

EFFECTS OF COAL BURNING IN NEW MEXICO
ON AIR QUALITY AND SURFACE WATER QUALITY:
RATON STUDY AREA

Technical Completion Report
Project No. 1345656

EFFECTS OF COAL BURNING IN NEW MEXICO ON AIR QUALITY
AND SURFACE WATER QUALITY: RATON STUDY AREA

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ABSTRACT

The phenomenon known as "acid rain" has focused attention on the possible adverse effects on air and water quality that may be a consequence of the increased demand for electricity and concomitant increase in coal burning. Population migration to the "sunbelt" coupled with large, strippable coal supplies has the potential to put more demands on a limited water supply and decrease the quality of life that is enjoyed in the Southwest. In this study, we have attempted to evaluate local effects of a small, coal burning power plant in Raton, New Mexico, on air, precipitation, soil, and surface water. Much of the work has involved establishing the methodology for such an evaluation which should prove extremely useful in similar evaluations of the effects of much larger regional facilities. The presence of precipitation with pH values lower than predicted for rain influenced only by carbon dioxide has been established. The effects of the lower pH values are masked by the neutralization capacity of regional airborne particulates. The presence of fly ash in the air and precipitation has been verified. No adverse environmental effects were noted in the study area.

Keywords: aerosols, air pollution, chemistry of precipitation, fly ash, heavy metals, precipitation (atmospheric), rain water, soil chemistry, trace elements, water chemistry

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I. INTRODUCTION

The purpose of the research has been to evaluate the environmental consequences of coal burning in the Raton, New Mexico, area with regard to precipitation chemistry and to estimate potential long term effects on surface water quality and air quality. The fly ash and sulfur dioxide produced may travel great distances before settling or washing out and may present health and ecological hazards. Acid precipitation has not been documented adequately in the Southwest and preliminary data indicate it may be a problem. Aerosols have been collected and analyzed directly to determine their characteristics including distribution and heavy metal content. Precipitation samples have been collected and analyzed to determine pH, metal content, and associated chemistry. Surface water systems and soil in the proximity of the plume have been analyzed to ascertain the effects of both wet and dry deposition in the vicinity of the power plants. Study of the effects of this small power generating facility may allow comparison for modeling when contrasted to the much larger power plants in northwestern New Mexico. The relationship of the city of Raton to the Four Corners area and other areas of the state is shown in Figure 1.

The larger problem to be studied is to ascertain the potential and present effects of large scale coal combustion on New Mexico's air and surface water quality. The 1978 combustion of coal in the Four Corners area was more than 7 million tons (National Coal Association, 1978) and as a result of the current energy picture, it will be necessary to utilize more coal-produced energy. This increased dependence on coal necessitates a thorough study of the long term effects.

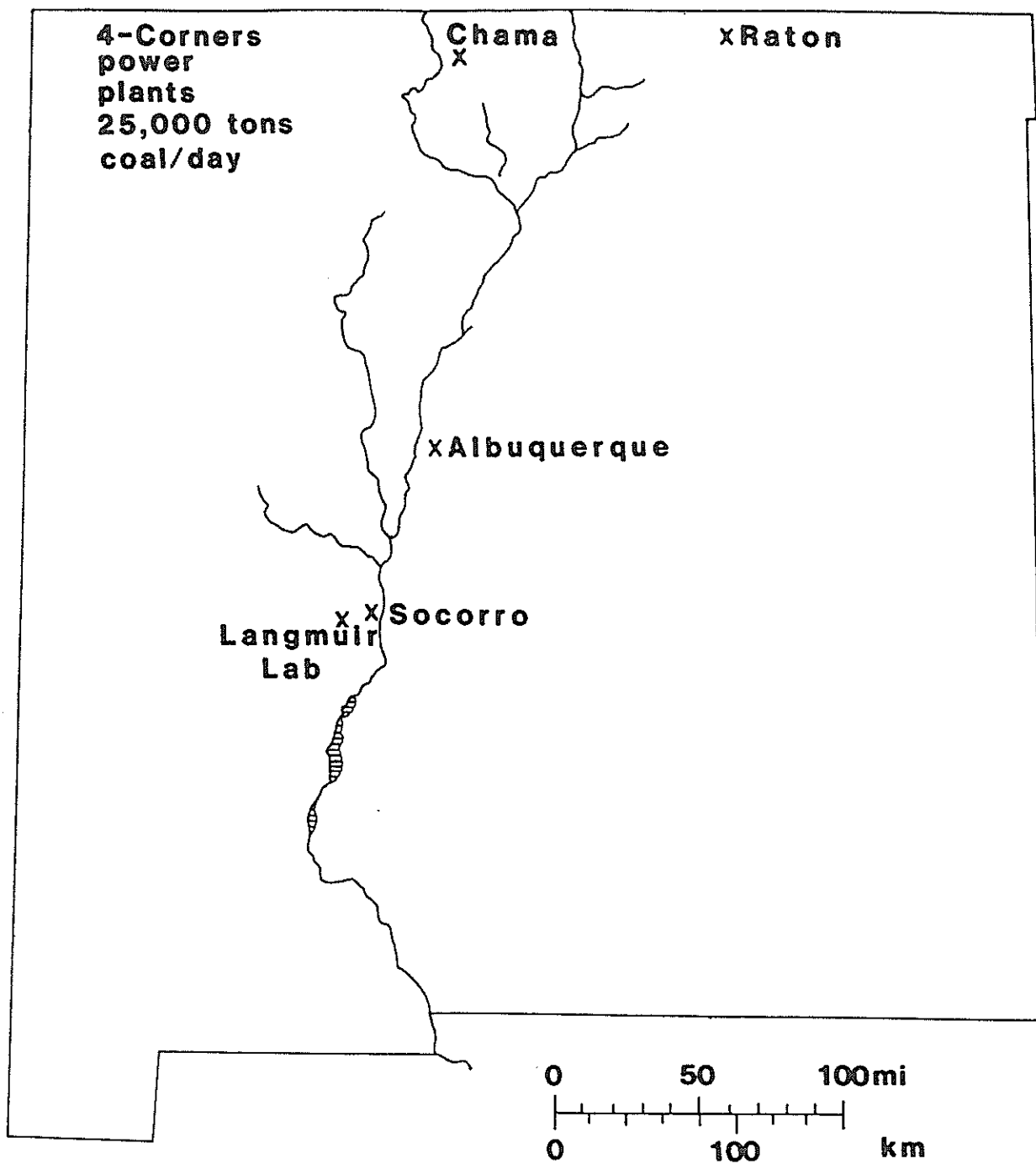


Figure 1. State Map of Sample Region.

The coal-burning facility studied at Raton is operated by the Raton Public Service Company. This facility burns approximately 25,000 tons of coal per year with a heat content of 11,500 BTU/lb (all data from Raton Public Service Company). This is equivalent to one day's capacity at the Four Corners area. Power plant capacity is 7,500 kilowatts with an average production of 5,000 kilowatts. The service area is about 25 square miles with 3,800 hook-ups. Fly ash is recirculated through the stoker and precipitated using a cyclone-type collector. The coal used has a low ash (~11 percent) and sulfur (~.7 percent) content which appears to contribute greatly to the operating efficiency. The basic plant was constructed in 1926 with two 750 KW units on line in 1927, a 1,875 KW unit was added in 1937, a 3,500 KW unit in 1947, and a 7,500 KW unit in 1972. The latter is the primary unit and is equipped with the pollution control equipment described.

Preliminary examination of the study area and discussion with Raton Public Service indicated that there was no apparent degradation of air quality from the standpoint of visibility as has occurred in recent years in the upper Río Grande Valley areas such as Santa Fe and Los Alamos. It is likely that the efficiency of the Raton power plant coupled with its small size may allow for sufficient dilution of particulates.

The project objectives are:

- (1) to survey the chemical nature of precipitation (both rain and snow) in the Raton area;
- (2) to determine the rate of aqueous leaching of components associated with the aerosols and fly ash;

- (3) to collect data available on elemental analysis of coal and fly ash used and generated in the Raton power plant and to determine the average density of fly ash particles both in the atmosphere and in surface soil and streams; and
- (4) to determine the chemical composition and physical nature and regional distribution and concentration of aerosols generated in the Raton power plant.

In addition, it was hoped that the proposed work would provide experience on the identification of fly ash in the New Mexico environment. Previously published data (McCrone and Delly, 1973) on identification with the energy dispersive X-ray analyzer have shown convincingly that this is possible. It is possible also to identify fly ash as a function of fuel type (e.g. oil, cellulosic, or coal fuels), and as a function of boiler configuration and flame temperature using the scanning electron microscope. In addition, elemental analysis of the major constituents usually are sufficient to identify the source (Wangen, 1976). Confirming data would be obtained using neutron activation analysis.

Acid rain has become a serious concern both on a global (Kerr, 1979) and national scale (Likens, 1976). The pH of rain would be 5.6 if it were controlled solely by carbon dioxide dissolution. Serious ecological problems occur when pH values drop much below 5. Although the neutralization capacity of water and soil in the study area is quite high (i.e. the soils and waters are generally alkaline with the exception of high mountain samples), the flora and fauna have adapted to the alkaline environment. It is not clear what the effect of lowered pH would be under such conditions, but it is probable that organisms would have difficulty adjusting.

Data from surface water studies (Brandvold, Brierley, and Popp, 1979; Brandvold and Popp, 1979; Dauchy, 1976) indicated that heavy metals in New Mexico surface waters may be higher than expected based on point and nonpoint source contamination. It is possible that the heavy metals enter the atmosphere from coal combustion and ultimately enter surface waters. This especially may be true of mercury which escapes coal-burning facilities almost undiminished in concentration (Klein, 1975; Block, 1976).

In a recent article (Handler, 1979), Philip Handler, president of the National Academy of Sciences, comments on the status of research in the United States. He notes that many basic processes -- photosynthesis, denitrification, mineralization, and so on -- are understood at the primary level. However, they are not understood in the gross dimensions of real concern which are the large-scale exchanges and fluxes that may be beneficial or injurious to the environment. In his discussion of the environment he lists six major subjects demanding examination:

- (1) cleansing of the atmosphere by forests and other natural and managed vegetation;
- (2) impoverishment of soils caused by acid precipitation;
- (3) influence of precipitation on the quality of lakes and streams, and the alterations in aquatic vegetation and fauna caused by deposition of acid substances;
- (4) increases in the abundance of heavy metals in food crops and natural food chains as a result of direct deposition from the atmosphere and mobilization in soils due to acid precipitation;

- (5) the fates of volatile pesticides and other chemicals used in agriculture and forestry; and
- (6) substances and processes involved in atmosphere-biosphere exchange.

Topics numbered 1, 3, 4, and 6 are addressed in this report.

Products of coal combustion include organics such as polyaromatics, oxides of sulfur, carbon and nitrogen, gaseous forms of some elements, and particulate emissions of an inorganic nature. These particles contain varying amounts of the constituents of the original coal including heavy metals. A major portion of the particulate matter is removed by devices such as electrostatic precipitators and scrubbers. However, a large percentage of the smaller-sized aerosols which escape are washed out by precipitation. Precipitation may be the most important mechanism of removal of small aerosols ($<5\mu$) released. These particles also tend to have the highest concentration of volatile, adsorbed trace metals (Muhlbaier and Zoller, 1979). A portion of the larger particles also is released and these particles tend to deposit close to the power plant. These larger particles tend to be lower in elements of concern than the original coal and outside of aesthetic problems are at present of minimal concern (Cannon and Swanson, 1975; Storjan and Turner, 1977). The small particles, however, have been found to be enriched in a number of elements (Natusch, 1974; Kaabinen, et al., 1975; Davidson, 1974; Muhlbaier and Zoller, 1979; Klein, 1975; Lee, et al., 1975; Block and Dams, 1976; Coles, et al., 1979; Smith et al., 1979). The elements most frequently mentioned as being concentrated are arsenic, cadmium, copper, lead, molybdenum, selenium, and zinc, although individual studies

have implicated other elements. These smaller particles may travel great distances before settling out or coming down with precipitation. Also a few elements such as mercury, selenium, arsenic, and cadmium are emitted at least partially in gaseous form (Klein, 1975; Crocket and Kinnison, 1979). The ultimate fate of these is unknown.

