Observations of Metals and Metaloids in Sediment Porewater Associated with the Tennessee Valley Authority, Kingston, TN Ash Recovery

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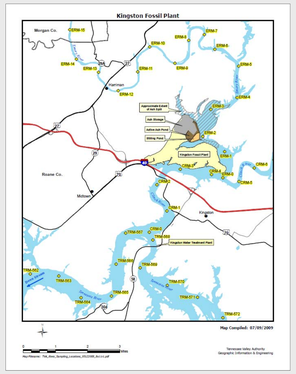
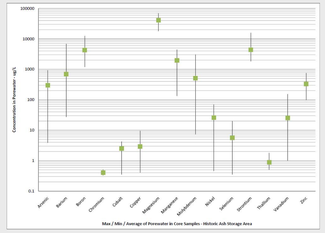
Confluence of Rivers: River Miles Relative to Ash Spill

The Kingston Ash Release occurred at approximately mile 2.1 on the Emory River (e.g., ERM 2.1). Higher river miles indicate locations upstream of the ash release. Lower river miles are downstream toward the confluence with the Clinch River. The Emory River enters the Clinch at about CRM 4.4. Upstream on the Clinch, Manhattan project wastes enter near CRM 22 and have contributed substantial amounts of mercury and other toxic compounds to the sediment for miles downstream. Further, managed water flow for cooling water at the Kingston Fossil Plant at times causes water to flow upstream on the Emory into the plant cooling water intake channel at approximately ERM 1.9. Measureable mercury in sediments in the final mile of the Emory are attributable to backflow from the Clinch and its contamination from the Manhattan Project era.



Porewater - Historic Ash Storage Area



Porewater - Historic Ash Borings (µg/L)

Ash had been accumulated at Kingston Fossil Plant for approximately 50 years. Geoprobe® cores collected of this ash and the standing porewater within those core samples was measured. The results of the Geoprobe porewater samples indicated much higher concentrations of the species of interest than were observed in river sediment porewater. This would represent perhaps the maximum possible accumulation of these metals and metaloids in the porewater from dissolution over a long-term timeframe. Initial core samples were taken to estimate the steady state within the slowly flowing or perched groundwater that has existed in the historic storage area over decades. Subsequent groundwater monitoring studies are discussed elsewhere.

The variation in observed metals concentrations is noteworthy in that variance over orders of magnitude was observed for several parameters.

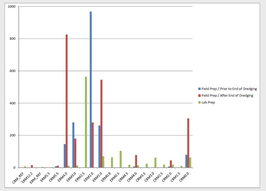
Porewater Studies - River System

A variety of sampling events have attempted to quantitate the concentrations of various soluble species in sediment porewater in conjunction with third-party research and under TVA's Non-Time Critical Removal Action (NTCRA) River System Investigation.

Three separate sediment collection series were performed:

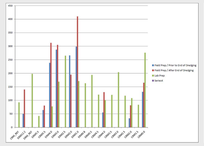
1. Prior to completion of dredging, porewater samples were collected via field filtration of sediments using a battery-operated vacuum filtration apparatus. This sampling was a third-party sampling event from which TVA obtained split samples for analysis at TVA's contract laboratory.
2. Post-dredging, porewater samples were collected via field filtration of sediments using a battery-operated vacuum filtration apparatus. This sampling was a third-party sampling event from which TVA obtained split samples for analysis at TVA's contract laboratory.
3. Post-dredging, TVA conducted sampling in support of the NTCRA River System Investigation. Sediment samples were collected using box cores; plastic tubes were pushed into the collected sample while still submerged to avoid changes in oxidation state of various species. Cores collected from box cores were submitted to TVA's contracted analytical laboratory for porewater extraction via centifugation and filtration.

In the graphs that follow, there is an apparent difference in concentrations depending on whether field processing or laboratory processing was employed to obtain the porewater. Both methods had a final filtration step through a 0.45 micron filter. The differences are not easily understood.

