metals or effects the other sites all equally.

The pattern for the fine particles can be generalized in much the same manner. JHE and CH Show the same pattern throughout the remaining four events. The SC site also shows the same general pattern except for the value of Ca for SC-7 and SC-8. The PC site shows more variability thoughout the events especially PC-5b which has higher loadings for Ca, Cl and Mn. Except for that event, PC usually has values just higher than the other sites for Al , Ca and Mn while the other metals (Cl, Na, and Ti) are similar for all four sites.

For the small scale metals all the sites except for PC, there does not seem to be much variation between the gauges. The values for JHE-1 are similar except for gauge 2 where Br is only half the loading compared to the other five gauges. Only three of the six small scale metals (Br, I, and V) show levels above detection. The SC-5a event have levels for all metals except Cu, and the highest loading is for Ba. The other metals especially Co, I and V are just above detection do not contribute much to the total loading. The site at CH show levels for Br, Cu. I and V and are consistent between gauges. In this case Cu is the largest loading while it is not even detected at JHE and SC. Cu is also detected at PC where again it is the largest loading. The two gauges at this site are variable but both illustrate the large level of Cu. Due to the levels of Cu at PC and also at CH , the nearest two sites to the industrial zone, the contamination of Cu must be due to the influence of the industries.

The loadings for JHE for the remaining four events show much the same pattern as the first event. There are only three metals

above detection (Br, I and V). The loadings are largest for Br, I then V. The loading for CH show the same pattern as JHE except Cu is also included. The PC site is more variable for the loading with Br and Cu the predominant metals. The pattern for SC displays large values for Ba and Br. The remaining metal loadings are very low and would not contribute much to the total loadings.

CHAPTER FOUR

4.1 Conclusions

The purpose of this study was to examine the process of dry deposition. The results showed that the amount of dustfall decreased rapidly as the distance from the industrial zone increased. The industrial emissions contain particulate matter, most of which fall within a short time after release. The larger particles (> 5 um) were not affected much by wind and was deposited within a short distance surrounding the industrial area.

The metal analysis of the dustfall displayed enriched values of Al, Ca and Mn near the industrial area. The presence of Cu was another indicator of the industrial effects. The metal was first detected at CH but was found to be larger at the PC site. By comparing the SC values to those from the other three sites, there were enriched values of most metals due to the urban environment. Therefore the industrial emissions of particulate matter was found to have a pronounced effect on the city of Hamilton.

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APPENDIX A

Statisical Analysis

A1.1 : Linear Regression for JHE.

H_o : The slope of the line is not significantly different from zero.

H_a : There is a significant difference.

Significance level = 0.05

THE REGRESSION EQUATION IS
C5 = 41.1 - 1.65 C9

COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	41.090	1.579	26.02
C9	-1.6500	0.6448	-2.56

S = 2.884

R-SQUARED = 45.0 PERCENT
R-SQUARED = 38.1 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	1	54.450	54.450
RESIDUAL	8	66.519	8.315
TOTAL	9	120.969	

$t^* = -2.56$

$t_{crit} = t_{9, .025} = -2.262$

$t^* < t_{crit}$

Therefore we reject H_o, and conclude that the dustfall rates change significantly with time.

Regression line: Rate = 41.1 - 1.65 Time (mg m^{-2} day^{-1})

A1.2 : Linear Regression for CH.

H_o : The slope of the line is not significantly different from zero.

H_a : There is a significant difference.

Significance level = 0.05

THE REGRESSION EQUATION IS
06 80.3 - 0.90 C10

COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	80.250	3.285	24.43
C10	-0.900	1.075	-0.84

S = 3.926

R-SQUARED = 14.9 PERCENT
R-SQUARED = .0 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	1	10.80	10.80
RESIDUAL	4	61.66	15.41
TOTAL	5	72.46	

$t^* = -0.84$

$t_{crit} = t_{4, .025} = -2.776$

$t^* \not< t_{crit}$

Therefore we do not reject H_o, and conclude that the dustfall rates do not significantly change with time.

Regression line: Rate = 80.3 - 0.90 Time (mg m^{-2} day^{-1})

A1.3 : Linear Regression for PC.

H_o : The slope of the line is not significantly different from zero.

H_a : There is a significant difference.

Significance level = 0.05

THE REGRESSION EQUATION IS
C7 = 254 - 4.66 C10

COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	254.100	2.701	94.06
C10	-4.6625	0.8843	-5.27

S = 3.229

R-SQUARED = 87.4 PERCENT
R-SQUARED = 84.3 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	1	289.85	289.85
RESIDUAL	4	41.70	10.43
TOTAL	5	331.55	

$t^* = -5.27$

$t_{crit} = t_{4,\ .025} = -2.776$

$t^* < t_{crit}$

Therefore we reject H_o, and conclude that the dustfall rates change significantly with time.

Regression line: Rate = 254 - 4.66 Time (mg m^{-2} day^{-1})

A1.4 : Linear Regression for SC.

H_o : The slope of the line is not significantly different from zero.

H_a : There is a significant difference.

Significance level = 0.05

THE REGRESSION EQUATION IS
C8 = 29.3 + 0.470 C10

COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	29.330	1.662	17.65
C10	0.4700	0.5440	0.86

S = 1.986

R-SQUARED = 15.7 PERCENT
R-SQUARED = .0 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	1	2.945	2.945
RESIDUAL	4	15.783	3.946
TOTAL	5	18.728	

$t^* = 0.86$

$t_{crit} = t_{4,\ .025} = -2.776$

$t^* \not< t_{crit}$

Therefore we do not reject H_o, and conclude that the dustfall rates do not significantly change with time.

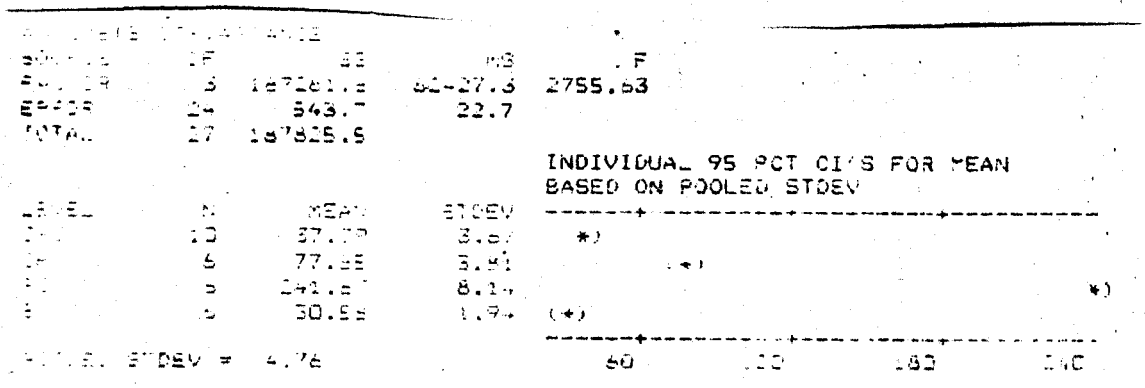
Regression line: Rate = 29.3 + 0.47 Time (mg m^{-2} day^{-1})

A2.1 : Analysis of Variance between JHE, CH, PC and SC.

H_o : The slope of the line is not significantly different from zero.

H_a : There is a significant difference.

Significance level = 0.05



$F^* = 2755.6$

$F_{crit} = F_{3,24,0.05} = 3.01$

$F^* > F_{crit}$

Therefore we reject H_o, and conclude that the dustfall rates are is a significantly differnce between the sites.

A2.2 : Analysis of Variance between JHE, CH, and SC.

H_o : The slope of the line is not significantly different from zero.

H_a : There is a significant difference.

Significance level = 0.05

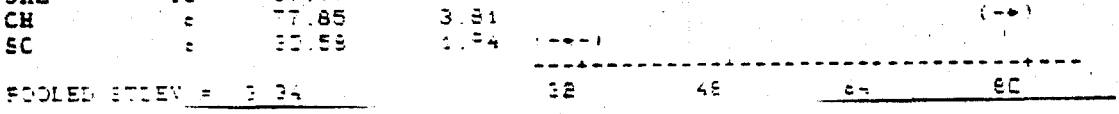
ANALYSIS OF VARIANCE

SOURCE	DF	SS	MS	F
FACTOR	2	8174.2	4087.1	366.04
ERROR	19	212.2	11.2	
TOTAL	21	8386.4		

LEVEL	N	MEAN	STDEV
JHE	10	37.79	3.87
CH	6	77.85	3.81
SC	6	80.58	1.94

POOLED STDEV = 3.34

INDIVIDUAL 95 PCT CI'S FOR MEAN BASED ON POOLED STDEV



$F^* = 366.0$

$F_{crit} = F_{2,19,0.05} = 3.52$

$F^* > F_{crit}$

Therefore we reject H_o, and conclude that the dustfall rates are is a significantly difference between the sites.

A2.3 : Analysis of Variance between JHE and SC.

H_o : The slope of the line is not significantly different from zero.

H_a : There is a significant difference.

Significance level = 0.05

ANALYSIS OF VARIANCE

SOURCE	DF	SS	MS	F
FACTOR	1	194.76	194.76	19.52
ERROR	14	139.70	9.98	
TOTAL	15	334.46		

LEVEL	N	MEAN	STDEV
JHE	8	37.79	3.67
SC	8	30.56	1.84

INDIVIDUAL 95 PCT CI'S FOR MEAN BASED ON POOLED STDEV

POOLED STDEV = 3.16

26.0 32.0 38.0 44.0

$F^* = 19.52$

$F_{crit} = F_{1,14,0.05} = 4.60$

$F^* > F_{crit}$

Therefore we reject H_o, and conclude that the dustfall rates are is a significantly difference between the sites.

