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Leaching Behavior of Coal Combustion Products and the Environmental Implication in Road Construction



Project Progress Report

by

Jianmin Wang



**NUTC
R201**

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16. Abstract <p>The use of coal fly ash in road base and sub-base applications can provide better properties and performance, and is superior to it being otherwise disposed and becoming a possible environmental liability. Understanding the metal leaching behavior for various fly ashes can help the construction industry and the energy industry in selecting the environmentally benign fly ash for road construction and for other beneficial use applications, and determining the long term environmental impact of fly ash during road construction. Coal fly ash contains many regulated cationic and oxyanionic elements such as antimony, arsenic, barium, boron, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, and selenium. Due to the implantation of several new air emission control regulations, future fly ash may contain elevated concentrations of volatile trace elements especially oxyanionic elements. Since oxyanionic elements have greater mobility in the environment, being less studied previously, and are generally more toxic than cationic elements, understanding the leaching behavior of oxyanionic elements from fly ash is significant in determining the potential environmental impact of fly ash during disposal or beneficial use, selecting the appropriate fly ash for road construction, and developing methods to control the leaching of oxyanionic elements. This research becomes more urgent due to the implementation of more stringent arsenic standards in drinking water that will become effective in January 2006. This research will focus on the leaching behavior of 6 major oxyanionic elements, antimony, arsenic, boron, chromium, molybdenum, and selenium, for various fly ashes under different management scenarios, using both batch and column experiments. Mathematical models will be developed to quantify the leaching behavior of these elements. Speciation of these oxyanionic elements will be determined using the most advanced Perkin-Elmer HPLC-ICP-MS system available at Missouri S&T.</p>			
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1. Introduction

1.1. Background

This is the third annual report for Project #043352. Project #043352 is designed to establish the leaching characteristics for several different types of ash using a relatively rigorous leaching procedure developed by Kosson et al (2002) for a wide range of constituents. That data will ultimately become part of a broader database of leaching characteristics that will be used to identify families of curves for a range of constituents and ash types, for prediction of leaching potential.

In addition to the previous work at Missouri S&T (Former UMR) on the leaching of arsenic and selenium from a few selected fly ash samples, more detailed work on arsenic and selenium, including their dominant aqueous species, will be performed in this project. This will include development of data on intrinsic leaching parameters, such as total leachable mass and adsorption constants.

The metal leaching behavior information for various coal fly ashes will help the construction industry in determining the types of fly ash that yield the minimum environmental impact for road construction. It will also help the energy industry in determining the potential environmental impact of the fly ash during disposal and other beneficial use applications.

1.2. Objectives

This project will (1) evaluate the leaching behavior of several different ash types under possible field management scenarios using the Kosson procedure. (2) Determine control mechanisms for arsenic and selenium release, including evaluation of individual species. (3) Establish a protocol for the determination of total leaching potential of arsenic and selenium in fly ash.

1.3. Work accomplished

This part of the project investigates equilibrium leaching behavior of fourteen fly ash samples. NRT #169, NRT #170, NRT #182, NRT #183, NRT #1020, NRT #189, NRT #186, NRT #034, NRT #089, NRT #094, NRT #103, NRT #104, NRT #153, NRT #1021. Previous reports have presented results for the basic sample characterization, equilibrium based assessment for NRT

#169, NRT #170, NRT #182, NRT #183, NRT #1020, NRT #189, and NRT #186. Mass transfer based assessment on arsenic, and selenium speciation was also studied in our previous report, using paired trona samples. This study will present (1) The recent sample characterization data for all the 14 ashes. (2) The equilibrium based leaching results for the seven ash samples we received on July 21st 2008: NRT #034, NRT #089, NRT #094, NRT #103, NRT #104, NRT #153, NRT #1021. (3) Impact of pH and sulfate on the leaching characteristics of trona ash.

2. Sample Collection and Characterization

2.1. Fly ash samples

A total of fourteen ash samples were studied in this project. Two samples were generated from sub-bituminous coal: NRT#1021, and NRT #186. The rest twelve samples were generated from bituminous coal. The detailed sample information is shown in Table 1.

2.2. Moisture content and LOI

Moisture content was determined for quantifying purpose. Loss-on-ignition (LOI) was determined to indicate the carbon content levels in fly ash. Empty crucibles were dried at 105 °C overnight until stable (W_e), cooled in a desiccator, and weighed. About 10 grams of ash was weighed into the crucibles (W_s), and dried at 105 °C for at least 2 hours, cooled in a desiccator and weighed (W_w). The samples were then heated to 500 °C for four hours, cooled in a desiccator, and weighed again (W_c). The moisture content is given by ratio of $(W_s + W_e - W_w) / (W_s)$, the LOI is given by the ratio of $(W_w - W_c) / (W_w - W_e)$. Three replicates were made for each of the 14 fly ash samples. Table 2 shows the results.

The moisture content for each ash was no more than 0.5 %. The paired sample NRT #182, NRT #183 have much higher LOI value(8.75%, and 10.59% respectively) than other ash samples, LOI values of samples NRT #034, NRT#153, NRT#169, NRT#170 were close to 5%, LOI values of NRT #094, NRT#103, NRT#104, NRT#1020, and NRT #189 ranged from 1.37% to 2.11 %, ash NRT#089, and the two class C ashes NRT #1021 and NRT #186 have the lowest LOI values of less than 1%.

Table 1. Fly ash sample information.

Sample NRT #	Plant ID	Unit	Sample Type	Sample Date*	Unit MW	Type	Source	Sulfur	SCR/SNCR	FA Control	SO3 Control	SO2 Control	Hg Control	FGC
34	40109	3	FA	01/06/04		Bit				ESPh	Trona	LSFO	No	None
89	35015	6	FA	12/01/05	400	Bit	Ohio	High	None	ESPc	None	FSI	No	None
94	33102		FA	01/02/05		Bit				ESPc?	None	None	No	S
103	17154	4	FA	04/05/05		Bit			SCR on?	ESPc	None	SDA	No	None
104	17154	1	FA	04/05/05		Bit			None?	ESPc	None	LSFO	No	None
153	35406	1	FA	07/06/06		Bit				ESPc?	None	Trona	No	None?
1021	50207	1&2	FA	09/06/08	512	Sub	Wyoming	Low	SCR on	ESPc	None	None	No	None?
169	14650		FA			Bit			None?	ESPc				
170	14650		FA/FSI			Bit			None?	ESPc				
182	33103		FA			Bit			None?	ESPh				
183	33103		FA			Bit			None?	ESPh				
186	6191		SDAA			Sub			None	FF				
1020*	35085		FA			Bit			SCR	ESPc				
189	35085		FA			Bit			SCR	ESPc				

Table 2. LOI and moisture content.

Sample ID	Moisture content (%)	LOI (%)
NRT #034	0.08	5.22
NRT #089	0.029	0.30
NRT #094	0.12	2.00
NRT #103	0.19	2.11
NRT #104	0.10	1.92
NRT #153	0.027	4.65
NRT #1021	0.015	0.45
NRT#169	0.06	4.97
NRT#170	0.20	5.65
NRT#182	0.24	8.75
NRT#183	0.23	10.59
NRT#186	0.50	0.56
NRT#1020	0.02	1.41
NRT#189	0.45	1.37

2.3. Total composition of 14 fly ashes

2.3.1. XRF results for major and trace elements

The total composition of major elements and some trace elements of the 14 ashes were analyzed with XRF (NITON Analyzer, XL3T 900, Thermoscientific). The detection limit of XRF was approximately 10 ppm (mg/kg). Elements undetectable with XRF and those lighter than Mg (including Na, Cd, Hg, B, Be and Li) was analyzed with complete acid digestion, and total extractable procedure following EPA method 3051A, followed by ICP-OES, ICP-MS or Mercury analyzer.

The XRF results of the fourteen ashes were listed in Table 3. As for the typical fly ash samples, the four major elements in all the fourteen fly ashes are Si, Al, Ca, and Fe. Calcium content in ashes NRT #169, and the two class C ashes NRT #1021 and NRT #186 are much higher than other ash samples. Sulfur content is high in samples NRT #186 (5.3%), and NRT #169 (3.71%). Iron content is high in ashes NRT #089, NRT #103, NRT #104, NRT #170, NRT #1020, and NRT #189. Samples NRT #034, NRT #1021, and NRT #186 showed higher strontium content. Mg content was the highest in NRT #1021, it is undetectable in other ash samples using the XRF method.

Table 3. Major element content in the 14 fly ash samples (XRF).

Ash ID	Major Elements										Trace Elements		
	Al %	Si %	S %	Ca %	Fe %	Mg %	P %	Ba %	Sr %	Cl %	Pb ppm	Zn ppm	Cr ppm
NRT#034	12.45	23.07	0.44	1.27	6.50	ND	0.21	0.18	1.25	0.05	130	150	170
NRT#089	12.49	21.76	0.35	1.39	17.29	ND	0.23	0.08	0.40	0.07	70	220	160
NRT#094	12.02	25.55	0.22	0.92	4.51	ND	0.19	0.10	0.45	0.02	90	90	200
NRT#103	10.46	23.36	0.87	3.45	13.27	ND	0.17	0.09	0.14	0.10	100	370	200
NRT#104	11.03	24.77	0.51	2.64	13.59	ND	0.21	0.07	0.16	0.05	90	470	190
NRT#153	13.67	28.73	0.18	0.67	2.93	ND	0.12	0.06	0.34	ND	80	110	200
NRT#1021	9.22	16.45	1.23	14.22	3.37	1.59	0.62	0.74	1.83	0.07	50	100	170
NRT#169	7.98	13.28	3.71	20.43	4.98	ND	ND	0.03	0.46	0.26	70	170	100
NRT#170	10.95	20.64	1.40	4.92	10.70	ND	0.13	0.07	0.55	0.08	90	200	160
NRT#182	12.60	26.73	0.17	0.64	4.86	ND	0.19	0.07	0.30	0.03	80	160	180
NRT#183	10.22	22.28	1.76	0.60	4.25	ND	ND	0.03	0.26	0.31	60	120	170
NRT#186	6.44	14.60	5.30	13.19	1.92	ND	0.44	0.43	0.98	0.18	30	50	140
NRT#1020	11.39	20.07	0.65	1.82	20.65	ND	0.17	0.05	0.35	0.09	40	140	140
NRT#189	11.26	19.72	1.54	1.94	18.39	ND	0.26	0.05	0.35	0.14	40	110	170

ND - Non Detectable.

2.3.2. Trace elements

The fourteen fly ash samples were initially tried for complete acid digestion, with Multiwave 3000 microwave digester (Anton Paar USA), a procedure with 9 ml HNO₃, 3 ml HCl, and 3 ml HF (Table 4) was recommended by the manufacture for coal fly ash digestion with eight-rotor set up. Table 5 shows the complete acid digestion results. For each batch of digestion, sample duplicate, sample spike, reference material SRM1633b, and reagent blank were included for QA/QC check. Due to the instrumental problems occurred during the digestion procedure, all the 14 fly ashes were digested at least twice, liquid samples generated from the digestion was filtrated with 0.2 µm filter and analyzed on ICP-MS, ICP-OES, and Tekran Mercury analyzer. The QA/QC for Be, Mo, Se, Ag, Cd, Li, Re were good, but part of the QA/QC for As, Co, Cu, Mn, Ni, Pb, Sb, Sr, Tl, V, and Zn was not satisfactory. In complete digestion procedure, the digestion liquid was clear in the beginning, but after overnight settling, white colloidal particulates formed, and they precipitated at the bottom of the tube in a longer time. After dump the supernatant, adding 10 ml concentrated HF can not dissolve these white particles, and they are not dissolvable even by heating on the hot plate at 105 °C for 2 hours.

There are several literatures on the digestion of coal fly ash, most of them concluded that complete digestion is not possible or at least hard to reach, which was proved in our case also. Total extractable digestion is used in most studies, which is sufficient for environmental concern research. Therefore, we tried total extractable digestion for all the 14 fly ashes following EPA method 3051A. The digestion procedure is shown in Table 4, and Table 6 shows the total extractable digestion results.

Table 4. Complete acid digestion procedure.

Method	Sample Weight	Acid	hold time (min)
Complete Digestion	0.1 g	HNO ₃ 9mL HCl 3mL HF 3mL	Temperature 240°C Ramp Time 10min Hold Time 30min
EPA 3051A	0.1 g	HNO ₃ 9mL HCl 3mL	Temperature 175°C Ramp Time 5.5 min Hold Time 4.5min

Table 5. Complete acid digestion results.

Ash ID	Ba	Sr	Mn	Cu	Cr	Zn	Ni	Li	Mo	Pb	Co	Se
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
NRT#034	128.27	374.46	163.97	201.62	147.51	171.67	129.63	130.38	14.99	106.45	75.28	0.64
NRT#089	261.10	320.43	189.97	73.53	104.77	182.02	85.72	118.29	25.47	65.24	42.25	4.17
NRT#094	175.94	57.37	237.70	121.22	157.00	91.47	109.40	96.59	14.22	60.87	61.27	15.40
NRT#103	217.39	63.39	281.82	75.06	208.91	376.97	117.67	64.02	77.78	75.78	32.34	8.31
NRT#104	234.56	93.76	233.88	90.33	189.92	421.53	119.39	59.41	66.72	89.01	35.39	2.27
NRT#153	251.35	106.72	94.56	115.77	123.36	83.71	91.29	103.85	13.99	56.41	51.15	10.29
NRT#1021	1296.48	602.18	143.30	186.93	37.23	125.05	66.45	27.21	18.05	44.98	28.40	9.58
NRT#169	184.11	41.52	152.28	39.59	21.61	162.98	66.50	64.10	7.79	45.68	24.50	9.09
NRT#170	121.99	213.47	199.81	72.67	162.92	185.74	113.75	94.03	12.10	69.14	42.07	7.60
NRT#182	125.63	36.23	75.37	132.77	102.12	115.20	72.84	73.39	8.31	47.08	33.56	0.56
NRT#183	137.63	120.77	142.05	95.76	130.65	131.65	89.54	90.68	8.76	57.97	39.81	13.47
NRT#186	1028.20	652.72	133.86	42.67	21.86	55.45	29.25	33.75	6.76	33.24	12.60	5.70
NRT#1020	183.25	177.45	163.16	62.10	154.61	109.84	82.00	70.93	15.79	38.88	34.64	2.84
NRT#189	82.85	90.13	158.41	56.89	150.68	122.48	71.42	71.49	16.10	43.02	29.07	10.18
Ash ID	V	As	Be	Sb	Tl	Cd	Ag	Re	Hg			
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppb)			
NRT#034	375.75	172.48	30.40	9.28	4.36	1.03	1.94	0.02	70.84			
NRT#089	228.45	102.89	18.68	3.90	12.87	0.94	1.12	0.00	55.55			
NRT#094	312.35	38.41	15.64	5.19	2.27	0.56	1.21	0.01	129.07			
NRT#103	584.64	61.22	12.14	11.12	11.59	9.55	1.53	0.04	172.24			
NRT#104	520.87	66.35	13.40	10.78	11.74	9.38	1.62	0.02	86.52			
NRT#153	309.58	19.45	18.84	4.59	2.01	0.62	1.25	0.00	56.80			
NRT#1021	307.27	25.22	4.10	3.24	0.79	1.44	1.33	0.05	411.64			
NRT#169	175.08	36.42	7.87	3.97	1.84	0.88	0.55	0.02	453.43			
NRT#170	185.74	162.92	1.14	1.06	0.02	5.66	7.60	3.60	250.66			
NRT#182	115.20	102.12	1.19	0.67	0.02	6.31	0.56	3.22	4.77			
NRT#183	131.65	130.65	1.06	0.74	0.02	5.06	13.47	2.94	0.83			

NRT#186	55.45	21.86	0.60	0.62	0.01	4.08	5.70	1.09	111.20
NRT#1020	109.84	154.61	1.21	1.02	0.01	1.42	2.84	5.10	35.86
NRT#189	122.48	150.68	1.18	1.15	0.02	1.40	10.18	7.40	67.08

Table 6. Total extractable digestion results.