The amount of fly ash escaping stack-capturing devices generally varies in the region from 1-3 percent or about 0.1 percent of the mass of coal burned (Klein, 1975). These airborne particles which escape range in the 40 μm and less size category (Davison, 1974). In the case of many of the trace metals, the concentrations are much higher as the size of the particle decreases (Davison, 1974; Muhlbaier and Zoller, 1979; Klein, 1975). Examples from the literature are shown in Table 1 (Klein, 1975).

<u>Element</u>	<u>Conc. in Coal</u>	<u>Conc. in Slag (Bottom Ash)</u>	<u>Conc. in Outlet Fly Ash</u>
As	4.5	18	440
Ba	65	500	750
Cd	0.47	1.1	51
Mn	34	295	430
V	29	260	1180
Zn	46	100	4900

Table 1

Selected Metal Concentrations as Coal is Reduced to Ash.

Concentrations in ppm

Little was known regarding the nature and distribution of aerosol emissions from the Raton Public Service power plant. Limited data is available regarding the chemical components in the coals which provide

the fuel (Swanson, 1976). There is also limited data available on the fly ash (Swanson, 1976) and the trace elements extractable from the fly ash (Dreesen, et al., 1977). A comprehensive survey of fly ash from the Four Corners power plant and effects on local soils and waters was performed by Wangen and Weinke (1976). Their summary remark regarding water quality was that insufficient data exist to draw quantitative conclusions concerning trace element concentrations.

The increased use of coal in the future makes investigation of the aerosols imperative as to environmental consequences. Using a figure of New Mexico coal usage in 1980 as 10^{10} kg, a mercury content of the coal as $0.2 \mu\text{g/g}$ and a conservative removal percentage of 50, approximately 1,000 kg of mercury alone may be emitted, and subsequently deposited on important watersheds. If a power plant burns 2.5×10^4 tons of coal/day (an average for a 2,000 MW plant such as the Four Corners power plant--Data from Public Service Company of New Mexico) and if the coal has a concentration of $0.2 \mu\text{g/g}$ of mercury, the amount of mercury present is 10 lb and anywhere from 2,190-3,285 lb (60-90 percent) is lost to the atmosphere on a yearly basis. All of these calculations need to be scaled considerably to the Raton power facility.

The deposited fly ash often contains some elements in a very soluble form that is easily leached (Cox, et al., 1978; Dreesen, et al., 1977) such as boron, molybdenum, fluorine, selenium, arsenic, and cadmium. These elements and others could be concentrated on watersheds and ultimately be further concentrated in bodies of water and biomagnified in aquatic life.

Anderson reports (1978) that the San Juan Basin contains 6.3 billion tons of strippable coal. About 20 percent of this would be lost during

mining and preparation, leaving about 5 billion tons of coal that could be utilized. At the current nominal use rate of about 7.6 million tons/year, this coal supply would last about 700 years. At the current atmospheric emission rate of about 0.2 percent of the coal burned (Wangen, 1976), about 10^7 tons of atmospheric fly ash would be generated over the 700 year period. Aerosols of the type currently eluted into the atmosphere have about a 2 percent toxic metal content. This means approximately 200,000 tons of toxic metals would be introduced into the atmosphere in highly respirable form during the life of the strippable coal reserve. Part of the purpose of this work has been to add to the data base needed to predict the effect of the 200,000 tons of heavy metals on the air, waters, and soils of New Mexico.

II. METHODS

A. Sample Sites, Sampling, and Sample Handling

The area around Raton and the location of two of the surface waters sampled, Lake Maloya and the Canadian River, are shown in Figure 2. The Vermijo River is not shown and is a tributary of the Canadian River upstream. The TO Ranch Pond, located about 16 km west of Raton was also sampled. Surface water samples were collected as grab samples using a polyethylene bucket. The pH and carbonate concentrations were determined in the field using an Orion Model 407 pH meter and a Hach Carbonate/Bicarbonate Titration kit. The samples were then placed on ice for return to the laboratory.

Soil samples were collected at Lake Maloya and in a radial pattern around the power plant. Sample sites in proximity to the power plant are shown in Figure 3. Surface samples were collected at a number of random places at each site and stored in polyethylene whirlpack bags. A soil auger was used to collect samples at a depth of approximately 15 cm. As with the surface samples, a number of samples were collected in a single bag. The soil samples were crushed and split in the laboratory with a riffle splitter. Portions of the samples were digested in Teflon beakers using hydrofluoric and nitric acids followed by perchloric acid. The ratios were approximately 1 g of solid and 5 ml each of the acids.

Samples of particulates in the air were obtained on 8 x 10 inch .45 micron Gelman glass fiber filters using a high volume air sampler manufactured by GCA Corporation. Air samples were obtained at the sites shown in Figure 3. The filters were analyzed microscopically by optical and scanning electron microscopy and also were subjected to leaching with distilled water.

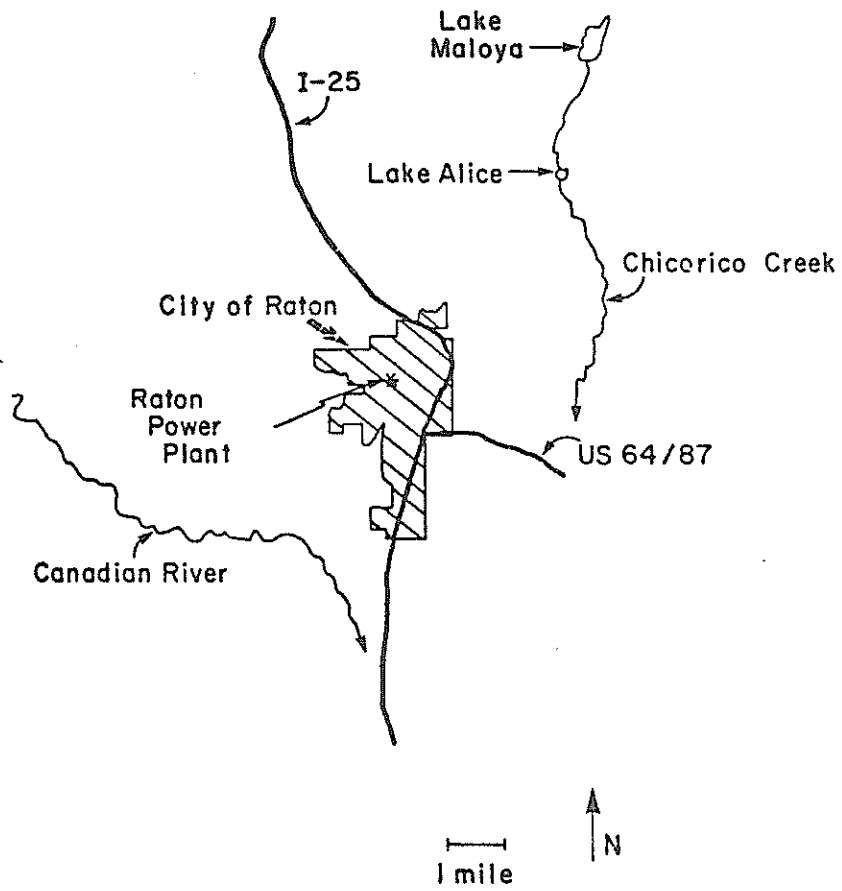


Figure 2. Overview of Raton Area.

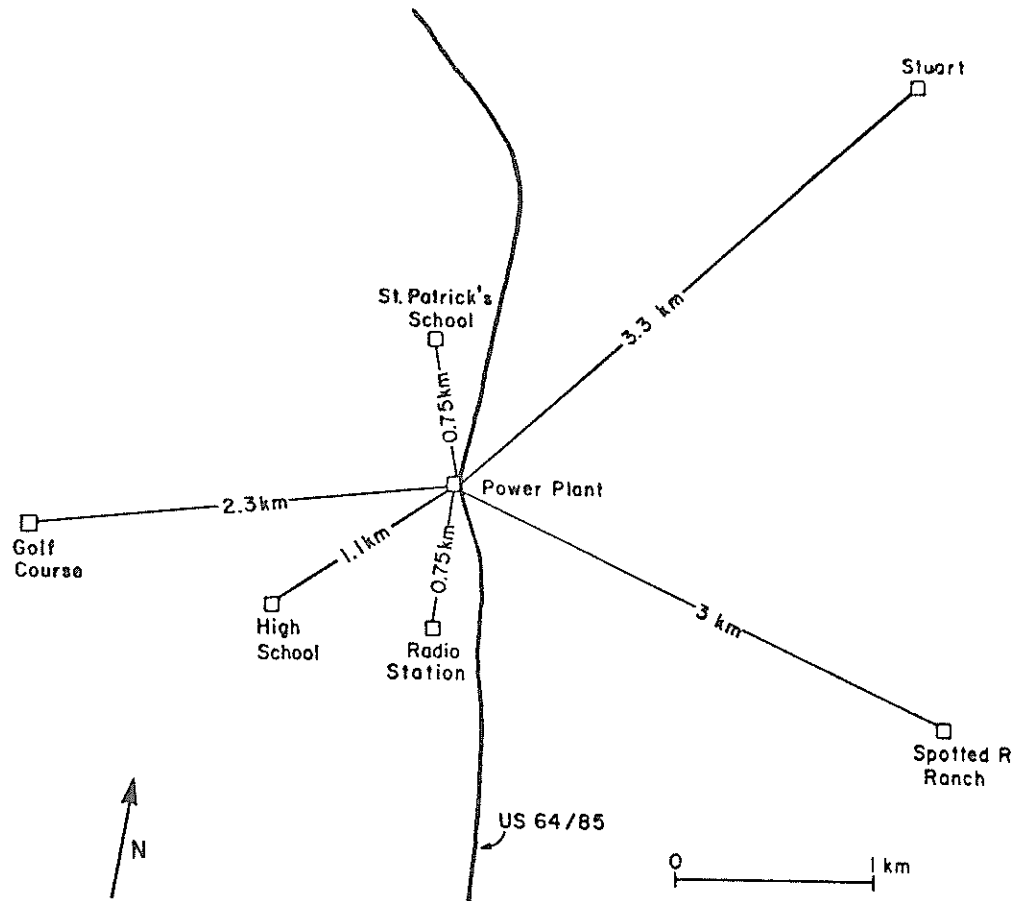


Figure 3. Raton Sample Site Distances to Power Plant.

Stack samples of particulates were obtained on 47 mm 0.45 micron glass fiber filters mounted in a stainless steel Gelman filter holder preceded by a water trap. Stack air was drawn through the filters using a portable vacuum pump. The sampling set-up is shown in Figure 4.