APPENDIX B

Trace Metal Tables

JHE-1

ELEMENT	#1			#2			#3		
Al	48000	+-	1600	44900	+-	1500	58800	+-	1900
Ba		<	2200		<	2200		<	1500
Br	560	+-	70	240	+-	40	480	+-	60
Ca	42600	+-	54000	61000	+-	6000	49000	+-	5000
Cl	36000	+-	3600	2540	+-	190	2380	+-	170
Co		<	50		<	37		<	29
Cu		<	500		<	370		<	500
I		<	31	52	+-	20	72	+-	25
Mn	11300	+-	800	15700	+-	1100	13400	+-	1000
Na	8600	+-	700	7700	+-	600	8100	+-	600
Tl	6000	+-	700	5050	+-	390	6800	+-	400
V	105	+-	9	104	+-	8	133	+-	10

ELEMENT	#4			#5			#6		
Al	69400	+-	2300	72500	+-	2300	57200	+-	1900
Ba		<	2700		<	2300		+-	900
Br	320	+-	60	320	+-	50	430	+-	50
Ca	96000	+-	9000	80000	+-	8000	84000	+-	8000
Cl	1910	+-	130	2400	+-	500	3440	+-	170
Co		<	22		<	40		<	22
Cu		<	260		<	500		<	270
I	130	+-	40	104	+-	36		<	16
Mn	17700	+-	1300	25500	+-	1800	21700	+-	1600
Na	9900	+-	800	9600	+-	600	10400	+-	500
Tl	7000	+-	500	6800	+-	500	6000	+-	400
V	152	+-	11	164	+-	12	129	+-	9

JHE-2

ELEMENT	62 um			5 um			45 um		
Al	92000	+-	3200	31000	+-		12000	+-	
Ba		<	1100		<	1200		<	2100
Br	1900	+-		450	+-		2200	+-	
Ca	142000	+-		92000	+-		78000	+-	
Cl	24000	+-		1980	+-		11000	+-	
Co		<	90		<	110		<	90
Cu		<	350		<	280		<	500
I	300	+-		200	+-		650	+-	
Mn	37000	+-		84000	+-		6300	+-	
Na	41500	+-		10500	+-		7250	+-	
Tl	41000	+-		3500	+-		16500	+-	
V	475	+-	17	300	+-		20	+-	

JHE-3

ELEMENT	62 um			5 um			45 um		
Al	95000	+-		33600	+-	1100	8840	+-	310
Ba		<	900		<	1100		<	4000
Br	1800	+-	190	280	+-	50	2580	+-	250
Ca	120000	+-		119000	+-	11000	82000	+-	10000
Cl	25000	+-		1990	+-	370	12700	+-	900
Co		<	60		<	24		<	70
Cu		<	400		<	310		<	500
I	140	+-	50		<	25	120	+-	40
Mn	65000	+-		60000	+-	4000	10100	+-	700
Na	12000	+-		5250	+-	330	13300	+-	1100
Ti	15000	+-		3000	+-	400	11500	+-	900
V	350	+-	150	165	+-	12	35	+-	4000

JHE-4

ELEMENT	62 um			5 um			45 um		
Al	115100	+-	3800	33600	+-	1100	11260	+-	400
Ba		<	11000		<	1100		<	8000
Br	1680	+-	240	280	+-	150	1960	+-	220
Ca	253000	+-	27000	119000	+-	11000	32000	+-	6000
Cl	21500	+-	1300	1990	+-	370	12400	+-	900
Co		<	180		<	24		<	120
Cu		<	1700		<	310		<	800
I	460	+-	160		<	25	820	+-	280
Mn	56000	+-	4000	60000	+-	4000	6000	+-	500
Na	26300	+-	2600	5250	+-	330	12800	+-	1200
Ti	94700	+-	3500	3000	+-	400	13600	+-	1200
V	690	+-	50	165	+-	12	45	+-	6

86-5-JHE

ELEMENT	62 um			5 um			45 um		
Al	75000	+-	3200	26000	+-	800	6300	+-	210
Ba		+-	980		+-	750		+-	1000
Br	2000	+-	90	250	+-	112	2100	+-	2700
Ca	160000	+-	12000	105000	+-	10100	55000	+-	7500
Cl	18000	+-	980	2500	+-	410	14000	+-	775
Co		+-	75		+-	35		+-	125
Cu		+-	320		+-	310		+-	650
I	350	+-	45	175	+-	19	630	+-	150
Mn	42000	+-	3700	73000	+-	4500	7500	+-	625
Na	37000	+-	3900	9800	+-	470	10500	+-	110
Ti	30000	+-	2700	4000	+-	350	12500	+-	1200
V	440	+-	19	140	+-	25	44	+-	7

PC-2

ELEMENT	#1			#2		
Al	14400	+-	500	26100	+-	800
Ba		<	400		<	800
Br		<	31	113	+-	25
Ca	66000	+-	6000	118000	+-	11000
Cl	690	+-	90	1160	+-	80
Co		<	8		<	16
Cu	500	+-	40	970	+-	80
I		<	8	22	+-	9
Mn	2220	+-	160	29500	+-	2100 *
Na	1510	+-	90	3110	+-	220
Tl	970	+-	130	7920	+-	290
V	32	+-	2	49	+-	4

PC-3

ELEMENT	62 um			5 um			45 um		
Al	15200	+-	810	35200	+-	1200	37900	+-	1200
Ba		<	4000	1160	+-	240		<	5000
Br	175	+-	36	94	+-	27	1750	+-	200
Ca	85000	+-	8700	150000	+-	14000	110000	+-	12000
Cl	10100	+-	1150	1120	+-	80	10600	+-	1200
Co		<	60	26	+-	5		<	70
Cu	550	+-	80	1300	+-	90	1560	+-	280
I	43	+-	21		<	13		<	70
Mn	15400	+-	1100	32900	+-	2400	29200	+-	2100
Na	2100	+-	110	5040	+-	210	11100	+-	1100
Tl	10400	+-	800	4850	+-	380	13600	+-	1000
V	40	+-	4	52	+-	4	67	+-	6

PC-4

ELEMENT	62 um			5 um			45 um		
Al	29200	+-	900	98600	+-	3200	42600	+-	1400
Ba		<	1800		<	1000		<	9000
Br	155	+-	32	103	+-	27	2320	+-	260
Ca	90000	+-	9000	198000	+-	18000	129000	+-	15000
Cl	3060	+-	180	1560	+-	110	16700	+-	1100
Co		<	30		<	26		<	140
Cu	1430	+-	110	1520	+-	130	2100	+-	400
I	93	+-	32	27	+-	10	250	+-	90
Mn	20300	+-	1500	38600	+-	2800	31500	+-	2300
Na	6300	+-	500	4020	+-	210	20400	+-	1800
Tl	11800	+-	500	4100	+-	500	14600	+-	1400
V	43	+-	4	109	+-	8	67	+-	8

PC-5a

ELEMENT	62 um			5 um			45 um		
Al	40300	+-	1300	38000	+-	1200	990	+-	40
Ba	1120	+-	220		<	700		<	2100
Br	65	+-	20		<	70	830	+-	90
Ca	108000	+-	10000	97000	+-	9000		<	2200
Cl	2340	+-	110	830	+-	80	690	+-	190
Co	22	+-	4		<	16		<	34
Cu	2310	+-	110	1810	+-	110	2160	+-	160
I	18	+-	7		<	14	140	+-	50
Mn	35700	+-	2600	33100	+-	2400	9600	+-	700
Na	6860	+-	260	3380	+-	190	7000	+-	600
Tl	8600	+-	400	4350	+-	370	5000	+-	400
V	81	+-	6	66	+-	5		<	6

PC-5b

ELEMENT	62 um			5 um			45 um		
Al	39300	+-	2900	42600	+-	3100	12000	+-	1100
Ba		<	2100		<	1000		<	7000
Br	250	+-	37	132	+-	31	970	+-	80
Ca	101000	+-	9500	240000	+-	20100	170000	+-	13000
Cl	4600	+-	210	2100	+-	140	147000	+-	1600
Co		<	210		<	15		<	21
Cu	2100	+-	230	1500	+-	190	1980	+-	320
I	95	+-	33		<	21	210	+-	70
Mn	20100	+-	1470	35600	+-	2800	28700	+-	2050
Na	6200	+-	500	5020	+-	250	10100	+-	1000
Tl	12000	+-	550	5010	+-	600	13300	+-	900
V	67	+-	8	105	+-	8	65	+-	6

SC-5a

ELEMENT	#1			#2		
Al	65900	+-	2100	62200	+-	2000
Ba	550	+-	120	410	+-	120
Br	51	+-	11	83	+-	32
Ca	96000	+-	9000	96000	+-	9000
Cl	920	+-	120	850	+-	100
Co	15	+-	7	11.7	+-	2.8
Cu		<	160		<	170
I	20	+-	7		<	7
Mn	5040	+-	360	5900	+-	400
Na	6880	+-	240	8270	+-	280
Tl	4520	+-	240	4280	+-	240
V	97	+-	7	82	+-	6

SC-6

ELEMENT	>62 µm			62-5 µm			5-<45 µm		
Al	84000	+-	2150	87000	+-	2200	12000	+-	1000
Ba	250	+-	80	210	+-	70	1000	+-	190
Br	56	+-	12	52	+-	11	300	+-	56
Ca	65000	+-	6500	170000	+-	13000	95000	+-	9000
Cl	83	+-	17	72	+-	15	3200	+-	200
Co	19	+-	7	10	+-	2	10	+-	2
Cu		<	160		<	140		<	150
I	14	+-	5		<	8	15	+-	6
Mn	3300	+-	280	2800	+-	250	6000	+-	400
Na	5040	+-	210	4080	+-	190	10100	+-	990
Ti	4800	+-	230	980	+-	150	5100	+-	250
V	106	+-	10	67	+-	7	33	+-	6

SC-7

ELEMENT	>62 µm			62-5 µm			5-<45 µm		
Al	15000	+-	140	10500	+-	1100	9800	+-	980
Ba	160	+-	90	150	+-	30	700	+-	150
Br	41	+-	10	43	+-	12	210	+-	40
Ca	43000	+-	6000	75000	+-	8500	55000	+-	8000
Cl	67	+-	20	65	+-	15	1500	+-	105
Co	14	+-	4		<	7		<	9
Cu		<	200		<	100		<	110
I	15	+-	7		<	9	21	+-	6
Mn	2200	+-	250	2100	+-	210	4010	+-	370
Na	4500	+-	180	6000	+-	250	7000	+-	890
Ti	3500	+-	200	1000	+-	160	52	+-	230
V	30	+-	5	65	+-	6	63	+-	6