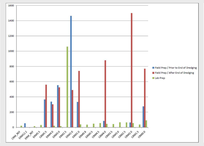


Arsenic in Sediment Porewater (µg/L)

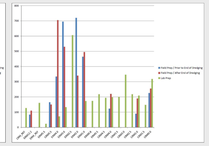
Arsenic concentrations are found on the Emory slightly upstream from and near the site of the spill (ERM 4.0, 3.0, and 2.5) and then downstream (ERM 2.0, 1.0, and CRM 0.0); arsenic was not observed significantly between CRM miles 0.0 and 4.4. Nor was significant arsenic found upstream on the Emory above ERM 5.



Barium in Sediment Porewater (µg/L)



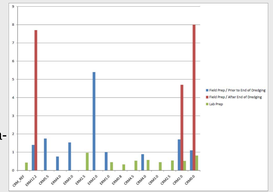
Boron in Sediment Porewater (µg/L)



Strontium in Sediment Porewater (µg/L)

Boron, strontium, and barium are somewhat similar in distribution, although all three are seen at CRM 5.5 at a location thought to be well away from the influence of the spill upstream of the confluence of the Emory and Clinch Rivers. Locations noted as "CRM_REF" and "ERM_REF" were well upstream on each river; these locations were sampled to serve as reference points without influence of ash.

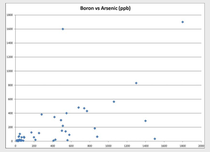
Selenium data however, shows an upstream source at ERM 12.2 which does not correlate with the presence of boron, the primary chemical indicator of the presence of coal ash. Otherwise, selenium appears to follow a similar pattern to that of arsenic although it was not detected in a sizeable fraction of the samples.

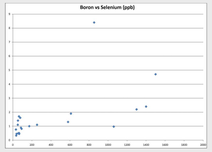


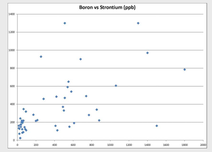
Selenium in Sediment Porewater (µg/L)

Correlation with Boron

Boron is a soluble element present in fly ash that is frequently used as an indicator of ash; strontium is sometimes used as an indicator of ash. The graphs below present the correlation between boron and arsenic and selenium based on the observed concentrations of these analytes in porewater.





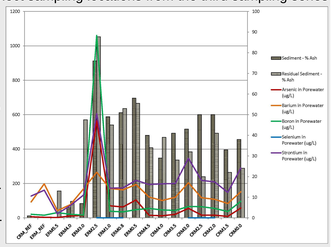


The correlations between arsenic and selenium and boron appear to be weakly linear. While there may be a slight correlation between arsenic and selenium and boron, it appears that trace levels of arsenic and selenium in many of the porewater samples may be influenced by naturally occurring background concentrations of these elements.

Strontium shows a strong correlation with boron concentration.

Percent Ash by Optical Microscopy (Point Counting)

Percent ash has been determined at select sampling locations from the third sampling series utilizing a point-counting technique using optical microscopy. Percent ash was not determined for the first two sampling series.



Sediment samples were collected from various river locations and subjected to porewater extraction. The porewater samples were analyzed for metals; the sediment and residual sediment samples were analyzed for percent ash. The graph presents the metals concentrations in porewater to the observed percent ash concentrations in the associated sediments and residual sediments.

Arsenic, barium, boron, and strontium porewater concentrations appear to correlate with the presence of ash in sediment and residual sediment. Selenium was not detected at concentrations significant enough to observe a correlation.