B. Precipitation Sampling

Wet deposition samples were collected in the study area from January 1980 through September 1981. Both snow and rain samples were collected because, commonly, winter temperature inversion conditions

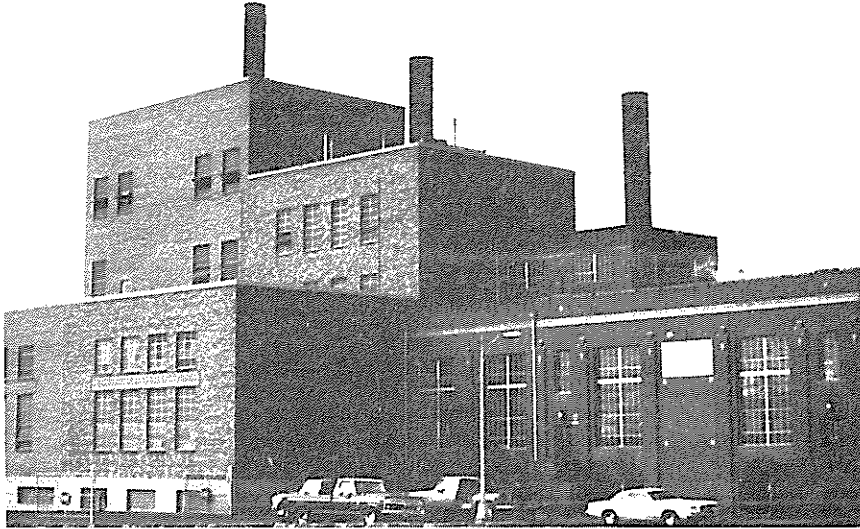


Figure 4a. Raton Power Plant. The Left Stack is the Principal Outlet and was the One Sampled.

could concentrate atmospheric pollutants at lower altitudes whereas summer conditions cause a good deal of atmospheric mixing to higher levels. Precipitation samples were collected with large plastic funnels which were only open when precipitation was falling in order to exclude air-blown dust which may contaminate the rain water (Popp, et al., 1982; Jensen, 1981). Bulk precipitation samples were collected using open funnels for comparison with rain-only samples. An automatic open/close rain sampler manufactured by Science Associates, Princeton, N.J., was used for a short period of time but the equipment broke down shortly after emplacement so its use was limited. The other closed collectors were opened manually before a precipitation event and rinsed

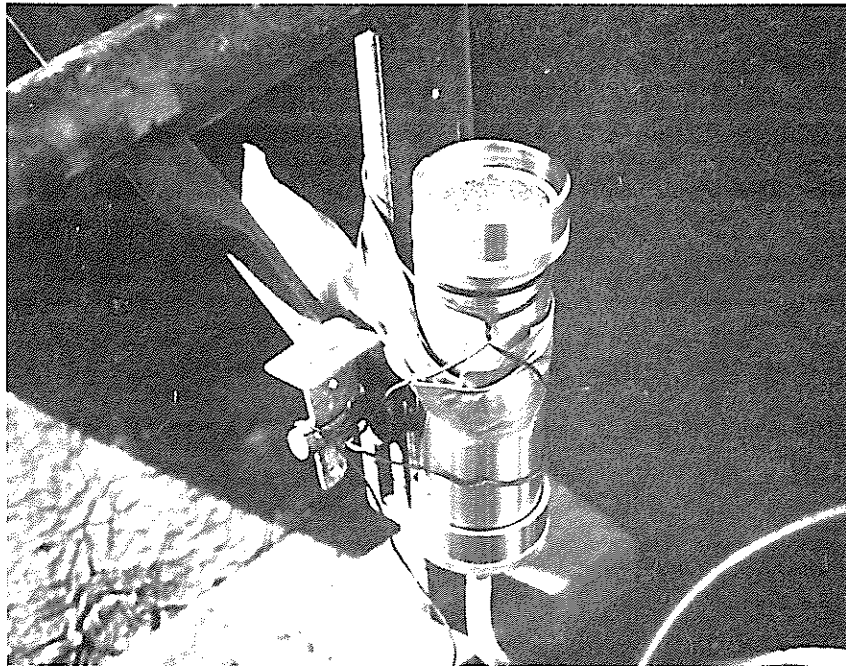
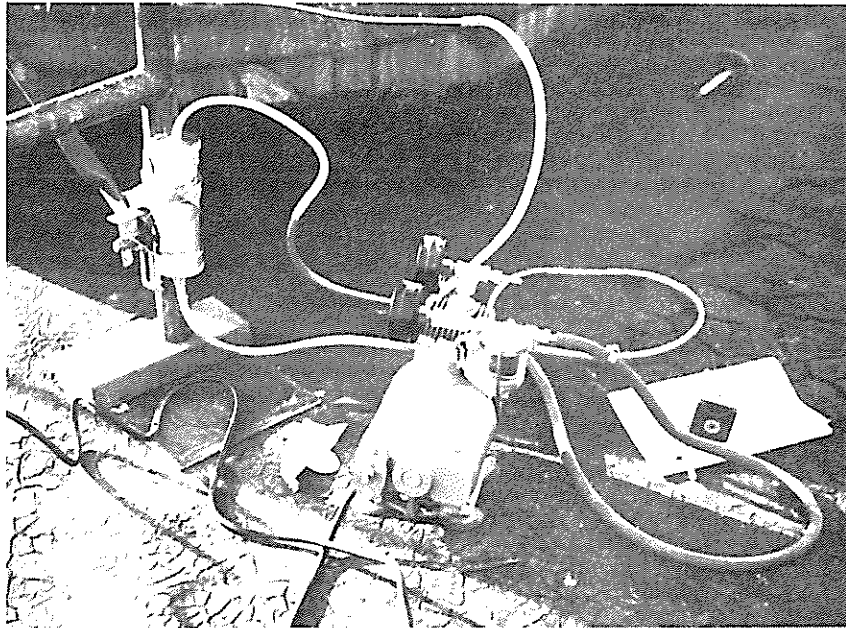


Figure 4b. Stack Sampling Apparatus Atop Power Plant Showing Vacuum Pump and Stainless Steel Filter Holder. Air was Drawn Directly from the Stack and Water was Condensed in a Cold Trap.

with distilled water before collection.

Sampling stations were located at Raton High School and at the Tracy Stuart residence in opposite directions from the power plant and detailed meteorological data was kept to determine wind direction, storm track, type of precipitation (i.e. thunderstorm or large frontal system and amount of precipitation).

Samples of wet precipitation and dry deposition on sticky tapes were collected by Mr. Tracy Stuart who lives in Raton and teaches chemistry at Raton High School. He cared for the wet precipitation samplers and collected air samples. The pH values of wet precipitation were taken immediately after collection using a glass electrode calibrated with two buffers. The samples were then filtered through 0.2 micron cellulose filters which stabilized the samples by preventing reaction with particulates (Popp, et al., 1982). The samples were placed in acid-washed polyethylene bottles, shipped to Socorro by bus and delivered to New Mexico Tech for sample splitting and analysis.

C. Water Chemical Analysis and Leaching of Fly Ash

Water analyses for general water chemistries and heavy metals were performed according to methods listed by the U.S. Environmental Protection Agency (1979) or in Standard Methods (1975). Leaching of fly ash samples was conducted using distilled water to determine the pH changes and other chemical effects of leaching. Fly ash was collected from the hopper at the power plant and split with a riffle splitter. A portion was digested in acid as described above (Sec. II. A) for A.A. analysis. Another portion (10 g) was stirred with both distilled water and 0.1 M hydrochloric acid for several hours and the leachate was analyzed by A.A.

The heavy metals were analyzed using both the HGA 2000 graphite furnace attachment to a Perkin-Elmer 403 atomic absorption spectrophotometer (A.A.) and a Perkin-Elmer 303 A.A. in the flame mode. Arsenic and selenium were determined using a Perkin-Elmer MS-10 hydride generator attached to the 403 A.A. Mercury was analyzed by the method of Hatch and Ott (1968) using a Coleman MAS-50 mercury analyzer.

Standard Reference Material fly ash (SRM 1633A) was analyzed to determine the accuracy of the analytical procedures and EPA standards were always run as analytical controls.

D. Aerosols and Dry Deposition

As previously described, high-volume air samplers were used for air analysis, and samples of soil were collected and examined as a function of depth. Water samples were collected from streams of minimum turbidity. Subsequent particulates collected on membrane filters were examined for the presence of fly ash among particulate washout.

Fly ash particles could be observed optically through a binocular microscope with 100X magnification giving the best results. Spherical particles to about 2 micrometers could be identified in this manner. When fly ash particles were found using 100X magnification, they were verified using higher magnification, usually 400X. Only spherical particles having little or no surface relief were identified as fly ash. The Particle Atlas (McCrone and Delly) was used to help identify these materials and aid in distinction between fly ash and other spherical material such as pollen. Particles identified as fly ash were analyzed using the energy-dispersive X-ray attachment to the SEM and

they proved to be alumino-silicate dominated material. The number of particles counted optically per sample ranged from zero to about 10. Because of the small number of fly ash counted, the mean average relative standard deviation is estimated to be at least 60 percent.

The lower resolution of the optical technique may have added to the uncertainty in particle identification. A counting analysis of over 50,000 particles has shown that the optical method of identification may not be entirely reliable, the probability of error being at least 75 percent using optical microscopy only. This error effect is probably due to the added apparent sphericity from the refraction of light. This effect is under further investigation.

In the actual counting of a slide optically, the slide was scanned in a television-type mode with the sample being moved back and forth. Each time a slightly different line of particles was observed. An observed particle was noted with a specific statement to an assistant, and the assistant would make a note in the laboratory record. After several thousand particles were counted in this manner, the record was reviewed with the total number of particles noted along with those which had been identified as fly ash.

A Hitachi HHS-2R scanning electron microscope equipped with an energy-dispersive X-ray unit was used to examine the particulates on various filters. The counting data from the scanning electron microscope were obtained directly from photographs. These photographs were obtained by focusing randomly on an area of interest. It was found that a magnification of 1000X allowed fly ash to be identified to about 0.7 micrometers, yet still showed a large enough field for a substantial number of particles to be found. Tracing paper was attached to the

photograph and each particle in the photograph was marked on the overlay. Fly ash particles received special notation. Master particle counts were then made directly from the traced overlays. Somewhat surprisingly, as different workers reviewed a photograph additional fly ash particles were almost always discovered. In some cases particle counts were doubled by careful inspection. This uncertainty of a factor of two seems to be present at each stage in the determination of fly ash number densities.

An arroyo soil sample from the Socorro area was determined to contain no fly ash particles. This sample was used as a control; it was periodically relabeled and given to the assistants making the optical counts. The assistants never found fly ash particles in this sample.

III. RESULTS AND DISCUSSION

A. Precipitation Sample Period and Sampling Conditions

Samples were collected over a 21-month period from January 1980 to September 1981 at Raton High School (RHS) and from February to September 1981 at the Stuart (STU) residence (see Figure 3). A total of 23 precipitation events were sampled at RHS with a closed collector open only during the event. Nineteen bulk samples were collected at RHS during this period while 15 bulk precipitation samples were collected at the STU site. Sample dates, precipitation amounts, and wind conditions are summarized in Table 2.

It should be noted that events often did not occur on the same day at RHS and STU sites even though they were only a few km apart. Because this type of sampling depends on the vagaries of weather, a relatively long sample period is necessary. The normal amount of precipitation for Raton is 41 cm/year and the total precipitation during this sampling period was 17 cm, so the period sampled represented below average precipitation. The 10.1 cm collected represents 59 percent of the available precipitation. It should also be noted that many of the events deposited only small amounts of precipitation so averages obtained on an event-only basis may underestimate the overall effect. This is discussed later.

B. Trace Metals in Precipitation

Fifteen trace metals were analyzed in the precipitation samples from the Raton area and the results are summarized in Table 3.