Ash ID	B	K	Mg	Na	Ba	Sr	Mn	Cu	Cr	Zn	Ni	Li	Mo
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
NRT#034	75.88	3319.98	1638.81	1154.72	646.30	913.51	83.73	125.69	26.18	47.69	48.29	61.71	13.48
NRT#089	352.10	2880.24	1520.74	495.10	241.20	227.26	113.61	32.95	62.70	86.16	36.46	39.23	23.52
NRT#094	34.79	1589.99	1189.87	382.67	382.89	214.13	184.20	48.67	60.16	72.48	42.54	25.63	13.83
NRT#103	683.27	2873.00	1601.34	924.43	349.60	85.80	230.52	36.75	105.67	185.29	53.46	13.57	71.17
NRT#104	696.81	2941.45	1457.88	850.42	266.79	89.98	172.32	36.54	94.43	142.03	47.47	12.35	60.47
NRT#153	9.08	1471.39	831.13	231.88	270.51	132.22	35.96	43.57	33.65	56.54	27.26	24.84	13.09
NRT#1021	686.12	1951.79	23219.05	7476.43	4679.23	2820.36	165.14	162.62	97.11	103.82	62.00	22.42	19.83
NRT#169	561.84	1171.24	3475.96	677.56	153.79	476.80	136.11	23.74	23.55	73.08	38.70	14.97	8.41
NRT#170	562.94	1904.60	2590.56	1049.55	253.60	419.14	197.30	40.02	51.79	67.09	64.05	30.42	11.56
NRT#182	35.65	4492.29	1334.95	459.77	296.23	115.44	53.03	73.09	13.30	49.35	30.60	29.95	7.71
NRT#183	28.57	2292.67	1212.95	77970.45	209.35	79.00	27.07	34.49	4.54	7.30	14.39	22.36	5.60
NRT#186	659.93	1319.91	6010.88	2641.40	2899.45	1251.13	148.35	28.15	28.39	24.70	21.30	13.83	6.76
NRT#1020	261.14	2058.29	1399.79	981.04	208.98	209.89	155.15	34.30	73.21	119.82	47.24	26.96	14.48
NRT#189	343.50	2165.11	1292.13	17181.22	130.46	203.19	131.50	29.92	77.87	44.00	37.43	18.80	16.09
Ash ID	Pb	Co	Se	V	As	Be	Sb	Tl	Cd	Ag	Re		Hg
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)		(ppb)
NRT#034	30.73	22.97	2.66	119.04	145.07	7.25	3.93	1.43	0.47	0.23	ND		83.64
NRT#089	27.14	16.37	6.90	ND	71.29	4.62	0.72	7.09	0.55	0.24	0.15		41.56
NRT#094	32.34	22.19	16.09	5.53	5.26	3.91	2.23	1.41	0.37	0.22	----		133.50
NRT#103	26.40	13.20	9.62	123.56	27.89	2.98	5.63	5.83	6.44	0.29	0.03		150.49
NRT#104	26.34	12.32	5.80	69.53	24.92	3.23	4.36	5.60	5.52	0.27	0.01		85.42
NRT#153	21.88	14.50	10.53	ND	ND	3.42	1.35	0.91	0.28	0.13	0.00		50.60

NRT#1021	34.62	22.89	10.90	269.26	51.06	3.01	1.30	0.31	1.56	1.07	ND		401.32
NRT#169	18.73	10.67	10.34	ND	ND	2.67	1.81	1.08	0.60	0.16	0.02		450.10
NRT#170	26.07	20.07	9.02	32.09	26.22	4.45	2.40	1.95	0.51	0.24	0.01		212.91
NRT#182	26.76	14.82	0.66	----	18.28	4.48	5.44	0.95	0.36	0.21	0.78		12.09
NRT#183	14.72	6.57	17.04	ND	ND	2.34	0.39	0.62	0.23	0.07	ND		5.80
NRT#186	21.70	7.11	6.89	103.21	25.50	4.29	1.67	0.25	0.53	0.52	0.01		100.62
NRT#1020	17.13	18.03	2.35	13.83	4.24	3.21	4.31	2.76	0.67	0.32	1.27		32.29
NRT#189	18.83	13.55	12.01	10.45	30.46	3.06	0.85	4.21	0.86	0.26	ND		60.64

3. Equilibrium-Based Assessment-Batch Leaching

The purpose of batch leaching experiments was to determine the leaching equilibrium as a function of pH and solid/liquid (S/L) ratio using batch leaching methods for the constituents listed in Table 2 of the proposal. Batch leaching experiments for the fourteen fly ash samples was carried out at S/L ratios 1:2, 1:5, 1:10, 1:20 without pH adjustment, and at S/L ratio 1:10 with pH adjusted to 2-12 (12 pH points) or pH 4-12 (6 pH points). The results for NRT #169, NRT #170, NRT#182, NRT#183, NRT #1020, NRT #189, and NRT #186 have been presented in previous two reports. This report will illustrate the batch leaching result for NRT #034, NRT #089, NRT #094, NRT #103, NRT #104, NRT #153, and NRT #1021(7 new ashes samples).

3.1. Leaching of seven new ashes at four S/L ratios without pH adjustment

Table 7 shows the leachate pH of NRT #034, NRT #089, NRT #094, NRT #103, NRT #104, NRT #153, and NRT #1021 at four S/L ratios. Leachate of ashes NRT #034 and NRT #153 was strongly acidic, close to pH 4. Leachate of ashes NRT #103, NRT #104, and NRT #1021 was strongly basic, with the pH greater than pH 12. Leachate of ashes NRT #089 and NRT #094 was slightly basic.

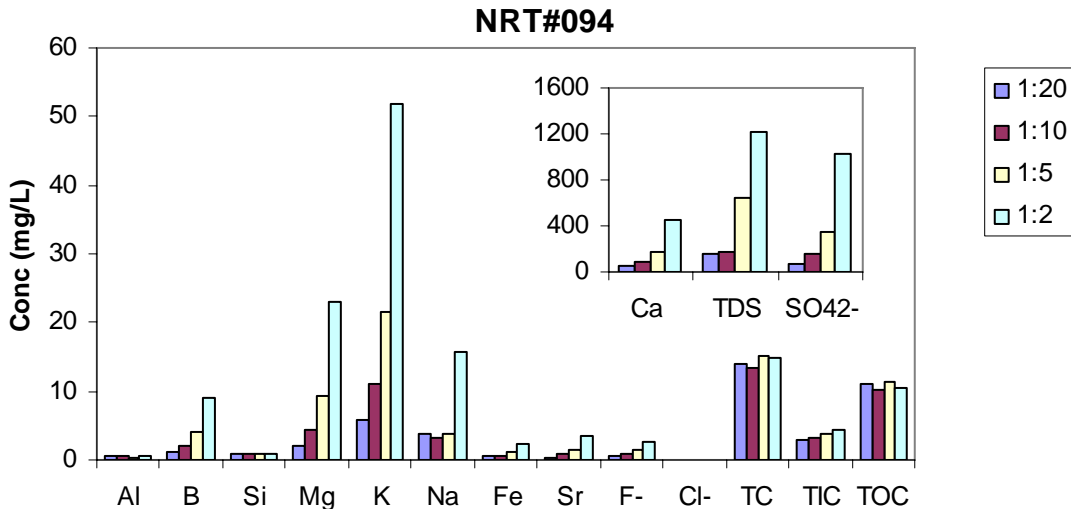
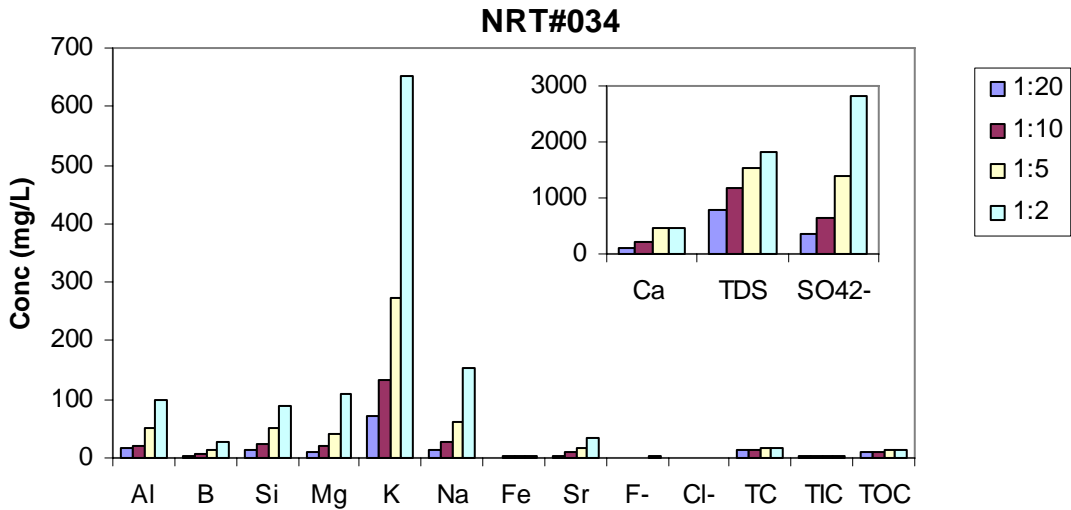
Table 7. Natural pH of NRT #034, NRT #089, NRT #094, NRT #103, NRT #104, NRT #153, and NRT #1021at S/L ratios 1:2, 1:5, 1:10, and 1:20.

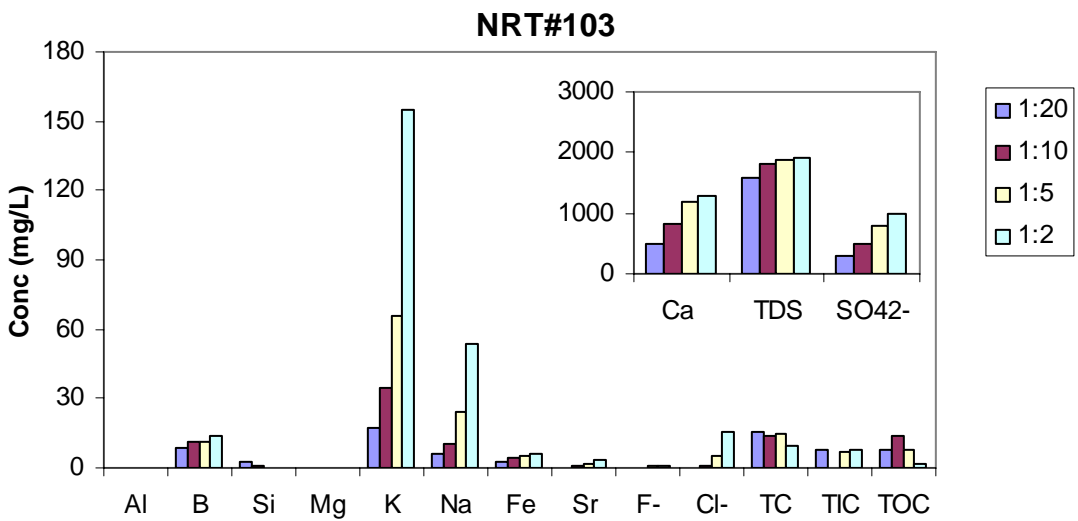
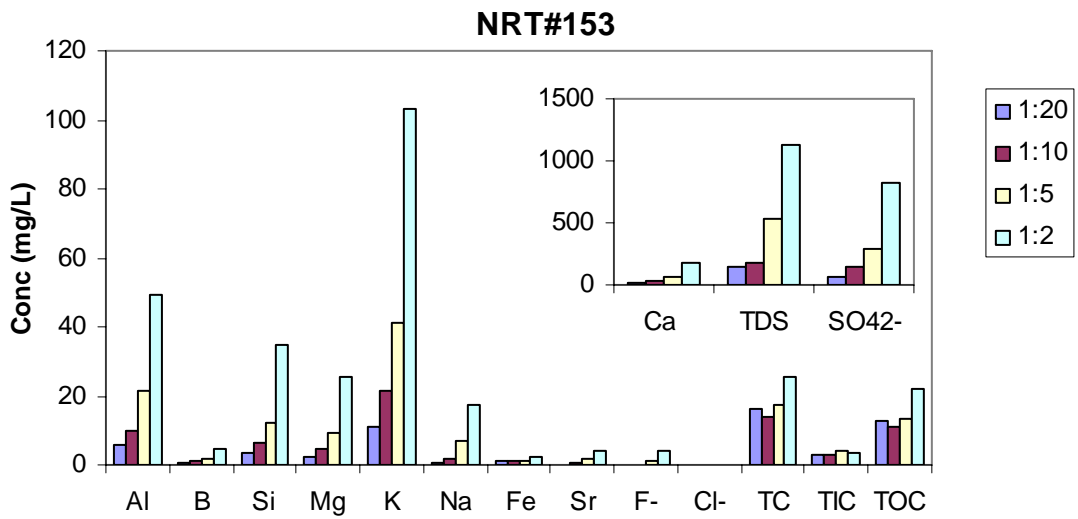
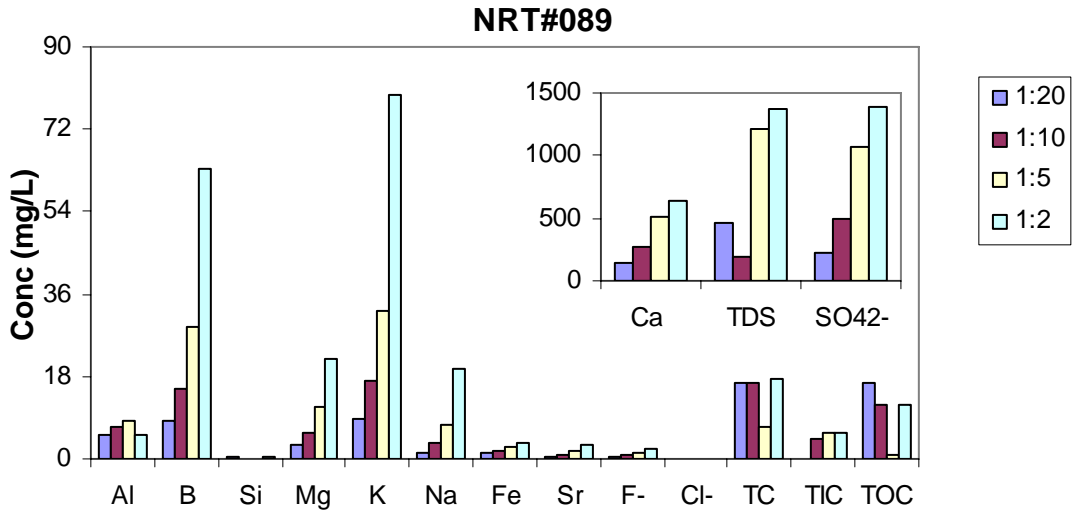
S/L Ratio	Leachate pH						
	NRT #034	NRT #089	NRT #094	NRT #103	NRT #104	NRT #153	NRT #1021
1:20	4.12	9.41	8.43	12.35	12.4	4.12	12.33
1:10	4.08	9.39	8.4	12.56	12.58	4.08	12.58
1:5	4.01	9.44	8.32	12.69	12.7	4.04	12.63
1:2	3.92	9.48	8.3	12.71	12.72	3.97	12.71

Figure 1 shows the leaching of major elements(in ppm level) under different S/L ratios 1:2, 1:5, 1:10, 1:20 without pH adjustment, while Figure 2 shows the leaching of trace elements (in ppb level). For all the 7 ashes, Ca, K concentrations were higher among major cationic elements leached out (in ppm level), while SO_4^{2-} leached out the most

among the major anions. Mg concentration was also high in the leachate of NRT #034, NRT #089, NRT #094, and NRT #153, B concentration was high in leachate of NRT #094, NRT #103, and NRT #104. Li, Mo, Zn concentration was the highest among all the trace elements, leachate of NRT #089, NRT#094, NRT #103, NRT #104, NRT #1021 also contained significant amount of Ba, while leachate of NRT #034, and NRT #153 contained high concentration of Cu.

For most elements, the soluble concentration increased with increase of S/L ratio, such as Li, B, K, Na, Sr, Mo, and Se. This may be because these elements tend to be in soluble phase at the natural pH condition; whereas others showed an opposite trend, such as As, Tl, and Ba in ash NRT #089, NRT #094, NRT #103, and NRT #104, and Al in ash NRT # 1021. This may be caused by the precipitation of them with other elements as the S/L ratio increased.





