Report

LA-6401-MS

Informal Report

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Reporting Date: June 1976

Issued: July 1976

7176

A Review of Trace Element Studies Related to Coal Combustion in the Four Corners Area of New Mexico

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UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINIS
CONTRACT W-7405-ENG. 36

7924

Work supported by the US Energy Research and Development Administration, Division of Biomedical and Environmental Research and the Environmental Protection Agency.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy $4.50 Microfiche $2.25

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A REVIEW OF TRACE ELEMENT STUDIES RELATED TO COAL COMBUSTION IN THE FOUR CORNERS AREA OF NEW MEXICO

by

Lawrence E. Wangen and Caroline L. Wienke

ABSTRACT

This document is a review of trace element studies related to coal combustion in northwestern New Mexico, which were performed with particular emphasis on the potential environmental effects of the Four Corners Power Plant. Trace element studies in coal, power plant bottom and precipitator ash, local soils, and local surface water systems are presented and discussed in relation to trace element mobilization and potential environmental contamination.

I. INTRODUCTION

Coal extraction and combustion changes the physical and chemical properties of trace species present in the original coal matrix. Some of these processes convert various potentially toxic species from relatively inert, immobile states to physical and/or chemical forms more readily available for uptake, movement, or chemical and biological transformation in the environment. In some cases, this mobilization may approach and even exceed that due to natural causes.[1] The mobilization of sulfur, for example, is well known, and there is considerable evidence for the emission of mercury from coal-fired power plants.[2] Further, it has been recently recognized that, on a world-wide basis, coal combustion results in the release of an estimated 50% more selenium to the environment than does natural weathering.

In recent years there has been a growing concern about the emission of larger amounts of trace substances into the atmosphere. Various studies have shown that certain trace elements appear to be present in air particulates at anomalously high concentrations, as compared to crustal concentrations, and it has been proposed that this may in part be due to coal combustion. The proposition appears feasible because: (1) coal combustion is ubiquitous; (2) coal is known to contain several elements in forms which are volatilized at combustion temperatures; (3) condensation of these volatilized species on available surfaces tends to concentrate them on smaller particles because of larger surface-to-volume ratios; (4) particulate control devices are least efficient at collecting particles in the smaller size range; and (5) smaller particles have longer atmospheric residence times and would thus be expected to be present in airborne particulate at great distances from the source. A good example of the last point is lead from combustion of leaded gasolines. This element, associated with small particles in the submicron size range, is now found in relatively high

quantities at remote locations far removed from man's technological activities.[4]

Another process, which has not been sufficiently studied, is the potential mobilization of trace species from coal ash after disposal, such as by wind and water erosion. One recent study[5] concluded that iron in the +3 oxidation state in coal ash is more soluble than if it were present simply as crystalline Fe_2O_3, as is often assumed. This suggests that other nonvolatile elements may also become more available as a result of the combustion process. The concentration of many trace, and some minor, elements on the outside of fly ash particles has recently been demonstrated,[6] and this concentration makes these elements more available to weathering processes than if they were associated with the bulk material.

These considerations have led to investigations into the significance and potential hazards of the nation's anticipated reliance on coal to meet its near-term energy demands. Extensive exploitation of Western coal resources is anticipated in partial solution to short-range energy needs. The five Rocky Mountain states of Arizona, Colorado, New Mexico, Utah, and Wyoming have estimated remaining coal resources of 743×10^{12} kg; 97×10^{12} kg are in thick, accessible beds which are of current economic interest. Approximately 0.25×10^{12} kg of this total are strippable, with about 0.20×10^{12} kg recoverable by present technology.[7]

Few systematic studies have been made on the environmental consequences of current and projected use of these extensive coal resources. The Los Alamos Scientific Laboratory (LASL) is involved in a study of the fate and ecological impact of trace elements resulting from coal usage in semi-arid regions of the western United States. The initial study area chosen for this research is the Four Corners area of northwestern New Mexico. Extensive coal mining, including the Navajo and Western Mines, and generation of electrical power are under way in this area. The Four Corners and San Juan Power Plants will soon be consuming coal on the order of 10^{10} kg/yr. The coal presently used in the San Juan and Four Corners Power Plants has an unusually high ash content, between 18 and 24%, and disposal of about 2×10^9 kg/yr of ash is anticipated. The bulk of this is to be returned to the mine. The possibility of water contamination by leaching and surface run-off of trace contaminants from strip-mined areas and ash disposal sites must be investigated in order to identify environmental hazards so that sufficient mitigating actions can be taken.

A. The Four Corners Power Plant[8]

Principal emphasis in the LASL investigation is to be initially centered around the Four Corners Power Plant, which is jointly owned by a number of western utilities. It consists of five pulverized coal-burning steam electric generating units: two 175-MW units, one 225-MW unit, and two 800-MW units (hereafter referred to as Units 1, 2, 3, 4, and 5, respectively). At full load these five units consume about 25.4×10^6 kg of subbituminous coal per day. Current daily consumption averages about 18.14×10^6 kg. The plant is situated adjacent to the Navajo Mine from which it receives its coal. Hot flue gases from the combustion process pass through a boiler, superheater, economizer, and air heater, and into pollution control devices before discharging out of the stack. Particulate control on Units 1, 2, and 3 is accomplished by variable-throat Chemico venturi wet scrubbers using forced draft fans before and induced draft fans after the scrubbers. In Units 4 and 5, gases are blown through Research-Cottrell electrostatic precipitators by forced draft fans.

The venturi scrubbers are designed to remove 99.2% by weight of the particulate matter from the flue stream, whereas the precipitator particulate collector specifications state a 97% removal efficiency. Exit gas temperature and stack height for Units 1, 2, and 3 are 50°C and 76.2 m, respectively. (Units 1 and 2 use the same stack.) Flue gases from Units 4 and 5 exit through separate stacks at a height of 91.4 m and a temperature of about 107°C.

The venturi scrubbers on units 1, 2, and 3 were installed in late 1971 and early 1972. Prior to this time these units were equipped with mechanical particulate collectors, installed in 1963-64, with a particulate collection efficiency rated at about 77%. Approximately 1.4×10^6 m^3 of water per year are used to transport fly ash from the scrubber systems to the ash disposal and settling ponds. After settling, 87% of this effluent water eventually reaches the Chaco River; lime is added to control the pH. The bottom ash from these units is sluiced to dewatering bins; the water is then recycled and the bottom ash is slurried to the ash ponds or used for fill and diking support.

The Research-Cottrell electrostatic precipitators, through which Units 4 and 5 flue gases pass at a temperature of about 115°C, collect particulates by an electrostatic field, on the order of 53 000 v, on a collecting surface which is rapped about once every 2.5 min. The rapping causes the particulates to fall downward, where they are collected in large hoppers located below the precipitators. The bottom and precipitator ash from Units 4 and 5 are returned to the Navajo Mine for disposal. Mill rejects from the coal pulverizer mill are also disposed in this manner.

About 25×10^6 m^3/yr of water are currently diverted from the San Juan River to Morgan Lake for use as process waters. This diversion represents about 2% of the annual average San Juan River flow. The water is used by the plant for condenser cooling, domestic water, plant boiler feed make-up, ash sluicing, and make-up to the venturi scrubbers. Blowdown of Morgan Lake water to the Chaco River is used to maintain total dissolved solids (TDS) in the lake below 900 to 1000 mg/ℓ. This TDS value constitutes an upper limit for prevention of scaling in the heat exchangers.

Various chemicals used in the process streams of the power plant are discharged into Morgan Lake or the ash pond. The chemicals used in substantial amounts are sulfuric acid, sodium hydroxide, aqua ammonia, lime, alum, hydrazine, chlorine, sodium chloride, and hydrated lime. Of these, hydrated lime (calcium hydroxide), for control of scrubber pH, and sodium chloride, as a water softener, are used in the greatest quantities. Effluent from both of these processes is discharged into the ash pond.

B. Other Studies

An initial task of the program was to review the literature and assess the trace element studies that have been performed at the Four Corners Power Plant and in the surrounding area. The intent was to assimilate available information and define potential problem areas.

To date there have been three studies undertaken to assess trace element impacts in the vicinity of the Four Corners Power Plant: 1) the Southwest Energy Study (SWES);[7] 2) a University of Nevada-Desert Research Station Study funded by the Federal Environmental Protection Agency (EPA);[9] and 3) private efforts funded jointly by Arizona Public Service (APS) and Utah International, Inc. (UII) with additional input from other interested utility and mining groups.[8,10,11] Additionally, there have been other investigations of a more limited scope. The SWES[7] and the APS-UII[8,10] studies included trace element analyses of coal, bottom and precipitator ash, soils, and flora. The APS-UII study also included some analyses of fauna. The EPA-funded

study[9] sampled soils and flora around the power plant.

The following components are defined for the purposes of this discussion of trace element movement: coal, bottom ash, precipitator ash, venturi scrubber ash, stack emissions, waters, soils, flora, and fauna. In subsequent sections the available trace element studies in each of these components, excepting flora and fauna, are discussed and compared with other studies and system components, as applicable.

II. IN-PLANT STUDIES ON COAL AND ASH

A. Coal

Trace element concentrations in coals show considerable variability depending on geographic location, location in the coal seam bed, and the grade of coal. The coal used at the Four Corners Power Plant is subbituminous with a low heating value of about 9000 BTU/lb. The trace element results for coal, bottom ash, and precipitator ash reported by APS-UII and the SWES are summarized in Tables A-I and A-II of Appendix A together with some descriptive information on sampling and analytical procedures. Average major element concentrations of Navajo Mine coal,[7] expressed as percent oxides in the ash are:

SiO_2	54.57	Na_2O	1.54
Al_2O_3	24.95	MgO	0.80
CaO	3.77	K_2O	0.70
SO_3	3.29	P_2O_5	0.16
Fe_2O_3	3.08	TiO_2	0.26

The average percent ash content of the coal upon which these data are based is 23.58. These figures, except for TiO_2, are within the normal range observed for subbituminous coals[12] except for the percent ash (22-24%), which is quite high; the majority of coals have ash contents between 6 and 12%. The silicon and aluminum concentrations of Four Corners coal ash are high, while the Ca, Mg, P, Fe, and S concentrations are lower than other western coals analyzed as part of the SWES.[7]

The elements considered in this report are listed in Table I, together with average concentrations in various coals,[7,13-16] expressed on a whole-coal basis. The Navajo Mine values are a composite of 21 samples from the SWES.[7] On a whole-coal basis, Navajo Mine coal contains less As, Cd, Co, Cr, Fe, Hg, Mo, Ni, S, Sb, V, and Zn; about the same B, Be, Cu, Ga, K, La, Mg, Mn, Pb, Sc, Se, Sr, and Zr; and more Al, Ba, F, Na, Si, Ti, and ash than eastern coals. Since the ash fraction of Navajo Mine coal is a factor of 2 or more greater than that of most other coals, the elemental mass concentrations on a coal ash basis would be lower by about a factor of 2 for Navajo Mine coal, assuming comparable volatilities of the trace compounds. Most of the sulfur in low-sulfur coal is thought to be organically bound,[12] implying low inorganic sulfur, and all of the elements in the low abundance group mentioned above (except Cr and V) are chalcophiles and are expected to be present in lower concentrations in the low-sulfur Navajo Mine coal. The following observations,[15,17] based on float-sink data, have been made concerning the organic/inorganic associations of trace elements in coals: Be, B, and Ge show marked "organic affinity" and Ga, P, Sb, Ti, V, Co, Ni, Cr, Se, and Cu are associated with both inorganic and organic phases, with the first three showing a preference for organic association and the latter five (Co-Cu) having an inorganic preference. Mercury, Zr, Zn, As, Cd, Pb, Mn, and Mo generally show inorganic affinities. The major and minor elements Al, Ba, Ca, Fe, K, Mg, Na, and Si are associated with inorganic phases. These generalizations are based primarily on analyses of coals from the eastern United States and therefore are not necessarily applicable to Navajo Mine coal. However, with the exception of antimony, all of the trace elements listed as having an organic preference (Be, B, Ga, Sb, V) are present in comparable or greater concentrations in the Navajo Mine

TABLE I

ELEMENTAL ABUNDANCES IN VARIOUS COALS ON A WHOLE-COAL BASIS (IN μG/G, UNLESS % INDICATED)

	Navajo Mine (21 Samples)	Rocky Mountain[a] Region	Valmont[b] Power Station	Chalk Point[c] Power Plant (Av of 9 Samples)	Illinois Coal (Av of 82 Samples)	Allen Steam Plant[d] (Av of >3 Composites)
%Al	3.11	0.79	0.49	1.93	1.22	1.04
As	2.2	1.02		26	14.9	4.45
B	105	92			113.8	
%Ba	0.052	0.0171		0.015		0.0065
Be	1.27	0.429		1.89	1.72	
%Ca	0.637	0.506		0.15	0.74	0.434
Cd	<0.12	<0.1			2.89	0.47
Ce		<15		25		8.2
Co	1.86	1.45		5.8	9.15	2.9
Cr	4.48	4.13		29	14.1	18
Cu	13.4	5.45	9.6		14.1	8.3
Eu		<10		0.53		0.1
F	160.5	127			59.3	
%Fe	0.507	0.281	0.37	1.36	2.06	1.085
Ga	9.20	2.55		12.9	3.04	4.5
Ge					7.51	
Hg	0.06	0.017	0.07	0.36	0.21	0.122
%K	0.137	0.037		0.23	0.16	0.154
La	16.5	6.26		12.8		3.8
Li	20.1	5.78				
%Mg	0.11	0.083		0.089	0.05	0.121
Mn	53.3	13.9		39	53.2	33.8
Mo	1.46	0.42	0.99		7.96	
%Na	0.269	0.11		0.029	0.05	0.0696
Nb	<4.7	<2	0.76			
Ni	<2.4	2.61		25	22.4	16
%P	0.017	0.02			0.0063	
Pb	13.2	3.49		9.6	39.8	4.9
%S	0.68	0.42	~0.6	1.78	3.51	3.25
Sb	0.32	0.40		1	1.35	0.5
Sc	3.14	1.14		5.7		2.2
Se	2	1.61	1.9	5.1	1.99	2.2
%Si	6.01	1.62		3.39	2.39	2.31
Sn					4.56	
Sr	69.6	98	120	86		23
Ta				0.29		0.11
Te	<0.04	<0.02				
%Ti	0.101	0.0315		0.119	0.06	0.0506
Tl	<0.34	<0.2				
U	2.56	0.69				2.18
V	22.4	7.6		40.2	33.13	28.5
Y	9.67	3.98	3			

TABLE I (CONTINUED)

	Navajo Mine (21 Samples)	Rocky Mountain[a] Region	Valmont[b] Power Station	Chalk Point[c] Power Plant (Av of 9 Samples)	Illinois Coal (Av of 82 Samples)	Allen Steam Plant[d] (Av of ≥3 Composites)
Zn	12.5	4.87	7.3	32	313.04	46
Zr	49.5	16.6	13	38	72.1	
%Ash	23.58	7.76	~6	12.8	11.28	~13

[a]Average from coals from six different mines used or to be used at various plants as presented in SWES.
[b]Coal from Rosebud Mine near Hannah, Wyoming.
[c]Coal used at Chalk Point is from West Virginia and Pennsylvania.
[d]Coal used at the Allen Steam Plant is from southern Illinois.

coal, and all trace elements listed as having inorganic affinities are present in Navajo Mine coals at concentrations less than, or about the same as, eastern coals. The higher concentrations exhibited by some of the matrix elements in Navajo Mine coal are principally due to the higher inorganic (ash) content of this coal. Fluorine is not included in the organic/inorganic work; however, it is geologically classed as a lithophilic element and therefore expected to be inorganic. Generally speaking, fluorine concentrations are considerably greater in rocks and soils than in plants and animals. Thus, higher fluorine levels in Navajo Mine coals may simply reflect the higher overall levels of inorganic ash.