SC-8

ELEMENT	>62 µm			62-5 µm			5-<45 µm		
Al	54000	+-	2000	65000	+-	2300	10500	+-	1010
Ba	250	+-	90	290	+-	80	1500	+-	210
Br	51	+-	10	53	+-	10	340	+-	50
Ca	91000	+-	8500	150000	+-	12000	9300	+-	8000
Cl	210	+-	20	250	+-	25	4100	+-	270
Co	18	+-	6	10	+-	2	11	+-	2
Cu		<	170		<	120		<	100
I	10	+-	2	9	+-	2	23	+-	6
Mn	2900	+-	270	3100	+-	290	5400	+-	350
Na	4400	+-	210	4300	+-	190	9000	+-	700
Ti	5300	+-	210	1100	+-	150	4500	+-	190
V	90	+-	9	57	+-	6	35	+-	5

CH-5a

ELEMENT	62 um			5 um			45 um		
Al	32000	+-	2100	21000	+-	1200	9900	+-	120
Ba		<	90		<	120		<	240
Br	840	+-	60	340	+-	70	630	+-	120
Ca	28000	+-	8100	91000	+-	3200	21000	+-	450
Cl	9800	+-	450	3500	+-	470	14000	+-	340
Co		<	14		<	50		<	70
Cu		<	120	280	+-	120	300	+-	110
I	180	+-	20	120	+-	30	350	+-	125
Mn	12500	+-	220	21500	+-	2100	3100	+-	1200
Na	7800	+-	4500	7900	+-	350	14500	+-	1400
Ti	32300	+-	340	21000	+-	360	15500	+-	2700
V	54	+-	30	67	+-	5	21	+-	3

CH-6

ELEMENT	62 um			5 um			45 um		
Al	41000	+-	3800	31000	+-	1200	5500	+-	1200
Ba		<	2000		<	45		<	2100
Br	550	+-	100	210	+-	50	850	+-	37
Ca	34500	+-	3600	57500	+-	9000	8500	+-	95
Cl	8700	+-	450	10100	+-	1000	17500	+-	12000
Co		<	33		<	8590		<	4506
Cu	120	+-	400	210	+-	150	290	+-	34
I	190	+-	60	140	+-	56	220	+-	50
Mn	18700	+-	650	17500	+-	380	11000	+-	1200
Na	9200	+-	700	4500	+-	210	17500	+-	1600
Ti	21000	+-	1200	15500	+-	160	2500	+-	125
V	53	+-	5	71	+-	6	42	+-	20

CH-8

ELEMENT	62 um			5 um			45 um		
Al	24000	+-	3200	11000	+-	890	7800	+-	210
Ba		<	980		<	750		<	110
Br	510	+-	90	340	+-	112	660	+-	2700
Ca	37000	+-	12000	45000	+-	10100	24500	+-	7500
Cl	11500	+-	980	9800	+-	410	16500	+-	775
Co		<	75		<	35		<	125
Cu	105	+-	320	180	+-	310	170	+-	650
I	205	+-	45	165	+-	19	195	+-	150
Mn	6050	+-	3700	31500	+-	4500	12500	+-	625
Na	12500	+-	3900	6300	+-	470	16500	+-	1100
Ti	35500	+-	2700	19300	+-	350	4500	+-	1200
V	47	+-	19	64	+-	25	43	+-	7

SC-9

ELEMENT	62 um			5 um			45 um		
Al	74000	+-	2100	92000	+-	2400	11500	+-	1100
Ba	280	+-	90	260	+-	70	1800	+-	200
Br	55	+-	9	70	+-	10	250	+-	50
Ca	71000	+-	8100	180000	+-	9500	91000	+-	8500
Cl	83	+-	16	80	+-	15	3500	+-	150
Co		<	7		<	8	10	+-	2
Cu		<	140		<	150		<	120
I	11	+-	2	11	+-	2	18	+-	3
Mn	3400	+-	300	3200	+-	290	6000	+-	380
Na	4200	+-	200	4500	+-	210	8200	+-	650
Ti	5500	+-	220	1200	+-	160	4800	+-	210
V	100	+-	9	60	+-	6	40	+-	5

CH-3

ELEMENT	#1			#2		
Al	28700	+-	900	35000	+-	1100
Ba		+-	2400		+-	3000
Br	150	+-	50	320	+-	70
Ca	132000	+-	12000	144000	+-	14000
Cl	2130	+-	180	2680	+-	240
Co		+-	39		+-	50
Cu	350	+-	100	340	+-	120
I	48	+-	19	57	+-	23
Mn	71000	+-	5000	78000	+-	6000
Na	4400	+-	500	5700	+-	600
Ti	3500	+-	400	4300	+-	500
V	167	+-	12	189	+-	13

CH-4

ELEMENT	62 um			5 um			45 um		
Al	23500	+-	800	21800	+-	700	9950	+-	330
Ba		+-	2300		+-	1600		+-	2400
Br	640	+-	80	420	+-	50	810	+-	90
Ca	29700	+-	3800	78000	+-	8000	16200	+-	2600
Cl	9400	+-	500	4130	+-	240	12100	+-	600
Co		+-	34		+-			+-	34
Cu		+-	400	290	+-	90	340	+-	110
I	190	+-	60	87	+-	30	230	+-	80
Mn	9500	+-	700	18200	+-	1300	4820	+-	360
Na	9000	+-	700	6700	+-	500	10700	+-	600
Ti	28900	+-	1000	24100	+-	800	5700	+-	500
V	43	+-	4	60	+-	5	22	+-	3

JHE-1

#1	#2	#3
.624	.4939	.7644
0	0	0
.00728	.00264	.00624
.5538	.671	.637
.468	.02794	.03094
0	0	0
0	0	0
0	.000572	.000936
.1469	.1727	.1742
.1118	.0847	.1053
.078	.05555	.0884
.001365	.001144	.001729

#4	#5	#6
.9716	.87	.7436
0	0	0
.00448	.00384	.00559
1.344	.96	1.092
.02674	.0288	.04472
0	0	0
0	0	0
.00182	.001248	0
.2478	.306	.2821
.1386	.1152	.1352
.098	.0816	.078
.002128	.001968	.001677

.45 um	62 & 5 um
.048	1.169
0	0
.0088	.02205
.312	2.29
.044	.23778
0	0
0	0
.0026	.0049
.0252	1.257
.029	.489
.066	.4075
.00008	.007575

JHE-3

.02652	1.096
0	0
.00774	.0172
.246	2.15
.0381	.2199
0	0
0	0
.00036	.00112
.0303	1.12
.0399	.1485
.0345	.15
.000105	.00445

JHE-4

.04504	1.1753
0	0
.00784	.01484
.128	3.08
.0496	.17239
0	0
0	0
.00328	.00322
.024	1.052
.0512	.24185
.0544	.6959
.00018	.006645

JHE-5b

.0189	.961
0	0
.0063	.02075
.165	2.595
.042	.1895
0	0
0	0
.00189	.005075
.0225	1.181
.0315	.4408
.0375	.314
.000132	.0055

PC-2

#1	#2
1.152	2.0619
0	0
0	.008927
5.28	9.322
.0552	.09164
0	0
.04	.07663
0	.001738
.1776	2.3305
.1208	.24569
.0776	.62568
.00256	.003871

PC-3

.1704	4.48
0	.1276
.00928	.01734
.516	19.9
.0668	.5272
0	.00286
.0084	.165
.001	.00172
.126	4.235
.0816	.6384
.0584	.9495
.000268	.00732

PC-4

.1516	
0	
.007	11.824
.44	0
.0424	.018203
0	25.218
.00624	.30918
0	0
.1168	.22833
.0444	.007233
.0544	5.0457
.000268	.72222
	.9892
	.013575

PC-5a

.0099	
0	5.2934
.0083	.04256
0	.00247
.0069	13.707
0	.17109
.0216	.000836
.0014	.26697
.096	.000684
.07	4.6335
.05	.5953
	.75745
0	.009612

PC-5b

.084	
0	5.9205
.00679	0
1.19	.023346
1.029	28.659
0	.3957
.01386	0
.00147	.2364
.2009	.003705
.0707	4.4507
.0931	.75886
.000455	.98403
	.013428

SC-6

.024	1.542
.002	.0041
.0006	.000968
.19	2.22
.0064	.001384
.00002	.000252
0	0
.00003	.000112
.012	.0544
.0202	.08112
.0102	.0482
.000066	.001518

SC-7

	1.155
.0098	.0127
.0007	.0033
.00021	3.76
.055	.00534
.0015	.00098
0	0
0	.00105
.000021	.175
.00401	.375
.007	.255
.000052	.00275
.000063	

SC-8

	1.082
.0315	.0049
.0045	.000938
.00102	2.228
.0279	.00418
.0123	.000244
.000033	0
0	.00017
.000069	.0542
.0162	.0782
.027	.0534
.0135	.00129
.000105	

SC-9

	1.494
.023	.00486
.0036	.001125
.0005	2.259
.182	.001467
.007	0
.00002	0
0	.000198
.000036	.0594
.012	.0783
.0164	.0603
.0096	.00144
.00008	

CH-3

#1	#2
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.0039	.00768
3.432	3.456
.05538	.06432
0	0
.0091	.00816
.001248	.001368
1.846	1.872
.1144	.1368
.091	.1032
.004342	.004536

CH-4

.04975	.981
0	0
.00405	.0189
.081	3.51
.0605	.18585
0	0
.0017	.01305
.00115	.003915
.0241	.819
.0535	.3015
.0285	1.0845
.00011	.0027

CH-5a

.0792	1.099
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.00504	.0223
.168	3.213
.112	.2457
0	0
.0024	.00868
.0028	.00624
.0248	.8415
.116	.3541
.124	1.1032
.000168	.002833