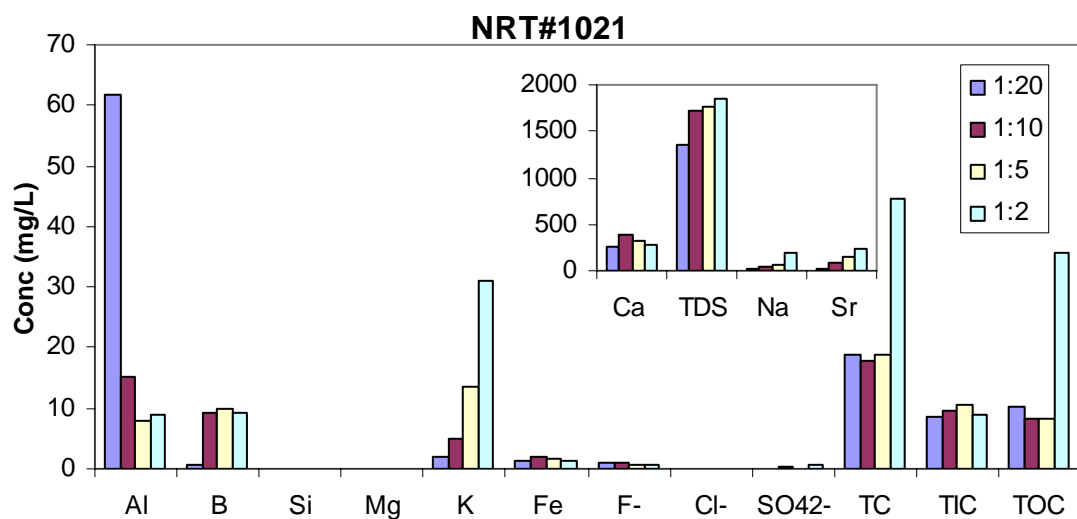
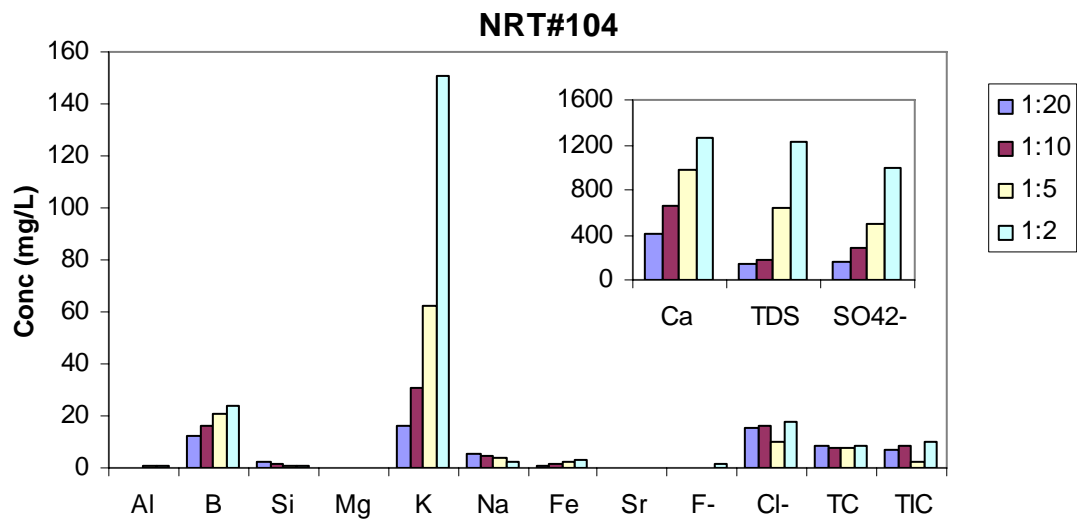
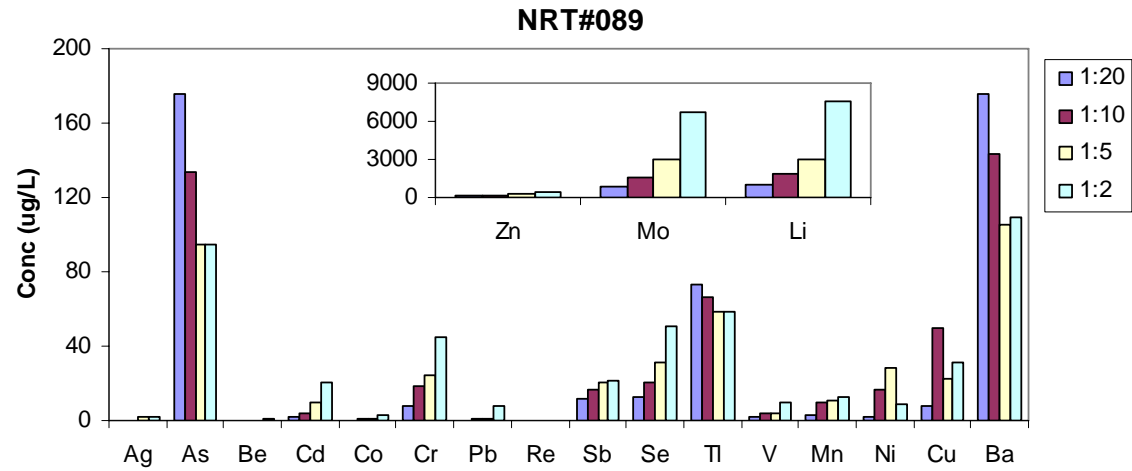
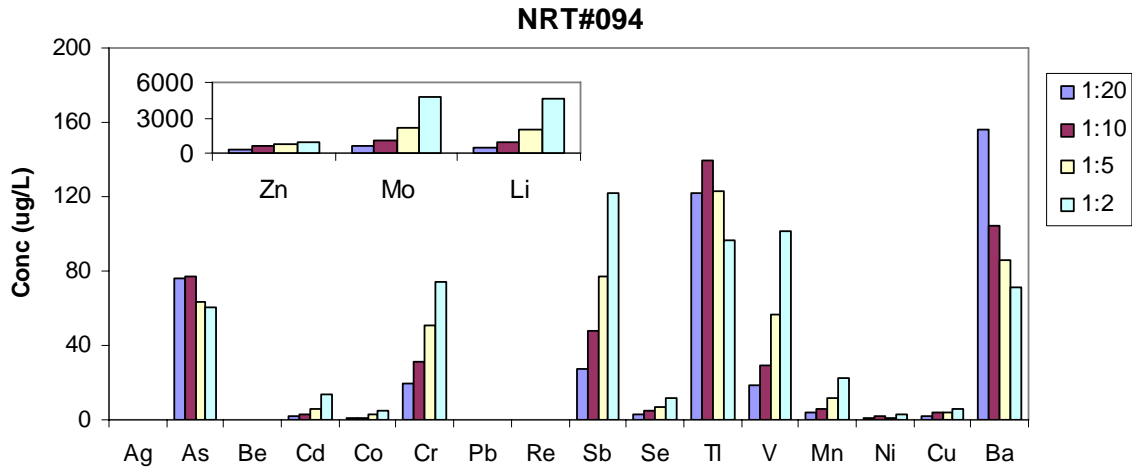
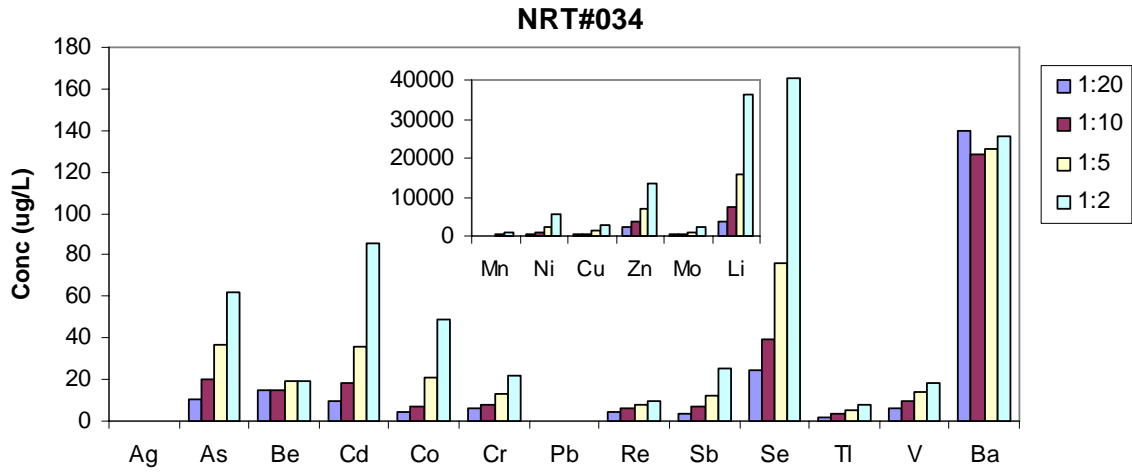
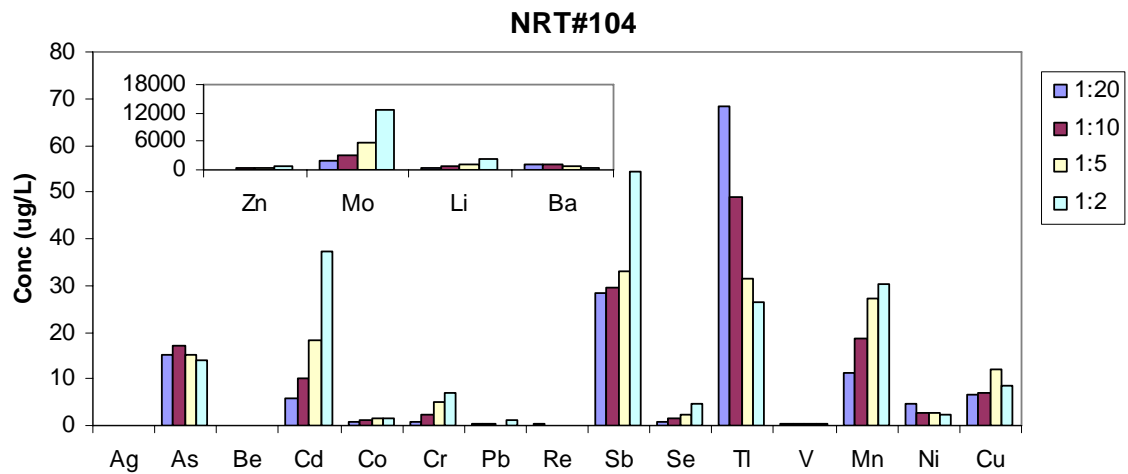
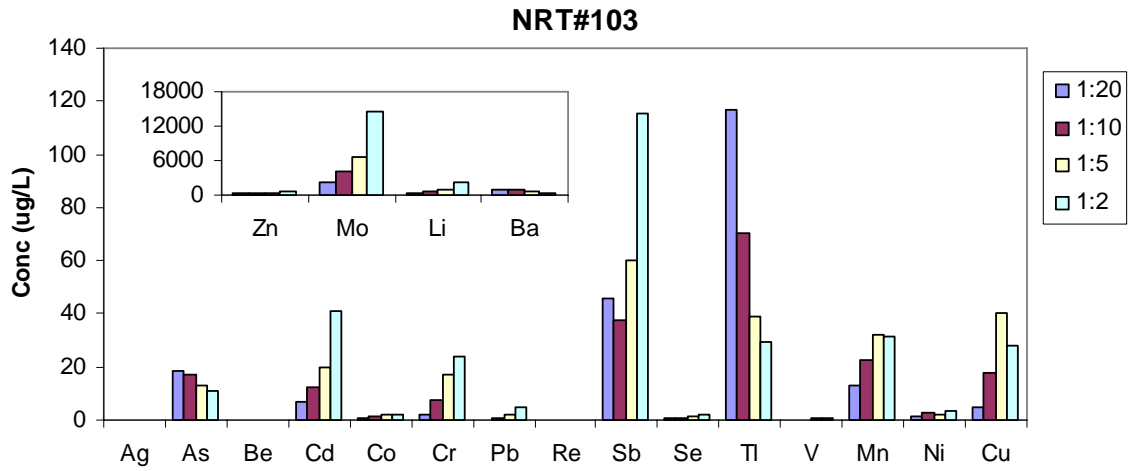
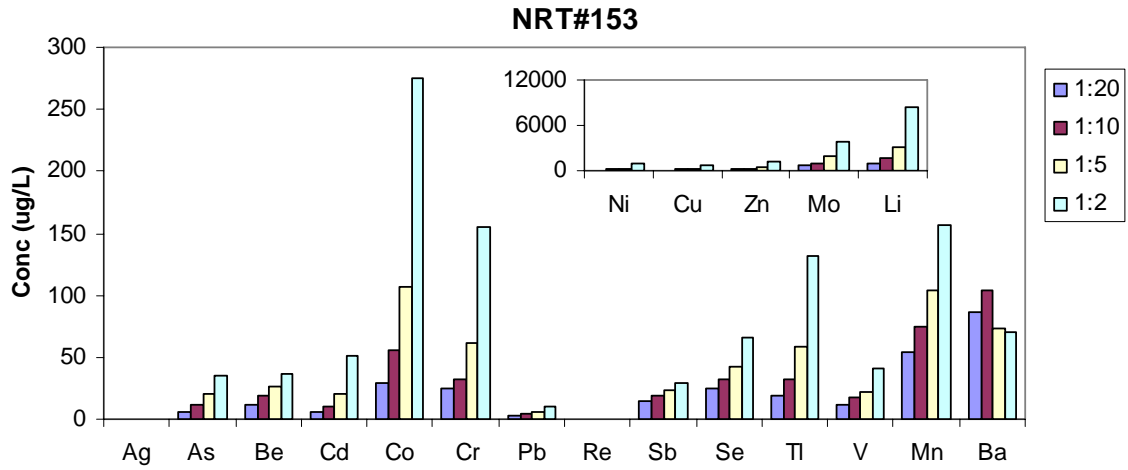


Figure 1. Leaching of major elements and anions at S/L ratios 1:2, 1:5, 1:10, and 1:20 without pH adjustment for NRT #034, NRT #089, NRT #094, NRT #103, NRT #104, NRT #153, and NRT #1021.





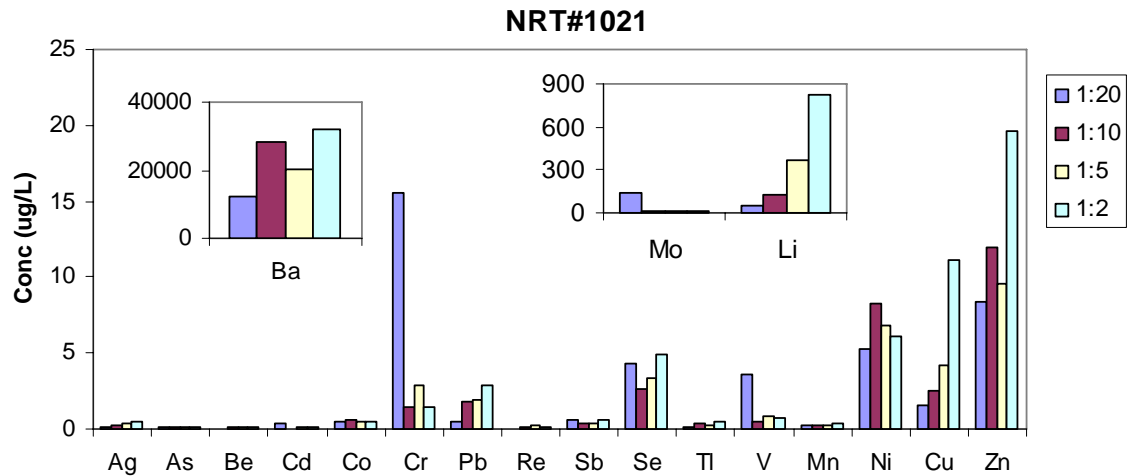


Figure 2. Leaching of trace elements at S/L ratios 1:2, 1:5, 1:10, and 1:20 without pH adjustment for NRT #034, NRT #089, NRT #094, NRT #103, NRT #104, NRT #153, and NRT #1021.

3.2. Leaching of seven new ashes at S/L ratio 1:10, pH 4-12

Figures 3 illustrates the leaching of major and trace cationic elements (Ca, Al, Mg, Fe, K, Na, Sr, Ba, Zn, Ni, Cu, Co, Be, Pb, Tl, Cd and Ag) at S/L ratio 1:10, and pH 4-12 (6 pHs). Figure 4 shows the leaching results of major and trace anionic elements (B, Si, V, Mo, Se, As, Cr, Sb, and Mn) and the major anion SO_4^{2-} .

Subbituminous coal ash NRT #1021 generally leached significantly higher amount of major elements (Al, Mg, Sr, B) than other 6 bituminous coal ash samples at pH 3, this could be cause by the fly ash dissolution at this pH, since this ash is highly alkaline (natural pH =12.6 at S/L 1:10), large amount of concentrated HNO_3 (2 ml 70% HNO_3) was added during titration to reach this pH level. During the leaching experiment, once MQ water was added into the bottle with NRT #1021 ash, cementation started, and it could not be easily dissolved even large amount of acid was added. This may contribute to the inconsistent leaching curve of NRT #1021.

Ca in the 7 ash samples displayed the highest leachability among all the elements, and its leaching decreased with increase of pH. Precipitation of $Ca(OH)_2$ may be the reason for the sharp decrease of Ca concentration at pH greater than 12 . The Ca leaching curve also

indicated that at the same pH, ash NRT #103 and NRT#104 can release significantly more Ca than other bituminous coal ashes.

The three major elements Al, Si, Mg and Fe, and nine trace elements Mn, Cu, Pb, Be, Tl, Cd, Zn, Ni, and Co showed a typical leaching behavior as other cationic metals. Their leaching generally was negligible at alkaline pH conditions, but increased significantly as pH is decreased to below a certain level, which was pH 8 here for the four elements. Similar leaching behavior was observed for other elements including Ca, Sr, Ba, and B, and SO_4^{2-} from NRT #1021. However, the release of these elements was decreasing gradually over pH 4-12. The remarkable release of these elements at low pH might be caused by not only surface desorption, but also by acid/base dissolution, because significant amount of acid was used to reduce pH for ashes NRT #103, NRT #104, and NRT #1021, while significant amount of strong base was added to adjust the pH for ash NRT #034, and NRT #153.

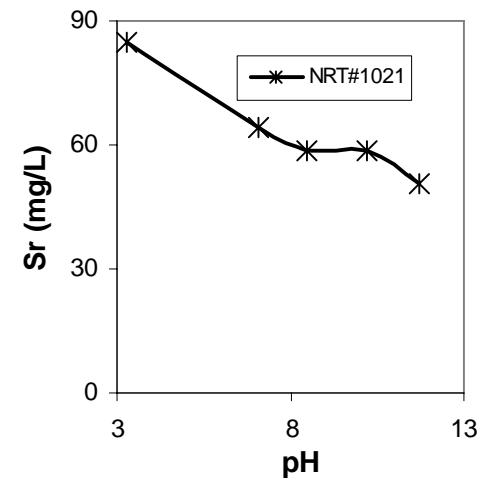
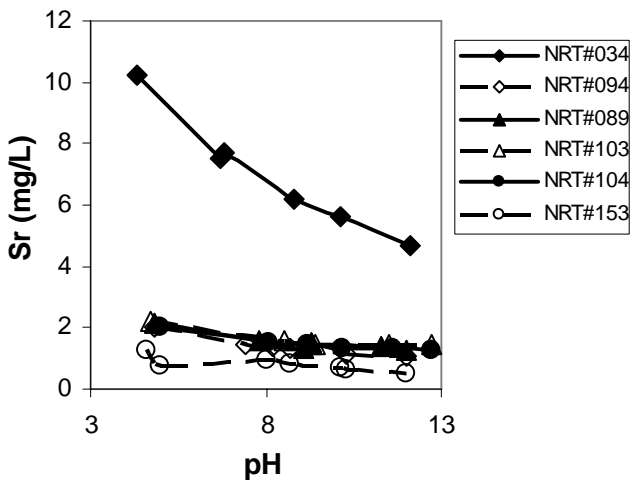
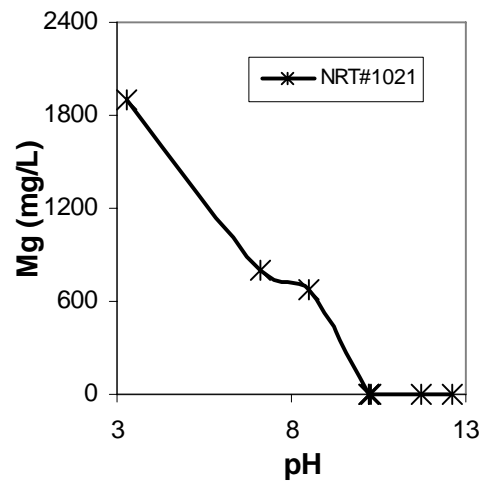
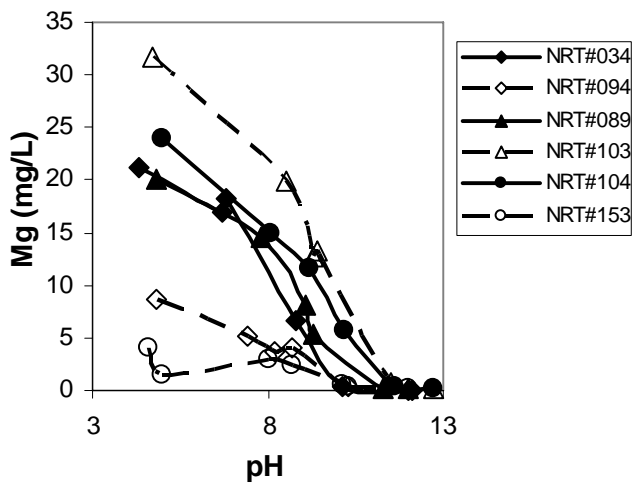
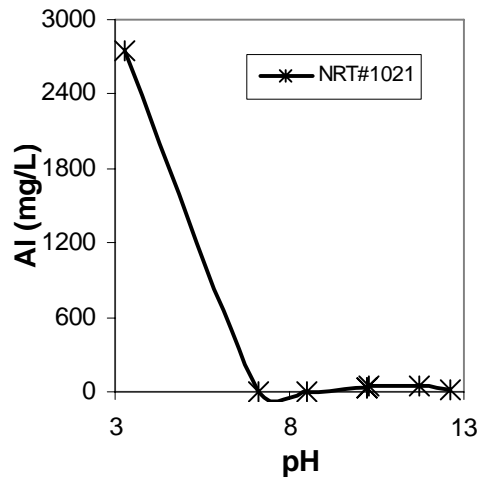
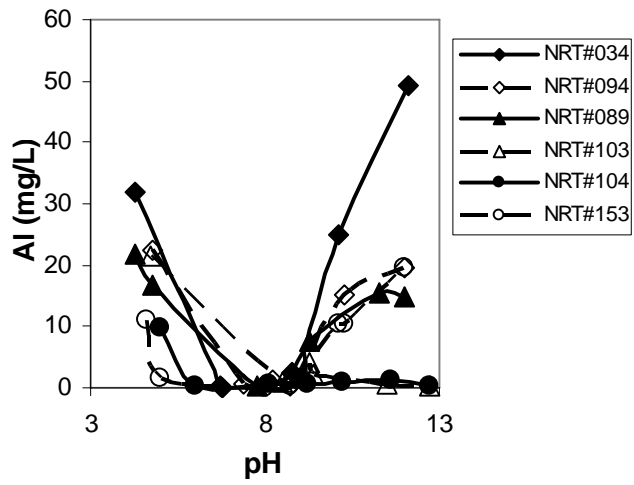
The leaching results of K, and Li indicated that they were in soluble phase in entire pH range. SO_4^{2-} from NRT #034, NRT #089, NRT #094, NRT #153 showed similar leaching trend, leaching of Re and SO_4^{2-} from NRT #103, NRT #104 are similar over pH < 9, but there is a sharp decrease at high pH, the sharp decrease at higher pH was probably caused by particle precipitation.