It is concluded from available data that the trace element concentrations in coal used at the Four Corners Power Plant are consistent (either the same or lower) with levels in other coals with the possible exception of fluorine and some of the inorganic matrix elements which appear to be present at levels about a factor of 2 to 3 higher.

B. Ash

In the analysis of trace element concentrations in coal ash, it is necessary to specify the pertinent variables. Coal analyses performed on ash remaining after heating the coal for several hours at elevated temperatures give erroneously low results for any species having appreciable volatility at the ashing temperature. On the other hand, if the interest is in the bottom ash from a power plant which has boiler combustion temperatures in the range of 1300-1500°C, data obtained at lower ashing temperatures would not be applicable for many elements.

Perhaps of more importance are potential misinterpretations when comparing data from different power plants with different operating procedures, such as different types of boilers and emission control devices. For example, for particulate control, the Four Corners Power Plant currently uses venturi scrubbers on Units 1, 2, and 3 and electrostatic precipitators on Units 4 and 5. Therefore, for comparative purposes, when samples are collected it is necessary to specify more than just the power plant name and approximate location in the process stream.

To date, only APS-UII and SWES have reported bottom ash and precipitator-collected ash trace element data from the Four Corners Power Plant. In addition, APS-UII have funded studies on trace elements in the venturi scrubber slurries and in the stack effluent downstream of the control devices. Elemental data reported by SWES and APS-UII for bottom and precipitator ash samples are reproduced in Table A-II of Appendix A. For the most part, these data are in agreement

TABLE II (CONTINUED)

	Four Corners[a] Power Plant	Other[b] Rocky Mountain Power Plants	Valmont Power Station (Av of 3 Daily Composites)	Allen Steam Plant (Av of 3 Composites)	Chalk Point Power Station (Av of 9 Samples)
Zn	16	34	58	100	150
Zr	184	233	220		240

[a]Composite of APS-UII and SWES data, cf Appendix A.

[b]Power plant average of bottom ash data reported in SWES excluding Four Corners and Naughton plants.

considering probable differences in analytical techniques, process parameters, and seam origin of the coal used. However, there are two- to five-fold differences among samples which might logically be expected to be quite similar since they are from the same plant; such examples are B, Ba, Cr, Ga, Hg, Li, Ni, Sb, and V in the precipitator ash data. These variabilities indicate the need for care in analytical procedures and interpretation of results.

As suggested above, it is difficult to compare the Four Corners Power Plant ash samples with other reported data on inplant ashes. Many studies do not provide sufficient information to allow interpretive comparisons. In particular, the ash data reported by the SWES from the various power plants are identified as only fly ash and bottom ash. Nevertheless, Tables II and III tabulate elemental concentrations in boiler residue and precipitator-collected ash from various power plants in the United States.[7,13,14,16,18] The first three columns in each table refer to Western coals while the last two columns refer to eastern coals.

Four Corners Power Plant trace element data reported by APS-UII and SWES for coal, bottom ash, and precipitator ash are tabulated in the Appendix A Tables A-I and A-II on a mass-concentrations basis. By comparing the coal concentrations converted to a coal-ash basis with the bottom and precipitator ash values, a rough mass balance can be calculated and some statements made about volatility of the elements. According to data presented in Ref. 8, approximately 20% of the ash remains as bottom ash while the remainder leaves the Unit 4 and 5 boilers as fly ash at the Four Corners Power Plant. Of this remaining 80%, 97% or more is captured by the electrostatic precipitators. Thus, about 98% of the total mass of ash is retained in the plant while less than 2% by weight escapes as stack emissions, assuming the particulate control systems are functioning up to specifications.

Rough mass balances calculated using only these components give the results shown in Table IV. The mass balances are presented separately for SWES and APS-UII. The third and fifth columns give the departure from balance as a ratio of output to input. A number larger than 1.0 implies more going out in the bottom and precipitator ash than is input in the coal, whereas a number less than 1.0 implies that some of that element escapes via stack emissions to the atmosphere. The data indicate, unambiguously, that Al, Ca, Co, Cu, Fe, K, La, Li, Mg, Na, Sc, Si, Ti, U, and Zr balance. That is, the output-to-input ratio is near 1.0, or if not, is greater than 1.0, but within 25%. The output-to-input ratios for As, Ba, Cr, Ga, Mn, Mo, Ni, Pb, Sr, V, and Zn are ambiguous in that the two mass-balance ratios differ considerably and, furthermore, at least one of the ratios indicates more of each element leaving the plant in

TABLE II

ELEMENTAL CONCENTRATIONS OF BOILER RESIDUE FROM VARIOUS POWER PLANTS

(IN μG/G, UNLESS % INDICATED)

	Four Corners[a] Power Plant	Other[b] Rocky Mountain Power Plants	Valmont Power Station (Av of 3 Daily Composites)	Allen Steam Plant (Av of 3 Composites)	Chalk Point Power Station (Av of 9 Samples)
%Al	13.53	10.47	8.8	10.2	11.4
As	0.98	1.92	15	18	7.3
B	158	165			
%Ba	0.4	0.24		0.05	0.103
Be	4	4.3			10.6
Ca	3.35	5.06		4.60	0.84
Ce		<300			143
Cd	<0.5	<0.5		1.1	
Co	6.9	8.8		20.8	42
Cr	18	43		152	165
Cu	46	41	82	20	2.8
Eu	15	13.3		1.1	
F	12	65.8			
%Fe	2.70	4.14	6.6	11.2	20.3
Ga	25	18		5	23
Hg	0.032	<0.01	0.14	0.028	0.015
%K	0.73	0.81		1.58	1.13
La	70	70		42	75
Li	78	60			
%Mg	0.45	0.74		1.24	0.60
Mn	284	317		295	340
Mo	3	<7	3.5		
%Na	1.31	0.51		0.50	0.18
Nb		<20	12		
Ni	12	16		85	125
%P	0.03	0.16			
Pb	25	27	<5	6.2	35
%S	0.06	0.09			
Sb	0.14	0.48	2.8	0.64	3.5
Sc	10	15		20.8	26
Se	0.52	0.87	7.7	0.08	1.7
%Si	27.3	26.15		22.9	18
Sr	367	966	1800	170	514
Ta				0.95	1.03
Te	<0.02	<0.02			
%Ti	0.60	0.33		0.40	0.721
Tl	0.30	0.25			
U	9.77 (Ue)	6.78		14.9	
V	65	75	44	260	212
Y	30	37			

TABLE III
ELEMENTAL CONCENTRATIONS OF PRECIPITATOR-COLLECTED FLY ASH FROM VARIOUS POWER PLANTS
(IN μG/G, UNLESS % INDICATED)

	Four Corners[a] Power Plant	Other[b] Rocky Mountain Power Plants	Valmont Power Station (Av of 3 Daily Composites)	Allen Steam[c] Plant (Inlet) (Av of 3 Composites)	Chalk Point Power Station (Av of 9 Samples)
%Al	14.4	11.5	10.2	9.09	13.3
As	11.5	9.7	120	110	161
B	394	400			
%Ba	0.52	0.33		0.046	0.114
Be	5.07	5.7			17.4
Bi	<10				
%Ca	2.97	6.29		2.52	1.06
Ce		<300		84	176
Cd	<0.5	<0.5		8	
Co	8.1	16.7		39	42
Cr	34.5	77		300	188
Cu	68	90	230	140	
Fu	13	16.7		1.3	3.7
F	120	320			
%Fe	2.62	3.45	6.9	12.10	12.3
Ga	67	33			78
Ge	<10				
Hg	0.10	0.04	0.31	0.05	
%K	0.72	0.83		2	1.36
La	67	70		40	89
Li	120	77			
%Mg	0.49	0.94		1.06	0.64
Mn	272	133		298	390
Mo	8.3	<7	41		
%Na	1.25	0.85		1.01	0.211
Nb	17	<20	19		
Ni	19.3	47		207	159
%P	0.06	0.25			
Pb	66	43	66	80	56
S	0.11	0.25			
Sb	0.87	2.54	14	12	6.2
Sc	11.5	18.3		26	34
Se	6.75	12.6	27	25	25
%Si	27.1	24		19.6	20.8
Sn	<3				
Sr	521	1567	2500	250	810
Ta				1.4	1.7
Te	0.13	0.11			
%Ti	0.69	0.63		0.59	0.81
Tl	1.4	1.1			
U	9.8	9.4		30.1	
V	147	133		440	255

TABLE III (CONTINUED)

	Four Corners[a] Power Plant	Other[b] Rocky Mountain Power Plants A	Valmont Power Station (Av of 3 Daily Composites)	Allen Steam[c] Plant (Inlet)B (Av of 3 Composites)	Chalk Point Power Station (Av of 9 Samples)
Y	30	63	68		
Zn	81.5	75	250	740	230
Zr	297	200	210		267

[a]Composite of APS-UII and SWES data, cf Appendix A.

[b]Power plant average of fly ash data reported in SWES excluding Four Corners and Naughton Plants.

[c]In-stack sample collected prior to electrostatic precipitator.

precipitator and bottom ash than enters in the coal. Because the plant is not expected to synthesize these elements, the disagreement is attributed to experimental error, and it could be assumed that on a total-mass basis most of these elements are retained in the plant. However, due to the large degree of uncertainty, these elements are in need of further study. Both sets of data for Be, F, Hg, Sb, and Se indicate a mass deficiency, suggesting loss to the atmosphere. Additionally, the phosphorus and sulfur data, although only one set of measurements is available for each, suggest loss of these elements to the atmosphere. The emission of sulfur gases to the atmosphere is not contestable; however, little is known about phosphorus behavior in coal-fired power plants.

The mass balances for boron are very ambiguous. The APS-UII data suggest a considerable mass excess while the SWES data suggest a substantial mass deficiency. Examination of the boron concentrations shows that the APS-UII mass-excess result is due to a boron concentration in precipitator ash of 700 μg/gm. Based on other information[19] this is known to be an anomalously high value and should perhaps be discounted. The SWES value of 0.469 for the boron-out-to-boron-in ratio is probably more accurate, suggesting loss of boron to the atmosphere either on small particles or in the gas phase.

The mass-balance data generally support current ideas about the volatility of elements in coal. Most of the elements that balance are major and/or nonvolatile ones with the possible exception of copper, which appears to be somewhat volatile as evidenced by a comparison of the bottom and precipitator ash concentrations. Some of these elements, considered to be ambiguous but assumed retained in the plant because of a mass excess, such as As, Cr, Ga, Mo, Pb, Sr, V, Zn, and perhaps Ni, show definite evidence of volatile behavior in a comparison of precipitator and bottom ash concentrations. These elements need to be more carefully studied with respect to stack emissions and particle size dependence.

With respect to stack emissions, the trace elements showing a mass output deficiency are of great interest. These elements and corresponding mass-balance ratios are B (0.47), Be (0.66, 0.85), F (0.18, 0.42), Hg (0.20, 0.32), P (0.77), Sb (0.82, 0.57), and Se (0.66, 0.44). Beryllium and phosphorus were analyzed by semiquantitative emission spectrography and the imbalances should be considered tentative until better data are obtained. The two sets of data for antimony and boron are quite different and thus also require verification. The analytical methods used for the remaining three elements were specific ion electrode for fluorine, flameless atomic absorption

TABLE IV

MASS BALANCE FOR UNITS 4 AND 5 AT FOUR CORNERS POWER PLANT

	SWES		APS-UII	
	0.2 Bottom Ash +0.8 Precipitator Ash	Output/ Input	0.2 Bottom Ash +0.8 Precipitator Ash	Output/ Input
Ag				
Al	14.08	1.07	14.37	0.99
As	9.8	1.05	9.02	1.82
B	210	0.469	600	1.65
Ba	0.3	1.36	0.90	2
Be	3.56	0.66	5.8	0.85
Bi				
Ca	2.81	1.04	3.28	1.02
Ce				
Cd				
Co	7	0.89		
Cr	19	1	52	2.85
Cu	50.6	0.89	74.6	1.17
Eu	13.4	> 1.34		
F	≤122	≥ 0.18	83.4	0.42
Fe	2.68	1.25	2.67	0.99
Ga	44	1.13	86	2.36
Ge				
Hg	≤ 0.05	0.20	0.12	0.32
K	0.74	1.27	0.75	1.06
La	70	1		
Li	78.8	0.92	200	0.88
Mg	0.57	1.20	0.40	0.98
Mn	287	1.27	280	1.54
Mo	≤ 7	1.13	8.6	2.36
Na	1.38	1.21	1.02	0.98
Nb				
Ni	~ 8.4	≳ 0.84	28	1.54
P	0.054	0.77		
Pb	61.4	1.10	55	1.92
S	0.1	0.035		
Sb	1.12	0.82	0.34	0.57
Sc	12.4	0.93	10	1.11
Se	5.53	0.66	5.58	0.44
Si	27.5	1.08	27.6	1.03
Sn				
Sr	354	1.20	460	2.53
Ta				
Te				
Ti	0.53	1.23		
Tl	1.19	≥ 0.82		
U	9.79	0.90		
V	86	0.91	170	1.87
Zn	55	1.04	82	3
Zr	247	1.18	280	1.23

spectroscopy for mercury, and x-ray fluorescence (SWES) or flameless atomic absorption spectroscopy (APS-UII) for selenium. The results from these techniques show satisfactory agreement between the separate studies and provide good evidence for the validity of the observed mass deficiences. These output mass deficiencies are also consistent with volatility considerations and results of other investigations. For example, Kaakinen et al.[13] reported a mass balance (output/input) of about 30% and 10% for selenium and mercury, respectively, as compared to the Four Corners values given above and in Table IV.

C. Enrichment Ratios

A fairly common method of displaying trace element concentration data is in the form of elemental ratios. Elements often used to normalize the data so as to remove variations due to different coals, different concentrations units or, in the case of ambient concentrations, differences due to meteorological and source variables, are Al, Fe, or Si. In the present case Al, Fe, and Si are present in coal ash, bottom ash, and precipitator ash at about the same concentrations and expressed in the same units. The concentration ratios listed in Table V were normalized to silicon. For example, the enrichment factor for element X in precipitator ash compared to bottom ash is

$$E_x = \frac{([x]/[Si])\ \text{precipitator ash}}{([x]/[Si])\ \text{bottom ash}} \quad (1)$$

Klein et al.[16] suggest that the observed elemental concentrations at the Allen Steam Plant show three different classes of partitioning behavior. Class I were those elements partitioned about equally between inlet-to-precipitator fly ash and bottom slag ([x] inlet/[x] slag ≤ 1.2). At the Four Corners plant this class is approximated by a combination of equal partitioning between precipitator and bottom ash and mass balance. Class II were those elements concentrated in the inlet fly ash compared to bottom slag ([x] inlet/[x] slag ≥ 6) and in outlet from precipitator ash compared to inlet fly ash ([x] outlet/[x] inlet ≥ 3.5). This class is approximated at Four Corners by those elements not showing a mass deficiency and exhibiting a precipitator-to-bottom-ash ratio greater than 2.5. Class III were elements depleted in ash and believed to persist essentially in the gas phase. At the Four Corners plant this class can be approximated by those elements showing depletion in both bottom and precipitator ash as compared to coal. The class assignments given to the elements in the Allen Steam Plant study are listed in Column 6 of Table V. The class assignments using the criteria described for the elements based on APS-UII, SWES data are listed in Column 5 of Table V. For the most part, the elemental behavior between the two plants agrees. Some elements at Four Corners appear to exhibit partitioning behavior intermediate between Oak Ridge's Class I and Class II and are listed as such. These could be due to differences in process parameters such as boiler design, combustion temperature, or electrostatic precipitator temperature. However, all of the elements classed as intermediate between I and II show definite volatility as evidenced by a comparison of enrichment ratios for precipitator ash and bottom ash and should probably be placed in Class II. Mercury, F, S, and Se are placed in Class III at Four Corners based on mass imbalance and precipitator-bottom ash concentration ratio considerations. This Four Corners plant elemental volatility behavior is generally consistent with the results reported[13] at the Valmont Power Station which burns Wyoming coal.

