

## Influences of coal ash leachates and emergent macrophytes on water quality in wetland microcosms

### *Water Air and Soil Pollution*

L. H. Olson • C. J. Richardson  
 Duke University Wetland Center, Nicholas School of the Environment  
 J. C. Misenheimer  
 Oak Ridge Institute for Science and Education  
 C. M. Nelson • K. D. Bradham  
 US EPA National Research Exposure Laboratory  
 email: leifolson89@gmail.com

### Online Resource 2. Quality and Quality Control Summaries

Table 2a. National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) used to evaluate acid digestion efficiency. SRMs were paired with study sample matrices used as part of QA/QC for elemental concentration determination. One SRM was run with each microwave digestion batch. Soil, fly ash, and plant tissue samples were also spiked with B, Mo and Mn at 0.1 ppm, 0.1 ppm and 0.2 ppm respectively. If SRM or matrix spike recoveries exceeded  $\pm 25\%$  of the expected value, associated batch samples were flagged as estimates. (\* = NIST SRM values below method reporting limit, \*\* = NIST SRM value listed but not certified)

SRM ID	Paired Sample Matrix	[Element] (mg/kg)		
		B	Mo	Mn
2710A Montana Soil	Soil, fly ash	20**	NA	2140
1573A Tomato Leaves	Plant tissue	33.3	0.46**	NA
1547 Peach Leaves	Plant tissue	29	0.06*	98
1570A	Plant tissue	37.7	NA	76

Table 2b. Elemental method reporting Limits (MRLs) for each analytical instrument. MRLs were determined by the lowest calibration standard (Cal 1) or low level calibration verification (LLCV) standard, with recovery within  $\pm 30\%$  of the expected value. LLCV samples were included at the beginning and end of each analytical run. Sample values below the MRL were flagged as estimates.

Leachate /Water	ICP-MS		Plant/Soil/Fly Ash	ICP-OES	
	LLCV	Cal 1		LLCV	Cal 1
B	0.5 ppb	5 ppb	B	10 ppb	100 ppb
Mn	0.5 ppb	5 ppb	Mn	20 ppb	200 ppb
Mo	0.5 ppb	5 ppb	Mo	10 ppb	100 ppb

Table 2c. Standard reference material (SRM) and matrix spike (MS) percent recovery values for microwave acid digestions.

Element	SRM Recovery				MS Recovery		
	SRM 2710a	SRM 1573A	SRM 1547	SRM 1570A	Soil	Plant	Fly Ash
B	NA	91-95%	82-91%	92-101%	91-95%	101-123%	103%
Mn	98-103%	NA	88-94%	90-98%	104-111%	94-129%	104-110%
Mo	NA	NA	NA	NA	90-95%	99-122%	102-103%

Table 2d. Summary of all elemental analysis samples used in study. Letter codes are used to indicate samples with one or more QA/QC failures. (a = values below MRL, b = MS greater than 25% deviation from expected value, c = SRM relative recovery greater than 25% from expected value, d = No certified SRM value, e = SRM value below MRL)