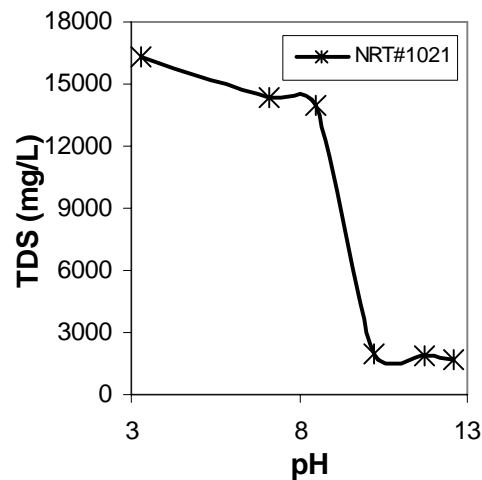
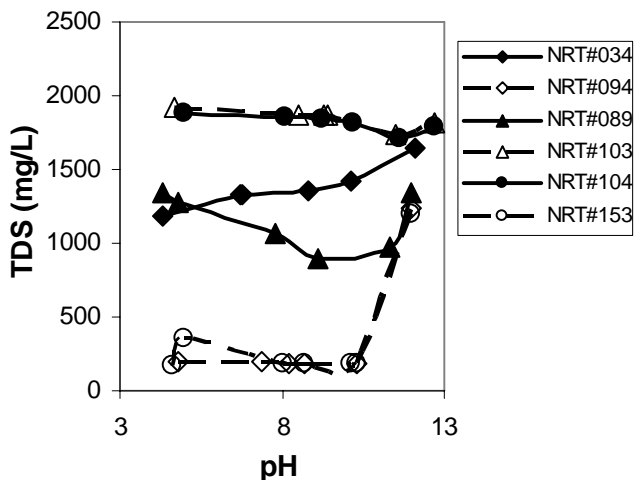
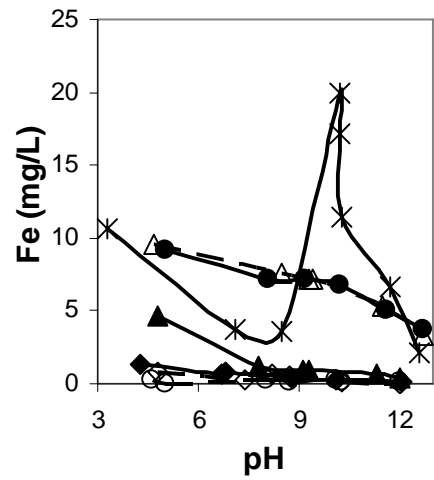
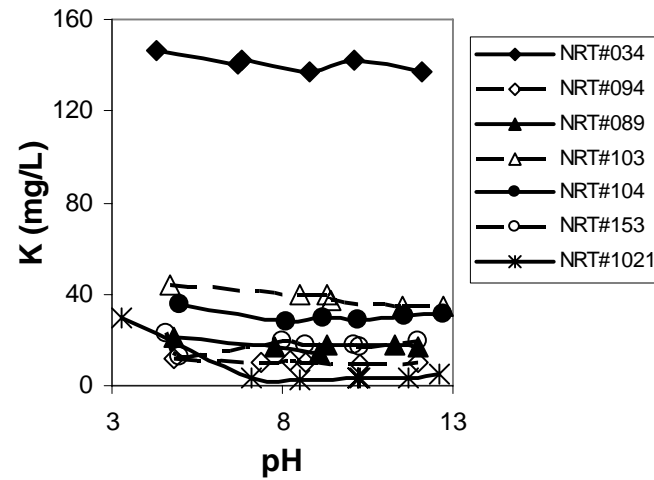
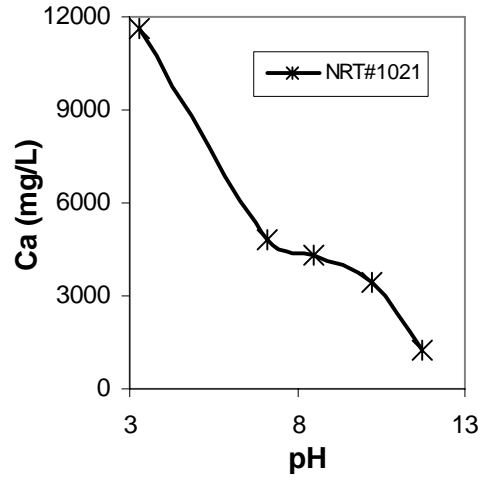
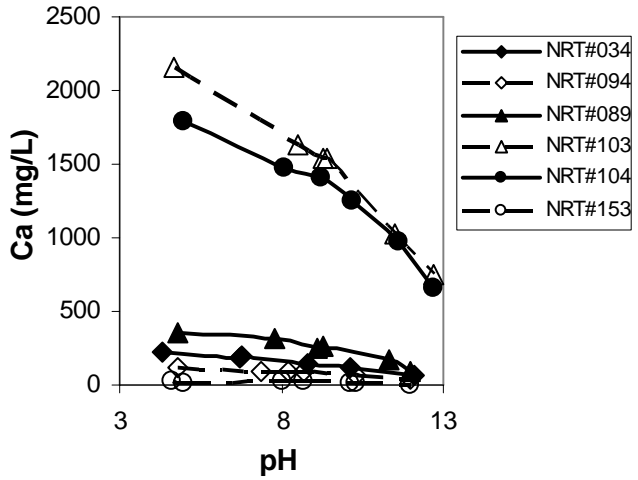
Pb, Be, Re, and Ag displayed the least leaching potential (< 10 ug/L), and larger error was expected for their analysis with ICP-MS, because the sample concentration were close to detection limit after dilution (10 to 100 times dilutions were required for most samples, because the high TDS in samples will shorten the life of cones in ICP-MS). F⁻, Cl⁻ release was not significant either, because their concentrations are below detection limit on IC after 5 times dilution. Therefore, the leaching curve for F⁻, and Cl⁻ were not presented in this report.

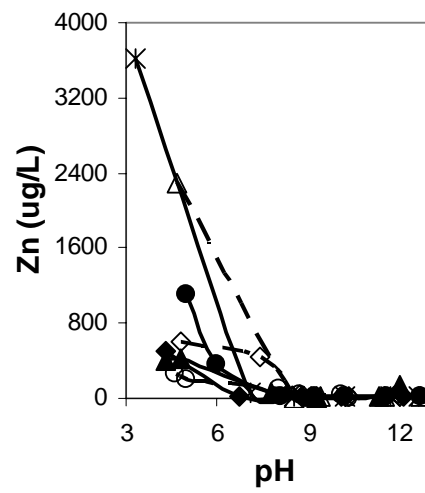
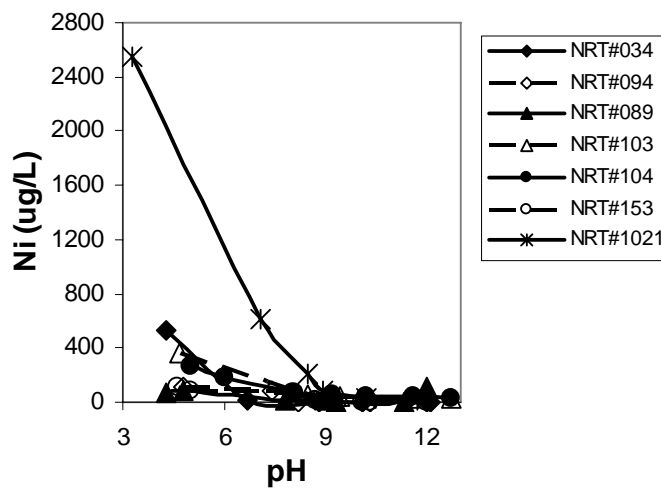
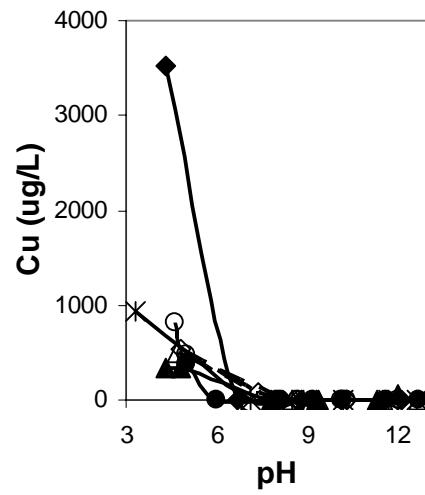
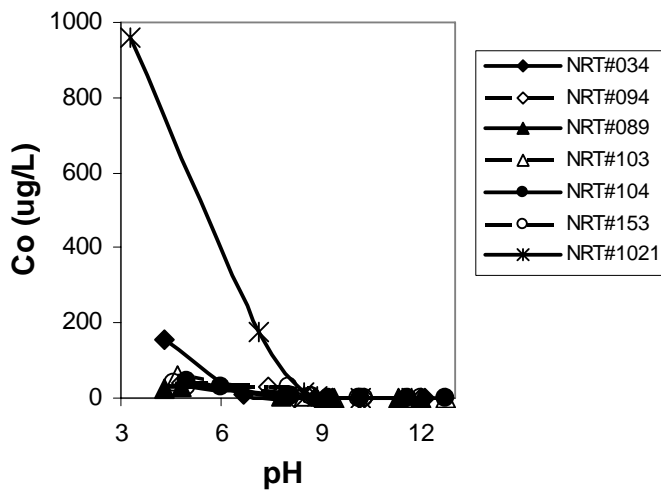
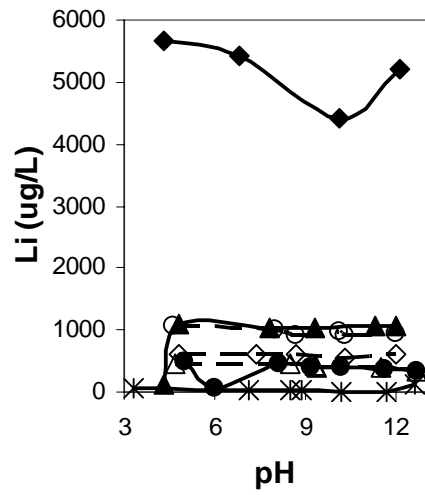
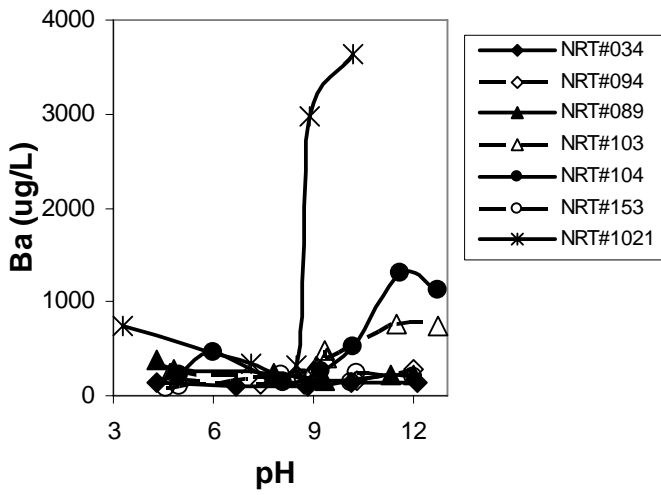
For all the seven ashes, B and Si showed the highest leachability among all oxyanions, and their leaching increased with the decrease of pH, similar trend was observed for Mn in Figure 4. For most of the seven ashes, leaching of As, V, Se, and Cr demonstrated similar trends, which had the least release pH range, and leaching is increased as pH was

at two extremes used in the experiment (to a lower pH range, and higher pH range), and the minimum release pH range was between 6 and 9 for these three elements. However, the leaching of As from NRT #089 was decreasing with the increase of pH over pH 4-12. Leaching of Mo generally increased with the increase of pH over pH 4-9.5, but decreased over pH >9.5, similar decrease of As, V, Se, Cr, and Sb was also observed for other ash samples (especially Cr, Sb leaching from NRT #103 and NRT #104) at this higher pH range, this could be because of the Ca precipitation impact.

NRT #103 and NRT #104 generally leached more Mg, Ca, Cd, Tl, Fe, B, Si, Mo, and Cr than other ashes over pH 4-12. NRT #034 released more Al, Sr, Cu, Li. The leachate of NRT #1021 had higher concentrations of Zn, Ni, Ba, and Co, and higher Se concentration at extreme acidic pH range. NRT #153 released more As, V, Sb, and Se at alkaline pH range. Al concentration was also high in leachate of NRT #094 over pH 4-12, and there was also a higher concentration of Se over alkaline pH range. The leachate of NRT #089 had higher concentration of Al, Mg over pH 4-12, and higher concentrations of As over pH <9.