Gladney[14] presents precipitator-ash-to-coal enrichment factors for the Chalk Point Power Station, where fly ash is collected with an electrostatic precipitator operating at about 125°C with approximately 96%

TABLE V

CONCENTRATION ENRICHMENT RATIOS AT FOUR CORNERS POWER PLANT FOR ASHES RETAINED IN THE PLANT

	Bottom Ash/ Coal	Precipitator Ash/ Coal	Precipitator Ash/ Bottom Ash	Approximate Class Based On FC Data	Assigned Class In Allen Steam Plant Work	Chalk Point Precipitator Ash/ Coal
Al	0.94	1	1.07	I	I	1
As	0.13	1.54	11.81	II	II	0.90
B	0.37	0.94	2.51	II	NA	
Ba	1.13	1.48	1.31	I	I	1
Be	0.63	0.80	1.27	I	NA	
Bi				NA	NA	
Ca	1.08	1.12	1.02	I	I	1
Ce					I	0.99
Cd					II	
Co	0.79	0.94	1.19	I	I	1
Cr	0.92	1.90	2.05	I- II	I- II	0.93
Cu	0.73	1.08	1.49	I	II	
Eu					I	1
F	0.014	0.14	10.06	III	NA	
Fe	1.10	1.17	1.07	I	I	1.3
Ga	0.64	1.71	2.69	II	II	0.89
Hg	0.096	0.31	3.16	III	III	0.028
K	1.09	1.09	1	I	I	0.85
La	0.96	0.92	0.96	I	I	1
Li	0.87	1.37	1.55	I- II	NA	
Mg	0.98	1.07	1.10	I	I	1
Mn	1.33	1.28	0.96	I	I	1.4
Mo	0.79	2.20	2.78	II	NA	
Na	1	1.10	1.10	I	I- II	1
Nb					NA	
Ni	0.63	1.02	1.62	I- II	I- II	0.92
P	0.41	0.82	2	I- II	NA	
Pb	0.84	1.91	2.28	I- II	II	0.85
S	0.02	0.035	1.8		NA	
Sb	0.14	0.85	6.24	II	II	0.89
Sc	0.90	1.04	1.16	I	I	0.9
Se	0.046	0.60	13.10	III	II	0.71
Si	≡1	≡1.00	≡1	I	I	0.86
Sn					NA	
Sr	1.20	1.85	1.53	I- II	I	1.4
Ti	0.87	1.01	1.16	I	I	0.96
Te					NA	
Tl	0.19	0.88	4.7	II	NA	
Ta					I	0.85
U	0.81	0.82	1.01	I	I- II	
V	0.67	1.52	2.28	I- II	I- II	0.94
Y	0.70	0.71	1.01	I	NA	

TABLE V (CONTINUED)

	Bottom Ash/ Coal	Precipitator Ash/ Coal	Precipitator Ash/ Bottom Ash	Approximate Class Based On FC Data	Assigned Class In Allen Steam Plant Work	Chalk Point Precipitator Ash/ Coal
Zn	0.29	1.48	5.13	II	II	1.0
Zr	0.81	1.31	1.63	I- II	NA	1.0

efficiency, and thus should provide data that can be compared with the corresponding enrichments at the Four Corners Plant. Although aluminum, rather than silicon, was used for normalization of the data, the Four Corners data could be considered normalized to aluminum as well as silicon since the aluminum enrichment factor for precipitator ash compared to coal was equal to 1. The Chalk Point enrichment factors are reproduced in Column 7 of Table V and should be compared to Column 3.

In nearly all cases where there is a substantial difference the ratios at Four Corners are greater. Chalk Point shows enrichment for only Fe (1.3), Mn (1.4), and Sr (1.4) when comparing precipitator ash to coal, whereas Four Corners data indicates enrichment for As (1.5), Ba (1.5), Cr (1.9), Ga (1.7), Li (1.4), Mn (1.3), Mo (2.2), Pb (1.9), Sr (1.8), V (1.5), Zn (1.5), and Zr (1.3). (However, consideration of Chalk Point post-precipitator fly ash enrichment ratios points out the hazards that exist if predictions about trace element volatility were made based only on precipitator-collected ash and coal trace element data.) It is difficult to explain the generally higher Four Corners enrichment ratios for precipitator ash compared to coal in view of similar precipitator temperatures and collection efficiencies. Consideration of other data from the Chalk Point plant and comparison with the available Four Corners Plant data suggest that volatile elements remain in the gas phase longer at Chalk Point and are, therefore, not collected by the precipitator. The Chalk Point Plant is a slag-type furnace with longer coal residence times in the boiler and higher combustion temperatures (∿1600°C) as compared to the dry-bottom Four Corners Plant (∿1350°C). These factors could account for the differences cited. On the other hand, they could be due to the trace elements being present in different chemical form in the coal.

Overall, the available data suggest that trace element behavior at the Four Corners Power Plant is consistent with that reported elsewhere. If different, it seems to be in the direction of less volatile behavior and, therefore, less emission of trace contaminants to the atmosphere than is the case for Eastern coals.

III. SOILS

A. Introduction

Soils have been collected in San Juan County, New Mexico, both near the Four Corners Power Plant and at sites remote from it. The data obtained from analysis of these samples and reduced for this report are presented in Appendix B along with pertinent information as to the date the samples were collected, the location of the sample sites, the depth at which samples were taken, and the methods of sample collection, preparation, and analysis. In many of the studies reported here the sampling schemes were designed to detect differences in elemental concentrations among the soils, dependent on either orientation to the power plant or with respect to the depth of sample collection. Because trace element mass impact on soils of the area from the Four Corners Power Plant can be expected to be quite small in relation to the natural trace element content of the soils, the problem of detecting a difference between areas of suspected high and suspected low impact is compounded. Other important complicating factors include routine problems

of judicious choice of sampling sites, the minimization of trace element contamination inherent in sample collection, preparation and analysis, the precision and accuracy of various analytic methods, the large natural variability of soils, and changing patterns of deposition due to varying meteorological conditions. Although there is a fairly impressive bulk of soil data, conclusions are difficult and tend to differ among the various investigators.

B. Summary of Findings

Data provided by Cannon and Anderson for the Southwest Energy Study, Report of the Coal Resources Work Group[7] (Appendix B) are graphed in that report for each element studied. As is apparent from those graphs, and as stated in the report, "Arsenic, copper, boron, beryllium, calcium, iron, titanium, magnesium, strontium, zinc, zirconium, and scandium values were all elevated at some points on traverse A-A' but were below the average for U. S. soils at points on traverse B-B'." However, if all data obtained for each traverse are averaged, (Appendix B, Tables I and II) the observations made when comparing traverse A-A' (<3.2 km from plant) are different from the original interpretation. Thus, when the mean value and standard deviation for each element for traverse A-A' is compared with similar data from traverse B-B', Cu, Ca, Fe, Mg, Zn, and possibly Be of the above mentioned 12 elements appear to be present in higher concentrations along traverse A-A' than B-B'. Analysis of the remaining elements suggests that there are also greater concentrations of Ni, V, and possibly Co and Cr along traverse A-A' than B-B'. Due to the location of traverse A-A', it is strongly suspected that any detectable difference, if attributable to power plant impact, is probably due to creep, saltation, and deposition of suspended material from the dried ash disposal ponds rather than from stack emissions. Table VI presents the means for the various elements as quantified for traverse A-A' minus the associated standard deviations and the means for traverse B-B' plus the associated standard deviations. Although this is not a classic statistical manipulation, it is used here only with the hope that rough trends might come to light. Of the elements already mentioned above, particular attention should be paid to zinc because it was one of the few elements in this study analyzed by atomic absorption. Consequently, those data should be more accurate and precise than the emission spectrographic results presented for most of the elements.

The preliminary work of Stark and Harris,[9] part of which is presented in Appendix B, was apparently a planning exercise for the more extensive work done at a later date in the "main" part of their study. Included in this preliminary work, however, are some data on soils digested with hydrogen fluoride (HF) which are of interest for comparison with work done by others. It was assumed that, for most elements, an HF digestion would dissolve essentially all of the sample. The HF digestion was not performed on the "main" samples. Too few preliminary samples were analyzed to permit a standard deviation calculation, and it is merely noted here that manganese was elevated at the preliminary impact site relative to the preliminary control site and that this elevated concentration was demonstrated at the 10- to 15-cm depth, but not at the 0- to 5-cm depth. Concentrations of molybdenum also appear to follow this same trend but are about two orders of magnitude greater than concentrations reported elsewhere.[10] There is no immediately obvious explanation for these high values. Also of some interest is work done in both the preliminary and main phases of the study in which 1N hydrochloric acid (HCl) extractions were conducted on soils in an effort to simulate concentrations of elements which "might be available to plant roots over a long period of acid action by roots." The preliminary work (Appendix B,

Table IV) indicates a possibly greater available amount of manganese at the impact site, both in an absolute sense and also when compared with the total manganese concentration (Appendix B, Table V) at the two sites. However, it should again be pointed out that there were too few determinations from which to calculate a standard deviation. The main samples (Appendix B, Table VI) for which it was possible to calculate a standard deviation do not exhibit a clear-cut increased manganese availability at the impact site as based on a 1N HCl extraction. Unfortunately an HF digestion was not performed on the main samples which would have made it possible to calculate the amount available (1N HCl extraction) at the control and impact sites in terms of the percentage of the total amount present (HF digestion) for the main samples.

Soil data for the Four Corners Power Plant environs, as reported by Woodward-Envicon[10] and reproduced and summarized in Ref. 8, are reduced and presented in Appendix B. There are no clear-cut differences between control and impact areas when viewed in light of the large standard deviations. However, it should be noted that one of the control sites is situated on the Utah International, Inc., Area III lease property which might be expected to differ from non-overburden areas. A comparison of means, both including and excluding this site, from samples follows in Table VII. No numerical significance should be attached to differences observed due to lack of sufficient sample size. There is, however, a rough indication that including the overburden of UII Area III in the control group may tend more often to increase, rather than decrease, concentrations reported for control samples at both the 0- to 1-cm and 15- to 18-cm depths. If such control samples are to be used in the future as standards against which possible impact on non-overburden areas is to be judged, it is advisable not to include overburden areas as part of the control group.

TABLE VI

SWES SOILS: 0-1/2 in.

(IN μG/G, UNLESS % INDICATED)

Element	Traverse A-A' $\bar{X}$ - Sx	Traverse B-B' $\bar{X}$ + Sx
As	3.91	4.37
B	26.77	28
Ba	641	825
Be	1.01	-
%Ca	1.49	1.31
Co	5.68	~5.61
Cr	24.79	20.90
Cu	17.38	11.33
%Fe	1.90	1.39
Hg	~0.01	-
%K	1.65	2.79
%Mg	0.85	0.48
Mn	179	340
%Na	0.83	1.40
Ni	9.79	-
Pb	17.65	27.58
Sb	0.22	-
Sc	4.99	-
Sr	160	176
%Ti	0.17	0.19
V	60	37
Zn	44	34
Zr	79	190

C. Discussion

The task of identifying the normal range of trace element concentrations for San Juan County soils is obviously germane to determining whether or not elevated concentrations can be observed in areas of possible impact. For purposes of comparison in this review, data from soil samples taken at depths not exceeding 5 cm in areas of suspected impact as well as control areas are presented in Table VIII as a range of the means obtained from various studies. Included are the data of Cannon and Anderson[7] from their traverse B-B', the total digestions of 0- to 5-cm soil samples from the preliminary control sites of Stark and Harris[9] and the 0- to 1-cm control data (excluding the overburden site) of Westinghouse

TABLE VII

WOODWARD-ENVICON CONTROL SOILS

(IN μG/G, UNLESS % INDICATED)

	With UII Area III		Without UII Area III	
Element	0-1 cm	15-18 cm	0-1 cm	15-18 cm
Ag	<1	<1	~0.75	~.75
%Al	>1	>1	>1	>1
As	4.2	4.6	3.2	3.8
B	16.7	16.7	15	15
Ba	1267	1267	1500	1500
Be	2	2	2	2
Bi	~8	~8	~10	>10
%Ca	≥1	≥1	≥1	≥1
Cd	~0.1	~0.19	~0.11	0.24
Co	30	33	40	45
Cr	10	10	10	10
Cu	11	7	6.4	8.3
F	150	220	108	140
%Fe	>1	>1	>1	>1
Ga	13	17	10	15
Ge	~4	~3.8	<10	<10
Hg	<0.02	<0.02	<0.02	<0.02
%K	>1	>1	>1	>1
Li	53	57	50	55
%Mg	≥1	≥1	≥1	≥1
Mn	367	233	200	200
Mo	<3	<3	<3	<3
%Na	>>1	>>1	>>1	>>1
Nb	<10	<10	<10	<10
Ni	~6.7	~6.7	~5	~5
Pb	7.4	10.5	7.8	8.25
Sb	1.1	0.20	1.6	0.18
Sc	10	10	10	10
Se	0.2	0.2	0.2	0.25
%Si	>>1	>>1	>>1	>>1
Sn	≤5	≤5	≤5	≤5
Sr	200	233	200	250
Ti	~933	~933	~900	~900
V	23	23	15	15
Zn	17	20	10	15
Zr	83	90	75	85

TABLE VIII

COMPOSITE SOIL DATA ≥2 MILES FROM PLANT: 0-5 CM DEPTH

(IN μG/G, UNLESS % INDICATED)

	0-5 cm CONTROL [a]			0-5 cm IMPACT		
	$\bar{X}$	Number of Investigators	Number of Samples	$\bar{X}$	Number of Investigators	Number of Samples
Ag	~0.75	1	2	<1.	1	3
%Al	>1	1	2	>1	1	3
As	3.2-~5.5	3	14	4.1-5.7	3	12
B	15-17	2	12	27-69	2	10
Ba	730-1500	2	12	1243-1600	2	10
Be	<1-2	3	14	1.5-2	3	12
Bi	<10	1	2	<10	1	3
%Ca	0.99-≥1	2	12	≥1.-2.7	2	10
Cd	~0.11-~0.75	2	4	~0.2-~0.75	2	5
Co	~4-40	3	14	7-33	3	12
Cr	10-36	3	14	13-29	3	12
Cu	6.4-8.7	2	12	12-37	2	10
F	108-460	2	12	170-222	2	5
%Fe	1.02->1	2	12	>1-2.43	2	10
Ga	10	1	2	13	1	3
Ge	<10	1	2	<10	1	3
Hg	<0.02-<0.11	2	12	<0.02-~0.02	2	10
%K	>1-2.25	2	12	>1-1.87	2	10
Li	50	1	2	60	1	3
%Mg	0.33-≥1	2	12	0.96-≥1.	2	10
Mn	200-296	3	14	200-286	3	12
Mo	<3	1	2	<3	1	3
%Na	1.09->>1	2	12	0.95->>1	2	9
Nb	<10	1	2	<10	1	3
Ni	<5-28	3	14	~6.5-13.57	3	12
Pb	~7.5-21	3	14	5-21.43	3	12
Sb	<0.5-1.6	2	12	0.2-0.79	2	10
Sc	<5-10	2	12	8.29-13	2	10
Se	0.2	1	2	0.2	1	3
%Si	>>1	1	2	>>1	1	3
Sn	≤5	1	2	≤5	1	3
Sr	159-200	2	12	200-271	2	10
Ti	~900-1600	2	12	~1000-3000	2	11
V	15-28	2	12	~17-67	2	10
Zn	10-27	2	12	~9-57	2	10
Zr	75-142	2	12	117-150	2	10

[a] Not an 'impact' site; not an overburden area.

