Distribution and Chemical Characterization of Fly Ash Bottom Sediments

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Introduction

During the early morning of December 22, 2008, a failure in an earth dike at Tennessee Valley Authority's Kingston Power Plant, released about 4.1 million m^3 of coal fly ash slurry into the waters and proximate riparian areas draining into Watts Bar Reservoir, principally into the Emory River. Within 3.2 km the Emory River discharges into the Clinch River, which flows into the Tennessee River after several kilometers.

Fly ash concentrates trace elements from coal during the combustion process (e.g., Van Herck and Vandecasteele, 2001; Bertocchi et al., 2006). Although much discussion has focused on whether fly ash is a toxic waste, the current EPA consensus is that it is not a toxic waste, rather it is a reusable material that can be used in the manufacture of cement and other products. Fly ash has also been occasionally used as an agricultural fertilizer (e.g., Mittra et al., 2005), but this practice is not widespread in the US. The composition of fly ash varies based on the chemical characteristics of coal burned in the power plant as well as the combustion process.

Following several high flows and initial fly ash dredging operations we began characterizing ash distribution within the affected rivers.

Objectives

- Assess the extent of fly ash distribution within the Emory, Clinch, and Tennessee Rivers.
- Determine the labile nature of various trace elements in sediment samples from the Emory, Clinch, and Tennessee Rivers.

Methods

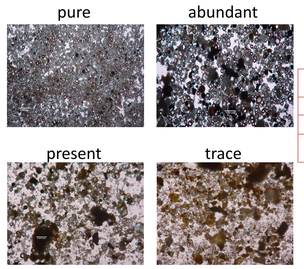
- High resolution seismic profiles were correlated against actual stratigraphy logged via box, gravity, and vibracore samples.
- Sequential extraction was used to determine the labile nature of trace elements from sediments. The water soluble, exchangeable, acid soluble, and reducible fractions were extracted using the method of Querol et al. (1996). Trace element concentrations were quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES).