Perhaps the most evident conclusion that can be made from examination of the data is that there was surprisingly little difference between trace metal levels in precipitation collected in the closed funnel and those collected from the bulk precipitation samplers. If

<u>RHS</u>			<u>STU</u>		
<u>Date</u>	<u>Amount-mm</u>	<u>Wind (mph)</u>	<u>Date</u>	<u>Amount-mm</u>	<u>Wind (mph)</u>
1980: 1/15	6	NW			
1/16	1	NW			
1/19	1				no samples collected
3/19	1				until February, '81
4/24	25	NW(20-25)			
9/10	8				
9/11	8		2/27	4	S(10-15)
1981: 3/4	5	S(6)	3/4	12	N-NW(15-20)
-			3/12	4	SW
4/29	4	W-SW(10-25)	4/29		W-SW(10-15)
-			5/5	2	SW
5/17	1	E-SE(5-10)	5/17		E-SE(5-10)
-			5/20		S-SW(20-30)
5/29	1	N(5-10)	5/29		N(5-10)
5/30	1	N	-		
6/2	1	SW	6/2		SW
-			6/29		S(5-10)
7/3	5		-		
7/12	1		-		
7/16	1	NW(25)	7/16		NW(25)
7/17	1	NW(5-10)	7/17		NW(5-10)

Table 2. Summary of Sample Dates, Precipitation Amounts, and Wind Conditions. (continued on next page)

<u>RHS</u>			<u>STU</u>		
<u>Date</u>	<u>Amount-mm</u>	<u>Wind(mph)</u>	<u>Date</u>	<u>Amount-mm</u>	<u>Wind(mph)</u>
1981: 8/2	2	N-NE(10-15)	-		
8/7	2	N-NE(10-15)	8/7		S(5-10)
8/17	2	S-SE(5)	8/17		N-NW(5-10)
8/18	6	N-NW(5-10)	-		
-			8/28		N-NW(10-13)
9/4	12	var(5-15)	9/4		var(5-15)
9/6	6	var(5-15)	-		
-			9/13		N-NW(10-15)

Table 2. (continued from previous page)

metals were being leached from the particulate material entrained from regional sources (windblown dust), then levels in the bulk precipitation would be expected to be higher than those in the sampler which remained covered. This suggests that the metal levels attained in the precipitation were already present before the samples were collected or they would have increased with exposure to more dust in the open collectors.

The values obtained for the Raton region are quite similar to those obtained in the Socorro area in central New Mexico (Popp, et al., 1982) and may indicate a regional continuity for the distribution of trace metals. In other words, the presence of the power plant in Raton does not seem to influence the trace metal pattern. It should also be noted that the highest levels attained for the trace metals analyzed were for Al, Ba, Fe, and Mn. Except for Ba, the other metals are quite abundant

<u>Metal</u>	<u>Sample Site</u>		
	<u>Raton High School-Closed¹</u>	<u>Raton High School-Open²</u>	<u>Stuart-Open²</u>
Ag	0.8	4.0	1.9
Al	44	42	96
As	0.3	3.0	1.2
Ba	21	26	180
Cd	0.65	1.2	0.68
Co	1.0	3.6	2.7
Cr	0.9	1.3	1.9
Cu	8.4	9.6	25
Fe	40	44	390
Hg	0.4	0.2	0.2
Mn	29	77	50
Ni	1.8	4.1	3.3
Pb	1.7	4.4	6.5
Se	2.2	1.5	1.6
V	3.9	5.0	5.0

1. Closed means "precipitation only". The collector was covered between events.

2. Open is a bulk sampler, always open.

Table 3. Trace Metals in Filtered Precipitation Samples. Values in ppb.

in both soils and fly ash and are also easily leached by slightly acidic solutions because of their basic character. Aluminum is also relatively toxic at low levels and would be one element of concern should precipitation become progressively more acidic.

C. Fly Ash Analysis and Leaching of Fly Ash

There are two primary concerns regarding fly ash. One concern is the potential health hazard associated with the small, respirable material released into the atmosphere. The second concern is the potential for leaching of trace metals from fly ash both by precipitation and by surface water. This study has addressed only the leaching potential as it might affect surface water quality. It is difficult to estimate the contribution from the leaching of trace metals by precipitation because some metals are leached from atmospherically entrained soil and dust as has been discussed in Section B above. In order to estimate the potential for leaching trace metals from fly ash locally derived, samples of Raton Power Plant precipitator ash were leached both with distilled water and with 0.1 molar hydrochloric acid. The distilled water has a pH of 5.6 and approximates what would happen if a large amount of fly ash were in contact with precipitation. The pH of the distilled water leach solution rose to 7.7 indicating the basic nature of the fly ash. The hydrochloric acid represents a "worst case" in which the ash was exposed to very acidic precipitation. The pH of the HCl leach solution rose to 1.7 during the experiment. The case of precipitation which has a pH lower than 5.6 would be intermediate. The pHs of some of the precipitation events at Raton were as low as 4.0. The leaching data and fly ash analyses are shown in Table 4.

Comparison of the fly ash analyses for the Raton ash and the NBS standard can be made by examining Table 4. In general, the trace metal values are comparable in the two samples. Selenium, lead, and cadmium are considerably lower in the Raton ash while manganese is much higher.

Element	Raton Ash		Raton Ash Leach		NBS Ash	
	Dig.-ppm	Leach-H ₂ O(%) ¹	0.1 M HCl(%) ¹		Dig.-ppm ²	
Al	-	4,940	54,800		-	
As	150	17 (1)	45 (3)		130 (145)	
Cd	<.1	.007(.7)	.56(60)		15 (1.0)	
Cu	52	2.2 (.4)	127 (24)		108 (118)	
Fe	60,000	51 (<.01)	-		86,000 (94,000)	
Hg	0.17	.18 (11)	.28(16)		0.10(0.16)	
Mo	17	5.6 (3)	150 (88)		28 (29)	
Mn	1,150	.44 (.4)	3,760 (33)		200 (190)	
Ni	180	3.6 (2)	400 (22)		-	
Pb	2.8	1.6 (6)	25 (90)		60 (72)	
Se	1	2.2 (22)	2.7 (27)		11 (10)	

1. Values are micrograms extracted from 10 g of fly ash by 1ℓ of solvent therefore numbers are µg/ℓ or ppb. The percentage extracted is shown in parentheses.

2. Accepted NBS values in parentheses.

Table 4. Fly Ash Digestions and Leaching of Fly Ash

The percentages of various metals extracted in the leaching experiments are also shown in Table 4. The elements Cd, Cu, Mo, Mn, Ni, Se, and Pb were all extracted to a much larger extent in the acid solution than in the distilled water. Almost 100 percent of the available Mo and Pb was extracted by the acid. A large amount of Fe was also extracted by the acid which was evidenced by the brown color of the solution but the analysis was not run. These metals which are extracted to a larger extent in the acid solution are therefore the ones which may pose problems with acidic precipitation. The metals and Se were extracted to a significant extent with distilled water and may be potential problems at higher pH values. With the exception of As and Al, the trace metals extracted by the distilled water have concentrations which are remarkably similar to those found for the precipitation as shown in Table 3. This similarity suggests that the distilled water leach may simulate the precipitation leach quite closely. The As and Al values are the only metals analyzed which are much higher in the water leach than in the precipitation.

D. Soil Analysis

Soil samples were collected in the Raton vicinity at St. Patrick's School, Lake Maloya, the golf course, the radio station, and at Raton High School. Locations of the sample sites are shown in Figure 3 except for Lake Maloya which is located about 20 km northeast of Raton. The Lake Maloya site was chosen because it is relatively remote from Raton, is in the mountains at a higher altitude, and is the site of a major portion of the water supply for the city of Raton. Data for analysis of selected trace metals in the soil are shown in Table 5. Samples were collected from the surface of the soil and at a depth of approximately 15 cm. If the dry deposition of fly ash were significant, the surface

<u>Element</u>	<u>St. Pat's School</u>		<u>Lake Maloya</u>		<u>Golf Course</u>		<u>Radio Station</u>		<u>Raton High School</u>		Average ¹ Crustal <u>Abundance</u>
	<u>Surface</u>	<u>15 cm</u>	<u>Surface</u>	<u>15 cm</u>	<u>Surface</u>	<u>15 cm</u>	<u>Surface</u>	<u>15 cm</u>	<u>Surface</u>	<u>15 cm</u>	
Cd	0.43	0.32	0.25	0.24	0.33	0.72	0.65	0.25	0.15	0.15	0.15
Cu	6.9	9.5	8.2	5.2	5.2	10.6	3.18	5.5	5.0	50	50
Pb	130	32	12	110	39	94	8.6	33	9.2	13	13
Cr	32	30	7.0	14	19	4.0	7.0	7.0	27	100	100
V	166	76	56	110	110	190	70	105	115	110	110

1. Krauskopf, 1979

Table 5. Raton Soil Sample Analyses for Selected Trace Metals

soils could show higher levels of metals than the subsurface soils. This assumes that the soils were not overturned and that leaching is minimal. Sites were chosen which appeared to be relatively undisturbed. Of the metals analyzed, only Pb seems to be consistently higher in the surface samples than in the subsurface samples. The levels of Pb in the surface soils are also higher than the average crustal abundance of Pb while the other metals are either lower than or equal to average crustal abundance. It is not clear what contributes to the anomalously higher levels of Pb in surface soils. Lead was relatively low in the Raton fly ash although it is possible that accumulation may occur over a long period of time. An alternative explanation is that the relatively high automobile traffic in town may be responsible for the apparent surface accumulation. This particular aspect warrants more study.

E. Leaching of Air Filters

Particulate samples which were collected in the Raton area on glass fiber filters were subjected to leaching with distilled water to determine the extent to which some trace metals and major ions could be easily dissolved. On the order of 50-100 mg of particulates could be collected using the high volume air sampler in a 24 hour period. It is this particulate material which could also be leached by precipitation. The data obtained for three air filters are shown in Table 6. Some trace metals were detected in significant amounts in the leach solution while others were below the detection limit. The Cd, Pb, and Ba concentrations were similar to values for the precipitation (see Table 3) suggesting that these metals are easily leached from the particulate material. Aluminum was high in the leach solution from two of the sites. The major ions calcium, sodium, sulfate, and chloride were also present in significant

amounts in the leachate. These major ions are also the most prevalent ions in the precipitation (see Section G.) and again suggest that the airborne particulates in the local area contain many of the easily dissolved chemical species.

	<u>RHS</u>	<u>STU</u>	<u>SPR</u> ^{1.}
Trace Metals ^{2.}			
Al	400	7	400
Cd	5.6	0.34	0.19
Cu	<blank	0.7	20
Ba	10	5	10
Pb	2.9	1.6	1.6
Major Ions ^{3.}			
Ca	3.0	1.6	0.6
Mg	0.02	0.06	0.04
Na	<0.5	1.6	1.6
SO ₄	6.5	3.8	6.0
Cl	5.8	3.8	1.3

1. SPR - Spotted R Ranch (see Figure 3).
2. Co, Cr, and Mn were less than the detection limit of approximately 0.5 ppb.
3. K was less than the blank.

Table 6. Results of Leaching Air Filters with Distilled Water. Values of Trace Metals in ppb; Ca²⁺, Mg²⁺, Na⁺, SO₄²⁻, and Cl⁻ in ppm.

F. Trace Metals in Surface Water in the Raton Area

Surface water samples were collected from two rivers (Canadian and Vermijo) and two impounded sources (Lake Maloya and the TO Ranch Pond). The Canadian River is south of Raton, the Vermijo River is west, Lake Maloya is northeast and the pond is east of town. As might be expected, the trace metal analyses shown in Table 7 were quite variable because of the different water types, yet most of the analytical results are comparable to trace metal values found in the Rio Grande (Popp and Laquer, 1980). Cadmium seemed to be considerably lower in the Raton samples than in the Rio Grande, while the Al value at Lake Maloya seems extraordinarily high. Because of the limited sampling, a great deal of significance should not be attached to the Al value, but it is recommended that several more samples from the lake be collected to verify the result. We plan to have Tracy Stuart collect several samples from the lake for us to analyze for Al.

G. pH, Major Cations, Anions, and Nutrients in Precipitation

The average values for pH and major cations are listed in Table 8. A complete tabulation of each set of analytical results is given in Appendix A. The higher pHs found in the bulk samples probably represent neutralization by "dust" already in the sampling funnel (Popp, et al., 1982). The same effect would account for the higher levels of major cations in the bulk samples. Differences between Bulk-RHS and Bulk-Stuart may reflect differences in fallout from the power plant emissions.