Environmental Systems Department as reported by Woodward-Envicon.[10] The control sites are all at least 3.2 km (2 mi) from the power plant, are not known overburden sites, and were not mentioned as possible impact sites by the authors of the cited reports. The control samples in Table VIII are all from a depth not exceeding 5 cm from the surface. Included in the range of means of samples taken at sites of suspected impact are the data of Cannon and Anderson[7] from their traverse A-A', the total digestions of 0- to 5-cm soil samples from the preliminary impact sites of Stark and Harris[9] and the 0- to 1-cm impact data of Westinghouse Research Laboratory as reported by Woodward-Envicon.[10]

Reviewing the data presented in Table VIII, it appears that there may be an increased concentration within the top 5 cm of soil of B, Ca, Cu, Fe, Sr, Ti, V, Zn, and possibly Sc at sites suggested by the various investigators as impacted by the power plant, as compared with control sites. These observations should certainly not be considered conclusive, due to differences among the investigators as to sample sites; sampling depths; methods of sample collection, preparation and analysis; date of sample collection; and sampling design considerations such as the number of sites, the number of samples per site, and the number of replicates per sample. Intuitively, the more data points available on which to base observations, the more credence is placed on those observations. The apparent differences between the ranges of means for concentrations of B, Ca, Cu, Fe, Sr, Ti, V, Zn, and Sc in the control and impact data of Table VIII were based on the work of at least two investigators and no fewer than 10 sample analyses.

Data for soil samples collected from 0- to 15-cm and 10- to 15-cm depths have been organized in similar fashion in Table IX. Possibly because of the small number of impact sample analyses, and/or because of no discernible impact at depths greater than 5 cm, there is no obvious increase in concentrations of elements listed as impact vs control sites. The range of means for the control group includes the data of Cannon and Anderson[7] from soils taken from 0- to 15-cm depths at sites ranging in distance from the power plant of 14.4 km (9 mi) to 54.4 km (34 mi), the 10- to 15-cm depth control data of Stark and Harris[9] and the 15- to 18-cm control soil data of WRL as reported by Woodward-Envicon.[10] Impact data include that of Stark and Harris and Cannon and Anderson as cited above.

In an effort to determine any apparent relationships between vegetation and soil, elemental content of specific plants and soils collected by Cannon and Anderson at the same site were ratioed and organized in order of increasing distance from the power plant. The values obtained represent the ratio of the elemental concentration in the vegetation to the concentration of that same element in soil at 18 sites. Ratios were calculated for Cu, Zn, Ni, V, V, and Cr. Because different species were analyzed at different sites, because the sites are in many directions from the power plant, and because the only soil samples within an 8-km radius are taken from a different depth from the remainder of the soil samples for which there is both soil and plant data available, there remain too few data which are similar enough to be compared relative to power plant emissions. However, it is worthwhile to point out that the species which show a relative concentration of the elements (highest ratios) are distinctly different from the group of species which show the lowest concentration of the elements relative to the amount in the associated soil (Table X). The soil data presented in Table X were reported by Cannon and Anderson[7] representing samples collected at a

TABLE IX

COMPOSITE SOIL DATA; > 5-CM DEPTH

(IN μG/G, UNLESS % INDICATED)

	CONTROL			IMPACT		
	$\bar{X}$	Number of Investigators	Number of Samples	$\bar{X}$	Number of Investigators	Number of Samples
Ag	~0.75	1	2	<1	1	3
%Al	>1	1	2	>1	1	3
As	3.8-~7	3	31	4.6-~5.5	2	5
B	15-~25	2	29	23	1	3
Ba	850-1500	2	29	1567	1	3
Be	~1.5-2.0	2	29	~1.5-2.0	2	5
Bi	<10	1	2	<10	1	3
%Ca	≥1-3	2	29	~0.75-≥1	2	5
Cd	0.24~0.75	3	31	0.16	1	3
Co	~6 -45	3	31	~12.6-27	2	5
Cr	10-30	3	31	13-27.5	2	5
Cu	8.3-15	2	29	13	1	2
F	140-224	2	4	180-268	2	5
%Fe	>1-1.5	2	29	>1	1	3
Ga	15	2	29	13	1	3
Ge	<10	1	2	<10	1	3
Hg	<0.02-~0.02	2	29	<0.02	1	3
%K	>1-2	2	29	>1	1	3
La	~25	1	27			
Li	55	1	2	63	1	3
%Mg	0.7-≥1	2	29	≥1	1	3
Mn	125-250	3	31	167-232	2	5
Mo	<3	1	2	<3	1	3
%Na	1->>1	2	29	>>1	1	3
Nb	<10	1	2	<10	1	3
Ni	~5-24	3	31	~3.8-<10	2	5
Pb	7.5-20	3	31	~7.5-21	2	5
Sb	0.18-<0.5	2	29	0.15	1	3
Sc	~5-10	2	29	13	1	3
Se	0.25	1	2	0.3	1	3
%Si	>>1	1	2	>>1	1	3
Sn	≤5	1	2	≤5	1	3
Sr	250-450	2	29	233	1	3
Ti	~900-1500	2	29	~1000	1	3
V	15-50	2	29	20	1	3
Y	20	1	27			
Zn	15-45	2	29	~9	1	3
Zr	85-150	2	29	120	1	3
Yb	2	1	27			

TABLE X.

SWES SOIL/VEGETATION DATA

	Data for site at which the highest ratio of elements in plant tissue to the same element in soil was found						Data for site at which the lowest ratio of elements in plant tissue to the same element in soil was found					
	Cu	Zn	Ni	V	B	Cr	Cu	Zn	Ni	V	B	Cr
Site No.	25	25	67	67	22	25	47	186	16	182	16	182
km from Power Plant	24	24	35	35	23	24	52	27	40	16	40	16
Direction from Power Plant	E	E	E	E	ENE	E	SSW	SW	SW	NW	SW	NW
Plant Analyzed	A	A	B	B	C	A	D	E	F	G	F	G
Conc in plant (μg/g)	500	1100	15	50	500	15	15	50	10	<15	100	7
Conc in soil (μg/g)	5	20	<2.5	30	Not detected (<10)	7	30	45	15	70	50	50
Plant Conc/ Soil Conc	100	55	>6	1.7	>50	2.1	0.5	1.1	0.7	<0.2	2	0.1
Total No. of sites at which this species was sampled	1	1	2	2	1	1	3	2	2	2	2	2
Ratio at other sites for this species is generally	-	-	>1	1	-	-	Low	1.5	<1	<0.3	2.0	0.2

A = *Chrysothamnus nauseosus*
B = *Artemesia tridentata*
C = *Gutierrezia lucida*
D = *Atriplex confertifolia*
E = *Atriplex corrugata*
F = *Atriplex powelli*
G = *Alfalfa*

depth of 0- to 1-cm. The plant samples for which data are presented were collected in 1971 and were not washed, but were ashed, before analysis. The analytical methods for the plant analyses were the same as those for soil and can be found in Appendix B.

Assuming that different plant species show different abilities to concentrate or take up trace elements, the question then becomes one of cause and effect. There are obviously not enough data to attempt an answer. However, typical questions relative to the copper data, as an example, are

1. Can Chrysothamnus nauseosus be found at site #47?
   A) If not, why not?
   - Is the copper concentration in the soil too high for the plant to tolerate?
   - Is the plant not present because of other environmental factors such as water availability (note that all sites with high ratios are east of the power plant and all sites with low ratios are west of the power plant)?
   - If so, what would the absolute concentration of copper be in the plant and what would the ratio of copper in the plant to copper in the soil be?
2. Is there an upper limit to the amount of copper that Chrysothamnus nauseosus will take up?
3. Is the amount of copper in the plant dependent on the amount in the soil?
4. Is there an upper limit to the ratio of copper in Chrysothamnus nauseosus to the copper in the soil?
5. Could species such as Chrysothamnus nauseosus be used as indicators of gross pollution by elements such as copper?
6. Is the ratio of Atriplex confertifolia copper content to soil copper content fixed at such a low value that A. confertifolia is able to grow only in soils with a copper content high enough to supply it with copper sufficient to fulfill nutrient needs?
7. Is A. confertifolia relatively indifferent to soil copper content?

Of ultimate importance is the impact which elevated trace element concentrations in soil may effect on the terrestrial ecosystems. In this light, it should be noted that even though a chemical species may be supplied to or resident in an abiotic medium as an insoluble and presumably biotically unavailable form, it may be transformed to an available form under certain conditions by microorganisms[20,21] or by extracellular metabolic by-products. A well-known example of this type of situation is the transformation of elemental mercury by microorganisms, especially in an anaerobic reducing environment, to the extremely toxic methyl mercury form which is concentrated in food chains. Biomethylation of both selenite[22] to dimethylselenide and inorganic arsenic[23] to di-and trimethylarsine is known to exist. There are also indications that Sn, Pd, Pt, Au, Tl, Te, and S[23] may also be methylated in the environment.

The literature documents microbially mediated solubilization of Mn[24], Zn[25], Co[26], and Cu[26]. It is also likely that microbial oxidation and reduction may affect the solubilities of As, Mo, Se, Te, U, and V.[20] Of these elements, Cu, Mn, Mo, and Zn are considered essential nutrients for all organisms, and Co, Se, and V are considered essential nutrients for some groups of organisms. Yet, these required trace elements are all moderately to highly toxic to large groups of organisms at concentrations above that required for nutrition.[20] Numerous factors affect toxicity, including individual organism susceptibility, the chemical species involved,

temperature, pH, moisture, oxygen tension, dose rate, route of exposure, and other synergistic or antagonistic factors. Because it is impractical to attempt measurement of all these parameters in the field, most toxicity studies are accomplished in laboratories under more controlled conditions. The information obtained from such studies is certainly useful but cannot easily be extrapolated to the real world. Nonetheless, it has been shown that the indigenous population of aerobic heterotrophs of a man-made reflecting pool is inhibited by as little as 0.001 ppm copper added as $CuCl_2$;[27] yet Bowen[20] references work which suggests a nutrient concentration of 0.005 ppm Cu for bacteria. It is possible that organically rich growth media bind a great portion of the copper and only a portion of the amount added is actually available to the microorganisms in ionic form to provide the required nutritive amount, or that all the copper is bound by organics in the media and organisms are able to render it available as it is needed.[28] It can be hypothesized that the reflecting pool, being less organically rich than laboratory growth media, has less metal binding capacity and that lesser concentrations of potentially toxic elements in such conditions have an adverse effect on the populations. Although this is only one of many possible explanations of the discrepancy in copper toxicity levels noted above, it is apparent that under certain conditions the threshold between harmless or essential concentrations and those which may be lethal can be small.

Of what possible consequence are these observations to the terrestrial ecology of the Four Corners Power Plant area? The immediate area is considered to be a dry, cold, desert with desert grasslands vegetation. Work done by the University of Utah as reported by Westinghouse Environmental Systems Department[8] indicates an average living cover of less than 19% during 1971 at 10 stands less than 4.8 km from the power plant. The organic content of the soil in the mine lease area is low, averaging much less than 1%.[8] Soils with very low organic content may be more susceptible to trace element impact than soils which are organically rich. For example, Martens et al.[26] demonstrated that an increase in the amount of organic matter in soils was significantly correlated with an increased amount of zinc bound by organo-clay complexes.

Studies of metals impact on terrestrial ecosystems are beginning to receive more attention. Work done in the Crooked Creek Watershed[30] in southeastern Missouri adjacent to a lead smelter and lead mine shows a decreasing amount of litter decomposition in the O_2 soil horizon with increasing amounts of lead. Bacteria isolated from zinc and copper tips[31] have been shown to have a much higher threshold for those elements than bacteria isolated from uncontaminated soils.

D. Elemental Concentrations in Soils Compared with Coal and In-plant Coal Ash

It is common practice to compare trace element concentrations in coal, power plant ashes, stack particulates, and ambient air particulates with crustal average values. One reason for this procedure is to enable some estimates to be made concerning the source of trace elements measured in samples collected from the ambient air. If the elemental ratios (to aluminum, for example) in an ambient sample were approximately the same as the crustal average ratios it could reasonably be assumed that the air particulate sample consisted principally of wind-blown dust. A weakness in this deduction is that the trace element composition of wind-blown dust at a particular site may be considerably different than the crustal average values due to variability in location, type of soil, vegetative cover, and other factors.

Elemental concentrations in Four Corners area soils, together with values given by others[7,20,32] as crustal averages or nominal soil values, are tabulated in Table XI. In all cases, except where the symbol

∿ is shown, the Four Corners concentrations are based on 27 or more samples. These concentrations are a composite of the control sites discussed above. The variations in Four Corners concentrations may be due to analytical uncertainty or natural variations. The relative standard deviations for many of the elements are near 50%, which is the appropriate one-sigma precision value for the emission spectrographic technique used for many of these same elements. However, natural variations of this order in trace elements concentrations may also be expected. The listed standard deviations are undoubtedly a combination of both of these factors and possibly others.

The Four Corners area soil elemental concentrations listed should be considered normal as compared to other soils and crustal averages. In most cases where there is an apparent difference, the Four Corners values are lower. However, based on the available data, this statement is only suggestive.

For potential environmental effects, it is useful to compare Four Corners soil averages with the values found in coal, bottom ash, and precipitator ash (Table IV). This is done by comparing the mass concentrations in bottom and precipitator ash to soils, as tabulated in Columns 6 and 7 of Table XI. Inferences of possible environmental effects from these ratios should carefully consider that the relative availability of a given chemical species in the soil or ash may have little relation to the total elemental content. Differences in chemical or physical form between the various matrices undoubtedly exist and would influence the availability. However, based only on differences in elemental concentrations we can state that:

1. Aluminum, B, Ba, Be, Cd, Cu, Fe, La, Sc, Se, and Ti are all present in the bottom ash at levels that are twice those in area soils, and B is in excess by at least a factor of 5.
2. Arsenic, F, K, Sb, and Zn appear to to be substantially depleted in the bottom ash compared to area soils.
3. With regard to precipitator ash, B and Se are greatly enriched (> X 10) compared to area soils, whereas Ba, Cu, and Hg are present at concentrations between 5 and 10 times their concentrations in soils; and Al, As, Be, Ga, La, Li, Pb, Sb, Se, Ti, V, Zn, and Zr may or may not be significantly more concentrated in the precipitator ash than in area soils.
4. Fluorine and potassium are the only elements apparently depleted in the precipitator ash as compared to area soils.