Sample Matrix	Treatment	[B] (mg/kg)	[Mn] (mg/kg)	[Mo] (mg/kg)	
Fly Ash	Low Sulfur	62.1bd	41.47b	13.79bd	
	Low Sulfur	57.07bd	37.15b	13.38bd	
	Low Sulfur	55.37d	34.93	12.62d	
	Low Sulfur	61.15d	38.85	14.39d	
	Low Sulfur	60.09d	37.8	14.97d	
	High Sulfur	297.78bd	106.98b	42.35bd	
	High Sulfur	342.9bd	135.7b	49.78bd	
	High Sulfur	377.23d	131.01	56.29d	
	High Sulfur	318.55d	112.05	47.44d	
	High Sulfur	357.16d	126.58	52.97d	
Plant Tissue					
Species	Organ	Treatment	[B] (mg/kg)	[Mn] (mg/kg)	[Mo] (mg/kg)
<i>Juncus effusus</i>	Root	High Sulfur	27.51	366.62	7.3e
		Water	10.53	332.48	0.19ae
		Water	24.45	395.4	14.36e
		Water	9.17	403.93	0.34ae
		High Sulfur	9.22	312.26	0.26ae
		Low Sulfur	12.08	363.67	1ae
		Low Sulfur	12.39	337.04	1.7ae
		Low Sulfur	14.83	489.79	5.89e
	High Sulfur	26.42	479.26	10.52e	
	Stem	High Sulfur	52.55	1005.81	6.4e
		Water	22.31	1145.39	2.3ae
		Low Sulfur	49.36	991.12	4.04ae
		Low Sulfur	18.13	1165.34	1.74ae
		High Sulfur	16.48	985.98	1.7ae
		Water	41.09	1220.01	3.14ae
		Low Sulfur	36.16	945.13	2.29e
High Sulfur		48.65	1625	2.22ae	
Water	73.65	1122.35	8.91e		
<i>Eleocharis quadrangulata</i>	Root	High Sulfur	16.08	537.59	9.05e
		Water	5.53	691.24	0ae
		Water	5.22	549.34	0ae
		Water	5.51	511.13	0ae
		High Sulfur	13.47	651.75	6.52e
		Low Sulfur	7.58	480.4	1.55ae
		Low Sulfur	6.89	359.23	0.59ae
		Low Sulfur	7.56	433.84	1.19ae
	High Sulfur	15.46	622.14	16.98e	
	Stem	High Sulfur	31.51	1508.14b	10.78e
		Water	6.56	1698.31b	0.45ae
		Low Sulfur	8.53	1804.43b	0.23ae
		Low Sulfur	11.91	2138.61b	0.35ae
		High Sulfur	28.07	1939.95	6.72e
		Water	13.34	1740.51	0.83ae
		Low Sulfur	11.7	1102.51	0.63ae
High Sulfur		12.83	1315.07	0.7ae	
Water	28.71	1486.17b	5.73e		

Sample Matrix					
Fly Ash Leachate					
Dosing Period	Treatment	[B] (mg/L)	[Mn] (mg/L)	[Mo] (mg/L)	
Acute (1 <sup>st</sup> )	Low Sulfur	2185	157.2	447.2	
	Low Sulfur	2219	174.3	439.2	
Chronic (2 <sup>nd</sup> )	Low Sulfur	2329	160.6	453.9	
	Low Sulfur	2290	160.4	447.3	
	Low Sulfur	2315	164	452.9	
	Low Sulfur	2314	165.5	454.1	
	Low Sulfur	2372	169.8	468.1	
	Low Sulfur	2082	146.2	477.8	
	Low Sulfur	2213	146.3	474.9	
	Low Sulfur	2168	145.9	466.5	
Acute (1 <sup>st</sup> )	High Sulfur	9470	0a	3859	
	High Sulfur	9747	0a	4038	
Chronic (2 <sup>nd</sup> )	High Sulfur	8710	0.38a	3941	
	High Sulfur	8568	0a	3873	
	High Sulfur	8753	0a	3972	
	High Sulfur	8671	0a	3979	
	High Sulfur	8817	0a	3960	
	High Sulfur	6898	0a	4221	
	High Sulfur	7663	0a	4056	
	High Sulfur	7982	0a	4228	
Surface Water					
Date	Species	Treatment	[B] (mg/L)	[Mn] (mg/L)	[Mo] (mg/L)
7/29/2015	Control	High Sulfur	52.06	794.1	0.93a
		Water	52.24	69.79	0.59a
		Low Sulfur	55.07	809.1	0.52a
		Low Sulfur	46.99a	625.7	0.34a
		High Sulfur	39.15a	575.7	0.38a
		Water	46.95a	1026	0.24a
		Low Sulfur	47.22a	853	0.19a
		High Sulfur	41.95a	801.4	0.15a
		Water	41.51a	842.6	0.21a
		<i>Juncus effusus</i>	High Sulfur	19.24a	5.56
	Water		18.93a	67.81	0.23a
	High Sulfur		14.05a	14.02	0.15a
	Water		17.3a	24.12	0.2a
	Water		17.32a	32.52	0.17a
	Low Sulfur		17.85a	2.01a	0.17a
	Low Sulfur		21.96a	10.24	0.14a
	Low Sulfur		11.88a	28.98	0.11a
	High Sulfur		13.13a	420.3	0.16a
	<i>Eleocharis quadrangulata</i>		High Sulfur	17.3a	12.85
		Water	7.84a	1.56a	0.1a
Water		9.89a	2.29a	0.03a	
Water		7.51a	13.4	0.11a	
High Sulfur		4.5a	5.85	0.13a	
Low Sulfur		8.94a	9.42	0.01a	
Low Sulfur		32.29a	1.17a	0.12a	
Low Sulfur		8.03a	3.23a	0.1a	
High Sulfur		9.43a	3.43a	0.06a	