	<u>Lake Maloya¹</u>	<u>Canadian River¹</u>	<u>Vermijo River²</u>	<u>TO Ranch Pond^{2,3}</u>	<u>Rio Grande</u> (Popp & Laquer, 1980)
Al	2280	170	30	-	-
As	0.9	3	-	-	16
Ba	39	76	-	120	45
Cd	0.03	0.27	0.26	-	2.3
Co	70	34	5	-	14
Cr	0.8	5	0.5	3.2	1.5
Cu	9.5	15	8.6	-	16
Fe	108	51	27	-	108
Hg	0.8	3.5	-	-	0.7
Mn	13	17	-	0.9	10
Ni	10	30	-	6	18
Pb	6.5	4	-	0.7	7.7
Se	0.9	2.8	2.5	-	<1
V	30	52	5	-	29

1. Average of two samples.

2. One sample.

3. 18 km east of Raton

Table 7. Trace Metal Analyses of Surface Water Samples from the Raton Area. Values in ppb.

	Bulk	Closed	Bulk
<u>Species</u>	<u>RHS</u>	<u>RHS</u>	<u>Stuart</u>
pH	6.1	5.5	5.8
Na	4.4	1.3	1.3
K	2.6	0.96	1.8
Ca	7.2	2.0	2.5
Mg	0.87	0.19	0.39

Table 8. Average Major Cation Concentrations (in ppm) and pH for Precipitation Sites.

The average pH value obtained using the covered collector located at Raton High School was 5.5 indicating equilibrium or control of the pH by atmospheric CO₂. However, the range was large with pH values from 4.3 to 6.9 for precipitation in the RHS closed collector. Because of variation in the amount of precipitation from event to event (see Table 2), it is useful to calculate a weighed average pH which accounts for the variation in rainfall amounts. In other words, a rain of 11 cm with a pH of 5 contributes much more total acid than a 5 cm rain of pH 6. The formula for calculating the weighed average is

$$\frac{\sum_{i=1}^n (H_i^+) (Vol_i)}{\sum_{i=1}^n (Vol_i)}$$

The volume is proportional to the measured amount of rainfall so the amount of rainfall in mm was substituted for the volume in the equation. Application of the formula to the data yields a weighed average pH of 4.9 which is considerably different and lower than the 5.5 event average

for RHS wet-only precipitation collected. Examination of the data in Table 2 suggest that events with greater amounts of precipitation have lower pH values. This may not be surprising because of the large amount of local dust which may tend to neutralize the acid in small amounts of precipitation. When washout occurs early in the event, the pH falls for samples collected later in the event. This effect was also noted in the Socorro area(Popp, et al., 1982).

Average values for major anions, silica, and nutrients are given in Table 9. Concentrations of sulfate, chloride, and silica were higher in the bulk samples reflecting dry deposition. Anion levels in the bulk samples showed the same trend as the cations being higher at RHS than at Stuart's. The most striking difference is the high level of phosphorus at RHS. This would have to be from an anthropogenic source. Nitrate levels are not greatly different indicating that the wet precipitation is the major source.

<u>Species</u>	Bulk	Closed	Bulk
	<u>RHS</u>	<u>RHS</u>	<u>Stuart</u>
SO ₄	9.1	3.2	6.4
Cl	8.4	2.9	7.2
NO ₃ -N	1.3	0.88	1.6
PO ₄ -P	1.7	0.05	0.16
SiO ₂	0.35	0.11	0.19
KN-N	0.41	7.0	0.4

Table 9. Average Major Anion, Silica, and Nutrient Concentrations for Precipitation Sites. Values in ppm.

H. Ion Mole Ratios

Selected ion mole ratios are shown in Table 10. The Cl/Na ratio for both wet and dry RHS samples is similar to the 1.4 average found previously in Socorro (Popp, et al., 1982). The high Cl/Na ratios found in precipitation at both Raton and Socorro suggest an anthropogenic and not a terrestrial source.

Ion Mole Ratio	Bulk RHS	Closed RHS	Bulk Stuart
Cl/Na	1.24	1.44	3.59
SO ₄ /Ca	0.53	0.67	1.07
NO ₃ /SO ₄	0.97	1.85	1.68
SO ₄ /Na	0.50	0.59	1.18

Table 10. Selected Ion Mole Ratios

The SO₄/Ca ratios are also similar to those reported previously (Popp, et al., 1982). Calcium rich terrestrial dust is probably a major source of calcium here.

Nitrate to sulfate ratios are similar to those reported for the Los Angeles, California region (Liljestrang, 1978). These may indicate long distance transport of nitrogen oxides since the amount generated locally would be expected to be small. The following table is presented for comparison.

<u>Site</u>	<u>NO₃/SO₄</u>
Albuquerque, N.M.	1.2
Socorro, N.M.	0.65
Chama, N.M.	3.0
Pasadena, California(Liljestrang, 1978)	2.5

Table 11. NO₃/SO₄ Ratios for Comparison to Raton

I. Particle Identification in Study Areas

Several series of studies were performed to ascertain whether fly ash sources could be identified in terms of their energy-dispersive X-ray spectra. These studies included the following:

- (1) individual particle studies on NBS standard fly ash;
- (2) particle analysis on San Juan fine precipitator ash; and
- (3) analysis of stack and precipitator ash from the Raton plant.

In each case there seemed to be trends towards a specific elemental composition ratio. However, the differences from particle to particle within a given series always exceeded the uncertainty in the concentration ratio differences between sources. For instance, the iron/silicon ratio in the NBS standard material varied by a factor of 5. The San Juan fly ash particles showed the same wide elemental composition.

The wide variation in elemental compositions are apparent from the energy-dispersive X-ray spectra for Raton stack effluent particles given in Figure 5. A, B, and C are the spectra of spherical particles and the remainder are for nonspherical particles. It is difficult to make generalizations from these wide elemental compositions, but it seems

apparent that the spherical fly ash are enhanced with respect to calcium and the nonspherical particles have a higher than average sulfur content. Studies in this area are continuing.

J. Fly Ash Densities

Raton soil samples were taken at the surface and at a depth of 15 cm. All samples were ground with a mortar and pestle and placed through a sample splitter prior to microscopic analysis. Results of the soil fly ash counts are given in Table 12. The variations in estimated fly ash densities at a given location were considerable; but in general fly ash densities were fairly homogenous throughout the study area. A summary comparing optical with SEM data is given in Table 13. SEM photomicrographs of fly ash particles are given in Figure 6.

Results of total air filter particle counts are given in Table 14 along with comparison data from Socorro and Langmuir Laboratory. A spatial resolution of the Raton data is given in Table 15.

A total of 43 Raton precipitation samples was collected. Both the optical and SEM data yielded a total of 0.14 particle percent fly ash. These data are given in Table 16 along with data for the control sites.

	Surface		15 cm depth		Surface		15 cm depth	
	<u>#F.A./Total</u>	%	<u>#F.A./Total</u>	%	<u>#F.A./Total</u>	%	<u>#F.A./Total</u>	%
Lake Maloya	2/712	0.28	6/570	1.05	2/500	0.4	3/500	0.6
" "	-	-	2/500	0.4	-	-	-	-
Radio Station	5/240	2.1	6/500	1.2	5/500	1.0	3/500	0.6
Golf Course	7/607	1.15	1/500	0.2	2/500	0.4	1/900	0.1
High School	2/802	0.2	3/600	0.5	2/500	0.4	2/500	0.4
Stuart Residence	3/1708	0.17	6/650	0.57	-	-	-	-
Spotted R	4/704	0.57	2/502	0.39	-	-	-	-

Table 12. Fly Ash in Surface and Subsurface Soils in the Raton Area, Optical Counts

<u>Location</u>	<u>Optical</u>			<u>SEM</u>		
	<u>#Samples</u>	<u>#F.A./Total</u>	<u>Size-μ</u>	<u>#Samples</u>	<u>#F.A./Total</u>	<u>Size-μ</u>
Raton	34	72/34,956	17 \pm 8	7	15/4,161	3.4 \pm 2.2
Socorro	14	0/13,625	-	2	2/754	2.3 \pm 0.5
Isleta Pueblo	2	0/2,000	-	2	0/600	-
San Antonio, N.M.	1	0/2,000	-	1	0/600	-

Table 13. Fly Ash in Soils Using Both Optical and SEM Examination Including Control Areas.

Size Uncertainty is Standard Deviation.

<u>Location</u>	<u>Particle Density</u> <u>$\mu\text{g}/\text{m}^3$</u>	<u>Optical Counts</u>			<u>SEM</u>		
		<u>#F.A./Total</u>	<u>Mean F.A. Size-μ</u>	<u>#F.A./Total</u>	<u>Mean F.A. Size-μ</u>		
Raton	147	9/6,619	7 \pm 4.1	-	-		
Spotted R	-	-	-	7/1,192	6.5 \pm 2		
Stuart's	-	-	-	1/653	6.5 \pm 2		
Socorro	32	1/4,189	7 (one only)	11/1,379	1.0 \pm 0.2		
Langmuir	20	10/2,861	6 \pm 4.4	2/247	1.0 \pm 0.4		

Table 14. Air Filter Particle Counts Identifying Fly Ash Among Total Particulates.

Size Uncertainty is Standard Deviation.

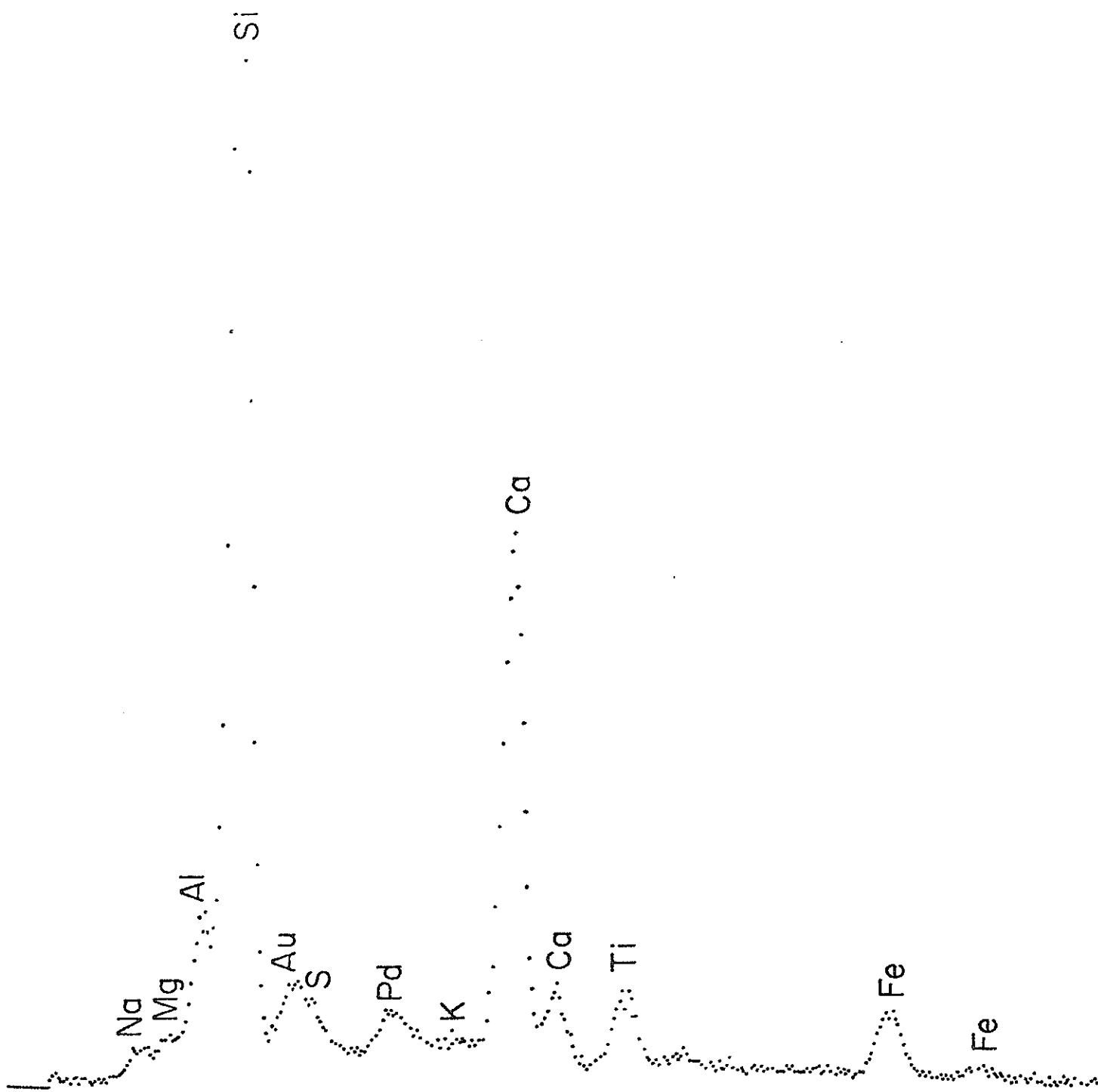
		Fly Ash/ <u>Total Particles</u>	Size of <u>Fly Ash-μ</u>	<u>Percentage</u>
A1 (11-25-80)	Radio Station	0/1000		0
A2 (1-x-81)	Radio Station	5/500	5,2,4,11,3	1.0
A3 (7-6-81)	St. Pat's School	2/822	14,8	0.24
A4 (7-9-81)	Spotted R	0/500		0
A5 (6-19-81)	Stuart Residence	1/500	5	0.2
A6 (6-24-81)	Golf Course	0/525		0
A7 (6-21-81)	Raton High School	1/530	10	0.19
A8 (6-17-81)	Radio Station	0/500		0
A9 (1-12-81)	Stuart Residence	0/526		0
A10 (1-10-81)	Raton High School	0/640		0
A11 (2-5-81)	Spotted R	<u>0/576</u>		0
Total		9/6619		