The elements considerably more enriched in precipitator ash than in bottom ash constitute the more volatile elements. Thus, we conjecture that the trend would continue in going from precipitator ash to stack emissions. Such a trend has been demonstrated at the Chalk Point and Valmont Power Stations.[13,14] This line of reasoning would indicate that As, B, F, Ga, Hg, Pb, Sb, Se, V, and Zn should be of most interest with respect to stack emissions.

Note, however, that species (elements) that are important in the atmosphere may be completely different than those important in the hydrosphere or soils. For example, solubility behavior may indicate a different set of priorities than volatility. (See Section IV.)

IV. WATER SYSTEMS

Water bodies are complex and often inhomogeneous in both space and time. As a consequence, characterization of trace elements in a water body may require extensive temporal and spatial sampling. Water quality may vary with depth, flow rate, time of year, rainfall, and its substrate. A single grab sample cannot usually be assumed to be representative of the water body and due care should be exercised when drawing conclusions from such data.

TABLE XI

FOUR CORNERS SURFACE SOILS COMPARED TO OTHER SOILS AND COAL ASH

(IN μG/G, UNLESS % INDICATED)

	Four Corners Area	Nominal Soils Values-Bowen	U. S. Average Soils	Wedepohl Crustal	Bottom Ash/ F. C. Soil	Precipitator Ash/ F. C. Soil
%Al	5.0 ± 2.32	7.1	6.6	7.83	2.7	2.9
As	4.53± 3.57	6	5	1.7	0.23	2.54
B	22.4 ±12.3	10(2-100)	35		7.1	17.6
%Ba	851±297	500	550	590	4.7	6.1
Be	1.55± 0.36	6(0.1-40)	1	2	2.6	3.3
Bi	~ 8 ± 6					
%Ca	2.46± 1.65	1.37(0.7-50.)	2.5-3	2.87	1.4	1.2
Cd	~0.36± 0.14	0.06		0.1	≲2.8	≲1.4
Co	7.86± 2.82	8	10	12	0.87	1.03
Cr	25.0 ±13.5	100(5-3000)	54	70	0.72	1.4
Cu	13.1 ± 4.15	20(2-100)	25	30	3.5	5.2
Eu						
F	~274±135	200		720	0.044	0.44
%Fe	1.37± 0.56	3.8	2.5	3.54	2	1.9
Ga	14.8 ± 4.4	(0.4-6)	-	17	1.7	4.5
Ge	~ 4 ± 2	1		1.3		
Hg	0.02± 0.03	(0.03-0.8)	0.05.0.11	0.03	1.6	5
%K	2.07± 0.41	1.4	2.4	2.82	0.35	0.35
La	25±13.4	30		4.4	2.8	2.7
Li	~ 53±6	30		30	1.5	2.3
%My	0.6 ± 0.3	0.5	0.9	1.39	0.75	0.82
Mn	257±109	850	580	690	1.1	1.1
Mo		2		1		
%Na	1.02± 0.42	0.63	1.2	2.45	1.1	1.2
Nb						
Ni	10.8 ± 8.7	40	20	44	1.1	1.8
P						
Pb	18.7 ± 2.8	10	20	15	1.3	3.5
S		700		310		
Sb	~0.31	(2-10)	<0.5	0.2	~0.45	~2.8
Sc	4.75± 2.25	7	10	14	2.1	2.4
Se	~0.2 ± 0.1	0.2	0.43	0.09	2.6	34
%Si		33		30.54		
Sn						
Sr	358±642	300	250	290	1	1.5
Ta						
Te						
%Ti	0.15± 0.05	0.5	0.3	0.47	4	4.6
Tl						
U		1		3.5		
V	42.5 ±16	100	80	95	1.5	3.5
Y	20±6	50		34	1.5	1.5
Zn	38±12	50	55	60	0.42	2.1
Zr	144±35	300	250	160	1.3	2.1

From an environmental and ecological effects viewpoint, chemical species that are mobilized by water systems are of interest for various reasons. In the context of the LASL program, comparison of trace element concentrations in various waters, including natural water bodies and process or disposal streams, can give important indications as to the solubility and availability of various elements in the residues remaining after combustion. For this reason, some of the available water quality data from the Four Corners, New Mexico, area have been considered and an attempt has been made to analyze and interpret them.

To date, the most extensive interpretive analysis of water quality in the vicinity of the Four Corners Power Generating Stations is that done in preparation for various environmental impact statements as required by Federal legislation.[8,11] Much of this work can be obtained from the Governmental agency (Bureau of Reclamation) responsible. For the purposes of this report, the data presented in this and other documents are used to provide direction for this study and to indicate possible gaps in current knowledge which suggest a need for additional studies. In connection with the above mentioned work, Arizona Public Service, Utah International, Inc., and others have sponsored environmental impact-related studies in which numerous trace element data on appropriate waters have been, and are being, collected.[8,10,11] An extensive water quality monitoring program is under way to assess water impacts due to the joint operations of Arizona Public Service, Utah International, Inc., and Western Coal Gasification Company. This program is being conducted by Syn-AN, Inc. (Billings and Rabinovitch), under contract to these same companies. The USGS, FWPCA, and USEPA are also sources of a limited amount of water quality data in the area, as are the New Mexico Environmental Improvement Agency and the New Mexico Surface Mining Commission.

The water bodies of interest for this report are the San Juan River, which constitutes the major drainage basin in the region; the Chaco River, a tributary of the San Juan which receives most of the surface drainage, effluent, and run-off from the Four Corners Power Plant and the Navajo Mine;[11] Morgan Lake, a man-made lake located adjacent to the Four Corners Power Plant, in which San Juan River water is stored and from which the power plant draws all process waters; and the ash slurry settling pond, where bottom ash and fly ash from boiler Units 1, 2, and 3 are placed for disposal. Also of interest are seepage waters from Morgan Lake and the ash disposal ponds, and underground aquifers.

The trace element and water quality information used in this report is given in Appendix C. Table XII summarizes these data by water body of interest. As noted in Appendix C, the available numbers may represent a single grab sample, an average of many grab samples, or an average of several years' samples; consequently, it is not possible to present a meaningful average or median and at the same time make use of all available information. Therefore, the data summary of Table XII is a subjective interpretation of the information presented in Tables I-IX of Appendix C and the original documents from which these tables were prepared. The considerations underlying these subjective judgments included (a) number of samples used in preparing a value; (b) how recently the samples were collected; and (c) in the case of single sample values, comparability with other data. The numbers given for each parameter are for dissolved components, are nominal, and are considered to be representative of current or recent conditions. In other words, they represent a reasonably probable or median value. Nominal fresh water values as presented by Bowen[20] are listed in Table XIII for comparison.

The water data for pH, TDS, HCO_3, Cl, SO_4, Ca, F, K, Mg, Na, Si, and perhaps B

TABLE XII

TYPICAL WATER QUALITY PARAMETER CONCENTRATIONS OF WATERS IN THE VICINITY OF THE FOUR CORNERS POWER PLANT [a,b,c]

	San Juan River	Morgan Lake	Ash Ponds	Chaco River	Seepage
TDS	350	1300	3300	2500	10000
pH	8.2	8.4	8.5	8.3	8
HCO_3	130		31	120	400
Cl	9	100	180	120	600
SO_4	120↑↓160	685	2100	1400	4000
Al	0.1(0.01-0.3)	0.5(0.3-1.0)	0.4		0.4(1)
As	0.001	<0.01	0.006		0.0008(1)
B	0.1(0.02-0.3)	2.3(2-4)	25(5-40)	5	2.0(0.5-5)
Ba	0.05	<0.1	<0.1	0.065(1)	0.04(1)
Be	0.005	<0.2		<0.2	<0.002
Bi	0.005	<0.2	ND	0.001	ND
Ca	65(35-100)	100(90-150)	300(200-600)	350(250-600)	400(300-600)
Cd	≤0.01	≤0.004	0.005(1)	0.005(0.0005-0.02)	0.0004,0.006
Co	0.002	<1	<0.001	<0.001	<0.001
Cr	0.005	<0.02	<0.02	<0.02	<0.001
Cu	0.03(0.005-0.07)	0.03	0.04	0.01(0.001-0.06)	0.0034(4)
F	0.4(0.1-0.9)	3.0(1-4)	14(5-20)	6(1-10)	1.0(0.5-5)
Fe	0.1(0.02-0.3)	0.05(0.03-0.2)	≤0.05	0.04(0.01-0.1)	0.2(0.1-0.3)
Hg	<0.001	<0.001	<0.001	<0.001	<0.001
K	3.0(1.0-5.0)	9(7-12)	7	20	50(20-100)
Li	0.03	ND	0.1	0.5	0.5(0.4-0.7)
Mg	8.0(4.0-15.0)	50(40-70)	50(20-150)	100	1000
Mn	0.5(0.1-1.0)	0.02	0.10	0.05	0.4
Mo	0.005	<0.01	0.4(0.05-0.9)	0.04	0.004(0.001-0.1)
Na	40(10-90)	200(150-250)	200(150-300)	300(200-1000)	4000(2000-5000)
Ni	0.005(0.001-0.02)	<0.02	<0.015	0.01(<0.001-0.02)	<0.001
Pb	0.02(0.001-0.05)	0.002	0.005	0.0005(<0.0001-0.001)	0.009
Sb	0.007	0.006(0.004-0.008)	0.007(1)	<0.0006	<0.0006
Se	0.001	0.001	0.03	0.005(1)	0.023(1)
Si	5(3-7)	2(1-6)	5(2-10)	5(2-9)	10(6-20)
Sr	4.3	ND	0.8(1)	2(1-5)	4
V	0.02(0.005-0.05)	<0.2	ND	ND	ND
Zn	0.01(0.01-0.2)	0.04	0.03	0.004(1)	<0.1

[a] Units are mg/ℓ, except pH.

[b] The integer in parentheses means the number of samples used to derive the value.

[c] Two numbers in parentheses are nominal ranges excluding very extreme values.

and Fe are fairly extensive. The data for Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Hg, Li, Mn, Mo, Ni, Pb, Sb, Se, V, and Zn are quite insufficient for intercomparison and drawing of meaningful scientific conclusions. The best that can be done with the data for the latter set of trace species is to look for qualitative features and areas of potential inquiry. In general, much more systematic monitoring is required before quantitative statements can be made.

Consideration of the information presented in Tables XII and XIII leads to some general tentative conclusions.

1. Concentrations of TDS, Cl, SO_4, B, F, Mg, and Mo generally increase in the following order: San Juan River, Morgan Lake, Chaco River, and ash pond effluent.
2. The concentrations of As, Be, Bi, Co, Cr, Hg, Ni, and V, if present, are less than the minimum detectable amount for the measurement technique. In the case of Co and Ni, these detection limits are sufficiently near nominal fresh water values to indicate that these elements are not present in abnormally high concentrations.
3. San Juan River values are quite high ($\geq$3X) for B, Ca, F, Mo, Na, and Zn and ($\sim$2X) for Cu and Mg, as compared to Bowen's nominal values for fresh waters.[20] In contrast, the Al, Fe, and Ni values in San Juan River samples are low.
4. Al, Cd, Fe, Ni, Pb, and Se values are highly variable, but generally low in all waters listed, with the exception of Se in the ash pond samples.
5. Morgan Lake and the ash pond have particularly high values compared to the San Juan River for B, Ca, F, Mg, and Na. In addition, the available data in these two waters indicate quite high concentrations (10X) of As, Be, Li, Mn, Mo, Sb, and Sr compared to Bowen's nominal values for fresh waters.
6. Seepage waters may be depleted in (As), B, (Ba), (Be), (Cu), F, Mo, and (Sb) as compared to ash pond values. (Parentheses indicate the statement for that element is considerably less certain.) Conversely, the seepage waters are enriched in TDS, HCO_3, Cl, SO_4, (Fe), K, Mg, Na, (Pb), and (Sr). The particularly high seepage values for K, Mg, and Na may be indicative of dissolution of soil rather than ash, as semiarid soils tend to be high in soluble salts due to lack of moisture penetration. Concentrations of Al, Ca, Cd, Mn, Se, Si, and Zn are generally comparable in the ash pond and seepage.

It cannot be overemphasized that the above conclusions are tentative, as based on available data, and in no way should be taken as quantitative factual statements. The principal conclusion to be drawn from these data is that for most elements there is insufficient trace element information available upon which to base quantitative or qualitative scientific statements about trace element concentrations in the area. Current water quality monitoring programs should, in time, provide statistically significant trace element data.

The available data are summarized in terms of relative concentrations in Table XIV. The numbers in the table are listed in order to give an idea of the magnitude of the relative concentrations. This information suggests that, of those species for which sufficient data exist, B, Mn, F, Cl, SO_4, Mg, and perhaps Ca, Na, and Al are of most interest with respect to materials solubilized and, perhaps, biological

availability. Additionally, consideration of Table XII suggests that Mo and Se are of interest.

TABLE XIII

TYPICAL FRESH WATER CONCENTRATIONS[a]

Al	0.24	Mn	0.012
As	0.0004	Mo	0.00035
B	0.013	Na	6.3
Ba	0.054	Ni	0.01
Be	<0.001	Pb	0.005
Bi	ND	S	3.7
Ca	15	Sb	0.00033
Cd	<0.08	Se	<0.02
Co	0.0009	Si	6.5
Cr	0.00018	Sr	0.08
Cu	0.01	Ta	<0.0000025
F	0.09	Te	ND
Fe	0.67	Tl	ND
Ga	<0.001	Ti	0.0086
Hg	0.00008	U	0.001
K	2.3	V	0.001
Li	0.0011	Zn	0.01
Mg	4.1	Zr	0.0026

[a]Units are in mg/ℓ.

TABLE XIV

CONCENTRATION RATIOS FOR MORGAN LAKE, ASH POND, AND SAN JUAN RIVER

Morgan Lake, San Juan River	B >	Cl >	F >	Mg >	SO_4 >	Al, Na >	TDS >	K >	Ca >	Fe, Si, Zn	
	25	10	8	6		5	4	3	2	1	
Ash Pond/ San Juan River	B >	F >	Cl,	SO_4 >	TDS >	Mg >	Ca, Na >	Al >	Ba, K >	Si, Fe >	HCO_3
	100	33	20	10	6	5	4	2	1/2	1/4	
Ash Pond/ Morgan Lake	Mn >	B >	TDS,	SO_4,	Ca >	Cl >	Al, K, Mg, Na, Sb, Zn				
	5	4	3		2		1				

APPENDIX A

SAMPLE-HANDLING PROCEDURES AND ANALYTICAL TECHNIQUES FOR COAL AND ASH

I. Southwest Energy Study[7]

A. Sample Preparation.

Air-dried at 38-40°C for up to 3 days, crushed, and pulverized with ceramic plates to pass 80-mesh, and mixed. Splits of these samples were distributed for analyses. Portions of the split of each coal sample were ashed at 530°C and submitted for spectrographic, x-ray fluorescence, and various wet chemical analyses.

B. Analytical Procedures.

(Coal analyses for As, F, Hg, Sb, Se, Te, and U were on whole-coal samples, whereas for all other elements the analyses were performed on coal first ashed at 530°C.)

As Heteropoly blue spectrophotometric method. Solubilized with nitric, perchloric, and sulfuric acid.

F Direct addition, ion selective electrode. Solubilization procedure: coal sample dried with slurry of magnesium oxide and nitrate, ashed at 600-700°C, fused with 2:1 mixture sodium carbonate and sodium nitrate, and dissolved in citrate-acetate buffer.

Hg Stannous-chloride flameless atomic absorption spectroscopic method.
Ash digested by heating with aqua regia, coal digested with sulfuric acid and potassium permanganate and subsequent reduction of excess permanganate with hydroxylamine hydrochloride.