CH-6

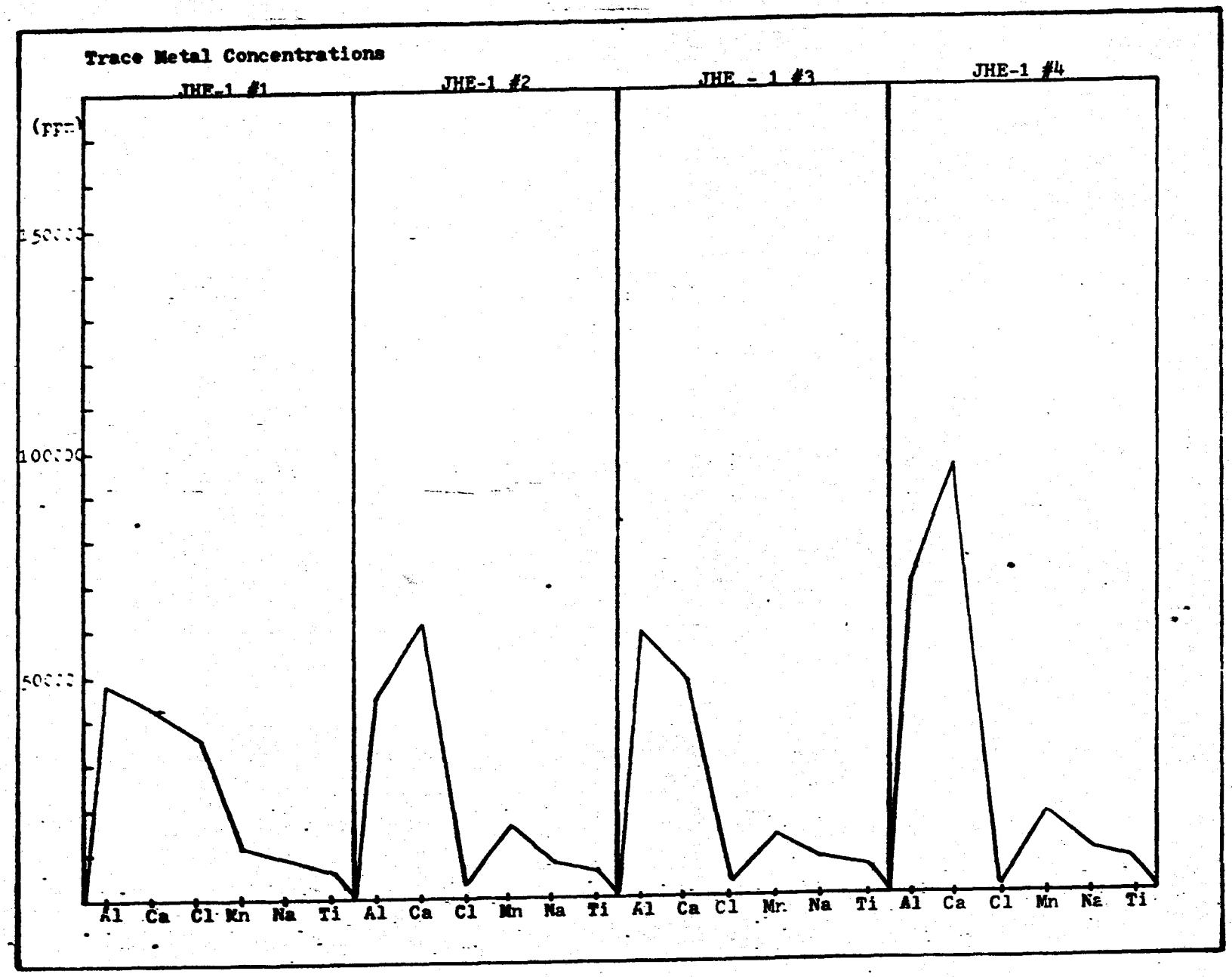
.044	1.319
0	0
.0068	.01193
.068	1.9895
.14	.3785
0	0
.00232	.0072
.00176	.00601
.088	.6957
.14	.2272
.02	.665
.000336	.002571

CH-8

.0468	.644
0	0
.00396	.01666
.147	1.778
.099	.4354
0	0
.00102	.00651
.00117	.00749
.075	.9667
.099	.3514
.027	1.0374
.000258	.00245