Summary of Metals Concentrations in Porewater

Location	Dredging	sample_date	Field or Lab	Aluminum	Antimony	Arsenic	Barium	Boron	Cadmium	Chromium	Cobalt	Copper	Magnesium	Manganese	Molybdenum	Nickel	Selenium	Strontium	Thallium	Vanadium
ERM12.2	Active	1/20/2010	Field Prep	14.2			50	53.2				0.9	18000	6.5		0.45	1.4	83.8		
ERM12.2	Complete	8/24/2010	Field Prep	740		15	140				4.1	3.2	20400	2300			7.7	110		
ERM_REF	Complete	6/9/2011	Lab Prep			3.68	198	15.4		2.44	11.6	0.86	8790	5530	0.44	5.65		161		
CRM_REF	Complete	2/25/2011	Lab Prep			6.87	92.5	20.8		0.81	2.14	0.77	16800	5290	0.84	1.72	0.429	127		
ERM5.5	Complete	6/8/2011	Lab Prep	467		2.08	42.1	30.5		0.82	4.59	1.93	1390	699		2.77		23.6		1.05
CRM5.5	Active	1/19/2010	Field Prep	49.3			51.2	77.1				3.4	12000	1210	2.9	1.2	1.6	145		
CRM5.5	Active	3/10/2010	Field Prep	230			51	610				4.5	13800	1500	1.2		1.9	190		
CRM5.5	Active	4/27/2010	Field Prep	120		8	90	410			0.63		11800	4100	3			160		
CRM5.5	Complete	6/3/2010	Field Prep	170		14	94	560				3.5	12100	5200	2.9	5.2		150		
CRM5.5	Complete	8/24/2010	Field Prep	360		9.6	67					8.2	11200	3400				150		
ERM4.0	Active	1/20/2010	Field Prep	22.3		15.5	263	31.8			14.8	0.54	13900	18400	2.1	5.5	0.76	242		
ERM4.0	Active	3/10/2010	Field Prep	230		22	63	430			2.4	2.1	5700	3300	0.52	2.1		110		
ERM4.0	Active	4/27/2010	Field Prep	83		400	390	550			6.4		17000	11300	4.3	4		650		
ERM4.0	Complete	6/2/2010	Field Prep	280		52	85	94			2.5	4.2	5800	3200	3.7	6.9		110		
ERM4.0	Complete	8/24/2010	Field Prep	200		1600	540	510			2.5	3.7	28600	10400	52			1300		
ERM4.0	Complete	6/8/2011	Lab Prep	118		11.5	77.4	20.9		3.28	2.87	0.89	4360	3980	1.01	1.77		72.1		
ERM3.0	Active	11/3/2009	Field Prep	78.8		345	134	420			0.81	21.7	6180	1870	57.7	2.1		484		
ERM3.0	Active	12/15/2009	Field Prep	32		19.8	178	215			2.7	1.6	7640	5560	4	2.7		223		
ERM3.0	Active	1/20/2010	Field Prep	95		116	554	254			13.5	0.8	30400	25800	37	4.4	1.1	928		
ERM3.0	Active	3/10/2010	Field Prep	80		91	150	580			0.58	2	11000	1100	75	2.1	1.3	540		
ERM3.0	Active	4/27/2010	Field Prep	84		830	420	1300	0.12		1.2		21400	2100	170		2.2	1300		
ERM3.0	Complete	6/2/2010	Field Prep			140	390	540			11	2.3	14900	12800	12	6.4		590		
ERM3.0	Complete	8/24/2010	Field Prep	210		220	220	510			2.2	3.9	13700	5100				470		
ERM3.0	Complete	6/8/2011	Lab Prep			13	169	15.8		0.55	7.77	2.84	8210	6670	0.73	3.51		133		
ERM2.5	Complete	6/6/2011	Lab Prep		0.65	564	265	1060		3.33	2.32	1.33	13000	4880	234	2.16	0.97	606		1.6
ERM2.0	Active	1/20/2010	Field Prep	75.6		183	53.9	854				0.93	6770	24	176	0.48	8.4	340		
ERM2.0	Active	4/27/2010	Field Prep	78		290	330	1400	0.081		0.79		19900	1700	120		2.4	970		
ERM2.0	Active	4/28/2010	Field Prep	21		1600	230	1800	0.071		1.5		10700	2100	73	3.9		470		
ERM2.0	Complete	6/2/2010	Field Prep	92		300	190	490				2.8	9100	2400	47	4.5		370		