Table 15. Data for Individual Air Filter Samples, Raton

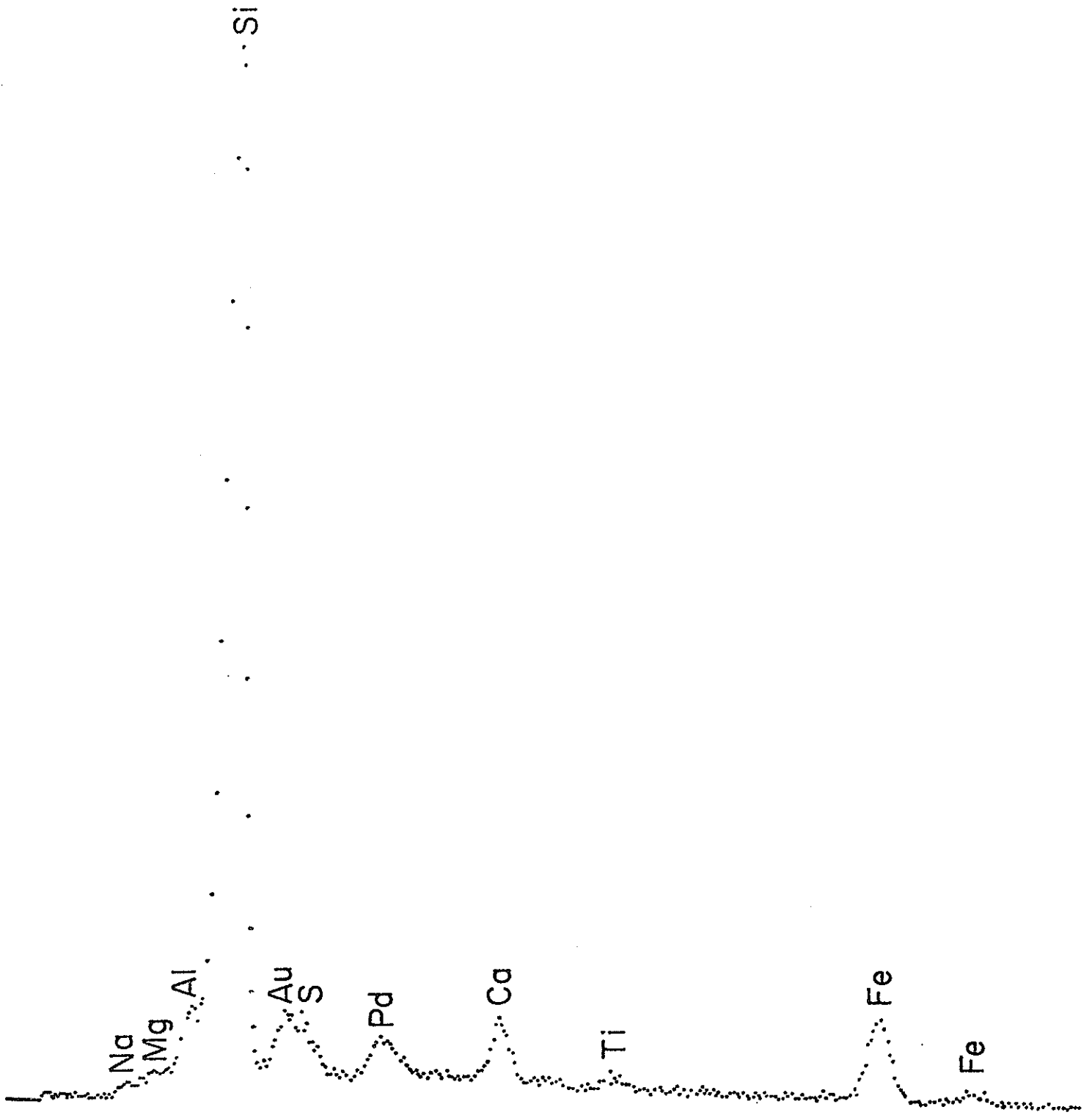
Site	Average Weight		Optical			SEM			
	Rain Filters	mg/l	#Samples	F.A./Total	Size- μ	Particle Percent	#Samples	F.A./Total	Size- μ
Raton	41		43	61/44,754	13 \pm 6.9	0.14	3	18/1,253	3 \pm 3.0
Socorro	36		60	9/70,043	12 \pm 2.9	0.01	3	5/1,184	4 \pm 5.3
Chama	39		25	11/18,483	16 \pm 4.6	0.06	17	55/4,495	4 \pm 4.8
Langmuir	5		11	2/8,735	11 \pm 2.8	0.02	4	11/1,898	3 \pm 3.6

Table 16. Fly Ash Densities in Precipitation Samples.

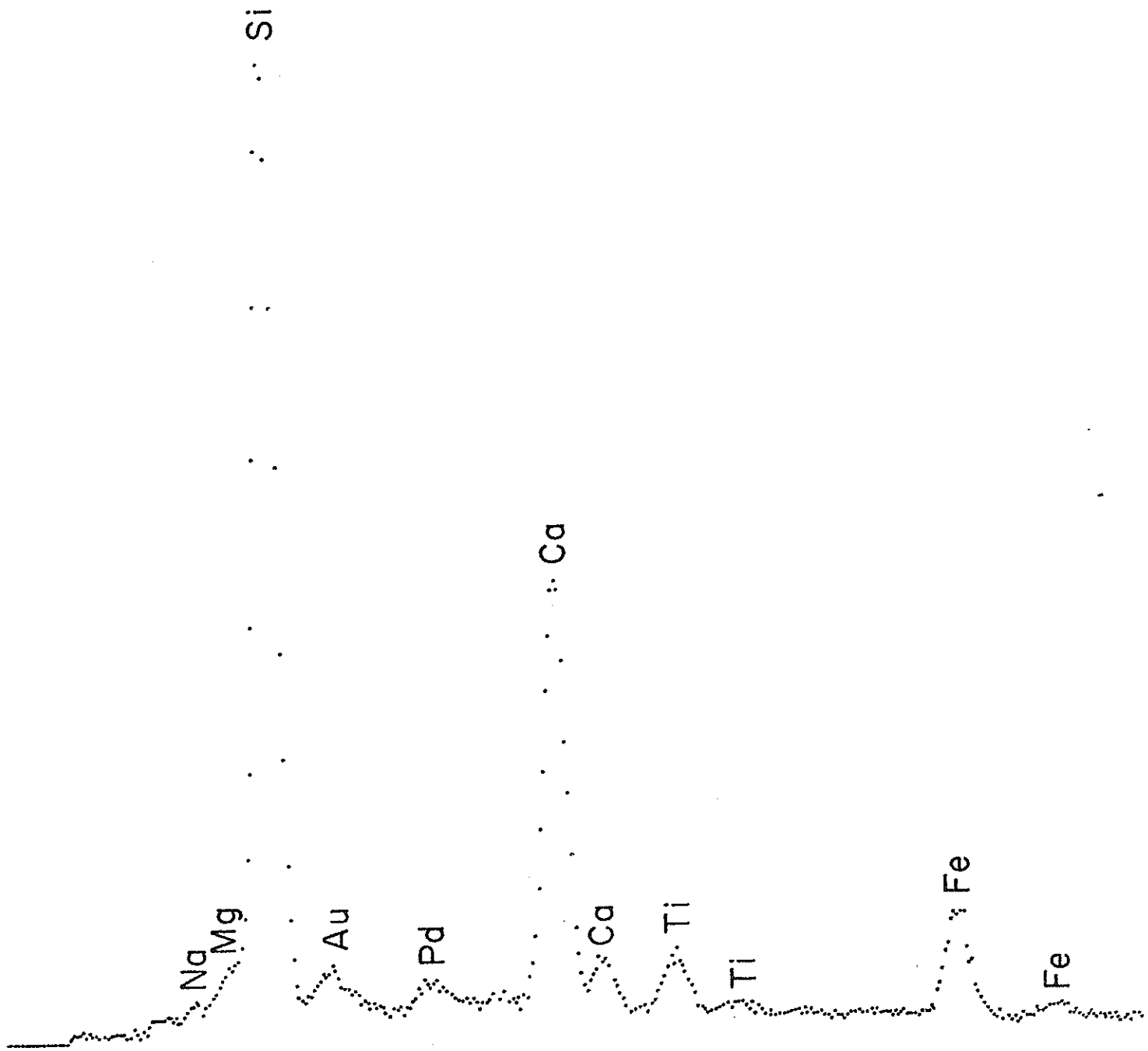
Figure 5. SEM X-ray Spectra of Raton Power Plant Stack Effluent. Particles A, B, and C are spherical and the Remainder are Nonspherical. A Gold-Palladium Film was Applied to Render the Particles Conductive. (These spectra are given on pages 41 through 48).