APPENDIX C

Trace Metal Graphs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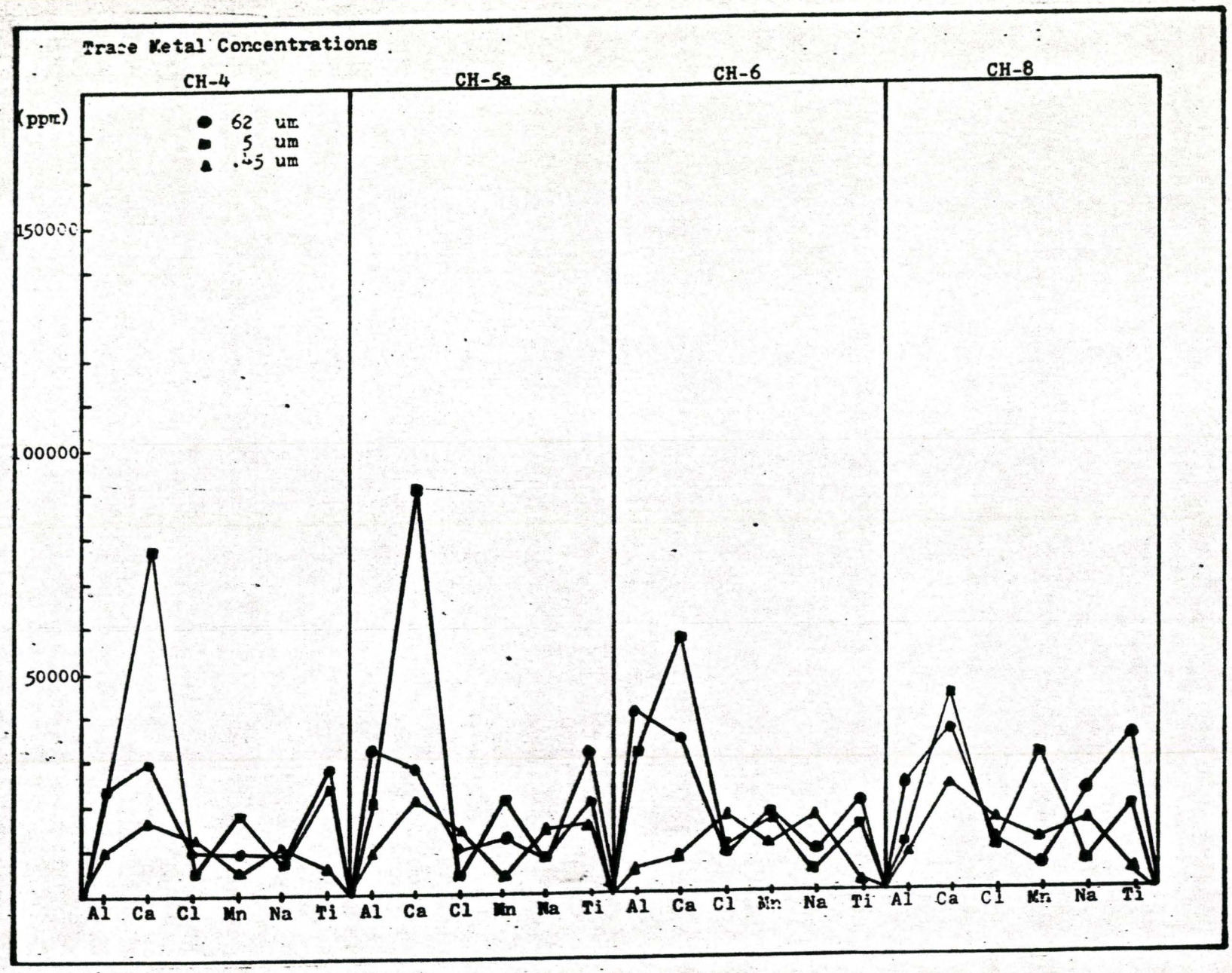
JHE-1 #1
JHE-1 #2
JHE - 1 #3
JHE-1 #4
(ppm)
150000
100000
50000
Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti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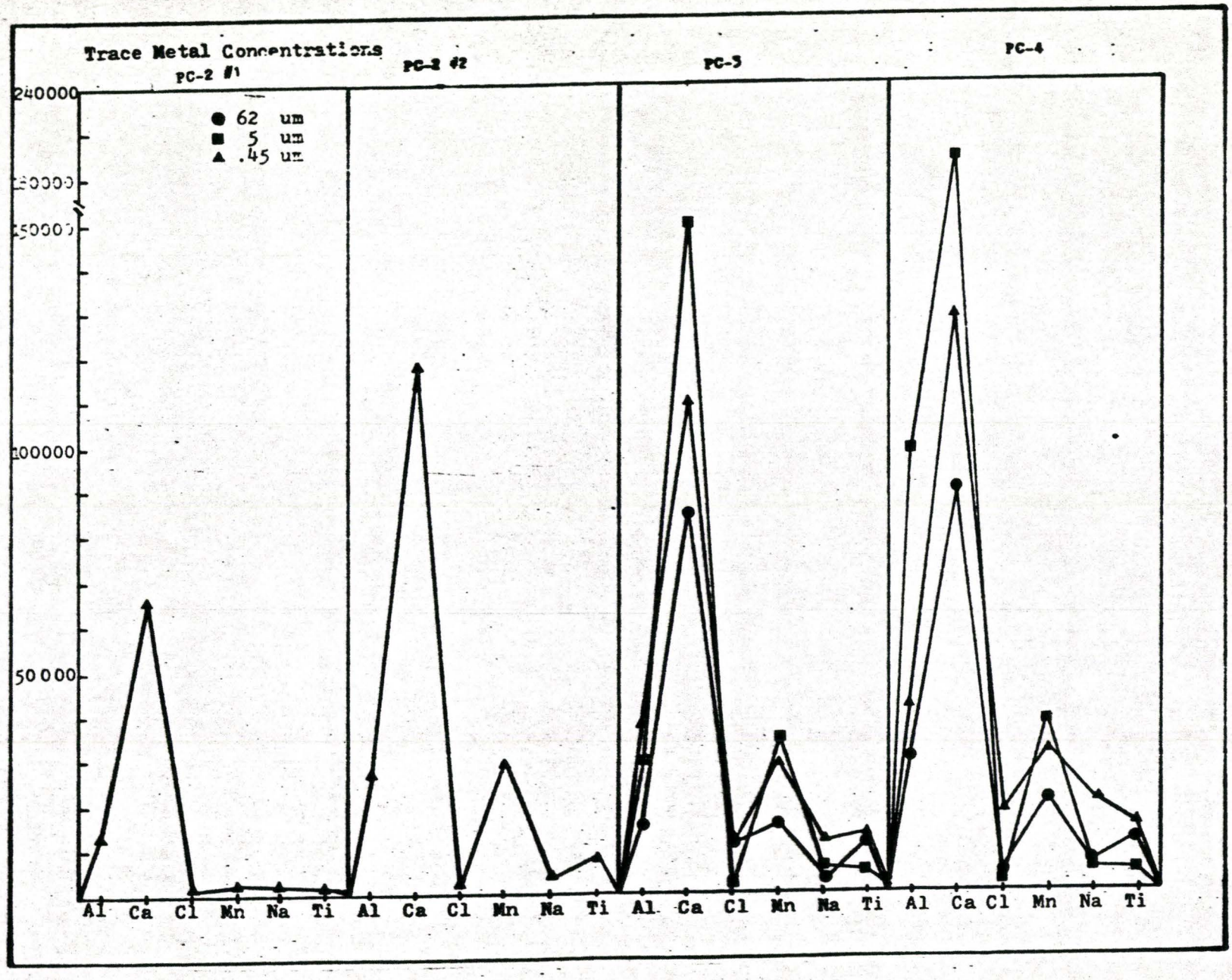
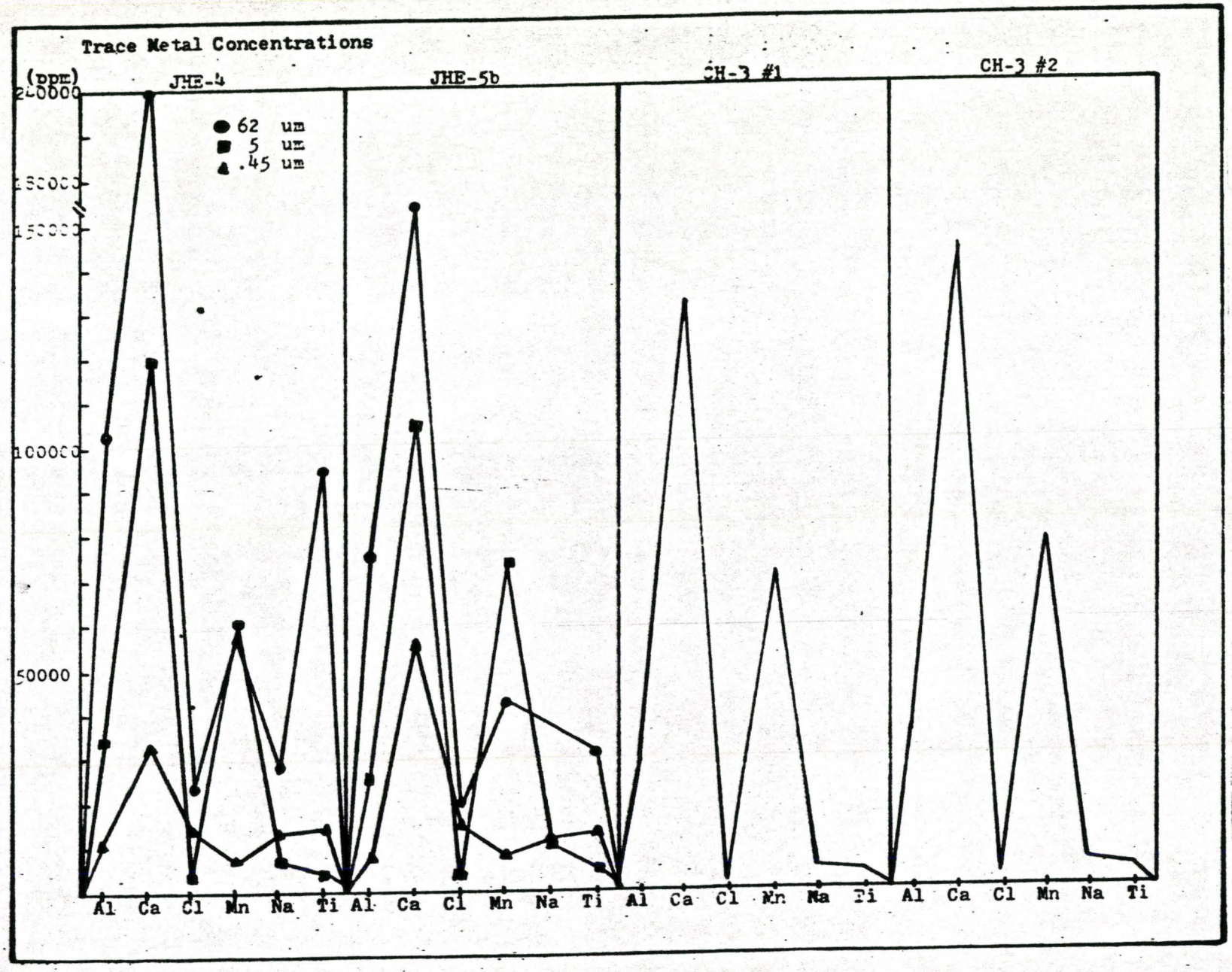
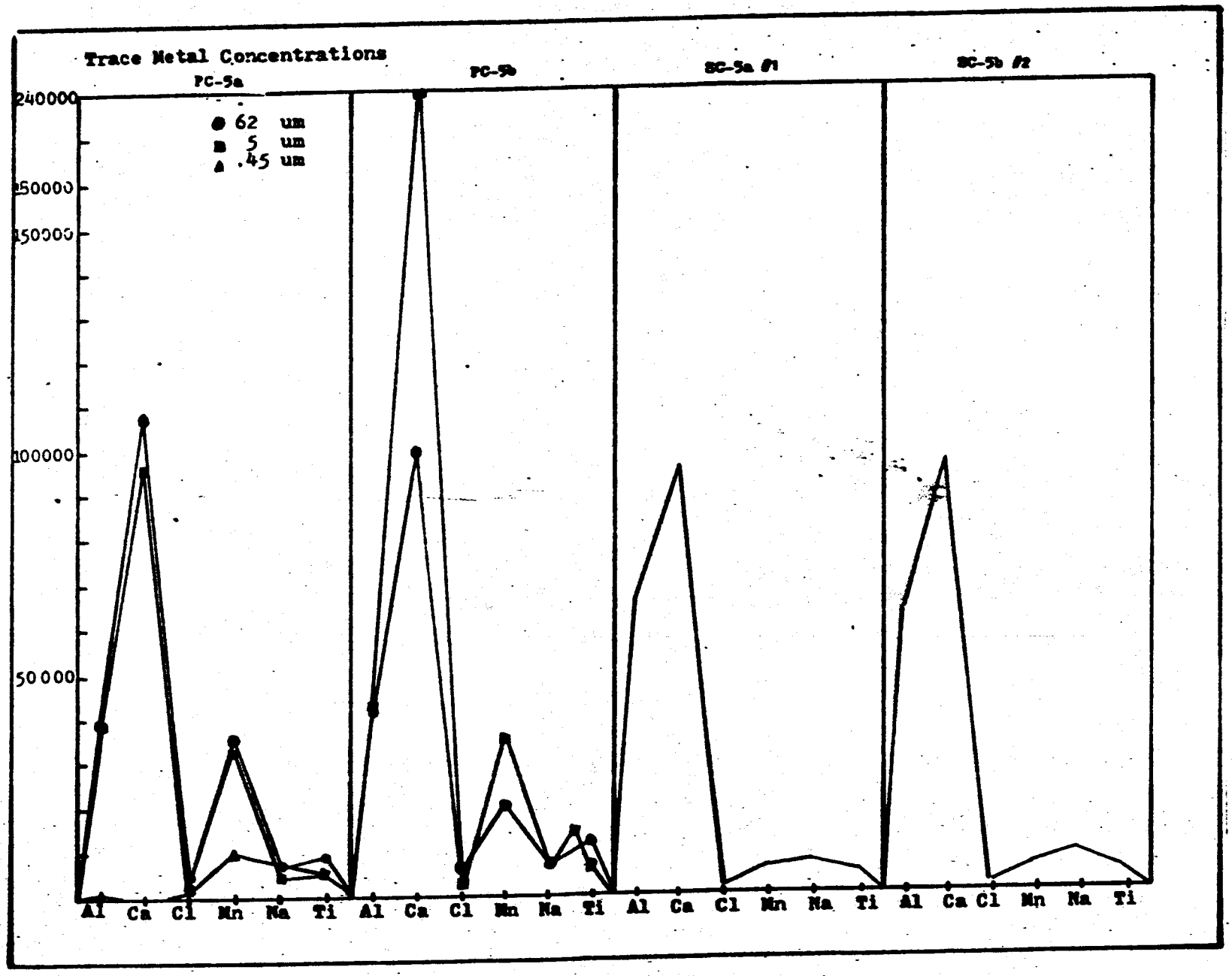
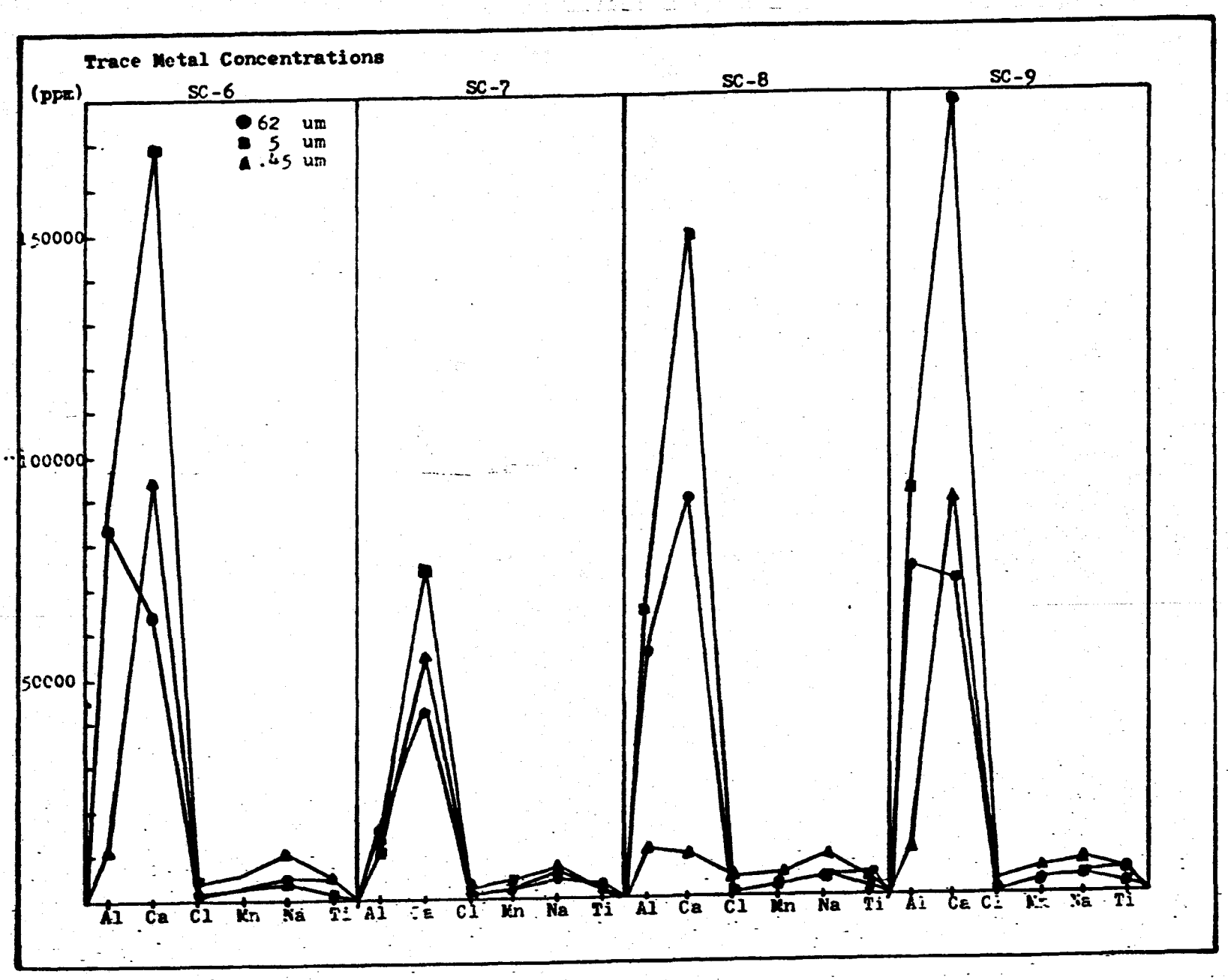
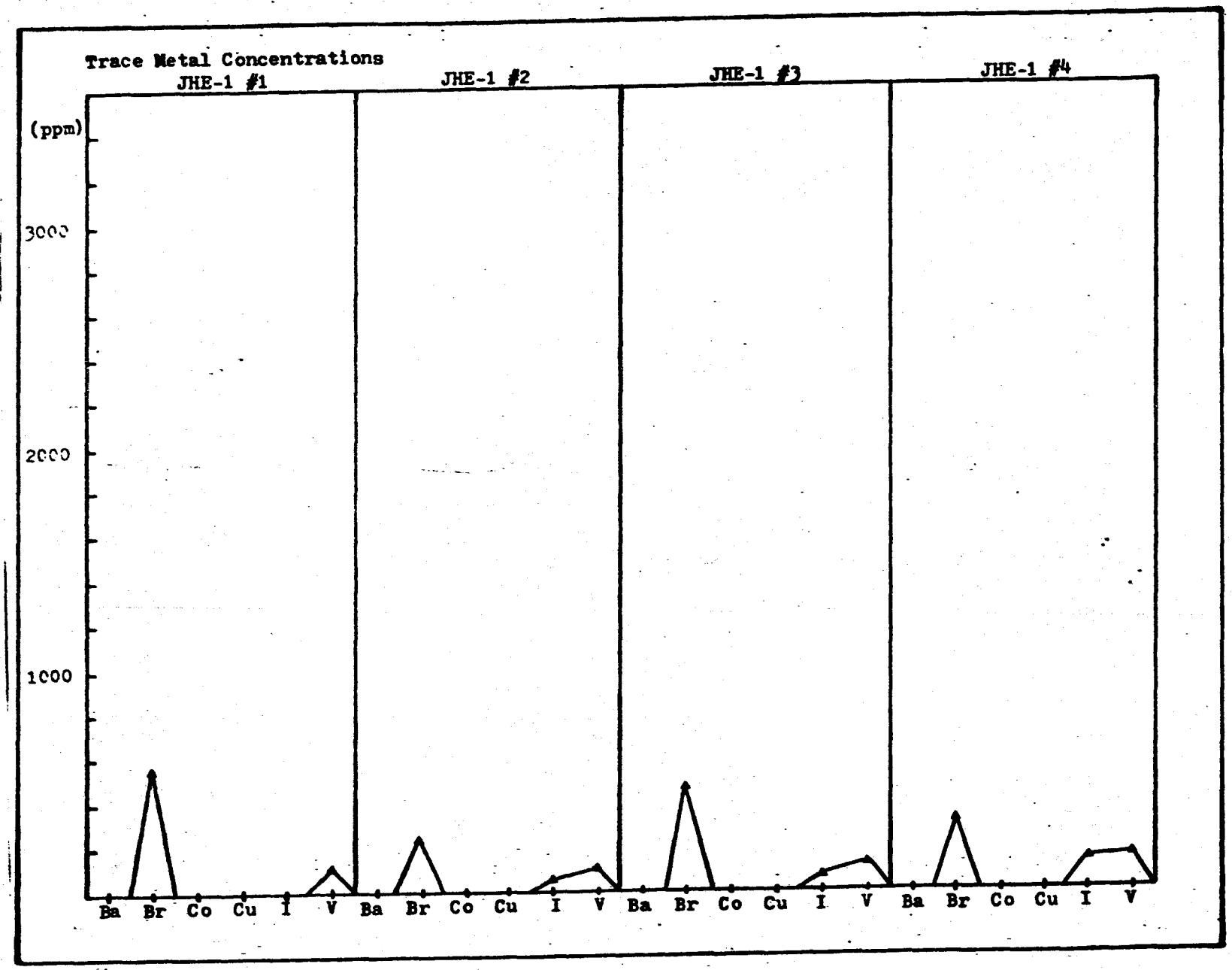
CH-4
CH-5a
CH-6
CH-8
(ppm)
62 um
5 um
.45 um
150000
100000
50000
Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti

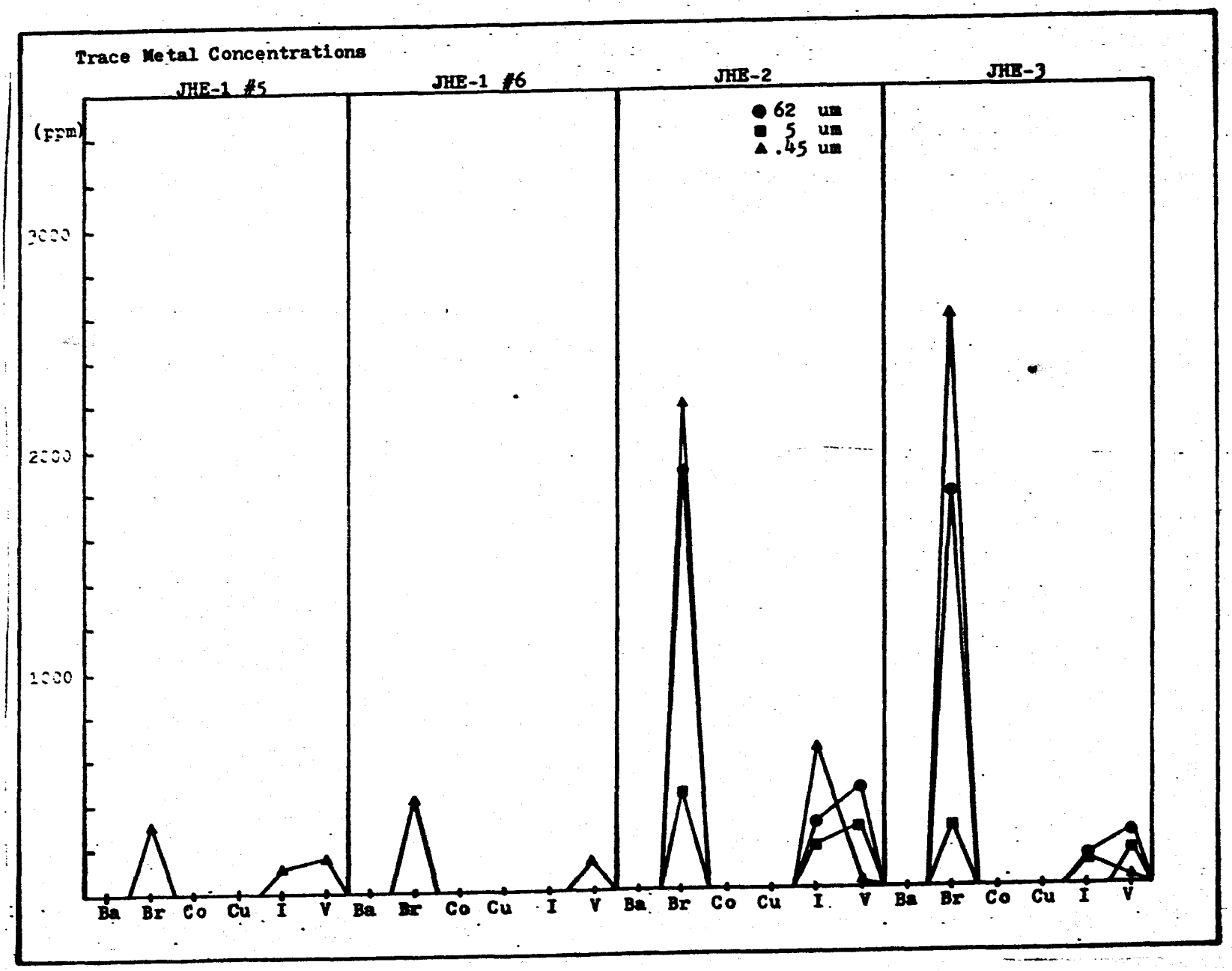

Trace Metal Concentrations
PC-2 #1
PC-2 #2
PC-3
PC-4
● 62 um
■ 5 um
▲ .45 um
240000
50000
200000
50 000
Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti

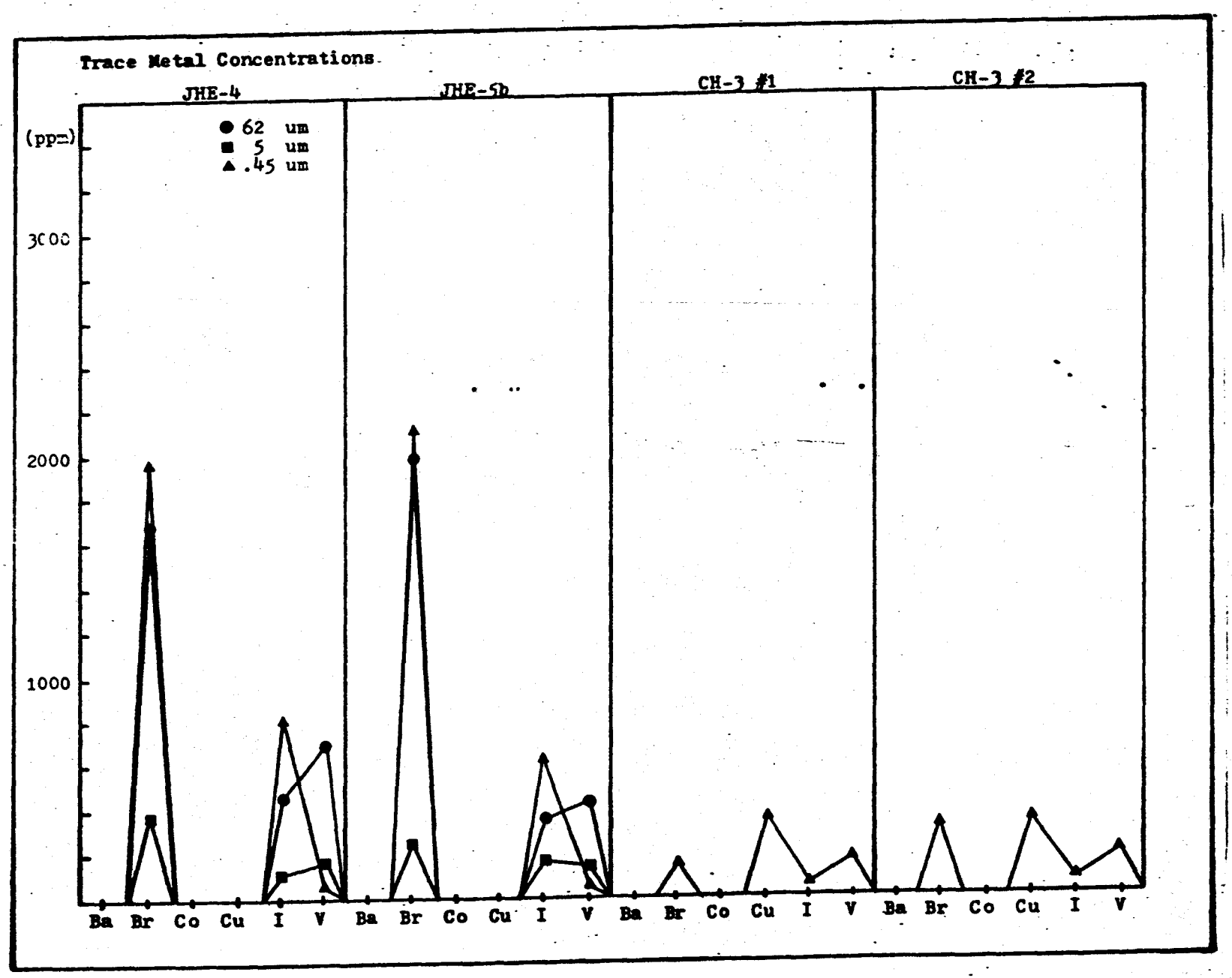

Trace Metal Concentrations
(ppm)
JHE-4
JHE-5b
CH-3 #1
CH-3 #2
62 um
5 um
.45 um
200000
150000
100000
50000
Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti

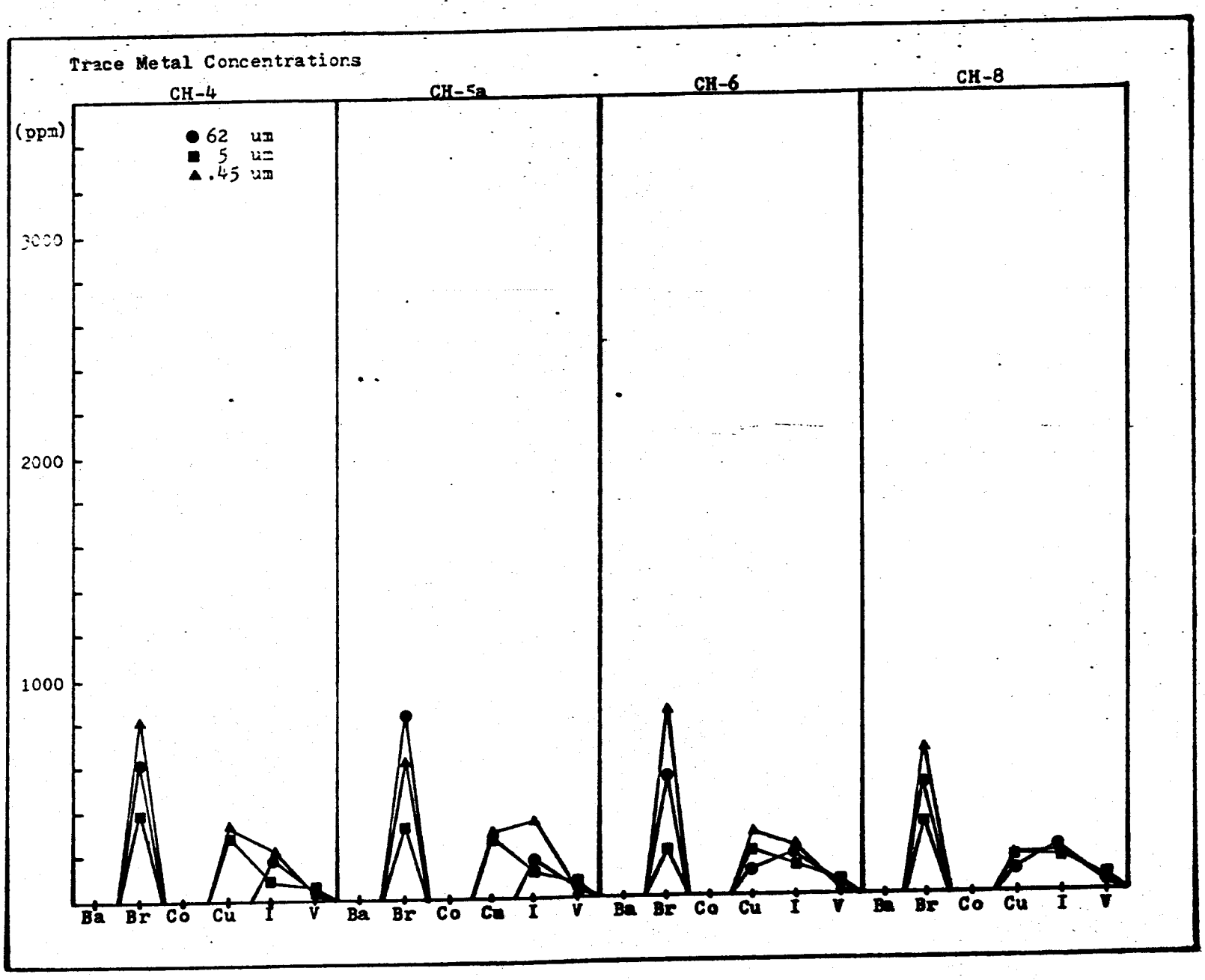

Trace Metal Concentrations
PC-5a
PC-5b
SC-5a #1
SC-5b #2
62 um
5 um
.45 um
240000
150000
100000
50000
Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti

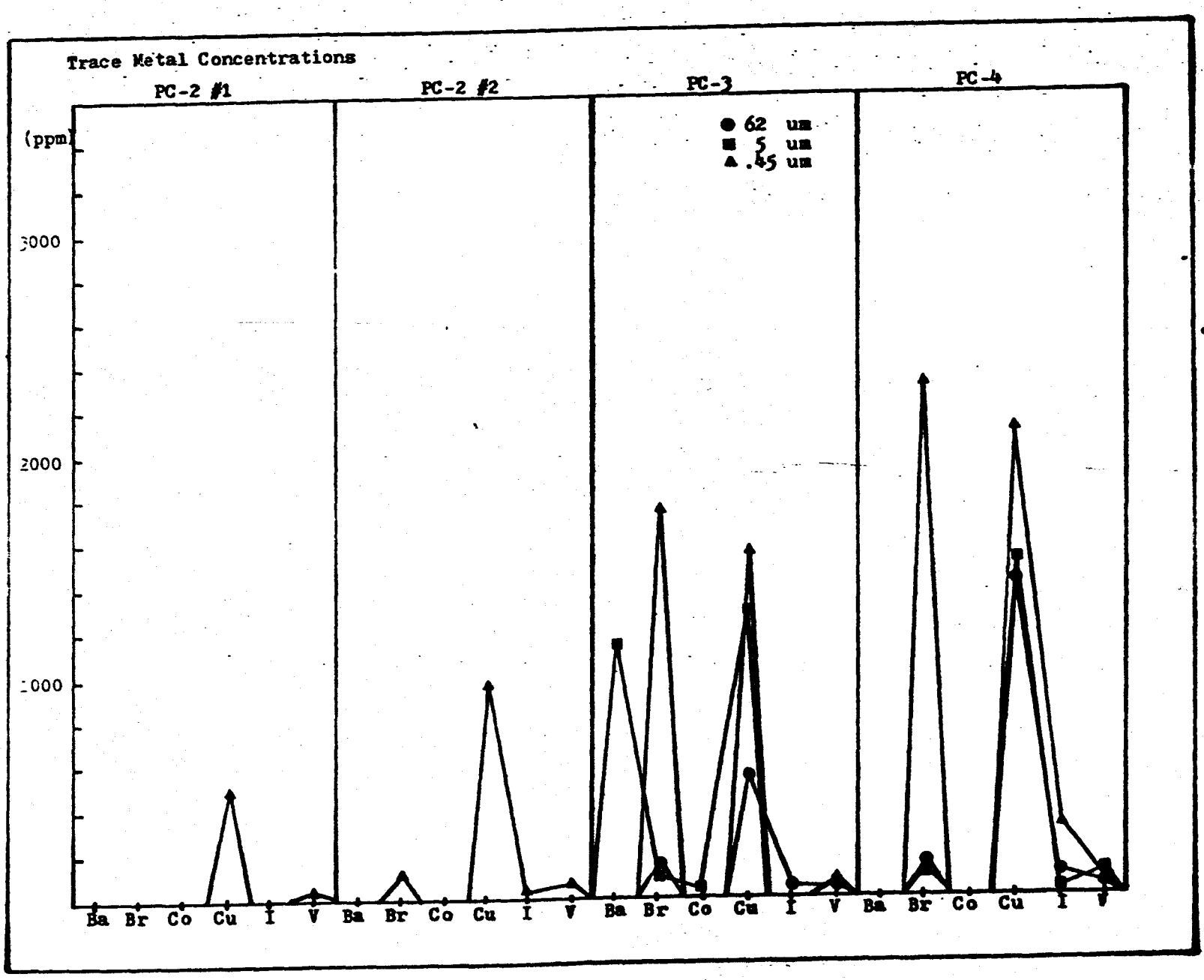

Trace Metal Concentrations
(ppm)
SC-6
SC-7
SC-8
SC-9
62 um
5 um
.45 um
150000
100000
50000
Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti Al Ca Cl Mn Na Ti