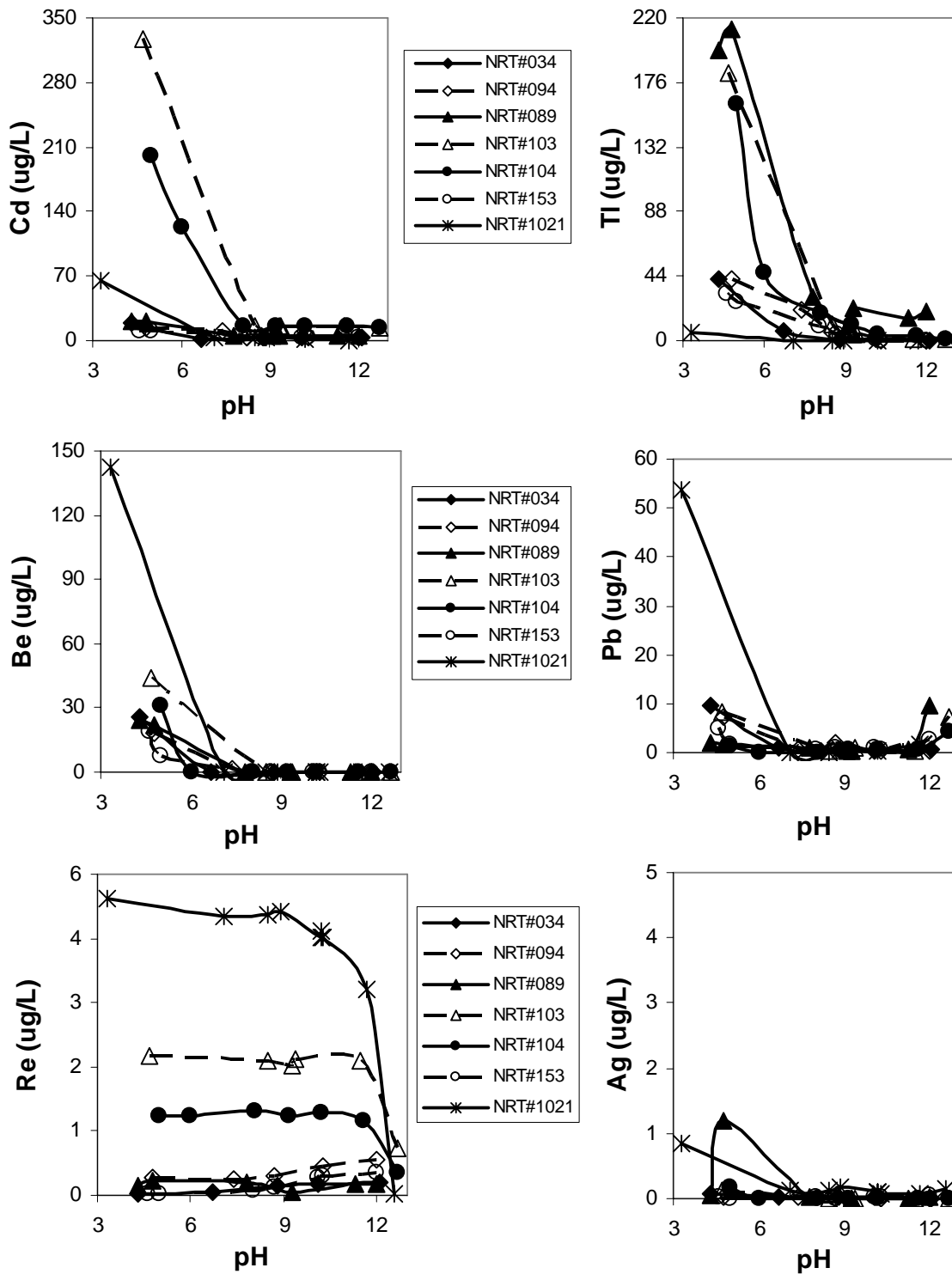
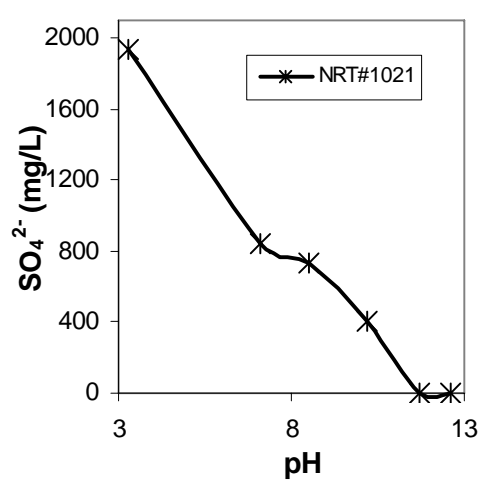
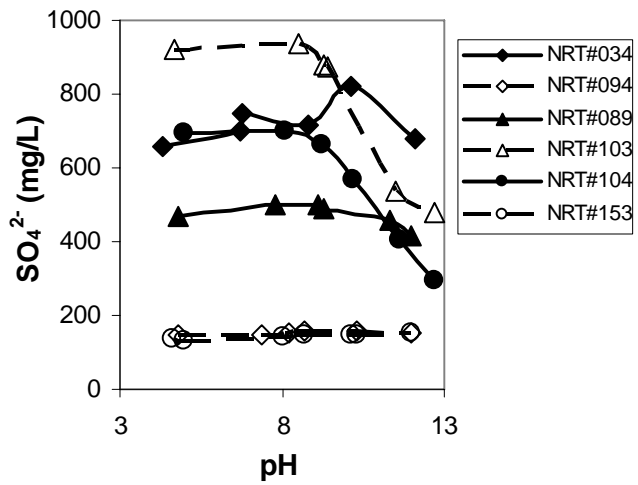
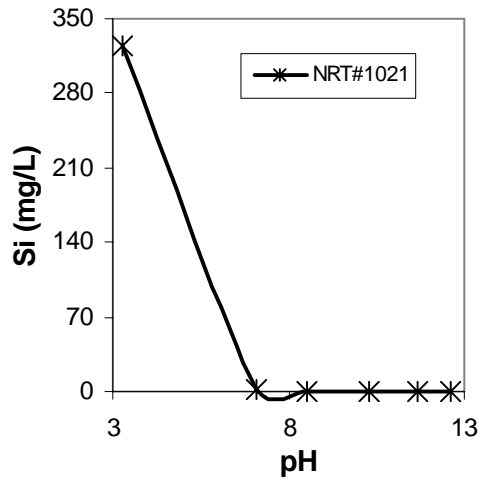
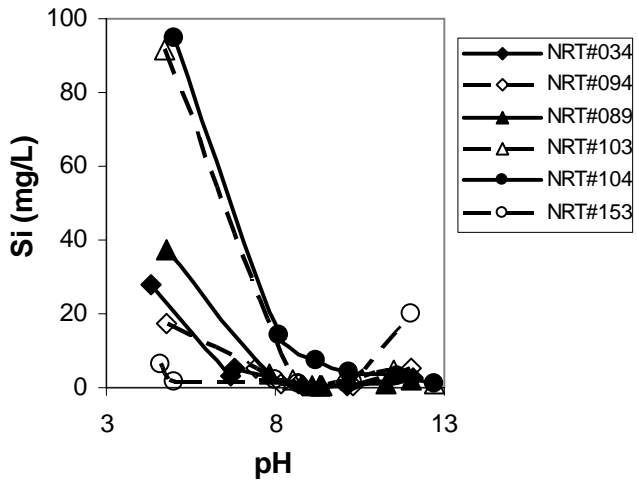
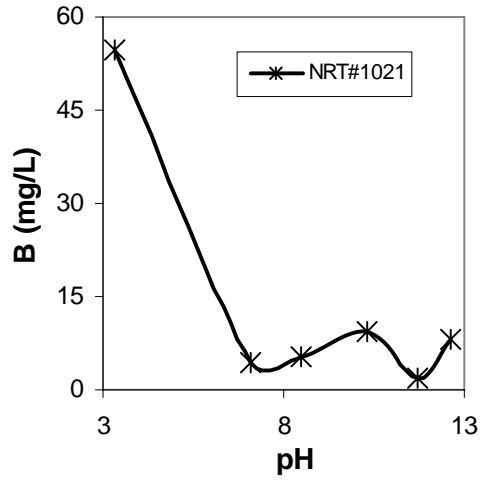
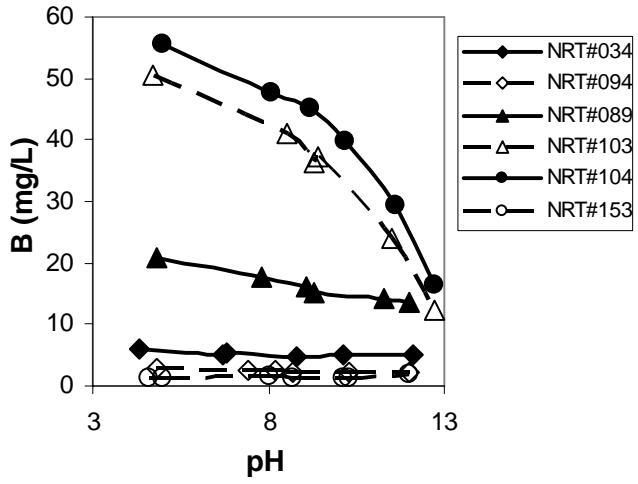
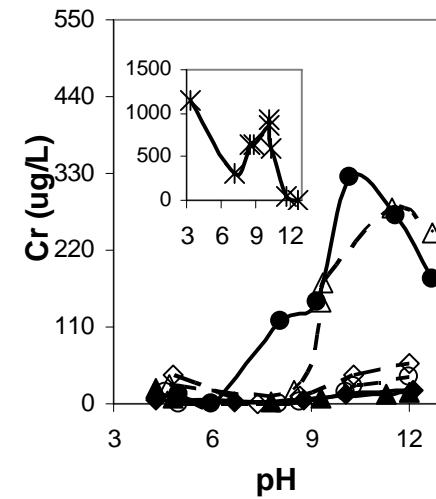
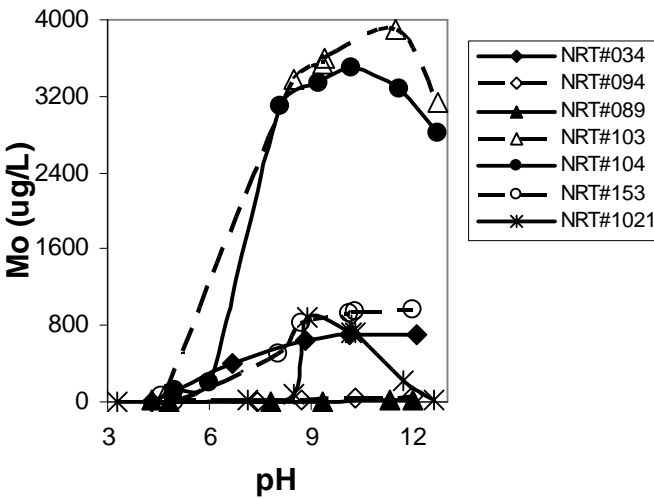
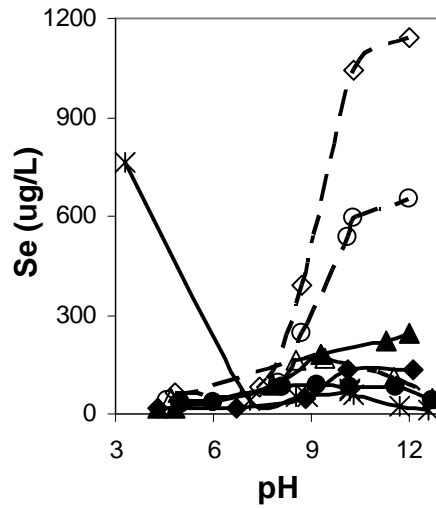
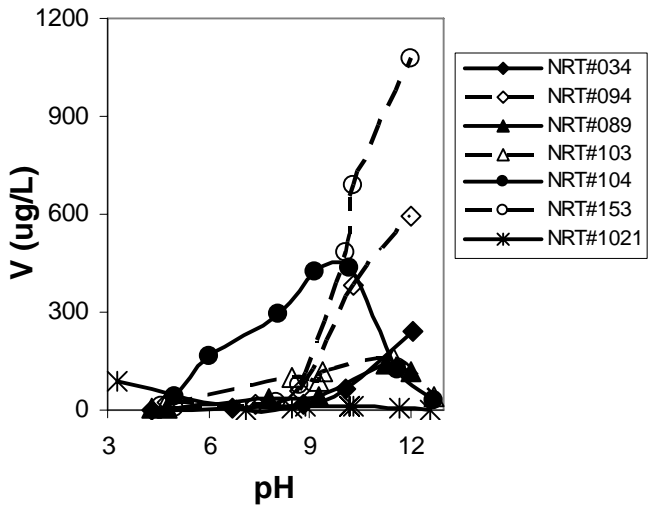
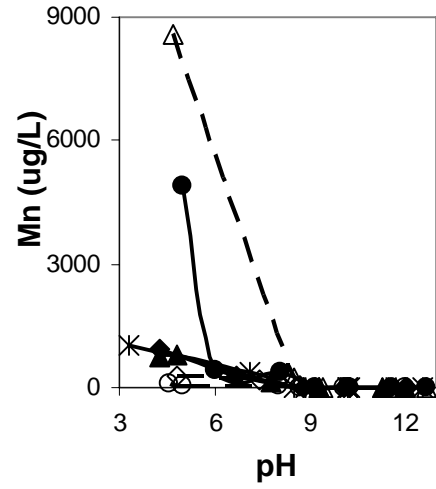
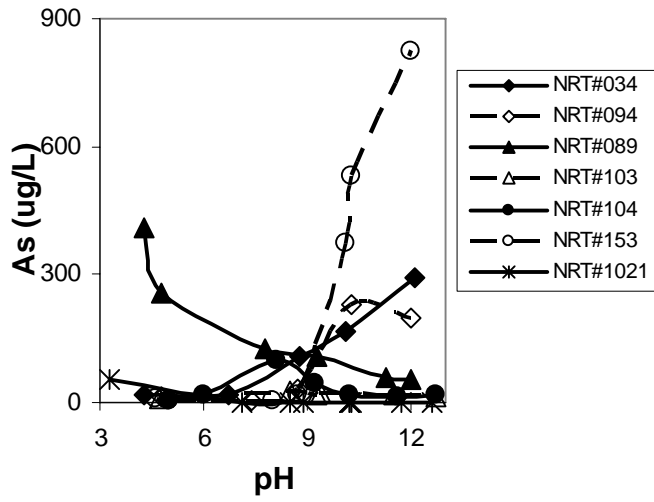


Figure 3. Leaching of major and trace cationic elements from NRT #034, NRT #089, NRT #094, NRT #103, NRT #104, NRT #153, and NRT #1021. S/L=1:10, pH 4-12.





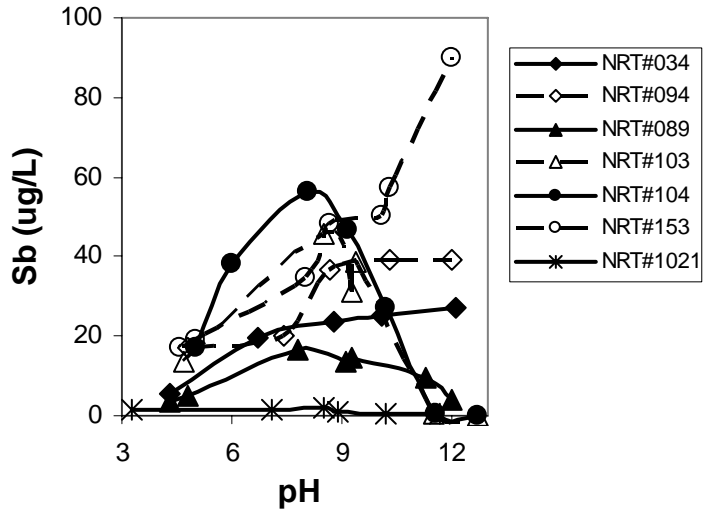


Figure 4. Leaching of major and trace anionic elements from NRT #034, NRT #089, NRT #094, NRT #103, NRT #104, NRT #153, and NRT #1021. S/L=1:10, pH 4-12.

Figure 5 shows the total organic carbon (TOC), total inorganic carbon (TIC), and total carbon (TC) concentrations in the seven new ash samples, similar to the case of former fly ash samples, the curves for TOC and TC do not show any consistent trend. Leachate of ashes NRT #034 and NRT #104 contained higher concentrations of TC and TOC than other five ashes. Except for ash NRT #103, the TIC in these fly ash leachates generally increased with the increase of pH, the TIC of which decreased at around pH 8.5, which could mean that precipitation occurred or analytical error.

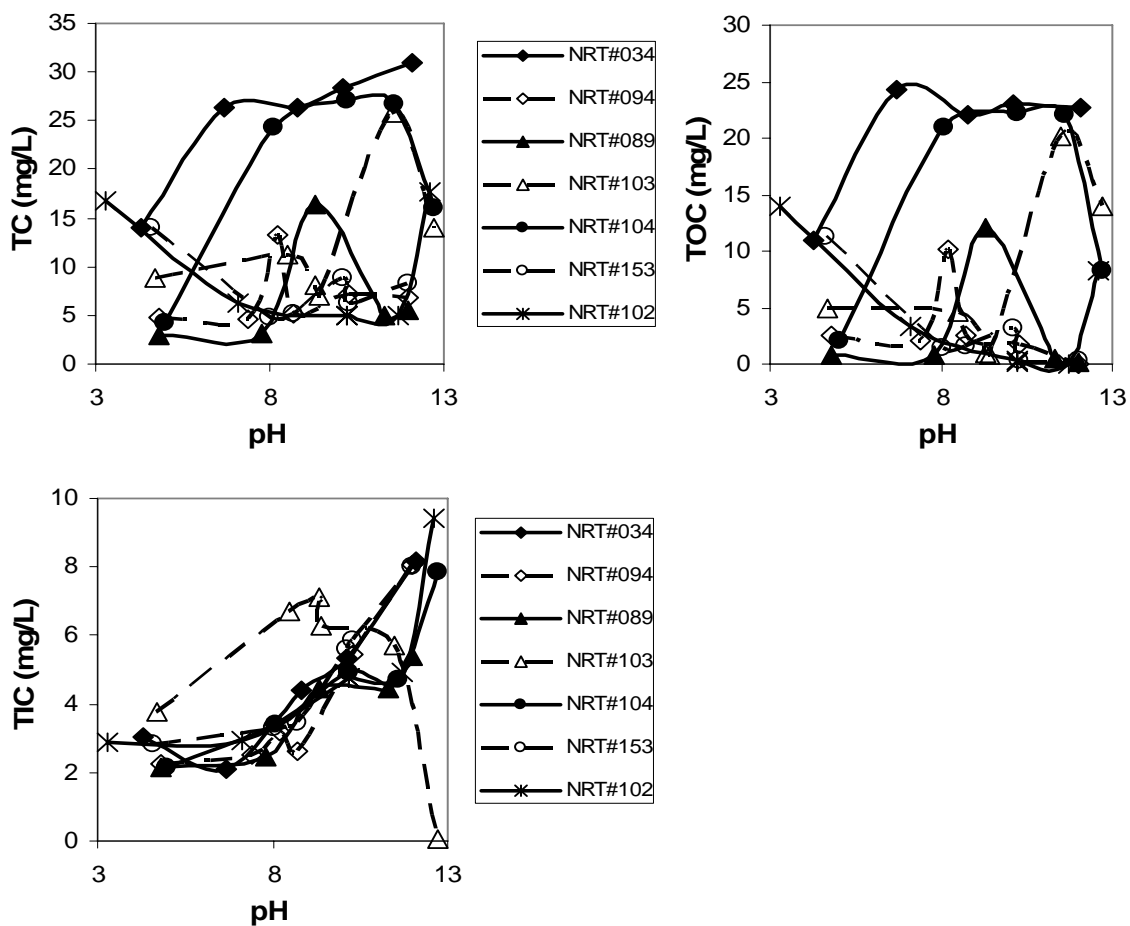


Figure 5. TOC, TIC, and TC in the leachate of NRT #034, NRT #089, NRT #094, NRT #103, NRT #104, NRT #153, and NRT #1021. S/L=1:10, pH 4-12.

4. Sulfate and pH Impact on Trona Ash Leaching

Our previous study compared the leaching results of two paired trona ash samples, and found that most trace elements concentrations in the Trona ash were higher than that of the according control ash, especially for the paired sample for SO₂ control, the leaching of oxyanionic elements enhanced significantly, which could pose great environmental concerns for the disposal of the trona ash. Based on the XRF and total composition result, the major difference between trona ash and the control ash was the sulfur, sodium content, and the pH of the leachate. We suspect higher sulfur content will compete with oxyanions such as As, Se, V, Mo, Cr for adsorption onto fly ash surface, and pH has been found to be an important factor impacting the leaching of these elements. So this study focused on the impact of sulfate and pH on the leaching of fly ash, using the two paired trona ash, which is NRT #182&NRT #183 for SO₂ control, NRT #1020&NRT #189 for SO₃ control.

4.1. Methods

Based on the XRF result, this study added sulfate into the control ash to reach the similar sulfur content as the according trona ash, the addition was 0.079 g K₂SO₄/ g NRT#182, and 0.043 g K₂SO₄/g NRT#1020. One batch leaching experiment for the control ash was carried out with only sulfate addition, and the other batch leaching experiment with not only sulfate addition, the pH was also adjusted to the level similar to the according trona ash. The leachate of these batch leaching experiments were filtered through 0.2 μm filters, and analyzed on ICP-MS and ICP-OES.

4.2. Results

The leaching results for major elements, trace elements were compared among the four batch experiments: (1) Control ash, (2) Control ash + sulfate addition, (3) Control ash + sulfate addition + pH adjustment, and (4) Trona ash. Figure 6 and Figure 7 illustrate the comparison for paired sample of SO₂ control. Figure 8 and Figure 9 present the comparison for paired sample of SO₃ control. Figure 6 and Figure 8 illustrate the leaching results for major and trace cationic elements; Figure 7 and Figure 9 illustrate the leaching

results for oxyanionic elements. Four S/L ratios 1:2, 1:5, 1:10, and 1:20 were used in the batch leaching study, the pH of the leachate is shown in Table 8.

Table 8. Leachate pH of the paired trona samples at S/L 1:2, 1:5, 1:10, and 1:20.