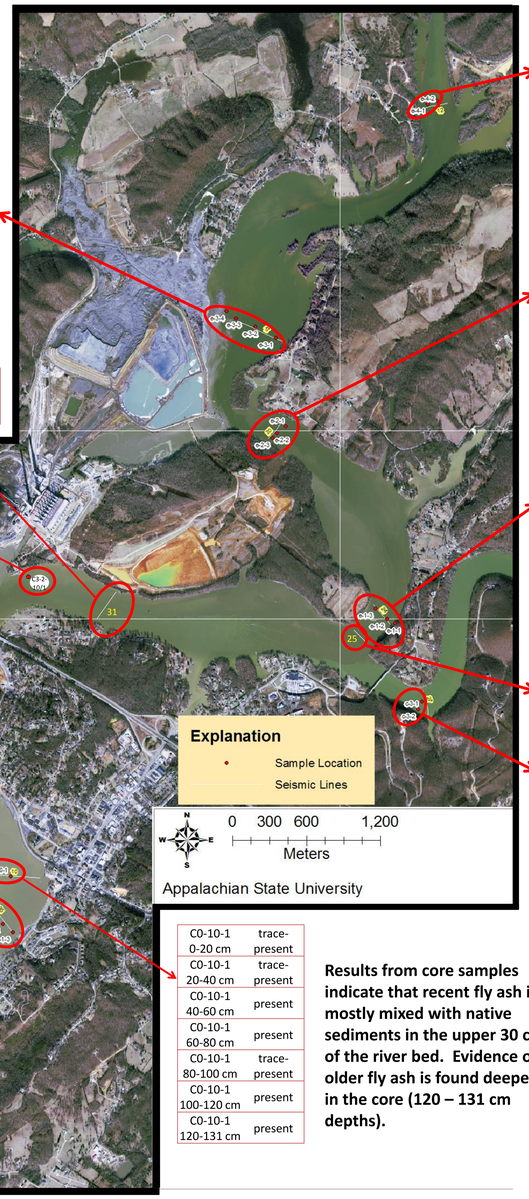
Main Findings

- Relatively pure ash deposits are confined to the Emory River.
- In the Clinch and TN Rivers, the recently deposited fly ash is mixed with native sediments in the upper 30 cm of the river bed. Evidence of older fly ash is found in deeper sediments (120-131 cm deep).
- The concentrations of extractable As, Cd, Cu, and Pb vary considerably along a downstream gradient from the spill. In general, the extractable concentrations of trace elements are lower in sediments from the TN River compared to sediments from the Emory and Clinch Rivers.
- There appears to be no relationship between the amount of ash in the sediment and extractable trace element concentrations.
- The sample with the highest concentrations of extractable elements is E4-1, located just upstream of the spill.
- The largest trace element concentrations are generally found in the reducible fraction.
- For Cd and Cu, the concentrations in each fraction are as follows: water soluble < exchangeable < acid soluble < reducible.
- Very little water soluble or exchangeable Pb is detected. Most Pb is found in the acid soluble and reducible fractions.
- Very little exchangeable As is detected in these sediments. Most As is found in the reducible fraction, followed by acid soluble and water soluble fractions.

Sampling Sites and Ash Concentrations

Smear slides are used to detect relative ash content in sediment samples based on relative number of ash spheres



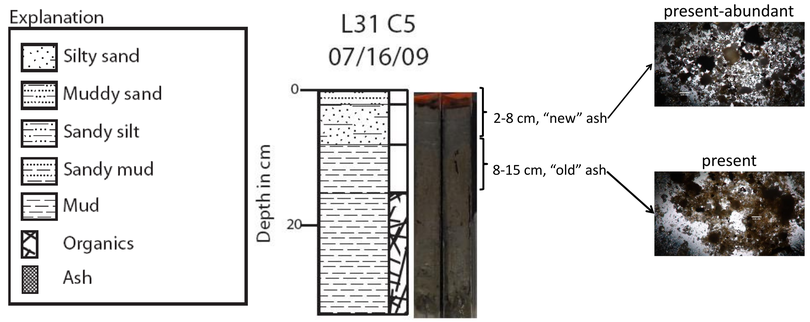


Results from core samples indicate that recent fly ash is mostly mixed with native sediments in the upper 30 cm of the river bed. Evidence of older fly ash is found deeper in the core (120 – 131 cm depths).