Sample Matrix							
Surface Water							
Date	Species	Treatment	[B] (mg/L)	[Mn] (mg/L)	[Mo] (mg/L)		
8/8/2015	No Plants	High Sulfur	1605	1079	349.5		
		Water	58.7	100.9	0.84a		
		Low Sulfur	399.6	1757	13.33a		
		Low Sulfur	348.5	1477	14.97a		
		High Sulfur	1502	1118	315.5		
		Water	59.51	1071	0.65a		
		Low Sulfur	331.1	1573	14.59a		
		High Sulfur	1463	1329	283.5		
		Water	64.66	981.8	0.76a		
		High Sulfur	1652	0.44a	110.6		
		Water	36.53a	40.99	0.26a		
		High Sulfur	1767	0.91a	152.7		
		Water	34.39a	5.72	0.72a		
		Water	29.7a	81.61	0.48a		
	Low Sulfur	411.3	170.9	2a			
	Low Sulfur	356.7	241.5	0.74a			
	Low Sulfur	377.2	418.7	1.12a			
	High Sulfur	1681	1351	214.4			
	<i>Juncus effusus</i>	High Sulfur	1582	1.2a	309.4		
		Water	36.18a	2.67a	1.02a		
		Water	26.58a	2.39a	0.31a		
		Water	21.25a	4.64a	0.17a		
		High Sulfur	1498	0.27a	280.3		
		Low Sulfur	402.5	486.6	11.5		
		Low Sulfur	427	373.6	5.85a		
		Low Sulfur	441.1	543.3	5.85a		
		High Sulfur	1560	12.55	283.5		
		8/30/2015	No Plants	High Sulfur	1331	304.2	73.73
Water				59.11	0.56a	0.1a	
Low Sulfur				338.1	1690	1.84a	
Low Sulfur				308.6	1421	1.3a	
High Sulfur				1342	0.78a	70.01	
Water	73.98			496	3.37a		
Low Sulfur	308.9			1837	4.32a		
High Sulfur	1178			491.9	73.67		
Water	67.36		327.6	1.65a			
<i>Juncus effusus</i>	High Sulfur		788.5	234.9	13.71a		
	Water		24.23a	4.46a	1.07a		
	High Sulfur		729.7	5.83	13.98a		
	Water		25.46a	15.96	0.85a		
	Water		22.55a	35.5	0.74a		
	Low Sulfur	221.6	129.1	0.48a			
Low Sulfur	183.8	205.7	0.32a				
Low Sulfur	202.5	2.78a	1.04a				
High Sulfur	805.4	38.84	9.81				