S/L	NRT#182	Sulfate	Sulfate+pH	NRT#183
1:20	7.51	7.56	11.3	10.98
1:10	7.57	7.5	11.2	11.04
1:5	7.52	7.4	11.04	11.1
1:2	7.46	7.18	10.78	11.13
S/L	NRT#1020	Sulfate	Sulfate+pH	NRT#189
1:20	9.11	9.44	7	7.74
1:10	9.41	9.74	7.3	7.59
1:5	9.33	9.79	7.5	7.53
1:2	9.81	10	7.5	7.67

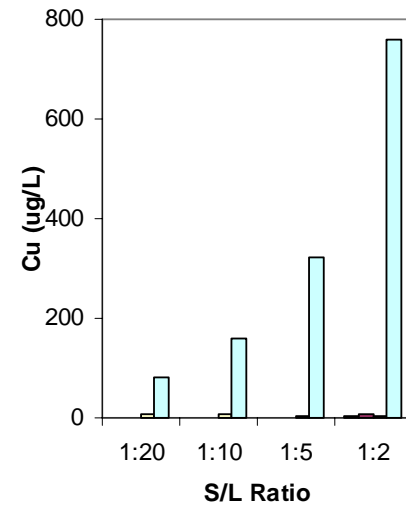
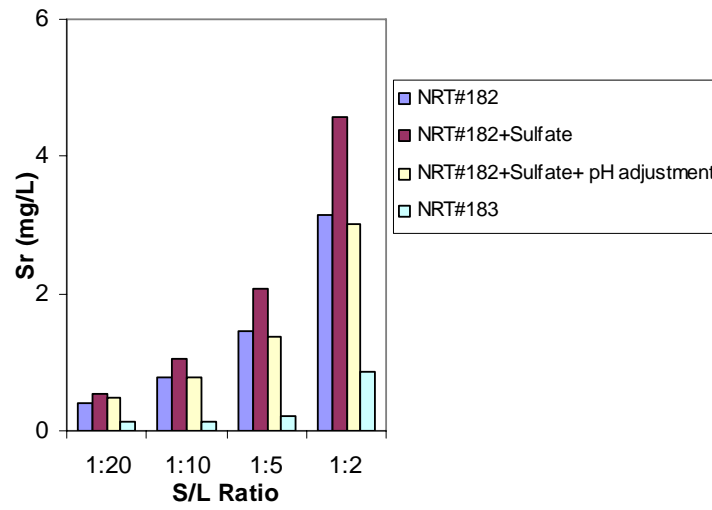
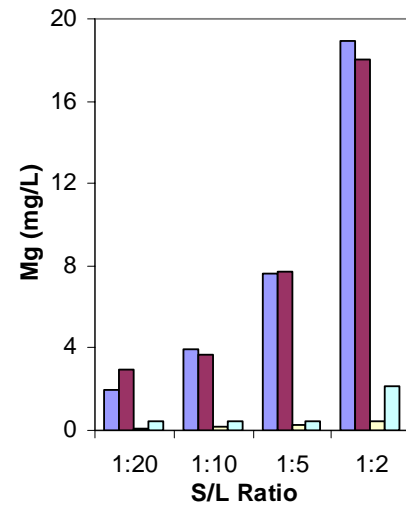
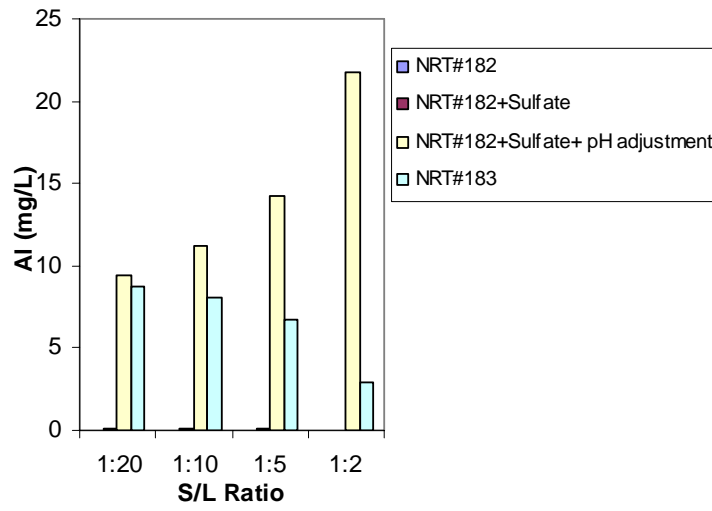
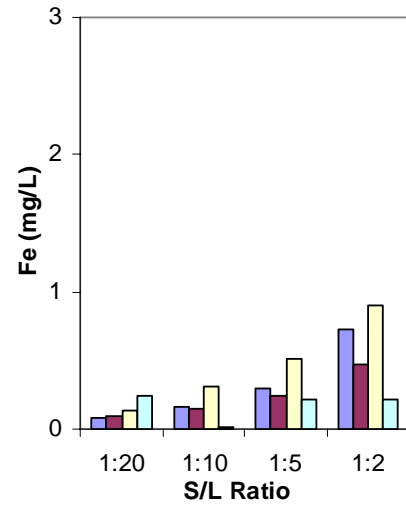
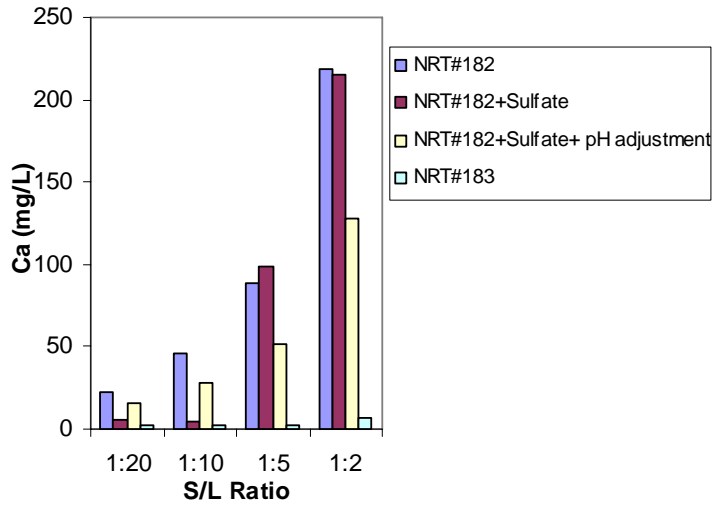
4.2.1. Comparison of leaching results for SO₂ control paired samples

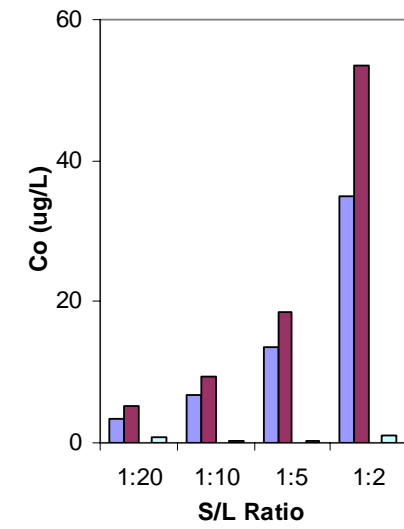
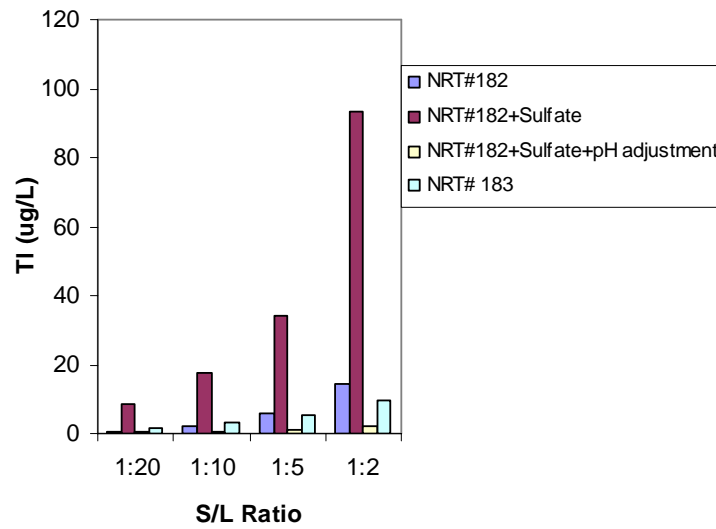
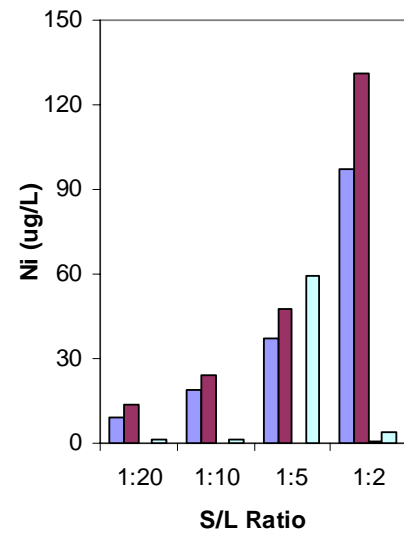
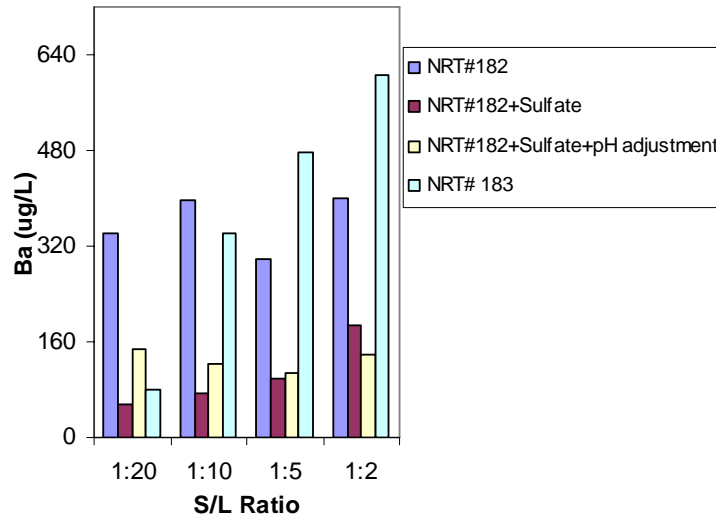
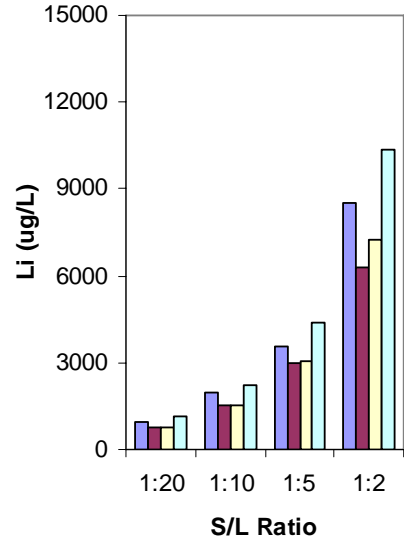
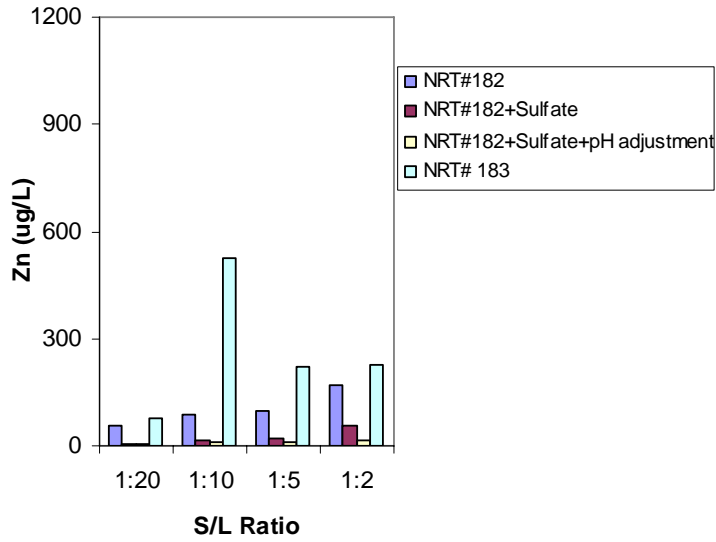
Figure 6 and Figure 7 demonstrated that, for the paired sample NRT #182 & NRT #183 (SO₂ control), both sulfate addition and pH adjustment reduced the leaching of Li, Zn, Sb, Ca, and Be, but the leaching of these elements in the trona ash NRT#183 was actually increased over the control ash NRT#182, indicating the different leaching characteristics observed between trona ash (NRT #183) and control ash (NRT #182) is not caused by the competitive adsorption from sulfate or the pH increase, further studies are needed to find out the mechanism. Results in Figure 6 and Figure 7 also indicate that the higher sulfur content and alkaline pH of the trona ash are responsible for the increased leaching of Cu, As, Cr, Mo, Al, Pb, because both sulfate addition and pH adjustment enhanced the leaching of these elements from the control ash. Sulfate addition increased the leaching of Se, B, and Cd from the control ash, but further increase the pH will reduce the leaching of these elements from the control ash. Contrary results were observed for V, Si, Re, and Ag, where sulfate reduced the leaching of these elements, but further increase the pH will enhance their leaching, all these elements released more in the trona ash than the control. Ba, Fe, Sr, Mn, Ni, Co, Tl, Mg was released less in the trona ash than the control, as the comparison in these two figures demonstrate, precipitation by sulfate could possibly explain the reduced leaching of Ba and Fe, while pH increase is more responsible for the reduced leaching of Sr, Mn, Ni, Co, Tl, and Mg.

4.2.2. Comparison of leaching results for SO₃ control paired samples

For the paired sample NRT #1020 & NRT #189 (SO₃ control) in Figure 8 and Figure 9, both sulfate addition and pH adjustment (decrease the pH from 9.7 to 7.1) reduced the leaching of Ba, but Ba leaching was much higher in the trona ash than the control, contrary results were observed for Sr, and Tl, indicating the increased leaching of Ba and decreased leaching of Sr, and Tl in the trona ash NRT #189 was caused by mechanism other than the competitive adsorption from sulfate or the pH change. The higher sulfur content and lower pH of the trona ash were responsible for the increased leaching of Sb, Mn, Pb, and Be, because both sulfate addition and pH adjustment enhanced the leaching of these elements from the control ash, as demonstrated by the leaching results in Figure 8 and Figure 9. Sulfate addition increased the leaching of As, Se, Cr, and V from the control ash, but further decrease the pH will reduce the leaching of these elements from the control, contrary results were observed for Si, Ni, Co, Mg, B, Cd, and Re, where sulfate reduced the leaching of these elements, but further decrease pH will enhance their leaching, all these elements released more in the trona ash than the control. Ca, Fe, Al was released less in the trona ash than the control; precipitation by sulfate could possibly explain the reduced leaching of Ca and Fe, while pH decrease is more responsible for the reduced leaching of Al.

It should be noted that sulfate addition + pH adjustment for the control ash NRT #182 almost reached the similar leaching levels of Mo, B, and Pb with that of the trona ash NRT #183. Similarly, sulfate addition + pH adjustment for the control ash NRT #1020 almost reached the similar leaching levels of Pb with that of the trona ash NRT #189. For the other elements, neither sulfate addition or sulfate addition + pH adjustment of the control ash got equivalent leaching results with that of the trona ash, indicating there are some other mechanisms responsible for the different leaching characteristics of these elements in the control ash and the trona ash, further studies are needed to find out the reason.