Sequential Extraction Results
Clinch River Sediments

		Water Soluble	Exch	Acid Soluble	Reducible	Sum
As	C3-1	0.19	0.13	0.61	12.75	13.67
	C3-2	0.08	< MDL	< MDL	36.29	36.42
	C3 L25 19-46 cm	< MDL	< MDL	< MDL	< MDL	< MDL
	C3 L25 47-79 cm	0.05	< MDL	< MDL	0.35	0.46
	C4-1	0.13	< MDL	0.22	3.97	4.34
	C2-1	< MDL	< MDL	0.12	2.81	2.98
	C2-2	0.05	< MDL	0.07	2.61	2.75
	C2-3	0.07	< MDL	0.26	4.29	4.65
	C2-4	< MDL	< MDL	< MDL	1.66	1.74
	C1-1	0.29	0.17	1.07	2.98	4.50
	C1-2	< MDL	< MDL	0.13	< MDL	0.25
	C1-3	0.05	< MDL	0.24	0.09	0.41
	C0-3-1 9/30	< MDL	< MDL	< MDL	< MDL	0.15
	C0-3-1 10/1	0.07	< MDL	0.21	2.25	2.56
	C0-10-1 10/01	0.07	< MDL	0.21	2.25	2.56
	C0-10-2 10/01	0.07	< MDL	< MDL	2.44	2.57
Cd	C3-1	< MDL	0.05	0.10	0.38	0.54
	C3-2	< MDL	0.06	0.12	0.51	0.69
	C3 L25 19-46 cm	< MDL	0.19	0.23	0.88	1.30
	C3 L25 47-79 cm	0.01	0.26	0.42	1.04	1.72
	C4-1	< MDL	0.07	0.13	0.31	0.52
	C2-1	< MDL	0.08	0.13	0.29	0.50
	C2-2	< MDL	0.08	0.14	0.37	0.59
	C2-3	< MDL	0.07	0.12	0.28	0.47
	C2-4	< MDL	0.07	0.14	0.56	0.78
	C1-1	0.01	0.05	0.10	0.12	0.28
	C1-2	0.007	0.08	0.14	0.24	0.47
	C1-3	0.01	0.04	0.08	0.17	0.29
	C0-3-1 9/30	0.01	0.14	0.18	0.83	1.15
	C0-3-1 10/1	< MDL	0.11	0.17	0.75	1.03
	C0-10-1 10/01	0.01	0.11	0.16	0.87	1.14
	C0-10-2 10/01	0.01	0.12	0.16	0.86	1.14
Cu	C3-1	0.18	0.49	0.85	25.42	26.92
	C3-2	0.20	0.67	0.61	40.67	42.14
	C3 L25 19-46 cm	0.19	0.31	0.98	23.81	25.28
	C3 L25 47-79 cm	0.30	0.35	1.45	27.55	29.65
	C4-1	0.51	2.22	5.26	21.23	29.22
	C2-1	0.31	0.76	2.90	12.50	16.47
	C2-2	0.34	0.70	2.83	8.77	12.64
	C2-3	0.33	0.73	2.11	6.60	9.77
	C2-4	0.32	1.18	1.95	45.82	49.28
	C1-1	0.47	0.26	1.27	4.67	6.68
	C1-2	0.610	0.59	2.25	3.99	7.44
	C1-3	0.28	0.30	1.12	5.89	7.59
	C0-3-1 9/30	0.42	0.64	1.88	38.53	41.47
	C0-3-1 10/1	0.69	0.68	2.24	37.06	40.66
	C0-10-1 10/01	0.87	1.16	2.64	43.21	47.88
	C0-10-2 10/01	0.66	0.87	2.54	49.62	53.69
Pb	C3-1	< MDL	< MDL	0.33	13.45	13.88
	C3-2	< MDL	< MDL	0.30	14.97	15.39
	C3 L25 19-46 cm	< MDL	< MDL	1.19	22.85	24.15
	C3 L25 47-79 cm	< MDL	< MDL	1.63	22.85	24.59
	C4-1	< MDL	< MDL	0.33	11.63	12.07
	C2-1	< MDL	< MDL	0.52	15.25	15.88
	C2-2	< MDL	0.10	0.34	16.65	17.16
	C2-3	< MDL	< MDL	0.30	11.59	12.00
	C2-4	< MDL	< MDL	0.16	17.73	18.00
	C1-1	0.20	< MDL	0.37	2.85	3.46
	C1-2	0.285	0.08	0.38	9.04	9.78
	C1-3	0.24	< MDL	0.19	5.42	5.88
	C0-3-1 9/30	< MDL	< MDL	1.19	21.44	22.73
	C0-3-1 10/1	< MDL	< MDL	1.36	18.10	19.57
	C0-10-1 10/01	< MDL	< MDL	1.37	18.85	20.32
	C0-10-2 10/01	< MDL	< MDL	0.83	< MDL	0.96

Geochemical Data for Core Sample from the Clinch



		Water Soluble	Exch	Acid Soluble	Reducible	Sum
As	2-8 cm	2.33	0.5	0.64	8.14	11.61
	8-15 cm	0.07	< MDL	0.04	2.80	2.93
Cd	2-8 cm	0.05	0.04	0.06	0.29	0.44
	8-15 cm	< MDL	0.08	0.13	0.65	0.87
Cu	2-8 cm	2.85	0.21	0.65	15.92	19.63
	8-15 cm	0.56	0.55	1.23	30.42	32.77
Pb	2-8 cm	1.21	< MDL	0.18	6.15	7.54
	8-15 cm	< MDL	< MDL	0.66	15.73	16.39