Sample Matrix					
Surface Water					
Date	Species	Treatment	[B] (mg/L)	[Mn] (mg/L)	[Mo] (mg/L)
8/30/2015	<i>Eleocharis quadrangulata</i>	High Sulfur Water	893.4 3.14a	0.73a 6.4	47.22 0.02a
		Water	0a	0.6a	-0.22a
		Water	0a	3.6a	-0.15a
		High Sulfur	848.6	0.35a	47.35
		Low Sulfur	188.7	23.75	1.05a
		Low Sulfur	218.2	659.9	1.34a
		Low Sulfur	232.1	113.9	0.66a
		High Sulfur	821.2	0.16a	29.97
		9/12/2015	No Plants	High Sulfur Water	3969 52.04
Low Sulfur	990.1			1721	74.24
Low Sulfur	964.5			1840	70.05
High Sulfur	3887			2.85a	1053
Water	37.85a			6.15	0.5a
Low Sulfur	918.5			2048	76.89
High Sulfur	3900			7.02	1035
Water	63.88			31.77	1.65a
<i>J. effusus</i>	High Sulfur Water			3850 21.99a	2.84a 0.98a
	High Sulfur		4085	11.3	1018
	Water		32.5a	28.27	2a
	Water		17a	28.95	0.74a
	Low Sulfur		954.3	990.5	23.59a
	Low Sulfur		1000	1271	22.66a
	Low Sulfur		1039	204.3	15.66a
	High Sulfur	3870	4.04a	888.7	
<i>Eleocharis quadrangulata</i>	High Sulfur Water	3896 29.34a	0.23a 8.54	1117 1.5a	
	Water	18.22a	13.43	0.47a	
	Water	15.79a	0.14a	0.17a	
	High Sulfur	3715	0.07a	1030	
	Low Sulfur	1135	1329	30.25	
	Low Sulfur	1117	2182	41.45	
	Low Sulfur	1101	1453	36.47	
	High Sulfur	4064	1a	1157	
	10/24/2015	No Plants	High Sulfur Water	3919 57.53	122.7 1.74a
Low Sulfur			907.1	1970	5.93a
Low Sulfur			844.4	1239	4.95a
High Sulfur			3588	3.99a	386
Water			74.97	1.82a	1.36a
Low Sulfur			879	2136	7.05a
High Sulfur			2963	24.04	220.8
Water			70.99	0.71a	0.49a

Sample Matrix					
Surface Water					
Date	Species	Treatment	[B] (mg/L)	[Mn] (mg/L)	[Mo] (mg/L)
10/24/2015	<i>J. effusus</i>	High Sulfur	1756	-0.07a	54.77
		Water	31.37a	0.15a	0.37a
		High Sulfur	1472	0.21a	42.48a
		Water	31.05a	0.78a	0.31a
		Water	26.36a	35.06	0.11a
		Low Sulfur	570.7	1852	1.82a
		Low Sulfur	387.9	241.1	1.06a
		Low Sulfur	510.6	0.2a	1.31a
		High Sulfur	1844	-0.09a	27.1a
	<i>Eleocharis quadrangulata</i>	High Sulfur	1605	0.29a	109.2
		Water	30.44a	2.61a	1.8a
		Water	22.39a	13.13	0.86a
		Water	15.05a	0.22a	0.43a
		High Sulfur	1971	1.75a	127.4
		Low Sulfur	502.7	743.2	2.99a
		Low Sulfur	539.5	676.1	1.22a
		Low Sulfur	564.5	1350	0.65a
		High Sulfur	1711	2.68a	96.02
Soil					
Date	Species	Treatment	[B] (mg/kg)	[Mn] (mg/kg)	[Mo] (mg/kg)
7/29/2015	No Plants	High Sulfur	0ac	193.75	0abc
		Water	0ac	177.89	0abc
		Low Sulfur	0ac	195.9	0abc
		Low Sulfur	0ac	201.61	0abc
		High Sulfur	0.25ac	191.73	0abc
		Water	0ac	181.97	0abc
		Low Sulfur	0ac	202.43	0abc
		High Sulfur	0ac	208.03	0abc
		Water	0ac	208.68	0ac
	<i>J. effusus</i>	High Sulfur	0ac	176.57	0ac
		Water	0ac	191.6	0ac
		High Sulfur	0ac	193.2	0ac
		Water	0ac	185.34	0abc
		Water	0ac	250.96	0abc
		Low Sulfur	0ac	178.5	0abc
		Low Sulfur	0ac	188.26	0abc
		High Sulfur	0ac	186.88	0abc
		<i>Eleocharis quadrangulata</i>	High Sulfur	0ac	206.87
	Water		0ac	221.37	0abc
	Water		0ac	195.02	0abc
	Water		0ac	188.45	0abc
	High Sulfur		0ac	158.98	0abc
	Low Sulfur		0ac	193.2	0abc
	Low Sulfur		0ac	170.35	0abc
	Low Sulfur		0ac	182.92	0abc
	High Sulfur		0ac	188.5	0abc