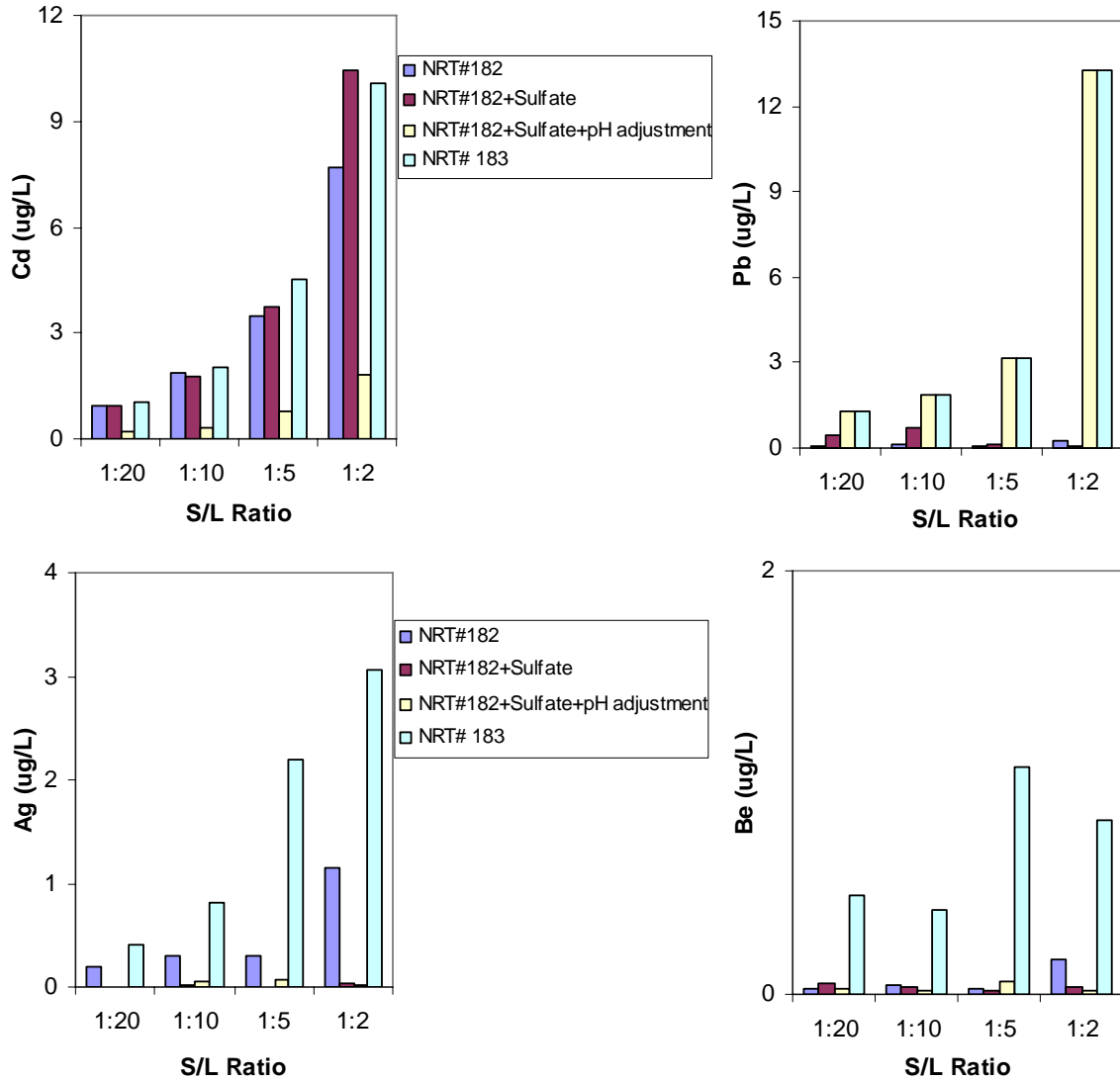
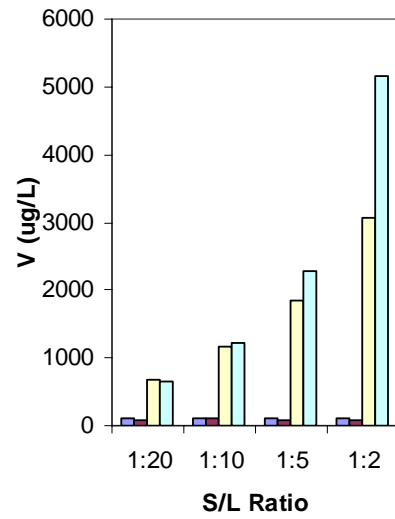
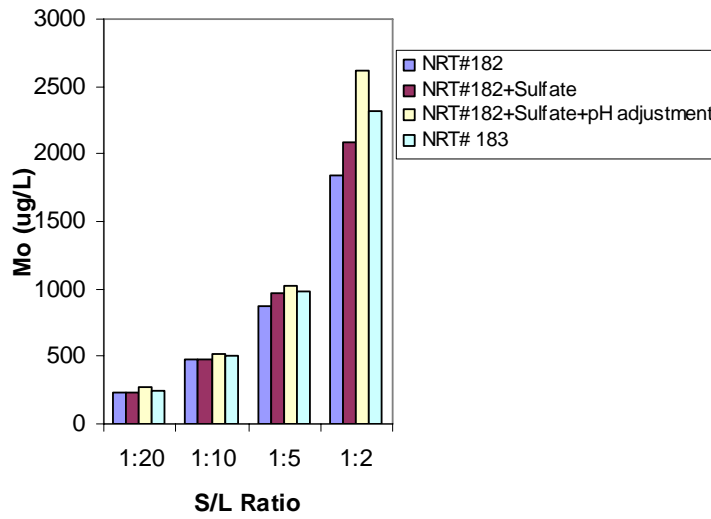
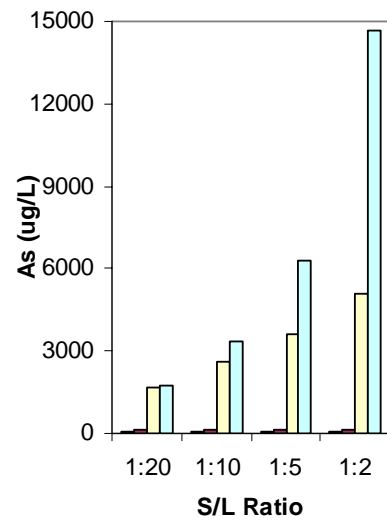
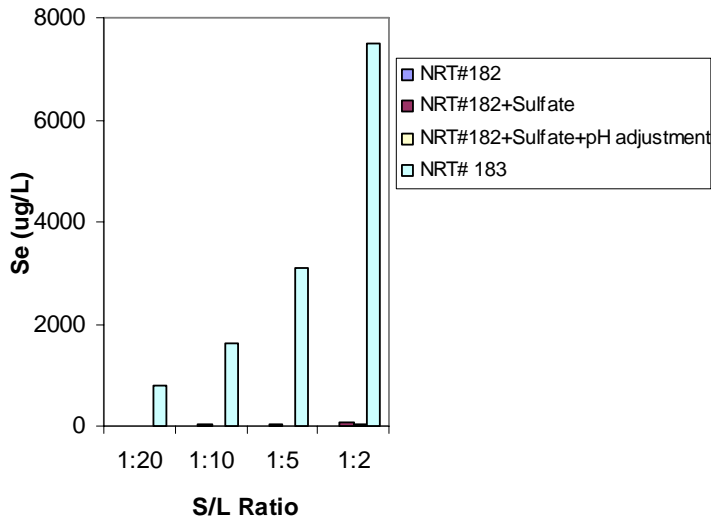
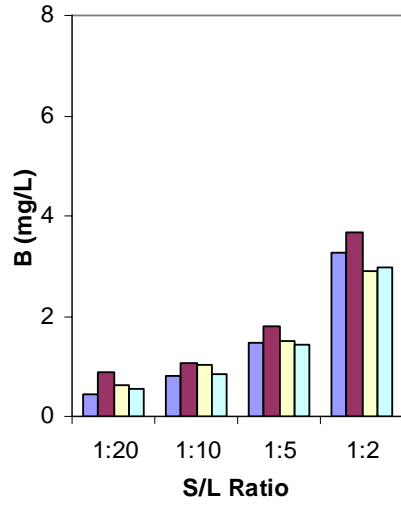
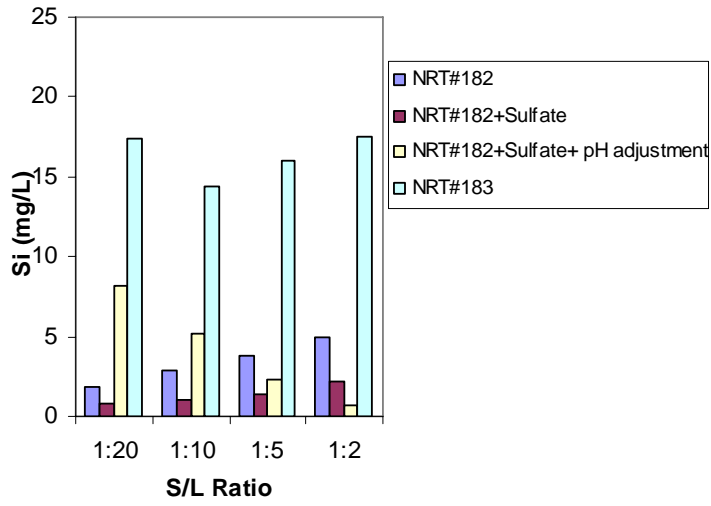


Figure 6. Comparison of leaching of major and trace cationic elements in the paired sample for SO₂ control. NRT #182 is the control ash, NRT #183 is the trona ash, S/L=1:10.



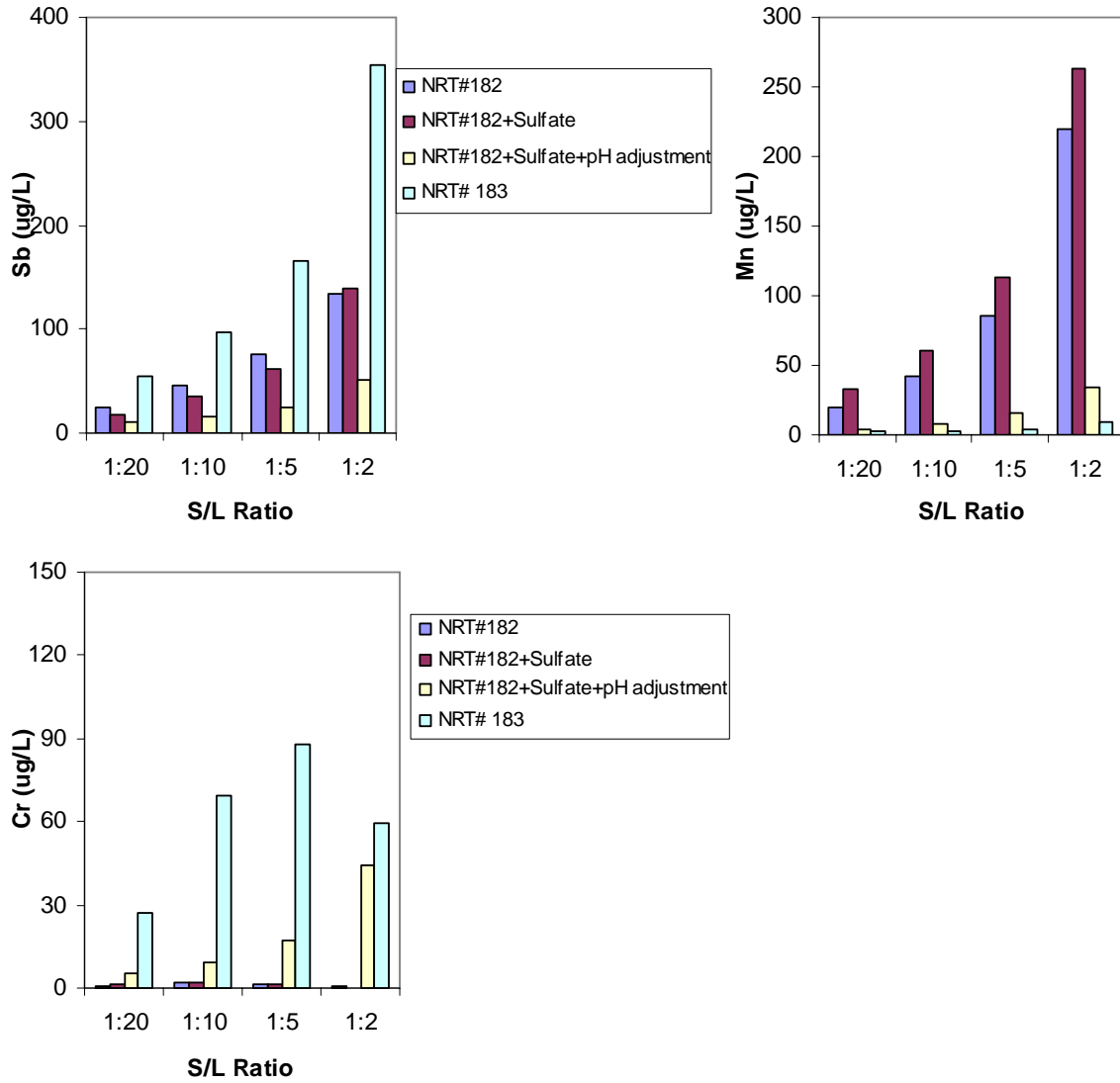
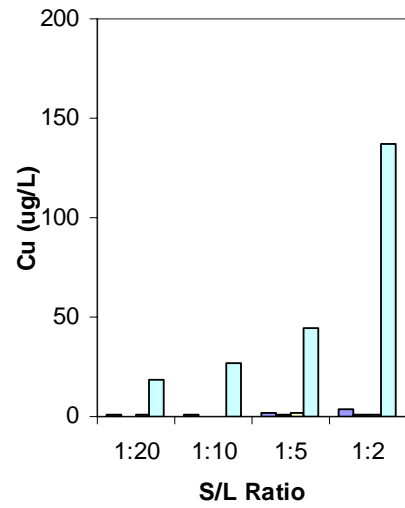
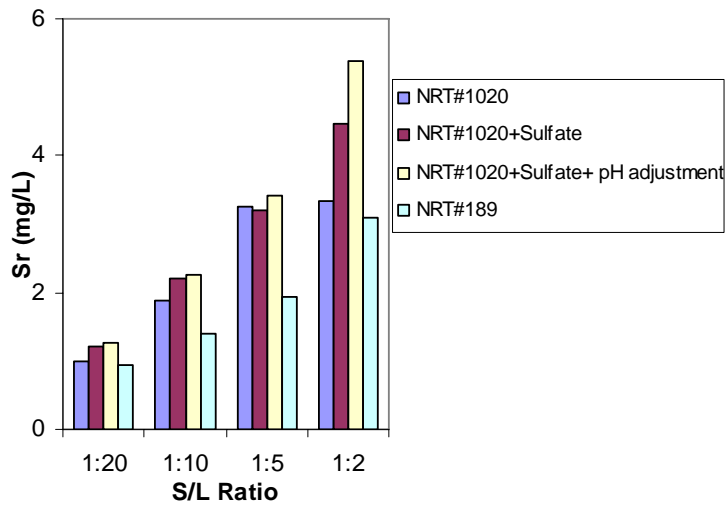
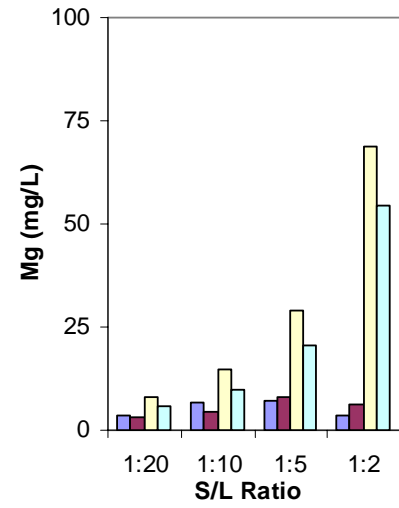
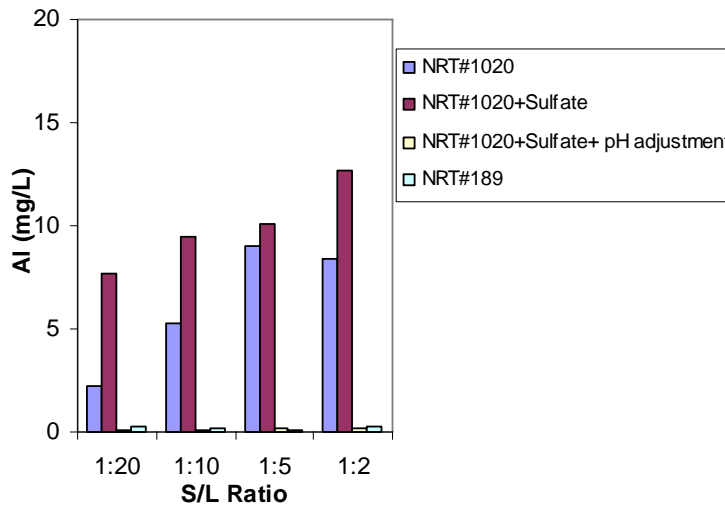
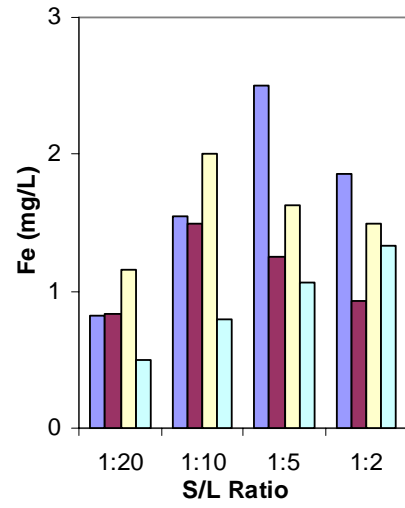
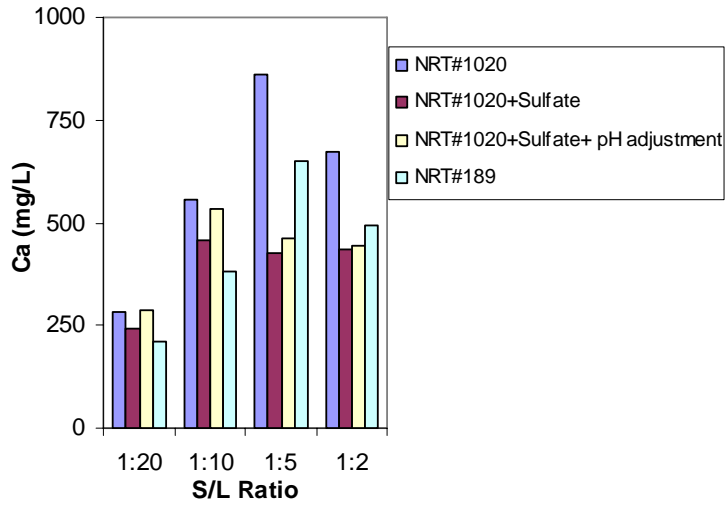
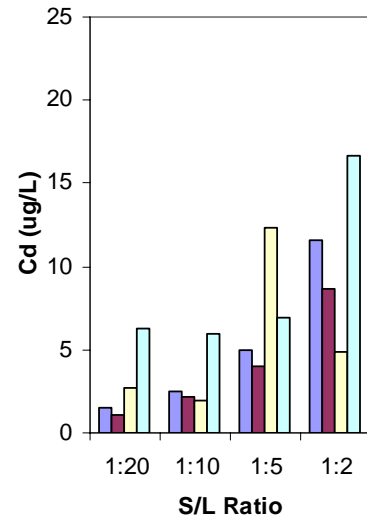
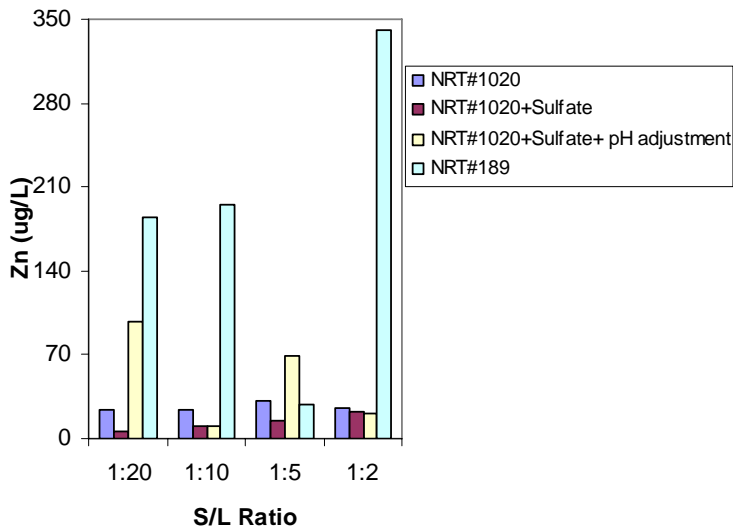
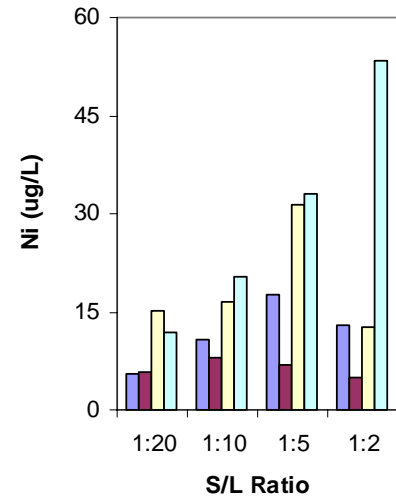
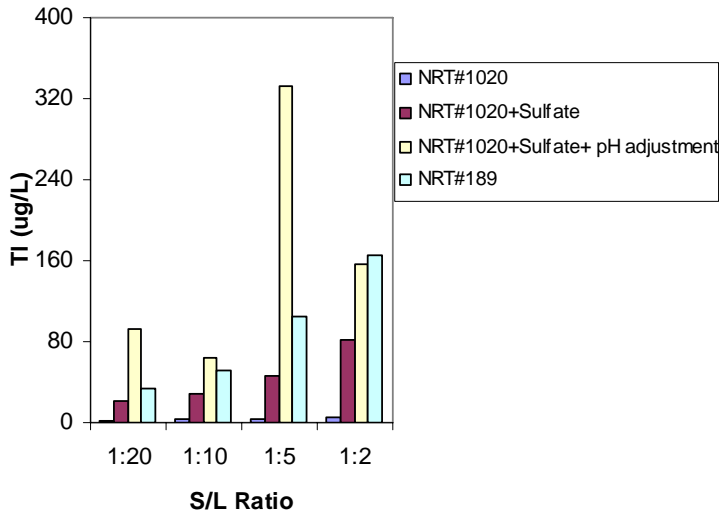
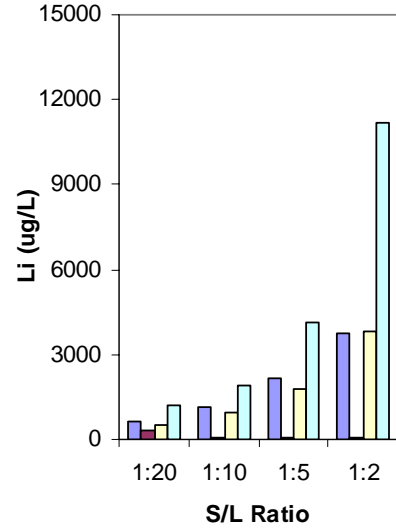
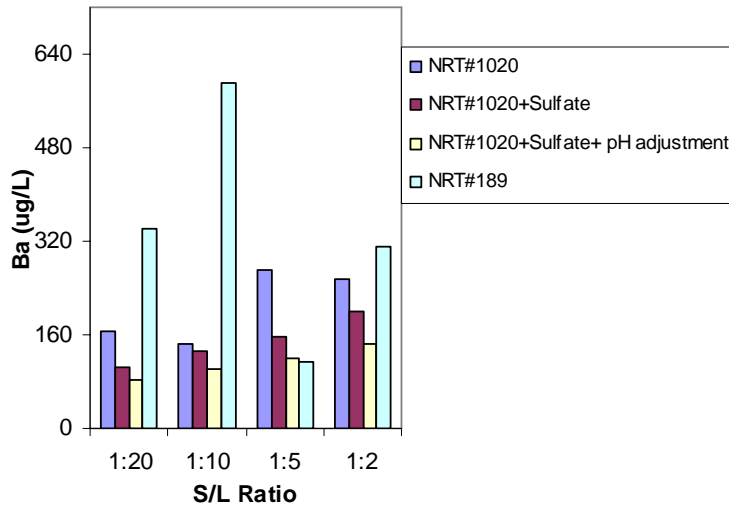