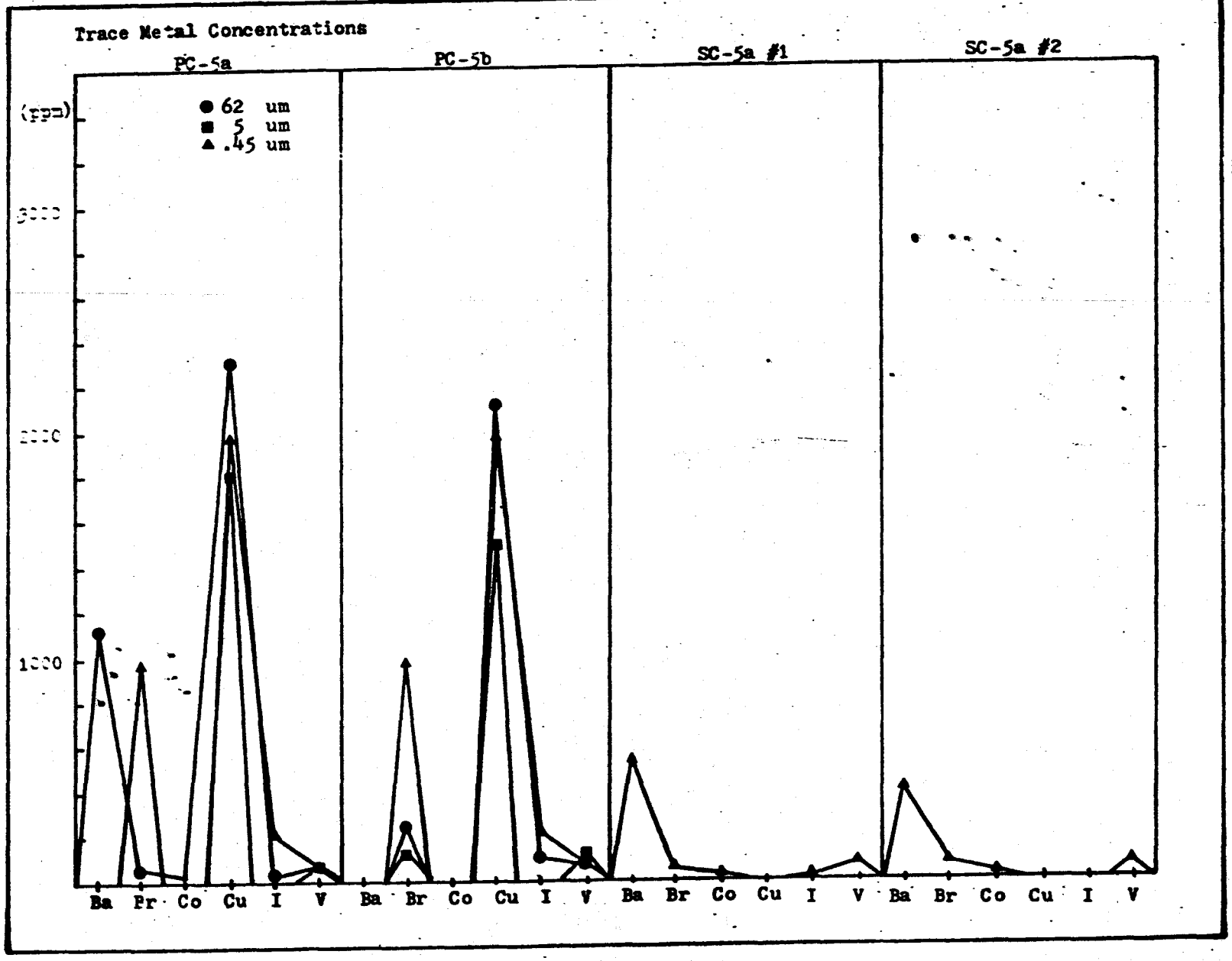

Trace Metal Concentrations
JHE-1 #1
JHE-1 #2
JHE-1 #3
JHE-1 #4
(ppm)
3000
2000
1000
Ba Br Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V

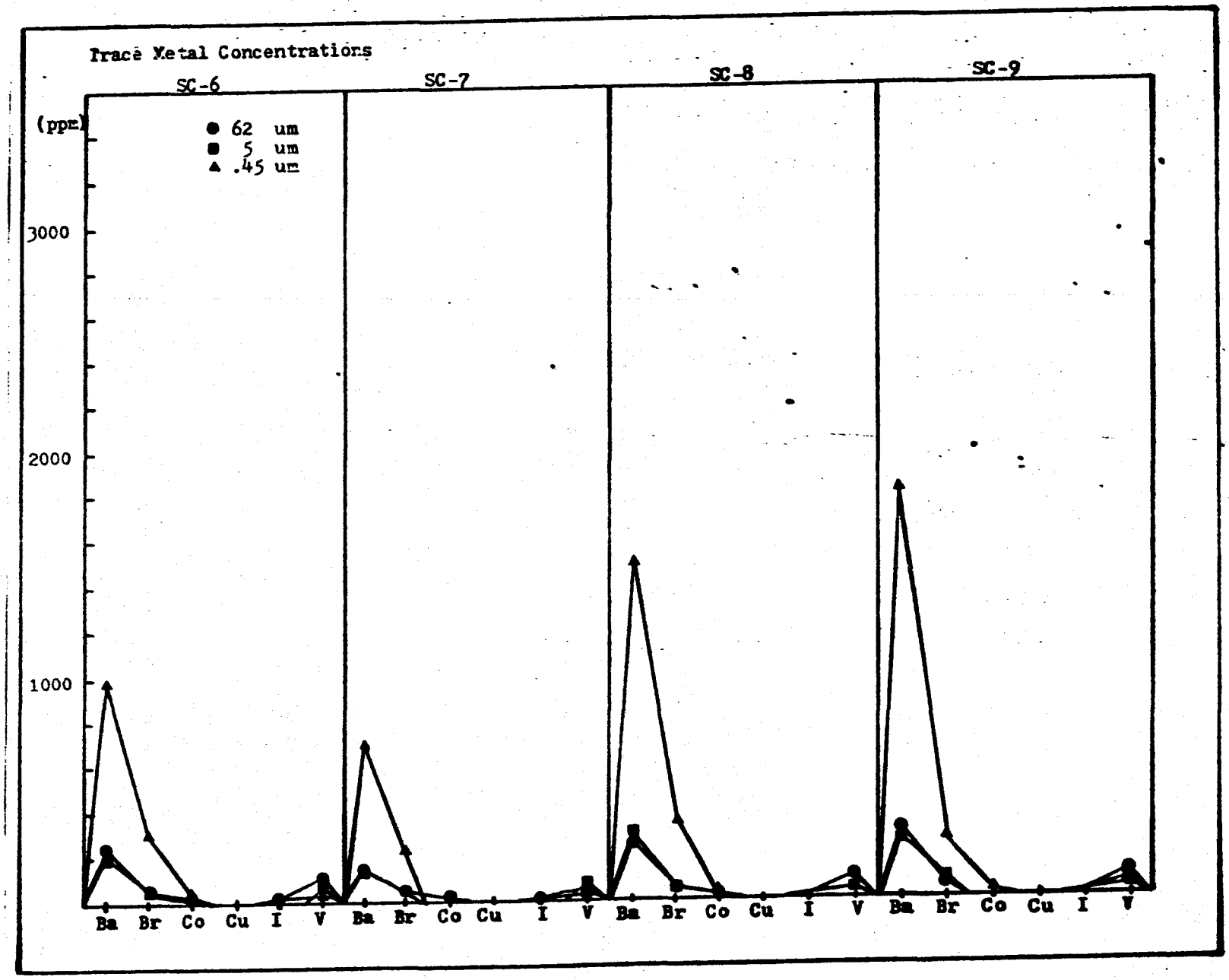

Trace Metal Concentrations
JHE-1 #5
JHE-1 #6
JHE-2
JHE-3
(ppm)
62 um
5 um
.45 um
3000
2000
1000
Ba Br Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V


Trace Metal Concentrations
JHE-4
JHE-5b
CH-3 #1
CH-3 #2
(ppm)
● 62 um
■ 5 um
▲ .45 um
3000
2000
1000
Ba Br Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V


Trace Metal Concentrations
CH-4
CH-5a
CH-6
CH-8
(ppm)
● 62 um
■ 5 um
▲ .45 um
3000
2000
1000
Ba Br Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V


Trace Metal Concentrations
PC-2 #1
PC-2 #2
PC-3
PC-4
(ppm)
3000
2000
1000
62 um
5 um
.45 um
Ba Br Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V


Trace Metal Concentrations
PC-5a
PC-5b
SC-5a #1
SC-5a #2
(ppm)
● 62 um
■ 5 um
▲ .45 um
3000
2000
1000
Ba Pr Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V


Trace Metal Concentrations
SC-6
SC-7
SC-8
SC-9
(ppm)
● 62 um
■ 5 um
▲ .45 um
3000
2000
1000
Ba Br Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V Ba Br Co Cu I V