Sb Colorimetric after reaction with rhodamine-B. Coal ignited at 500°C for 4 h in a slurry of magnesium oxide and nitrate, fused with sodium bisulfate and antimony subsequently extracted with ether from a hydrogen chloride leachate of the fused mass.

Se X-ray fluorescence.
Sodium peroxide fusion, reduction and precipitation with hydrazine sulfate, potassium iodide and sodium sulfite with tellurium added as carrier. Precipitate collected on a millipore filter for x-ray determination.

Te Catalytic.
Decomposition with sulfuric acid and hydrogen peroxide.

U Delayed neutron activation analysis.

Ca, Cd, Cu, Fe, Li and Mg
Atomic absorption flame spectroscopy.
All but Cd wet ashed with hydrofluoric, nitric, and perchloric acid and then solubilized with 5% hydrochloric acid. For cadmium, the sample is boiled in nitric acid, pH adjusted to 10 with ammonium hydroxide and cadmium extracted with 2-mercapto-benzothiazole into n-butyl acetate.

Na Flame photometric with lithium as internal standard.

Si Molybdenum blue spectrophotometric method.

S Combustion iodometric.

Tl Atomic absorption spectroscopy.
Dissolved with hydrofluoric acid, evaporated to dryness, dissolved with hydrobromic-bromine mixture and extracted with MIBK.

Si, Al, Ca, K, Fe, and S fused with sodium borate and determined by x-ray fluorescence.

TABLE A-I

ELEMENTAL CONCENTRATIONS IN NAVAJO MINE COAL USED AT FOUR CORNERS POWER PLANT[a]

(IN μG/G, UNLESS % INDICATED)

	SWES[b]	APS-UII[c]
Ag		0.9
%Al	13.2±0.9	14.5
As	2.2±0.8[d]	1.1[d]
B	447±147	363
%Ba	0.22±0.05	0.45
Be	5.4±1.5	6.8
%Ca	2.70±0.79	3.22
Cd	<0.5	<0.46
Co	7.9±1.4	<9
Cr	19.0±4.6	18.2
Cu	56.67±7.32	64
Eu	<10	
F	160.5±39.8[d]	44[d]
%Fe	2.15±0.29	2.7
Ga	39±10	36.4
Ge		<2.7
Hg	0.06±0.02[d]	0.08[d]
%K	0.58±0.12	0.71
La	70	
Li	85.3±9.6	227
%Mg	0.48±0.08	0.41
Mn	226.2±70	182
Mo	6.2	3.64
%Na	1.14±0.31	1.04
Nb	≤20	<9
Ni	≤10	18.2
%P	0.07±0.05	
Pb	56±9	28.6
%S	0.68±0.13	~0.7
Sb	0.32±0.13[d]	0.13[d]
Sc	13.3±2.4	9
Se	1.98±0.55[d]	2.8[d]
%Si	25.5±1.4	26.7
Sn		<2.7
Sr	295±59	182
Te	<0.04	
%Ti	0.43±0.12	0.9
Tl	<0.34[d]	
U	2.56±0.39[d]	
V	95±23	91
Y	41±12	

TABLE A-I (CONTINUED)

	SWES[b]	APS-UII[c]
Zn	53.05±7.5	27.3
Zr	210±49	227
%Ash	23.58±3.24	22.2

[a]Concentrations are in μg/g of coal-ash except where indicated; concentrations on coal ash basis converted to coal basis using ash fraction.

[b]Average and standard deviation of 21 different coal samples.

[c]Average of two 1-wk composite samples.

[d]Concentrations on whole-coal basis.

P Direct X-ray fluorescence on coal ash or plant ash.

Fe, Mg, Ca, Ti, Al, K, P, Ag, As, Au, B, Ba, Fe, Bi, Cd, Co, Cr, Cu, La, Mo, Nb, Ni, Pb, Pd, Pt, Sb, Sc, Sn, Te, U, V, W, Y, Zn, Zr, Ce, Ga, Ge, Hf, In, Li, Re, Ta, Th, Tl, Yb Six-step emission spectrographic technique.[40]

II. APS-UII[10]

A. Sampling

1. Coal - Each day for 10 days a composite sample was collected representing coal delivered to the plant during the previous 24 h.
2. Precipitator-collected fly ash from the hopper or hydrobins was sampled each day for 5 days.
3. Bottom ash from all five units was sampled daily for 5 days at each unit at the hydrobins.

TABLE A-II

ELEMENTAL ANALYSIS OF BOTTOM ASH AND PRECIPITATOR COLLECTED ASH FROM FOUR CORNERS POWER PLANT (IN μG/G, UNLESS % INDICATED)

	Bottom Ash			Precipitator-Collected Ash	
	SWES[a]	APS-UII[b] Units 1,2,3	APS-UII[b] Units 4,5	SWES[a]	APS-UII[b] Units 4,5
%Al	13.2		13.86	14.3	14.5
As	1	0.8	1.1	12	11
B	117	200	200	233	700
%Ba	0.3	0.5	0.5	0.30	1
Be	3	5	5	3.7	6
Bi		<10	<10		<10
%Ca	3.1		3.6	2.74	3.20
Cd	<0.50	3.2	<0.7	<0.50	<1.6
Co	7	<10	<10	7	<10
Cr	15	20	20	20	60
Cu	37	57	53	54	80
Eu	15			13	
F	<50	7	17	140	100
%Fe	2.78		2.73	2.66	2.66
Ga	20	30	30	50	100
Ge		<30	<30		<30
Hg	<0.01	0.03	0.06	0.06	0.13
%K	0.69		0.77	0.75	0.75
La	70			70	
Li	78	200	200	79	200
%Mg	0.54		0.36	0.58	0.41
Mn	367	200	200	267	300
Mo	<7	3	3	7	10
%Na	1.31		0.96	1.4	1.04
Nb	<20	<10	<10	17	<10
Ni	<10	20	20	8	30
%P	0.03			0.06	
Pb	27	23	26	70	62
S	0.06			0.11	
Sb	0.23	<0.05	0.08	1.34	0.4
Sc	10	10	10	13	10
Se	0.18	0.2	1.5	6.87	6.6
%Si	27.1		27.6	27.6	26.7
Sn		<3	<3		<3
Sr	300	300	300	367	500
Te	<0.02			0.13	
%Ti	0.37		0.84	0.57	
Tl	0.30			1.40	
U	9.77			9.80	
V	70	70	50	90	200

TABLE A-II (CONTINUED)

	Bottom Ash			Precipitator-Collected Ash	
	SWES[a]	APS-UII[b] Units 1,2,3	APS-UII[b] Units 4,5	SWES[a]	APS-UII[b] Units 4,5
Y	30			30	
Zn	24	10	<10	63	100
Zr	167	200	200	267	300

[a]Average of three samples.
[b]One 5-day composite.

B. Elements Analyzed by Special Analytical Techniques.

As Dissolution in concentrated nitric acid and hydrofluoric acid, evaporated to fumes with sulfuric acid, and diluted with water and analyzed by spectrophotometry after reduction of As (+5) with potassium iodide and stannous chloride, formation of AsH_3 with metallic zinc and absorption in silver diethyldithiocarbonate.

Cd Anodic stripping voltametry.

Cu Anodic stripping voltametry.

F Fusion, distillation with sodium bisulfate, collection in saturated ammonium carbonate and determination by ion selective electrode.

Hg Digestion with sulfuric, nitric, and perchloric acid, followed by addition of hydroxylamine hydrochloride and stannous chloride, and determination of metallic mercury by flameless atomic absorption spectroscopy.

Pb Anodic stripping voltametry.

Sb Spectrophotometry.

Se Same decomposition procedure as arsenic followed by flame atomic absorption spectrometric determination of Se as SeH_2 after addition of sodium borohydride and collection of the SeH_2 in a balloon.

C. Elements Determined by Emission Spectrographic Analysis.

Ag, Al, Ba, Be, Bi, Co, Cr, Fe, Ga, Ge, K, Li, Mg, Mn, Mo, Na, Nb, Ni, Sc, Si, Sn, Sr, Ti, V, Zn, Zr .. the general procedure involved complete oxidation, evaporation to dryness in presence of graphite followed by spectrographic analysis.

APPENDIX B

FOUR CORNERS SOIL DATA AND ANALYTICAL PROCEDURES

SOURCE: Southwest Energy Study, Report of the Coal Resources Work Group, Appendix J-III, trace element content of the soils and vegetation in the vicinity of the Four Corners Power Plant, prepared from data compiled by Helen L. Cannon and Barbara M. Anderson, February 1972.

SAMPLE SITE LOCATIONS: Traverse A-A' runs in a line due west of the power plant for 1.9 mi. Two samples were taken at each of three sampling stations along the traverse at distances of 0.5 mi, 1.0 mi, and 1.9 mi from the power plant. From the data reported, apparently only one sample was collected and/or analyzed in most cases for the station located along the traverse at a distance of 1.4 mi from the plant. When two samples were obtained at a station, they were collected at sites in different directions and at random distances within 150 ft. of each sample station on the traverse.

DEPTH: 0-1/2 in.

DATE COLLECTED: August-September, 1971

SAMPLE COLLECTION: Samples were collected in plastic bags.

SAMPLE PREPARATION: Samples were ground with a vertical Braun pulverizer using ceramic plates set to pass about 80-mesh. Samples were dried in aluminum pans in an air-circulating oven at 38-40°C.

ANALYTICAL METHODS: A six-step spectrographic method was used for Al, B, Ba, Be, Ca, Co, Cr, Cu, Fe, Ga, K, La, Mg, Mn, Na, Ni, Pb, Sc, Sr, Ti, V, Y, Yb, and Zr. The standard error for this technique is about 30 to 40%. Arsenic was determined by a heteropoly blue spectrophotometric method. Mercury, zinc, and cadmium were determined by atomic absorption spectrometry using wet digestion. Antimony was determined by fusion with sodium bisulfate, extraction from a hydrochloric acid leachate, and colorometric determination using rhodamine-B.

TABLE B-I

SOUTHWEST ENERGY STUDY, TRAVERSE A-A'

(IN μG/G, UNLESS % INDICATED)

Element	No. Of Samples	$\bar{X}$	Sx
As	7	5.71	1.80
B	7	68.57	41.80
Ba	7	1243	602.38
Be	7	1.86	0.85
%Ca	7	2.71	1.22
Co	7	7.14	1.46
Cr	7	28.57	3.78
Cu	7	37.14	19.76
%Fe	7	2.43	0.53
Hg	7	~0.02	~0.01
%K	7	1.87	0.22
%Mg	7	0.96	0.11
Mn	7	286	106.90
%Na	6	0.95	0.12
Ni	7	13.57	3.78
Pb	7	21.43	3.78
Sb	7	0.79	0.57
Sc	7	8.29	3.30
Sr	7	271.43	111.27
%Ti	8	0.30	0.13
V	7	67.14	7.56
Zn	7	57.14	13.50
Zr	7	150	70.71

SOURCE: Same

SAMPLE SITE LOCATIONS: Traverse B-B' started 2 mi north of the power plant and was made for 6-1/2 mi to the west through a gap in the Hogback. Two samples were taken at each of five sampling stations along the traverse at distances of 2 mi, 3 mi, 4 mi, 5 mi, and 6.3 mi from the plant. The two samples were collected in different directions and at random distances within 150 ft of each sample station on the traverse.

DEPTH: Same

DATE COLLECTED: Same

SAMPLE COLLECTION: Same

SAMPLE PREPARATION: Same

ANALYTIC METHODS: Same

TABLE B-II
SOUTHWEST ENERGY STUDY, TRAVERSE B-B'
(IN μG/G, UNLESS % INDICATED)

Element	No. of Samples	$\bar{X}$	Sx
As	10	3.70	0.67
B	10	~17	~11.11
Ba	10	730	94.87
Be	10	<1	
%Ca	10	0.99	0.32
Co	10	~4.10	1.51
Cr	10	13.90	7
Cu	10	8.70	2.63
%Fe	10	1.02	0.37
Hg	10	<0.11	
%K	10	2.25	0.54
%Mg	10	0.33	0.15
Mn	10	235	105.12
%Na	10	1.09	0.31
Ni	10	<5	
Pb	10	21	6.58
Sb	10	<0.5	
Sc	10	<5	
Sr	10	159	16.63
%Ti	10	0.16	0.03
V	10	28	9.19
Zn	10	26.80	7.02
Zr	10	142	48.03

SOURCE: Same

SAMPLE SITE LOCATIONS: One sample was collected at each of 27 sites varying in radius from 9.0 mi to 34 mi of the power plant. Direction of these sites from the plant varies in a clockwise direction from SSW to SSE. Eleven of the 27 sites are within a 15-mi radius of the plant.

DEPTH: 0-6 in.

DATE COLLECTED: Same

SAMPLE COLLECTION: Same

SAMPLE PREPARATION: Same

ANALYTIC METHODS: Same

TABLE B-III
SOUTHWEST ENERGY STUDY
0- to 6-in. SOILS
9-34 MILES FROM POWER PLANT
(IN μG/G, UNLESS % INDICATED)

Element	No. of Samples	$\bar{X}$	Sx
%Al	27	5	2.32
As	27	4.8	4.33
B	27	~25	~17.83
Ba	27	850	433.53
Be	27	~1.5	~0.42
%Ca	27	3	2.24
Cd	27	<1	
Co	27	~6	~3.54
Cr	27	30	19.82
Cu	27	15	5.95
%Fe	27	1.5	0.55
Ga	27	15	4.77
Hg	27	~0.02	~0.03
%K	27	2	0.53
La	26	~25	13.35
%Mg	27	0.7	0.39
Mn	27	250	154.4
%Na	27	1	0.57
Ni	27	~10	9.71
Pb	27	20	3.40
Sb	27	<0.5	
Sc	27	~5	~2.52
Sr	27	450	941.03
%Ti	27	0.15	0.07
V	27	50	23.37
Y	27	20	6.25

TABLE B-III (CONTINUED)

Element	No. of Samples	$\bar{X}$	Sx
Yb	27	2	0.58
Zn	27	45	16.76
Zr	27	150	48.71

SOURCE: Studies of Trace Elements In Soils and Plants From the Four Corners Area of New Mexico; Nellie B. Stark and Patricia F. Harris, final report to the U. S. Environmental Protection Agency, September 1972.

SAMPLE SITE LOCATIONS: Two preliminary, survey samples were collected at each of two sites for each of two depths. One site, designated "control" was 5 to 6 mi north of the power plant on a ridge. The other site, designated "impact" was about 4 mi south of the plant on a ridge.

DEPTHS: 0-5 cm
10-15 cm

DATE COLLECTED: March 12-15, 1972

SAMPLE COLLECTION: Not reported

SAMPLE PREPARATION: A total digestion using HF was used for all but F analysis for which a Na_2CO_3 fusion technique was used. In addition, 1N NH_4OAc, 0.002N H_2SO_4, and 1N HCl extractions were made on aliquots of each of the preliminary samples. Glassware preparation not given. Sieving and/or grinding technique not given.

ANALYTIC METHODS: A standard atomic absorption technique with a hydrogen continuum lamp and without scale expansion, extractions, or background corrections was used for Be, Cd, Co, Cr, Pb, Mn, Mo, and Ni. Fluoride was determined with a specific ion electrode or Na_2CO_3 fusion. The method for As analysis was not given but is assumed to be the same as the "main" samples (see following).