Figure 7. Comparison of leaching of major and trace oxyanionic elements in the paired sample for SO₂ control. NRT #182 is the control ash, NRT #183 is the trona ash, S/L=1:10.





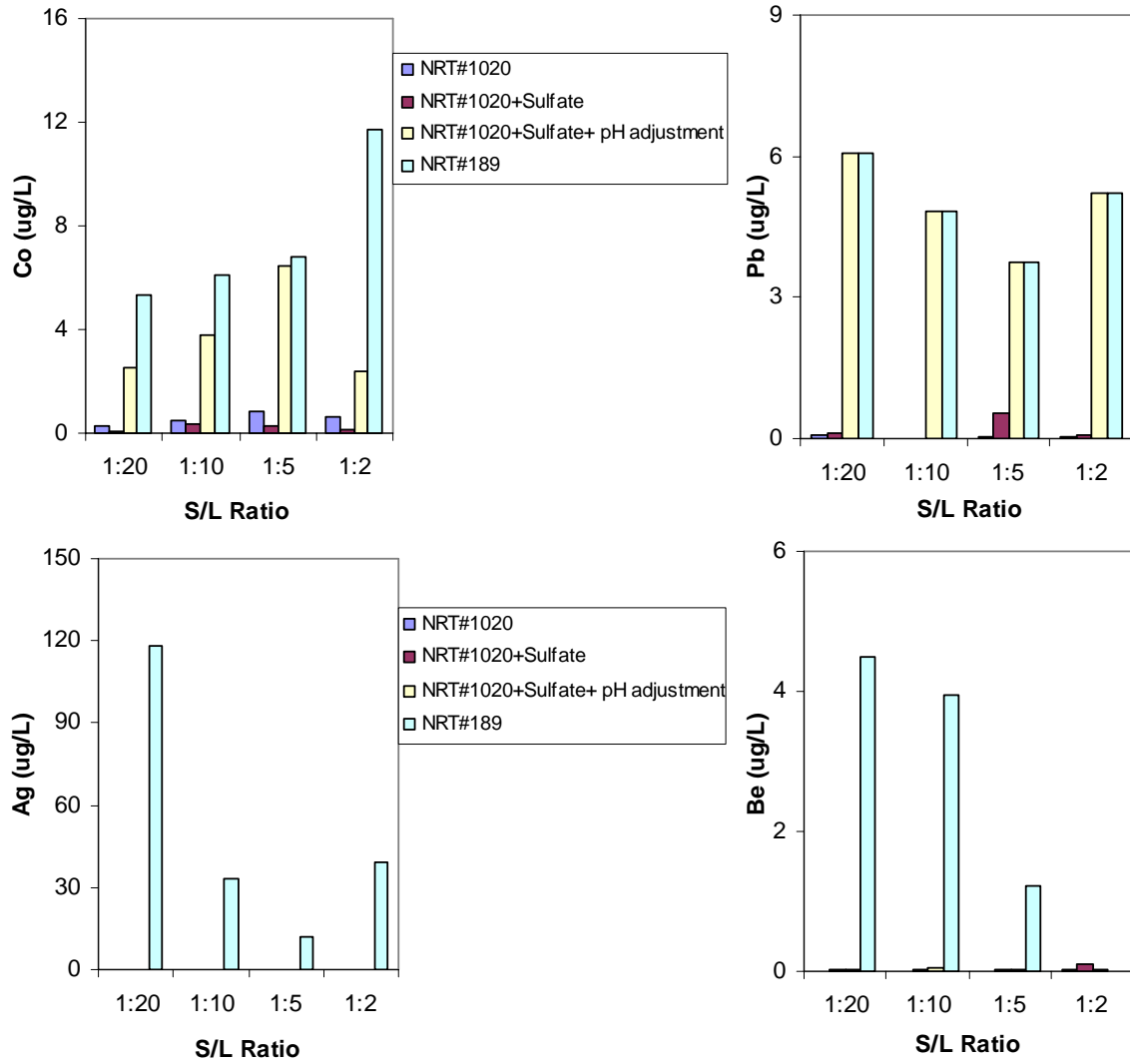
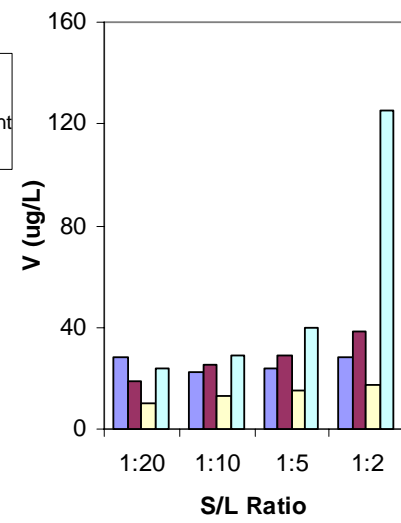
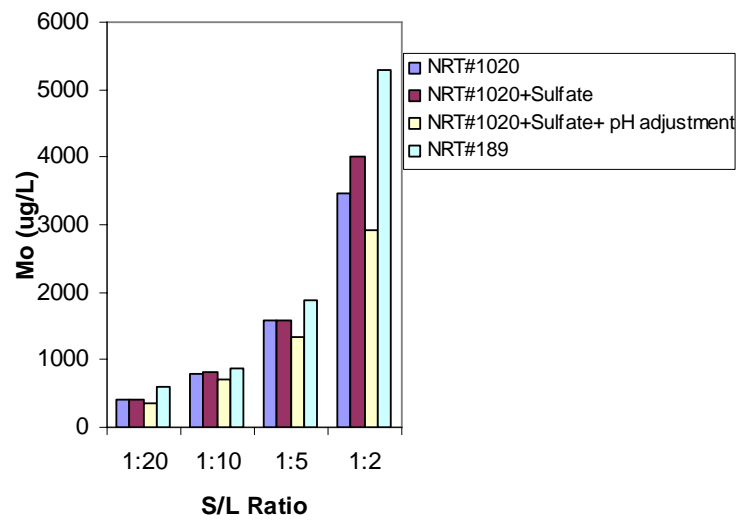
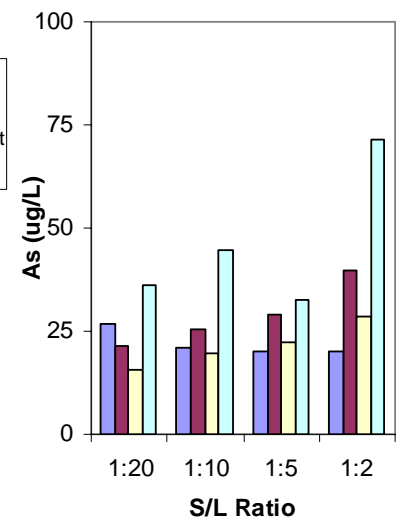
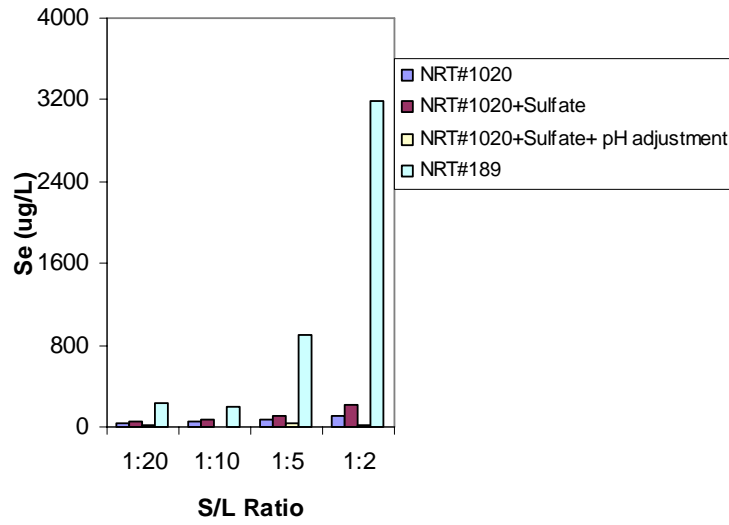
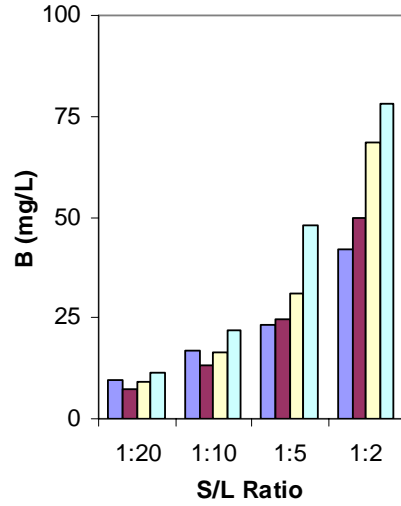
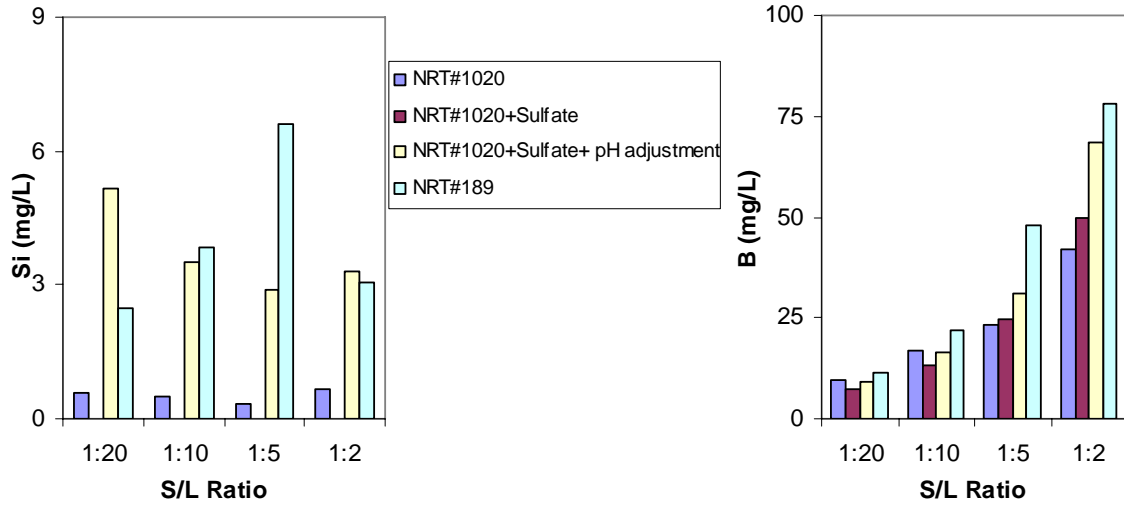


Figure 8. Comparison of leaching of major and trace cationic elements in the paired sample for SO_3 control. NRT #1020 is the control ash, NRT #189 is the trona ash, S/L=1:10.



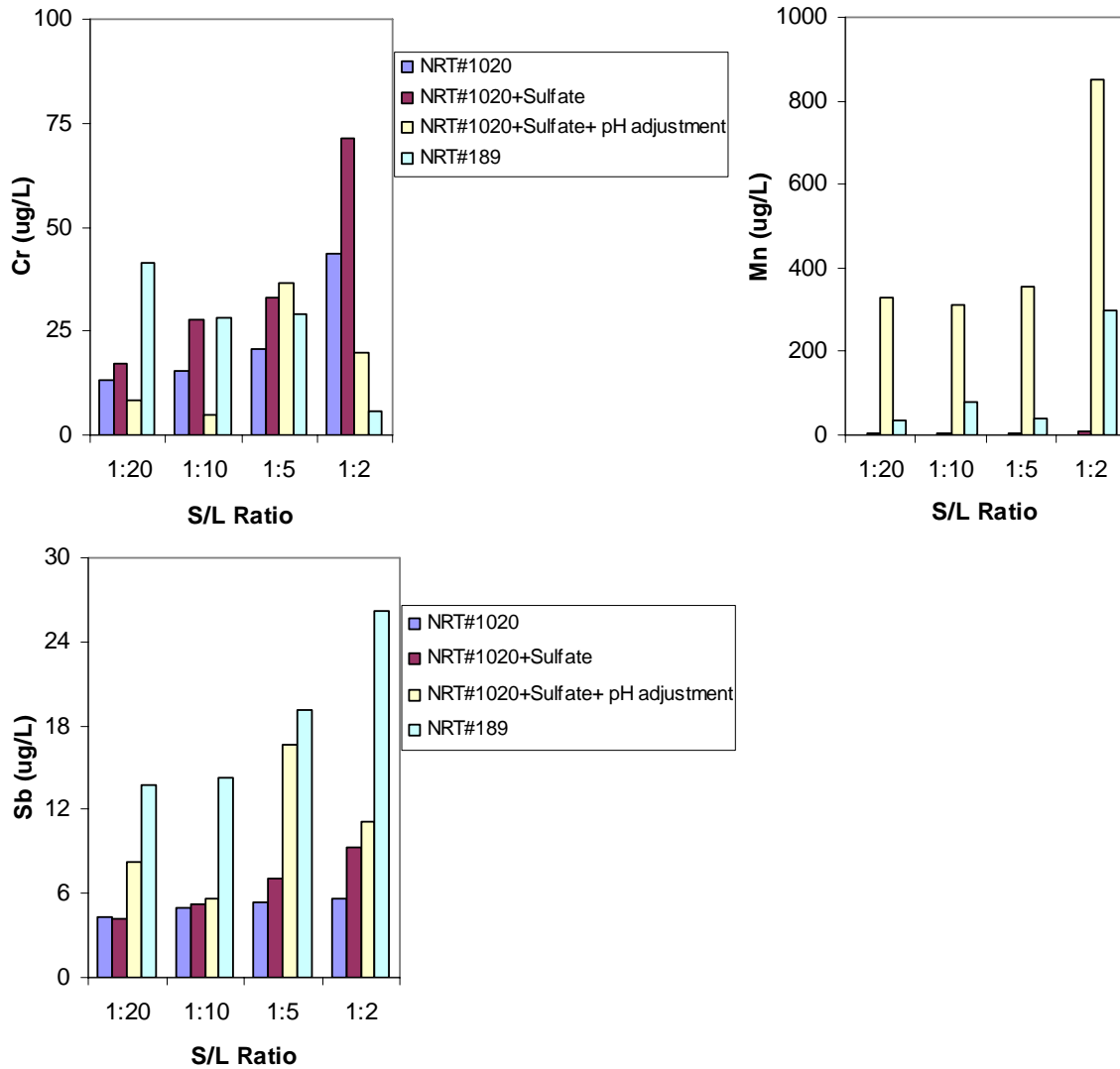


Figure 9. Comparison of leaching of major and trace oxyanionic elements in the paired sample for SO₃ control. NRT #1020 is the control ash, NRT #189 is the trona ash, S/L=1:10.