ERM2.0	Complete	8/25/2010	Field Prep	720		260	200				1.3	4.4	15100	5900	12			310		
ERM1.0	Active	11/3/2009	Field Prep	74		382	216	282			0.98	2.6	8430	2340	28.4	2.5		459		
ERM1.0	Active	12/15/2009	Field Prep	62.1		56.4	154	199			1.1	2	7030	2780	19.5	2.1		215		
ERM1.0	Active	1/20/2010	Field Prep	53.6		125	144	172			1.2	1.2	9940	2500	13.5	1.2	1	283		
ERM1.0	Active	4/27/2010	Field Prep	160		480	680	680			10		22400	19800	25	3.4		900		
ERM1.0	Complete	6/2/2010	Field Prep	180		470	450	740			4	2.9	15200	9300	12	5.5		490		
ERM1.0	Complete	8/25/2010	Field Prep	240		620	370				1.7		22100	8100				500		
ERM1.0	Complete	6/7/2011	Lab Prep		0.34	70.3	171	38.6		1.03	3.22	0.69	11100	4140	1.84	2.35	0.45	173		
ERM0.8	Complete	6/6/2011	Lab Prep			63.3	163	34.9		2.35	3.33	2.68	9920	5340	1.98	2.71	0.33	174		1.17
ERM0.5	Complete	6/6/2011	Lab Prep			104	194	47.6			2.9	1.04	12600	4850	2.15	1.86		218		
CRM4.5	Complete	2/25/2011	Lab Prep		0.65	15.1	121	54.9		1.07	0.87	3.07	13300	3930	1.88	1.45	0.49	194		2.33
CRM4.0	Active	1/19/2010	Field Prep	45.1		6.9	54.8	84.5			0.22	2	8130	1510	1.4	1.4	0.89	123		
CRM4.0	Complete	6/3/2010	Field Prep	580		64	140	880				4.7	11900	3700	7.1	5.4		220		
CRM4.0	Complete	8/24/2010	Field Prep	210		91	120					5.4	11700	3300				220		
CRM4.0	Complete	2/25/2011	Lab Prep		0.55	12.2	101	45.9		2.16	0.72	2.78	14000	2260	2.27	1.48	0.571	198		
CRM3.5	Complete	2/25/2011	Lab Prep		0.42	21	120	43.4		0.44	0.93	2.84	13600	4840	3.31	1.37		200		1.5
CRM3.0	Complete	2/24/2011	Lab Prep		0.38	55.3	204	66.3			2.32	1.99	20700	9920	15.2	2.62	0.45	346		1.04
CRM2.5	Complete	2/23/2011	Lab Prep		0.47	16.4	117	64.9			0.44	5.97	12800	1440	3.65	1.01	0.51	218		1.41
CRM2.0	Active	1/19/2010	Field Prep	52.9		6.5	33.2	63.3				3.5	7170	791	3.9	1.9	1.7	89.7		
CRM2.0	Complete	6/3/2010	Field Prep	410		34	78	1500				8.2	11400	2300	8.8	6.3	4.7	160		
CRM2.0	Complete	8/24/2010	Field Prep	910		55	85					10	16500	2500				220		
CRM2.0	Complete	2/23/2011	Lab Prep	53.9	0.4	15.8	108	55			0.65	4.52	13200	3080	8.2	1.47	0.49	209		1.75
CRM1.5	Complete	2/24/2011	Lab Prep		0.34	8.43	83.6	36.7		1.51	0.71	4.05	11100	3800	0.95	1.23		148		1.33
CRM0.0	Active	1/19/2010	Field Prep	26.8		8.9	72.7	51.4			1.3	2.3	9340	2140	2.4	1.9	1.1	122		
CRM0.0	Active	4/28/2010	Field Prep	130		150	190	500			2.4		14700	10400	18	2.8		330		
CRM0.0	Complete	6/3/2010	Field Prep	410		430	200	770				3	12700	5700	18	6.2		280		
CRM0.0	Complete	8/24/2010	Field Prep	730		180	130						12000	4700			8	230		
CRM0.0	Complete	2/22/2011	Lab Prep	11300	0.57	57.3	152	86.5	0.38	12	0.93	1.95	16400	2620	5.75	1.81	0.75	290	0.81	1.64

Notes: Aluminum result at CRM0.0 on 2/22/11 sample potentially biased high due to sample filtration failure.
Arsenic analyzed by two laboratories for 2/22/11-2/25/11 and 6/6/11-6/9/11 porewater samples. Results presented as average.