TABLE B-IV
'PRELIMINARY' SOIL SAMPLES
TOTAL DIGESTION
(IN μG/G, UNLESS % INDICATED)

Element	No. Of Samples	Control		Impact	
		$\bar{X}$(0-5 cm)	$\bar{X}$(10-15 cm)	$\bar{X}$(0-5 cm)	$\bar{X}$(10-15 cm)
As	2	~5.5	~7.	~5.5	~5.5
Be[a]	2	~1.5	~1.5	~1.5	~1.5
Cd[a]	2	~0.75	~0.75	~0.75	~0.75
Co	2	18.5	~12	~8.6	~12.6
Cr	2	36.25	27.5	22.5	27.5
F	2	460	224	222	268
Mn	2	296	125	268	232
Mo[b]	2	338	195	250	257
Ni[a]	2	28	24	~6.5	~3.8
Pb	2	~7.5	~7.5	~7.5	~7.5

[a]Values may be erroneously high due to lack of background corrections.
[b]Values are about two orders of magnitude greater than those reported elsewhere.[10]

TABLE B-V
"PRELIMINARY" SOIL SAMPLES
1N HCl EXTRACTION (IN μG/G)

Element	No. Of Samples	Control		Impact	
		$\bar{X}$(0-5 cm)	$\bar{X}$(10-15 cm)	$\bar{X}$(0-5 cm)	$\bar{X}$(10-15 cm)
As	2	~0.4	~0.4	~0.4	~.43
Be[a]	2	<0.2	<0.2	<0.2	<0.2
Cd[a]	2	0.20	~0.13	0.20	~0.24
Co	2	1.75	2	1.7	2
Cr	2	1.63	1.5	1	1.25
F	2	134	163	88	102
Mn	2	71	12.7	93.5	55.5
Mo	2	<5	<5	~4.7	<5
Ni[a]	2	2.6	2.1	1.6	2.6
Pb	2	5.4	3.8	4.1	3.8

[a]Values may be erroneously high due to lack of background corrections.

SOURCE: Same

SAMPLE SITE LOCATIONS: Main soil samples were taken at new sites designated "control" and "impact." The new control area was about 8 mi SW of the plant. The new impact area was about 1.5 mi WSW of the power plant. Eight soil samples from each of two depths were collected at eight sites along a transect in both the control and impact areas.

DEPTHS: Same

DATE COLLECTED: April 6-9, 1972

SAMPLE COLLECTION: Samples were collected in glass jars which had been washed with 1:1 hydrochloric or nitric acid and "throughly" rinsed with distilled-deionized water.

SAMPLE PREPARATION: Samples were dried for 60 h at 70°C ±3°C and then sieved through a "clean 0.7-mm screen, homogenized, and quartered on waxed paper." Four, 10-g aliquots, weighed to the fourth place, of each sample were extracted for analysis. Two of the aliquots from each sample were extracted with 0.002N H_2SO_4 and the other two were extracted with 1N HCl.

ANALYTICAL METHODS: Standard atomic absorption techniques with scale expansion were used for Be, Cd, Cr, Mn, Mo, Ni, and Pb. A flameless atomic absorption technique was used for Hg analysis. Fluoride analyses were accomplished with a specific electrode and a fluorometric procedure was used for selenium analyses. A standard method, colorimetric procedure, was used for arsenic determinations.

TABLE B-VI

'MAIN' SOIL SAMPLES

1N HCl EXTRACTION (IN μG/G)

		Control				Impact			
		0-5 cm		10-15 cm		0-5 cm		10-15 cm	
Element	No. Of Samples	$\bar{X}$	Sx	$\bar{X}$	Sx	$\bar{X}$	Sx	$\bar{X}$	Sx
As	8	~0.18		~0.19		~0.20		~0.17	
Be	8	0.11	0.05	0.10	0.07	0.06	0.02	0.07	0.01
Cd	8	~0.04		~0.03		<0.05		~0.12	~0.20
Cr	8	0.73	0.46	0.52	0.21	1.09	0.69	0.74	0.31
F	8	~1.81		~2.81		3.90	2.59	~5.74	~4.80
Hg	8	0.02	0.01	0.02		~0.01		~0.01	~0.01
Mn	8	125	36	114	20	134	33	128	51
Mo	8	<0.5		<0.5		<0.5		<0.5	
Ni	8	1.48	0.83	1.20	0.47	1.12	0.34	1.02	0.26
Pb	8	1.75	0.74	2.43	0.72	2.21	0.73	1.70	0.88
Se	8	<0.05		<0.05		<0.05		<0.05	

SOURCE: Trace Element Study for Four Corners Power Generating Plant and Navajo Mine for Arizona Public Service Company, Phoenix, Arizona. Woodward-Envicon, Inc., Scottsdale, Arizona, August 1974.

SAMPLE SITE LOCATIONS: Three control 'transects' varying in distance from the power plant, of 2.6 mi to 11.0 mi, and three impact 'transects' varying in distance from the power plant, of 3.0 mi to 5.0 mi, are mentioned. The control stations are all south of the power plant, and the impact stations are located in clockwise order from NW to ESE. It is assumed that one sample was taken at each of the three control "transects" and each of the three impact "transects".

DEPTH: 0-1 cm
15-18 cm

DATE COLLECTED: Latter part of 1973

SAMPLE COLLECTION: In polyethylene bags

SAMPLE PREPARATION: Each sample was ground in a steel, heat-treated pulverizer which had been previously shown to contribute "negligibly small" iron contamination, then "passed through a sample divider in successive halves, thus redivided until approximately a pound of material was obtained". A pound of each sample obtained as above was then ground to pass a 60-mesh sieve by the same grinder and divided as above until about 1/4 lb was ground in a "shatterbox with tungsten carbide grinding surfaces to pass a 100-mesh sieve." The final portion was dried overnight at 110°C and stored in screw cap polyethylene bottles.

ANALYTIC METHODS: Sample data reported by Woodward-Envicon were provided by Westinghouse Research Laboratory, but methods not cited in Woodward-Envicon Report.

TABLE B-VII

WOODWARD-ENVICON (IN μG/G, UNLESS % INDICATED)

Element	No. Of Samples	Control 0-1 cm $\bar{X}$	Control 0-1 cm Sx	Control 15-18 cm $\bar{X}$	Control 15-18 cm Sx	Impact 0-1 cm $\bar{X}$	Impact 0-1 cm Sx	Impact 15-18 cm $\bar{X}$	Impact 15-18 cm Sx
Ag	3	<1		<1		<1		<1	
%Al	3	>1		>1		>1		>1	
As	3	4.2	1.7	4.6	1.5	4.1	2.6	4.6	3
B	3	16.7	6	16.7	6	27	15	23	23
Ba	3	1267	643	1267	643	1600	693	1567	751
Be	3	2	0	2	0	2	0	2	0
Bi	3	~8	~6	~8	~6	<10		<10	
%Ca	3	≥1		≥1		≥1		≥1	
Cd	3	~0.1	~0.04	~0.19	~0.10	~0.2	~0.2	0.16	~0.04
Co	3	30	20	33	21	33	6	27	6
Cr	3	10	0	10	0	13	6	13	6
Cu	3	11	8	7	3	12	6	13	10
F	3	150	72	220	140	170	140	180	140
%Fe	3	>1		>1		>1		>1	
Ga	3	13	6	17	6	13	6	13	6
Ge	3	~4	2	~3.8	~2	<10		<10	
Hg	3	<0.02		<0.02		<0.02		<0.02	
%K	3	>1		>1		>1		>1	
Li	3	53	6	57	6	60	35	63	32
%Mg	3	≥1		≥1		≥1		≥1	
Mn	3	367	289	233	58	200	100	167	115
Mo	3	<3		<3		<3		<3	
%Na	3	>>1		>>1		>>1		>>1	
Nb	3	<10		<10		<10		<10	
Ni	3	~6.7	~2.9	~6.7	~2.9	~6.7	~2.9	<10	
Pb	3	7.4	0.8	10.5	6.9	5	2.4	21	8
Sb	3	1.1	1.5	0.20	0.07	0.2	0.14	0.15	0.03
Sc	3	10	0	10	0	13	6	13	6
Se	3	0.2	0.1	0.2	0.11	0.2	0.06	0.3	0.06
%Si	3	>>1		>>1		>>1		>>1	
Sn	3	≤5		≤5		≤5		≤5	
Sr	3	200	0	233	58	200	0	233	58
Ti	3	~933	~115	~933	~115	~1000		~1000	
V	3	23	15	23	15	~17	~6	20	0
Zn	3	17	12	20	10	~9	~1.4	~9	~1.4
Zr	3	83	15	90	17	117	76	120	72

APPENDIX C

FOUR CORNERS WATER QUALITY DATA [8,10,11,33-39]

The data tabulated here are abstracted from data collected by and/or reported to the following agencies: the Federal EPA STORET system, U. S. Geological Survey files, New Mexico Environmental Improvement Agency files, Federal Water Pollution Control Administration, various environmental statements issued by the Bureau of Reclamation, and studies performed and/or funded by private interests including the Arizona Public Service Company, Utah International, Inc., and the Western Coal Gasification Company.[8,10,11,33-39]

It is not practical to reproduce here the various sampling and analyses techniques used in the gathering of these data. Suffice it to say that the analytical techniques used by Federal agencies and private consultants or firms must satisfy Federal and State government specifications when the analyses are performed in satisfaction of regulations. In general if there is no justification for excluding data they should be included. It is imprudent to exclude numbers just because they fall outside some preconceived range of values. On the other hand, undue credence should not be given to one or two single sample values that appear to deviate widely from other information. Such apparent outliers should, however, arouse the scientific curiosity of the investigator and motivate further study aimed at their explanation.

TABLE C-I

WATER QUALITY DATA FOR SAN JUAN RIVER,[a] 1962-1969

	1962 - 1965 Discharge Weighted Average		1966, 1967, 1969 Discharge Weighted Average	
	Farmington	Shiprock	Farmington	Shiprock
TDS	282(165-341)	421(290-589)	279(222-364)	380(302-515)
pH	7.7(7.6-7.7)	7.5(7.2-7.6)	7.7(7.7-7.7)	7.7(7.6-7.7)
HCO_3	119(81-144)	138(110-166)	122(107-138)	132(119-149)
Cl	8.9(4.8-17.0)	16.0(8.1-26.0)	6.4(4.5-9.4)	10.5(6.9-16.0)
SO_4	112(54-171)	189(116-281)	111(82-157)	169(125-246)
NO_3	0.9(0.6-1.2)	3.4(2.4-3.9)		
B[b]	0.06	0.06		
Ca	53(32-72)	68(49-90)	50(39-61)	60(50-75)
F	0.35(0.3-0.4)			0.3(0.3-0.3)
Fe	0.01			
K	2.5(2.0-3.0)[c]	4.0(3.6-4.7)[d]	1.1(0.8-1.4)	3.0(2.1-4.1)
Mg	6.3(4.0-9.1)	10.7(8.0-14.0)	7.2(5.4-8.3)	10.8(9.3-13.0)
Na	31(15-46)	54(34-81)	31(23-46)	49(35-76)
Si	4.9(4.5-5.6)	5.2(4.7-6.1)	5.1(4.7-5.6)	5.1(5.1-5.1)

[a] Data are for dissolved components; units, except pH, are mg/l; numbers in parentheses are ranges on an annual composite basis, i.e., each number corresponds to an annual discharge weighted average.

[b] Only data for 1962 available at both stations.

[c] Data for 1962, 1963, and 1965.

[d] Data for 1962, 1963, and 1964.

TABLE C-II

TRACE ELEMENT CONCENTRATIONS FOR SAN JUAN RIVER AND ANIMAS RIVER - FWPCA[a,b]

	San Juan River, Shiprock, NM		Animas River, Cedar Hill, NM[c]	
	Percent Freq Of Detection	Average and Range Of Observed Values	Percent Freq Of Detection	Average and Range Of Observed Values
Al	27.3	0.085(0.021-0.2)	40	0.031(0.007-0.095)
B	100	0.123(0.025-0.295)	95	0.053(0.011-0.176)
Ba	100	0.057(0.015-0.108)	100	0.043(0.013-0.113)
Cr			30	0.006(0.003-0.013)
Cu	36.4	0.01(0.005-0.018)	50	0.005(0.002-0.010)
Fe	90.9	0.056(0.014-0.245)	85	0.012(0.002-0.029)
Mn	43.4	0.007(0.0036-0.012)	35	0.0036(0.0013-0.0105)
Mo			20	0.046(0.0010-0.088)
Ni			20	0.007(0.003-0.016)
Pb			55	0.030(0.014-0.052)
V			15	0.029(0.007-0.048)
Zn	63.6	0.035(0.016-0.074)	65	0.024(0.007-0.076)

[a]Data are dissolved components; units, except pH, are mg/l.

[b]Twenty samples at each site.

[c]This location is upstream of the confluence of the Animas with the San Juan River at Farmington, NM.

TABLE C-III

WATER QUALITY DATA FOR SAN JUAN RIVER,[a] 1972-1975

	Morgan Lake Intake, 8/73 1 Sample	1972-1973[b,c] 7 Samples	Storet Output[d] (11/18/75) Farmington	Storet Output[d] (11/18/75) Shiprock	San Juan River Upstream 1974	San Juan River Upstream 1975	San Juan River Shiprock 1974	San Juan River Shiprock 1975
TDS			346.5±182.7	439.6±216.2	454.60 10/10±66.70	401.50 10/10±149.06	513.93 10/10±239	418.20 10/10±163.26
pH			7.80±0.32	7.73±0.52	8.25 10/10±0.17	8.31 10/10±0.11	8.20 10/10±.47	8.28 10/10±0.06
HCO_3			143.4±42.6	155.1±82.8				
Cl			9.61±6.09	17.9±15.5	10.40 10/10±1.71	6.10 10/10±2.60	27.20 10/10±41.54	6.90 10/10±2.96
SO_4			158.3±108.0	237.2±159.9	165.50 10/10 30.05	152.0 10/10±76.48	207.50 10/10±113.37	174.00 10/10±90.60
Al	0.35			0.015				
As	<0.01	<0.01 0/2	0.001	0.032±0.047				
B	2	0.1(<0.1)2/7	0.052±0.027	0.100±0.093	0.13(<0.1)4/9	0.1(<0.1)3/6		
Ba	<3	<0.01 0/7		0.14	<0.1 0/9	~<0.28 0/5		
Be	<0.1			0.0065				
Bi	<0.1			0.008				
Ca	93		63.7±23.8	75.4±33.9				
Cd	<0.001	<0.02 0/7		0.011±0.033	0.02(<0.02)1/9	<0.02 0/6		
Co	<1			0.0018±0.0031				
Cr	<0.02	<0.02 0/7		0.0056 0.0052	0.03(<0.02)1/9	<0.02 0/6		
Cu	0.1	0.017(<0.01)3/7	0.003	0.023±0.038	0.06(~<0.015)3/9	.03 6/6±.02		
F	2.3	0.2 1/1	0.36±0.14	0.41±0.18	0.35 9/9±0.12	0.41 7/7±0.17		
Fe	<0.1	0.05 1/1	0.076±0.271	.022±0.032	0.2(<0.05)1/9	0.14 6/6±0.19		
Ga				0.004				
Hg	<0.001	<0.001 0/7	0.0004	0.00003	<0.001 0/9	<0.001 0/6		
K	9		2.57±0.92	2.94±1.25				
Li				0.029±0.047				
Mg	43		8.4±3.3	13.8±9.2				
Mn	<0.1	0.17 7/7	0.008	0.12±0.29	0.80 9/9±1.96	.38 6/6±.40		
Mo		<0.05 0/7		0.004	1.0(<0.05)1/9	<0.01 0/6		
Na			45.8±40.2	72.0±55.1				
Ni		0.03(<0.05)1/7		0.008±0.008	<.02 0/9	<0.02 0/6		
Pb			0.004	0.012±0.015	0.05(~<0.02)1/9	0.02 6/6±.03		
Sb	0.007							
Se	0.001	<0.05 0/7	0.001	0.001±0.001	~<0.05 0/9	<0.02 0/6		
Si			5.34±1.50	5.32±1.75	4.03 10/10±0.59	3.45 10/10±0.72	4.11 10/10±0.60	3.36 10/10±0.91
Sr				4.33±9.84				

TABLE C-III (CONTINUED)

	Morgan Lake Intake, 8/73	1972-1973[b,c]	Storet Output[d] (11/18/75)		San Juan River			
					Upstream		Shiprock	
	1 Sample	7 Samples	Farmington	Shiprock	1974	1975	1974	1975
Ti	<0.1			0.009				
V	<0.1			0.0026				
Zn	<1	0.10(<0.05)4/7	0.017	0.15±0.30	0.10(<0.05)4/9	0.15(<0.01)5/6±0.12		
Zr	<0.1			0.011				

[a]Data are for dissolved components; units, except pH, are mg/l.