All units in mg/kg

Emory River Sediments

		Water Soluble	Exch	Acid Soluble	Reducible	Sum
As	E4-1	2.97	1.58	2.41	44.69	51.64
	E4-2	< MDL	< MDL	0.04	1.26	1.35
	E3-1	0.09	< MDL	0.20	11.72	12.03
	E3-2	0.05	< MDL	0.04	1.33	1.45
	E3-3	< MDL	< MDL	0.14	0.32	0.51
	E3-4	0.27	< MDL	0.21	10.25	10.75
	E2-1	0.73	0.25	1.22	8.72	10.92
	E2-2	0.16	0.06	0.66	2.02	2.90
	E2-3	0.73	1.14	1.47	33.66	36.99
	E1-1	0.26	< MDL	0.92	2.38	3.58
	E1-2	0.07	< MDL	0.37	1.43	1.89
	E1-3	0.14	< MDL	0.55	2.31	3.02
Cd	E4-1	0.03	0.04	0.09	0.43	0.59
	E4-2	< MDL	0.04	0.05	0.33	0.43
	E3-1	< MDL	0.07	0.12	0.52	0.71
	E3-2	< MDL	0.01	0.01	0.13	0.16
	E3-3	0.01	0.02	0.04	0.10	0.17
	E3-4	0.01	< MDL	0.03	0.19	0.25
	E2-1	0.01	0.03	0.06	0.13	0.23
	E2-2	0.01	0.04	0.07	0.13	0.24
	E2-3	< MDL	0.04	0.12	0.51	0.71
	E1-1	0.01	0.05	0.11	0.16	0.32
	E1-2	0.01	0.06	0.12	0.18	0.36
	E1-3	0.01	0.07	0.13	0.18	0.39
Cu	E4-1	1.75	0.21	1.43	33.80	37.19
	E4-2	< MDL	0.15	< MDL	5.86	6.13
	E3-1	< MDL	0.32	0.31	18.35	19.03
	E3-2	< MDL	0.06	< MDL	2.82	3.01
	E3-3	0.11	0.08	0.24	0.59	1.03
	E3-4	0.27	0.10	0.38	8.39	9.14
	E2-1	0.43	0.17	0.76	4.04	5.41
	E2-2	0.15	0.29	0.39	1.32	2.15
	E2-3	0.29	0.33	1.24	37.11	38.98
	E1-1	0.29	0.42	0.69	1.52	2.92
	E1-2	0.33	0.26	0.63	2.09	3.30
	E1-3	0.15	0.45	0.49	1.96	3.05
Pb	E4-1	0.80	< MDL	0.19	12.42	13.45
	E4-2	< MDL	< MDL	0.75	5.91	6.71
	E3-1	< MDL	< MDL	0.65	10.64	11.40
	E3-2	< MDL	< MDL	1.26	4.09	5.46
	E3-3	0.20	< MDL	0.46	2.33	3.03
	E3-4	< MDL	< MDL	0.34	4.65	5.10
	E2-1	0.20	< MDL	0.36	2.91	3.50
	E2-2	0.26	< MDL	0.57	2.56	3.43
	E2-3	< MDL	< MDL	0.22	14.36	14.69
	E1-1	< MDL	< MDL	0.55	2.89	3.55
	E1-2	< MDL	0.10	0.59	5.12	5.88
	E1-3	< MDL	< MDL	0.80	3.82	4.73

All units are in mg/kg. < MDL = less than method detection limit. "Sum" refers to the sum of the water soluble, exchangeable, acid soluble, and reducible fractions. A duplicate and blank were extraction with each batch of samples.

TN River Sediments

		Water Soluble	Exch	Acid Soluble	Reducible	Sum
As	T2-1	< MDL	< MDL	0.11	< MDL	0.23
	T2-2	< MDL	< MDL	0.12	< MDL	0.24
	T2-3	0.09	< MDL	0.62	0.94	1.67
	T1-1	0.10	< MDL	0.45	1.24	1.81
	T1-2	0.05	< MDL	0.36	0.59	1.03
	T1-3	0.05	< MDL	0.21	0.35	0.62
Cd	T2-1	< MDL	0.01	0.02	0.08	0.12
	T2-2	< MDL	0.07	0.10	0.19	0.35
	T2-3	0.01	0.04	0.07	0.13	0.25
	T1-1	0.01	0.06	0.10	0.17	0.34
	T1-2	0.01	0.06	0.11	0.17	0.34
	T1-3	0.01	0.07	0.21	0.21	0.49
Cu	T2-1	0.19	0.08	< MDL	0.93	1.28
	T2-2	0.29	0.32	0.59	0.84	2.05
	T2-3	0.29	0.23	0.77	1.72	3.02
	T1-1	0.31	0.27	0.97	3.61	5.16
	T1-2	0.37	0.32	0.90	2.16	3.76
	T1-3	0.01	0.07	0.21	0.21	0.49
Pb	T2-1	< MDL	< MDL	0.12	2.88	3.11
	T2-2	< MDL	0.07	0.26	7.93	8.34
	T2-3	< MDL	< MDL	0.20	4.94	5.25
	T1-1	0.36	0.07	0.25	5.39	6.07
	T1-2	0.30	< MDL	0.27	6.89	7.50
	T1-3	0.21	< MDL	0.23	7.73	8.21

Fraction	Extraction Solvent
Water Soluble	Deionized water
Exchangeable	1 M NH_4Ac, pH 7
Acid Soluble	1 M NH_4Ac, pH 5
Reducible	0.1 M NH_2OH-HCl in 25% (v/v) HAc

References

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