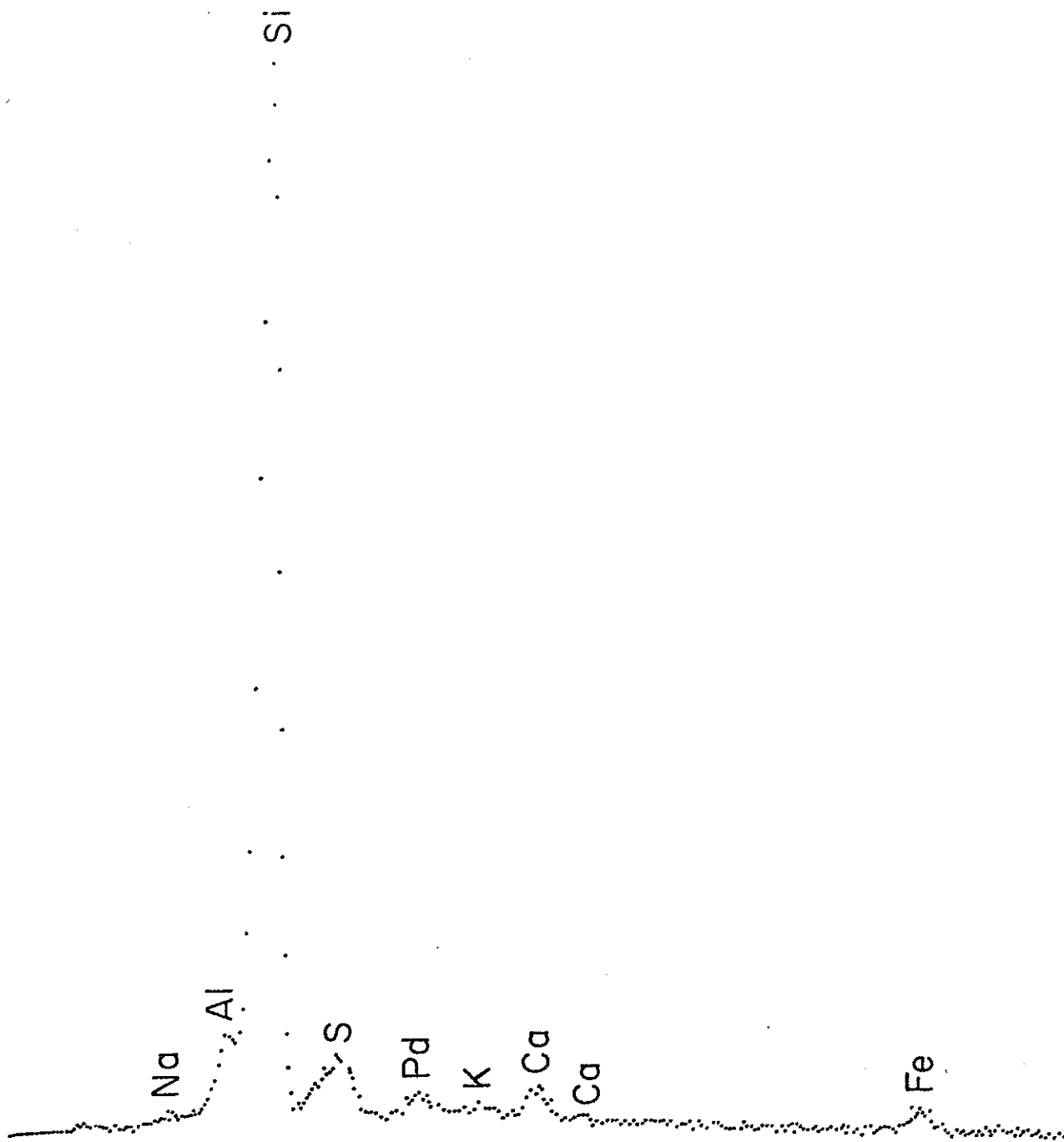
(A)



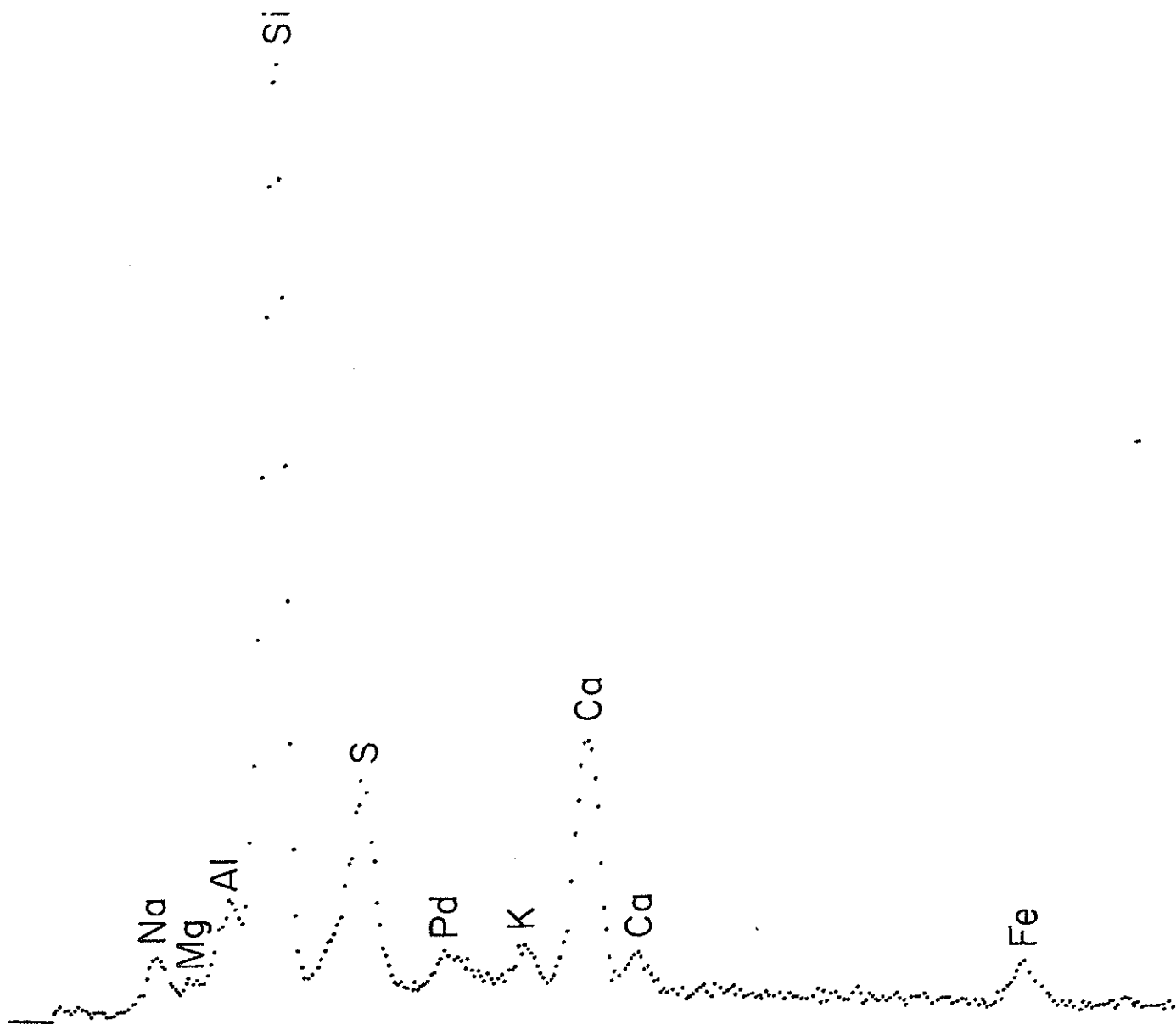
(B)



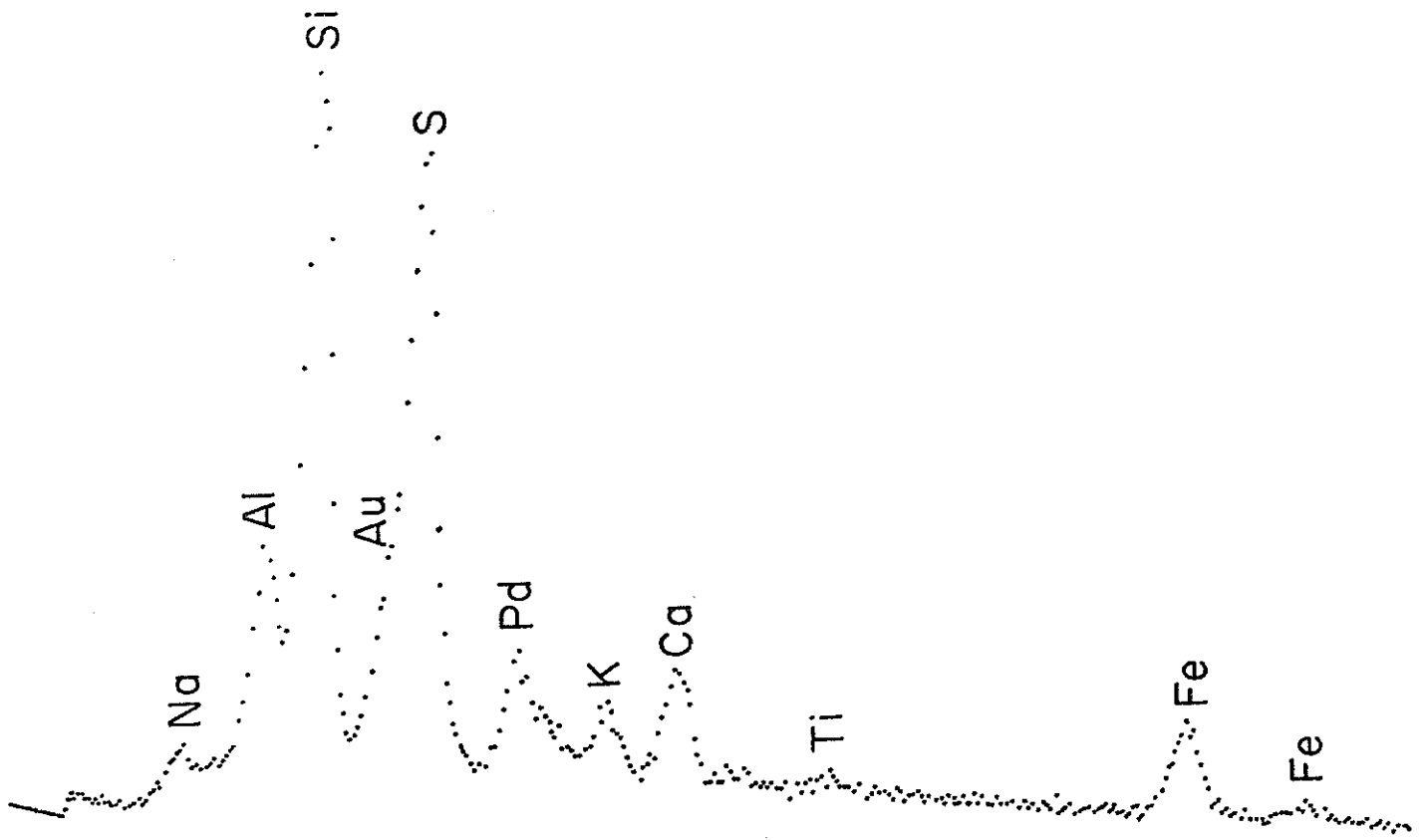
(c)