[b]Ratios are number of samples with element present greater than minimum detectable quantity to total number of samples analyzed for that element.

[c]Minimum detectable quantity varies depending on amount of dissolved solid per unit volume.

[d]Where more than five samples were reported, the standard deviation is listed.

TABLE C-IV

TRACE ELEMENT DATA FOR MORGAN LAKE[a]

	Intake 1 Sample (8/73)	Hot Pond 1 Sample	No. 3 Tower 1 Sample	Discharge 1 Sample (8/73)	Morgan Lake 1974	Morgan Lake 1975
TDS					1299.0 10/10±77.66	1270.30 10/10±143.11
pH					8.43 10/10±0.07	8.41 10/10±0.04
Cl					97.10 10/10±7.13	108.70 10/10±2.83
SO_4					704.60 10/10±45.44	666.50 10/10±90.04
Ag					<0.02 0/9	<0.02 0/6
Al	0.35	0.9	0.3	0.9		
As	<0.01	<0.01	<0.01	<0.01		
B	2	4	2	4	2.30 9/9±0.29	2.28 6/6±0.95
Ba	<3	<3	<3	<3	<0.1 0/9	<0.1 0/6
Be	<0.1	<0.2	<0.1	<0.2		
Bi	<0.1	<0.2	<0.1	<0.2		
Ca	93	130	9	130		
Cd	<0.001	0.004	<0.002	0.004	<0.02 0/9	<0.02 0/6
Co	<1	<2	<1	<2		
Cr	<0.02	<0.002	<0.02	0.02	<0.02 0/9	<0.02 0/6
Cu	<0.1	<0.1	<0.1	<0.1	~<0.02 0/9	0.03 6/6±0.02
F	2.3	2.7	2.1	2.7	2.89 9/9±0.52	3.27 6/6±0.45
Fe	0.1	<0.2	0.1	0.2	<0.05 0/9	<0.05 0/6
Hg	<0.001	<0.001	<0.001	<0.001	<0.001 0/9	0.01(<0.001) 3/6
K	9	10	9	10		
Mg	43	65	43	65		
Mn	0.1	<0.2	<0.1	<0.2	.03(~<0.02) 4/9	0.01 6/6±0.01
Mo	<1	<2	<1	<2	<0.05 0/9	<0.01 0/6
Na	165	250	160	250		
Ni	<0.1	<0.2	<0.1	<0.2	~<0.02 0/9	<0.02 0/6
Pb	<0.001	<0.001	0.001	<0.001	~<0.02 0/9	0.002(~<0.01) 1/6
Sb	0.007	0.006	0.005	0.006		
Se	<0.001	<0.001	0.001	0.001	~<0.04 0/9	<0.02 0/6
Si	4	6	4	6		1.24 10/10±0.64
Ti	<0.1	<0.2	<0.1	<0.2		
V	<0.1	<0.2	<0.1	<0.2		
Zn	<1	<2	<1	<2	<0.05 0/9	0.04 6/6±0.04
Zr	<0.1	<0.2	<0.1	<0.2		

[a] Data are for dissolved components; units, except pH, are mg/l; when less-than values are used in computing an average, one-half the less-than value is averaged.

TABLE C-V

TRACE ELEMENT DATA FOR ASH DISPOSAL PONDS AT FOUR CORNERS POWER GENERATING PLANT[a]

	USGS 1971 1 Sample	APS Files 1972-1973 16 Samples	Woodward Environ 1974 1 Sample	Ash Pond Effluent 1974	Ash Pond Effluent 1975
TDS	1100	3248		3303.33 9/9±361.20	3335.67 9/9±360.99
pH	11.3	8.47		8.29 9/9 ±0.68	8.88 9/9 ±0.17
HCO_3		31			
Cl	85	123		176.89 9/9 ±38.06	189.11 9/9 ±15.91
SO_4	580	2300		2063.22 9/9±231.09	2064.11 9/9±232.93
Ag				<0.02 0/9	<0.02 0/6
Al			0.4		
As	<0.12		0.006		
B	1.0		4	24.67 9/9 ±10.43	21.37 6/6 ±15.82
Ba	0.12		<3	<0.1 0/9	<0.1 0/5
Be			<0.002		
Bi	<0.0004		<0.2		
Ca	240	563	>200		
Cd	<0.025		0.005	<0.02 0/9	<0.02 0/6
Co	<0.001		<0.7		
Cr			<0.02	<0.02 0/9	<0.02 0/6
Cu	<0.003		<0.1	0.03(<0.02)3/9	0.05 6/6 ±0.05
F	1		6	13.24 0/9 ±4.09	14.85 6/6 ±4.93
Fe	0.06		<0.2	0.1(<0.05) 1/9	<0.05 0/6
Hg			<0.001	<0.001 0/9	<0.001 0/6
K	6.6		7		
Li	0.08		0.4		
Mg	0.1	102	20		
Mn	<0.005		<0.2	0.49 9/9 ±0.61	0.07 6/6 ±0.05
Mo	0.030		0.2	0.46 9/9 ±0.21	0.49 6/6 ±0.24
Na	170	294	>200		
Ni	0.003		<0.2	0.02(~<.04)1/9	<0.02 0/6
Pb	<0.005		0.0028	~<0.02 0/9	0.08 (~<0.015)1/6
Sb	0.012		0.007		
Se			0.021	~<0.05 0/9	0.03 6/6 ±0.03
Si	14	51	1	10.74 9/9 ±6.83	4.65 9/9 ±1.20
Sr	0.8				
Ta			<0.02		
Ti			<0.02		
V			<0.02		
Zn	<0.022			0.09(<0.05) 1/9	0.03 6/6 ±0.03
Zr			<0.07		

[a]Data are for dissolved components; units, except pH, are in mg/l; when less-than values are used, half the less-than value is averaged.

TABLE C-VI

CHACO RIVER WATER QUALITY DATA AT LOCATIONS UPSTREAM OF POWER PLANT INFLUENCE[a,b]

	Upstream of Power Plant[c] (1 Chaco 2 Arroyos to Chaco)	Chaco Baseflow Upstream[d] Of Power Plant
TDS	2700 (1500-3500)	2491 (1316-4049)
pH		7.64 (7.5-8.0)
HCO_3		388 (263-483)
Cl	18.7 (12-22)	42 (13-104)
SO_4	428 (105-625)	1272 (412-2170)
Al		<0.005
As	<0.005	
B	0.6 (<0.1) 1/3	<0.1
Ba		<1
Bi	<0.0005	<0.008 (<0.0005) 4/9
Ca	507 (276-738)	174 (17-480)
Cd	0.0074 (0.0005-0.021)	0.005 (<0.0001) 2/9
Co	<0.001	<0.001
Cu	0.031 (0.003-0.06)	0.012 (<0.001) 3
F	1.30 (0.81-1.96)	1.1 (0.62-1.5)
Fe	0.076 (0.027-0.06)	0.093 (0.027-0.17)
Hg	<0.001	<0.001
K	100 (60-160)	12 (3-20)
Li	0.023 (0.01-0.03)	0.08 (0.06-0.13)
Mg	48 (28-62)	44 (2-188)
Mn	0.147 (0.003-0.43)	0.79 (0.0006-3.0)
Mo	<0.003	<0.003
Na	1623 (750-2200)	607 (246-1100)
Ni	0.012 (<0.001) 1/3	0.01 (<0.001) 1/9
Pb	0.0004 (<0.0002) 1/3	0.0017 (<0.0002) 3/9
Sb	<0.0006	<0.0006
Si		14 (10-18)
Sr		3.5 (0.7-10.3)
Zn		0.21 (0.05-0.63)

[a] Data are for dissolved components; units, except pH, are mg/l followed by ranges in parentheses except where noted; less-than indicates all samples below minimum detectable quantity.

[b] Number followed by less-than in parentheses indicates most values were below detection limit, the fraction of values above detection limit follows the parentheses.

[c] Three samples, 1972, 1973; one from Chaco River, two from arroyos feeding Chaco.

[d] Nine samples, 1972-1973.

TABLE C-VII

CHACO RIVER WATER QUALITY DATA AT LOCATIONS DOWNSTREAM OF POWER PLANT INFLUENCE[a]

	Downstream[b] April, May 1969	USGS 8/71	APS, Chaco at Hogback 1 Sample	Near Mouth of Chaco River 1 Sample	APS, 9/73 1 Sample	APS, 1973 Av 10 Samples	Near Junction With San Juan 1974	Near Junction With San Juan 1975
TDS	4712	6830	6198		1140	2902	2789.89 9/9±1831.90	1862.11 9/9±638.34
pH	8.4	8.5	8.6		7.5	8.5	8.30 9/9±0.15	8.32 9/9±0.10
HCO_3	135[c]	136	227		161	98		
Cl	209	310	442		30	137	136.89 9/9±98.82	110.11 9/9 93.30
SO_4	2980	4400	2400		626	1716	1695.13 8/8±1282.51	1105.44 9/9±413.37
Al				<0.2				
As		<0.12	<0.005					
B	4.3	0.33	6.3	12				
Ba		0.065	<1	<3				
Be				<0.2				
Bi		<0.0004	<0.0005	<0.2				
Ca	302	390	442	288	110	407		
Cd		<0.025	<0.0001	<0.002				
Co		<0.001	<0.001	<2				
Cr				<0.02				
Cu		<0.015	0.013	<0.1				
F	0.6	1.2	4.8	9.6	1.2		5.18 4/4	6.60 6/6±1.56
Fe	0.03	0.01	0.002	0.2	<0.01			
Hg		<0.0001	<0.001	<0.001				
K	9.8	14	73	25	8.8			
Li		0.36	0.67					
Mg	308	440	884	168	11	116		
Mn		0.02	0.002	<0.2				
Mo		0.025	0.064	0.7				
Na	717	1000	1730	530	232	310		
Ni		0.009	<0.001	<0.2				
Pb		<0.005	<0.002	<0.001				
Sb		<0.012	<0.0006	0.008				
Se				0.005				
Si	4.5	4.7	11	24	19	14	4.67 9/9±0.70	3.98 9/9±1.75
Sr		1.6	4.2					
Ti				<0.2				

TABLE C-VII (CONTINUED)

	Downstream[b] April, May 1969	USGS 8/71	APS, Chaco at Hogback 1 Sample	Near Mouth of Chaco River 1 Sample	APS, 9/73 1 Sample	APS, 1973 Av 10 Samples	Near Junction With San Juan 1974	Near Junction With San Juan 1975
V				<0.2				
Zn		<0.022	0.004	<2				
Zr				<0.2				

[a]Data are for dissolved components; units, except pH, are mg/l.

[b]Four samples.

[c]Three samples.

TABLE C-VIII

TRACE ELEMENT CONCENTRATIONS IN SEEPAGE AROUND MORGAN LAKE AND ASH DISPOSAL PONDS AT FOUR CORNERS POWER PLANT[a]

	USGS 1 Sample 1971	USGS 1 Sample 1971	4 Samples 1973	Woodward-Envicon 1 Sample 1974	Morgan Lake 1 Sample 1973
TDS	13300	13900	9898		
pH	8.3	7.9	7.9		
HCO_3	251	274	855		
Cl	440	380	832		
SO_4	8700	9300	2362		
Al				0.4	
As	<0.12		<0.005	0.0008	<0.005
B	0.24		0.7	4	<0.1
Ba	0.04		<1	<3	<1
Be				<0.002	1
Bi	<0.0004		<0.0005	<0.2	<0.0005
Ca	500	430	335	>200	332
Cd	<0.025		0.00042	0.006	<0.0001
Co	<0.001		<0.001	<0.7	<0.001
Cr				<0.02	
Cu	<0.025		0.0034	<0.1	0.013
F	1.4	0.7	0.5	5.8	1.4
Fe	0.16		0.244	<0.2	0.12
Hg	0.0005		<0.001	<0.001	<0.001
K	23	20	91	7	115
Li	0.64		0.57	0.4	0.93
Mg	1000	1100	1023	20	2900
Mn	<0.02		0.443	<0.2	0.038
Mo	0.006		0.0036	0.2	0.012
Na	2100	2200	3965	>200	9920
Ni	0.02		<0.001	<0.2	0.007
Pb	<0.005		0.0009	0.0034	<0.00025
Sb	<0.0012		<0.0006	0.003	<0.0006
Se				0.023	
Si	8.1	8.3	14	1	17
Sr	2.8		4.7	<0.02	7.3
Ti				<0.02	
V				<0.2	
Zn	<0.022		0.1	<0.2	0.06
Zr				<0.07	

[a]Data are for dissolved components; units, except pH, are mg/l.

TABLE C-IX

GROUND WATER QUALITY DATA IN VICINITY OF FOUR CORNERS POWER PLANT AND NAVAJO MINE[a,b]

	Average[c] Pictured Cliffs Groundwater	Average of Seventeen Navajo Wells	Surface[d] Run-Off
TDS	23870	2609	
pH	8.4	7.68	
HCO_3	2590	347	
Cl	10000	53	22
SO_4	1571	1384	609
As		<0.005	<0.005
B	1.2	<0.1	<0.2
Ba		<1	<1
Bi	<0.0005	0.00094	0.0066
Ca	200	153	388
Cd	0.013	0.0009	0.006
Co	<0.001	<0.001	<0.001
Cu	0.042	0.0048	0.033
F	2.2	1.8	1.13
Fe	0.68	0.10	0.071
Hg	0.001	<0.001	<0.001
K	111	11	80
Li	0.023	0.07	0.04
Mg	91	31	41
Mn	0.038	0.415	0.0044
Mo	<0.003	0.0038	<0.003
Na	9430	631	1292
Ni	0.005	0.0046	0.004
Pb	0.126	0.00082	0.0003
Sb	<0.0006	<0.0006	<0.0006
Si	51	14	11
Sr		2.7	2.9
Zn	0.174	0.167	0.086

[a] Data are for dissolved components; units, except pH, are mg/l.

[b] In data as reported in references less-than values were averaged by using one-half the less-than value.

[c] Numbers in parentheses refer to the number of samples analyzed for that component.

[d] Average of surface runoff of four samples, two from Chaco River and two from arroyos feeding Chaco River during a flash flood in August 1973.

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