Sample Matrix							
Soil							
Date	Species	Treatment	[B] (mg/kg)	[Mn] (mg/kg)	[Mo] (mg/kg)		
8/8/2015	No Plants	High Sulfur	0ad	185.31	0ad		
		Water	0ad	185.81	0ad		
		Low Sulfur	0ad	178.58	0ad		
		Low Sulfur	0ad	222.18	0ad		
		High Sulfur	0ad	173.31	0ad		
		Water	0ad	192.24	0ad		
		Low Sulfur	0ad	175.11	0ad		
		High Sulfur	0ad	165.53	0ad		
		Water	1.28abd	229.11b	0abd		
		High Sulfur	0.63ad	169	0.37ad		
		Water	0.26ad	187.19	0ad		
		High Sulfur	0.74ad	174.9	0.43ad		
		Water	0.1ad	198.61	0ad		
		Water	0.16ad	185.86	0ad		
		Low Sulfur	0.16ad	156.53	0ad		
		Low Sulfur	0ad	169.95	0ad		
	Low Sulfur	0ad	176.44	0ad			
	High Sulfur	0ad	192.79	0ad			
	<i>Eleocharis quadrangulata</i>	High Sulfur	0ad	221.11	0ad		
		Water	0ad	176.31	0ad		
		Water	0ad	184.74	0ad		
		Water	0ad	199.95	0ad		
		High Sulfur	0ad	200.93	0ad		
		Low Sulfur	0ad	182.4	0ad		
		Low Sulfur	0ad	214.04	0ad		
		Low Sulfur	0ad	181.76	0ad		
		High Sulfur	0ad	165.29	0ad		
		No Plants	High Sulfur	0.97ad	178.59	0.72ad	
			Water	0ad	146.32	0ad	
			Low Sulfur	0ad	192.69	0.16ad	
			Low Sulfur	0ad	199.94	0ad	
			High Sulfur	0.69ad	201.67	0ad	
Water			0ad	167.19	0ad		
Low Sulfur			0ad	185.69	0ad		
High Sulfur	0.53ad		187.77	0ad			
Water	0ad		241.93	0ad			
<i>J. effusus</i>	High Sulfur		1.53ad	125.12	0.67ad		
	Water		0ad	153.96	0ad		
	High Sulfur		1.31ad	146.49	2.1ad		
	Water		0.01ad	144.57	0ad		
	Water		0.46ad	160.4	0ad		
	Low Sulfur		0.58ad	157.88	0ad		
	Low Sulfur		0.47ad	146.85	0ad		
	Low Sulfur	0.44ad	141.26	0ad			
	High Sulfur	1.43ad	152	0.2ad			

Sample Matrix						
Soil						
Date	Species	Treatment	[B] (mg/kg)	[Mn] (mg/kg)	[Mo] (mg/kg)	
10/24/2015	<i>Eleocharis quadrangulata</i>	High Sulfur	1.1ad	159.75	0ad	
		Water	0ad	143.83	0ad	
		Water	0ad	174.62	0ad	
		Water	0ad	180.97	0ad	
		High Sulfur	1.25ad	210.27	0ad	
		Low Sulfur	0.05ad	218.51	0ad	
		Low Sulfur	0.25ad	259.82	0ad	
		Low Sulfur	0ad	174.58	0ad	
		High Sulfur	0.92ad	156.42	1.43ad	