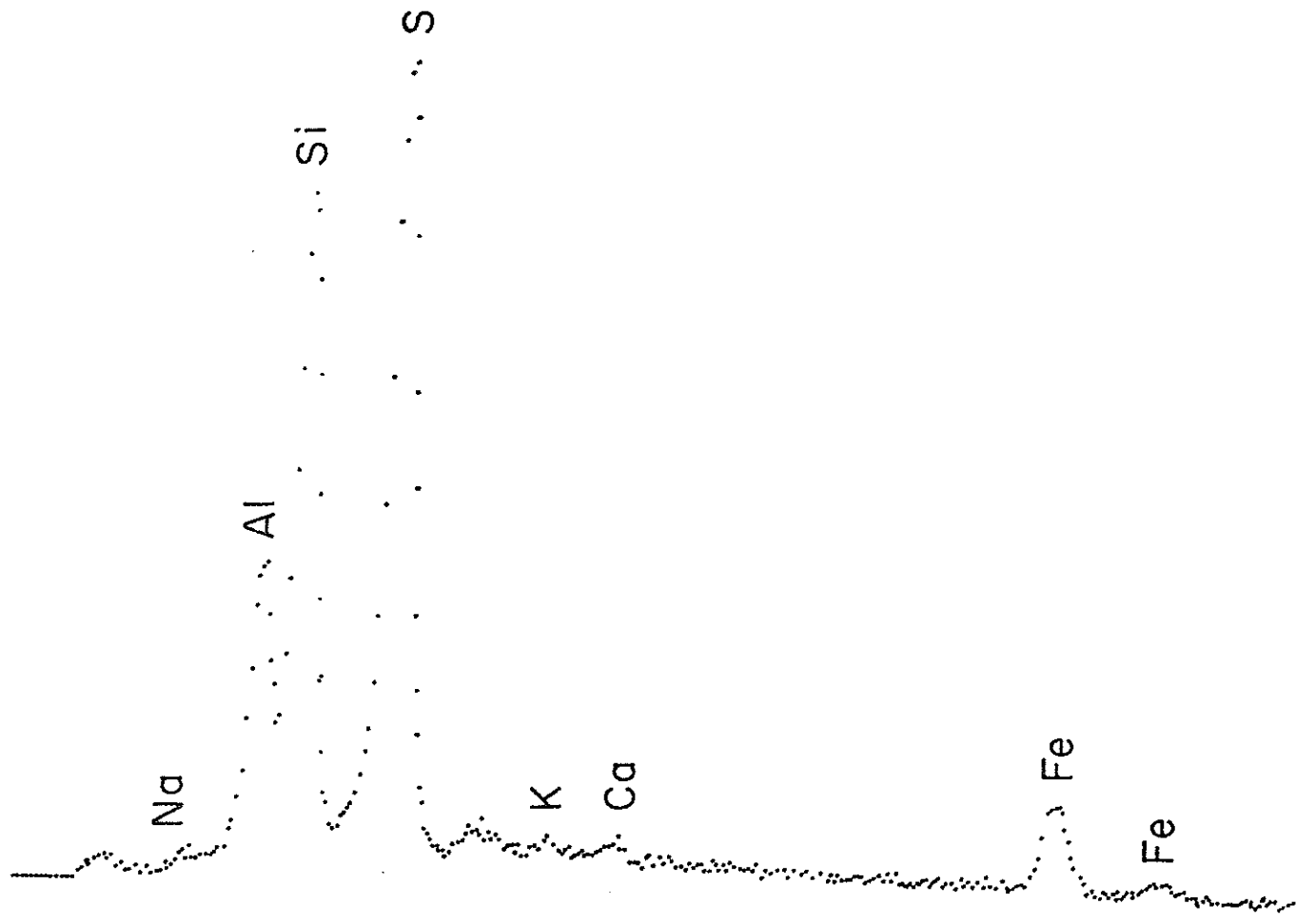
(D)



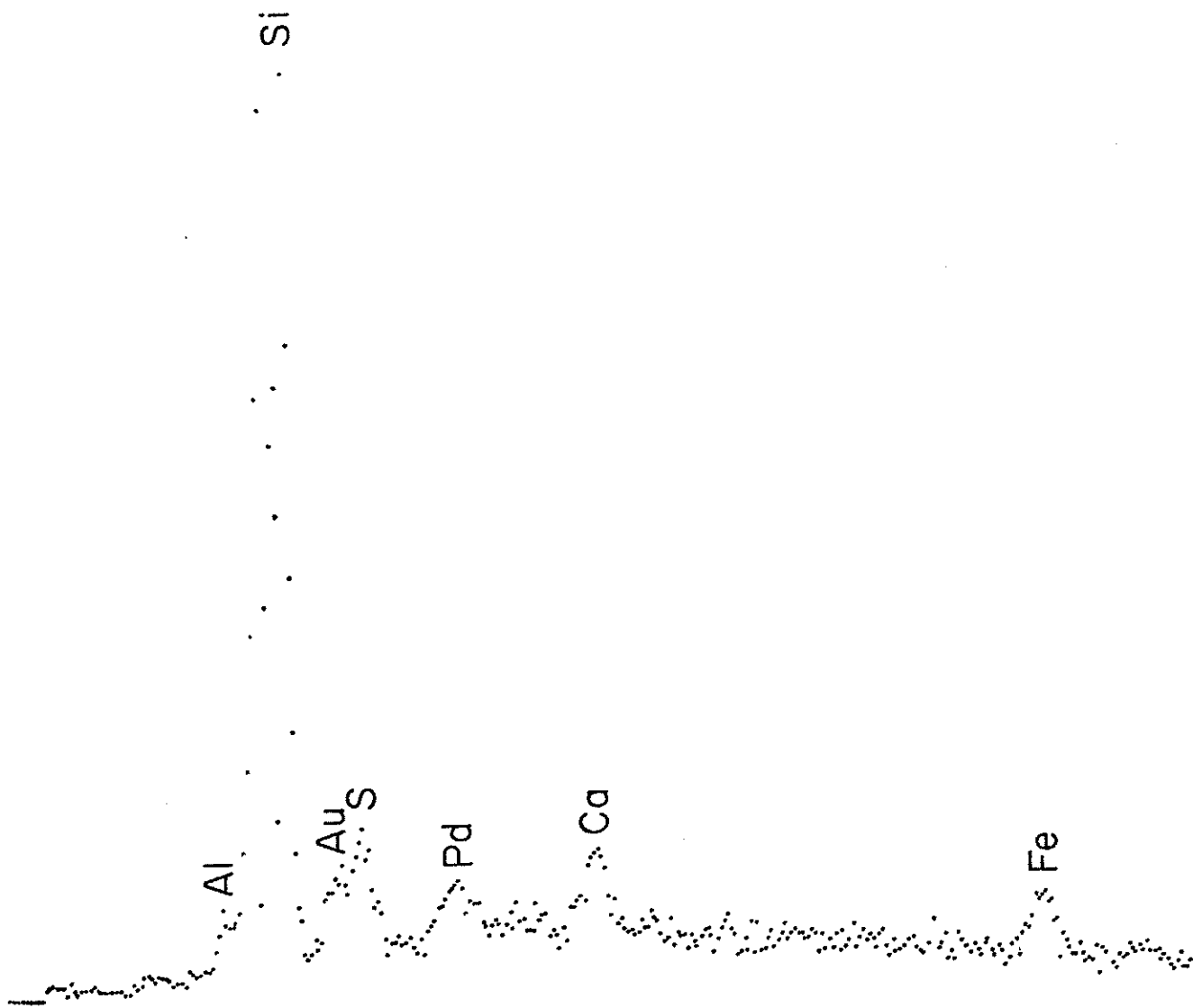
(E)



(F)



(G)



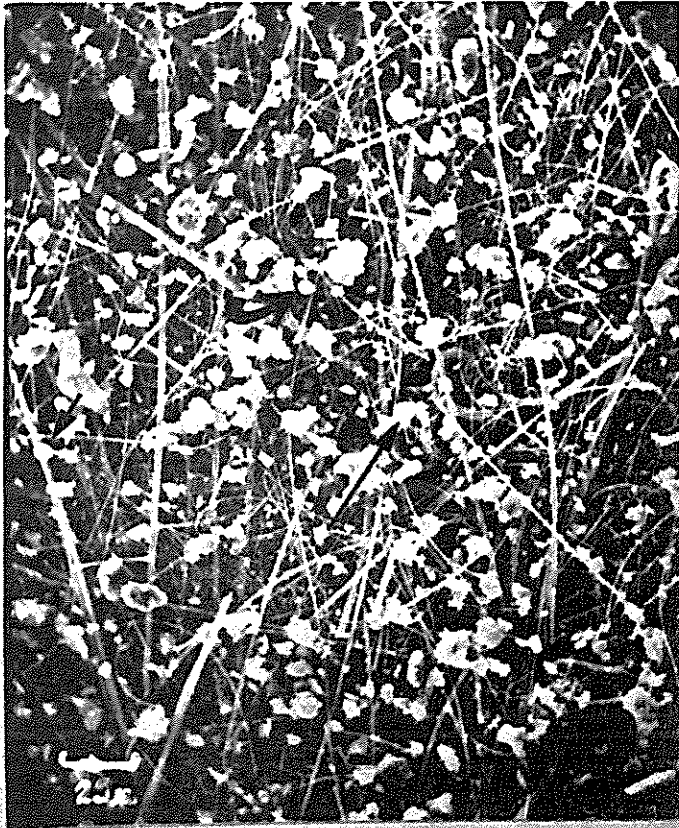
(H)

- (A) Raton power plant stack sample, June 26, 1981, 1000X. Analysis of the particle shape on this photograph yielded 38 spherical to 142 nonspherical particles.
- (B) Raton air sample, Spotted R. Ranch, 400X. Three spherical fly ash particles are visible.
- (C) Raton High School surface soil sample, 400X. Four spherical fly ash particles are noted.
- (D) Particulates removed from Raton rain, 1000X, 10/1/80. Two spherical fly ash particles are noted.

Figure 6. Scanning Electron Micrographs of Particulates from the Raton Area.



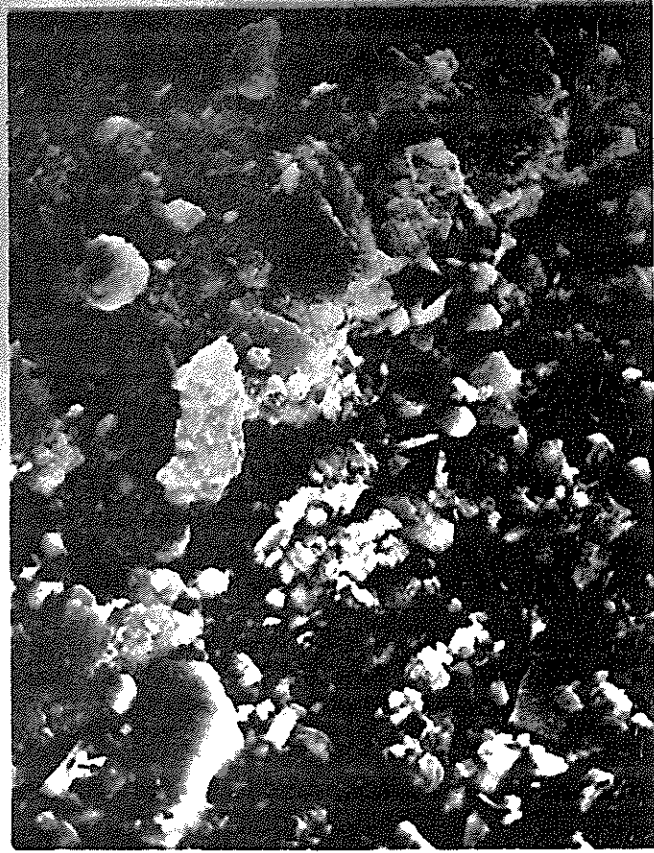
(A)



(B)



(C)



(D)

IV. CONCLUSIONS AND RECOMMENDATIONS

The presence of fly ash was determined in all atmospheric samples from the Raton area including precipitation and air filters. The fly ash in precipitation occurred as a result of washout. Fly ash was not identified in surface water but was found in surface soil samples around the power plant but at low number densities. More analytical work with the scanning electron microscope may allow the source(s) of the fly ash to be determined to separate local from regional effects.

A large number of the precipitation samples were more acidic than predicted simply from carbon dioxide equilibrium and the weighted average pH was 4.9 for wet-only precipitation. A continued downward trend in pH values could lead to problems such as leaching of trace metals from soils into surface water and damage of fragile ecosystems. A long-term and more widespread monitoring system should be established for precipitation. Research efforts should be increased to identify the source(s) of the acid-causing material.

Surface water samples in the Raton area seem to have normal trace metal content when compared to the Rio Grande in New Mexico. However, because some metals can be leached from fly ash by water, the ash should not be exposed to surface or ground water supplies. Release of fly ash to the environment should be kept as minimal as possible.

Publications: A paper resulting from this work entitled "Atmospheric Particulates in New Mexico: Identification of Fly Ash in Environmental Samples," has been submitted to Nature.

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