

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 m³ 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. The flow regime in this fly-ash affected continuum of these river systems is highly regulated due to the presence of the downstream Watts Bar Reservoir.

It is well known that 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.

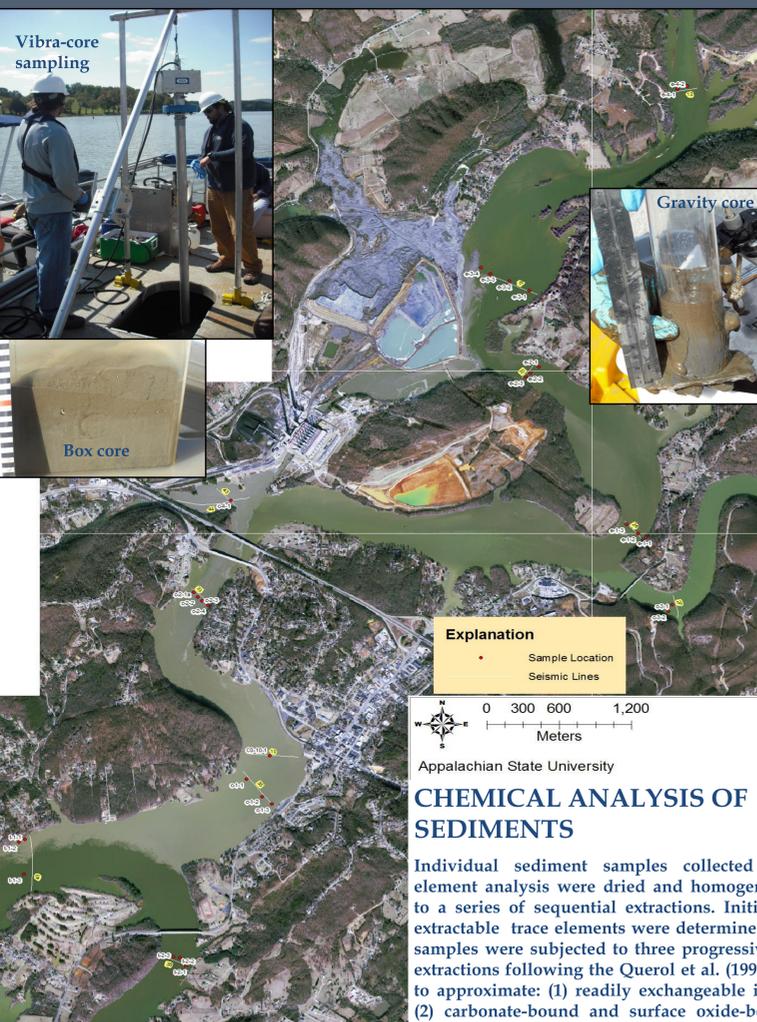
Following several high flows and initial fly ash dredging operations we began characterizing ash distribution within the affected rivers using a combination of high-resolution seismic reflection profiles correlated against actual stratigraphy logged via box, gravity, and vibra-cores. Additionally, selected river sediments affected by ash were collected and analyzed for trace elements via a sequential extraction continuum from water-extractable to reducible in order to assess the potential mobility and bioavailability of these elements.

OBJECTIVES

- Assess the extent of the fly ash distribution within the fluvial system
- Determine the labile nature of various trace elements in the fly ash and associated river bed sediments along a downstream gradient from the spill site

STUDY AREA and SEDIMENT SAMPLING METHODS

Vibra-corer Box core samplers Gravity core samplers



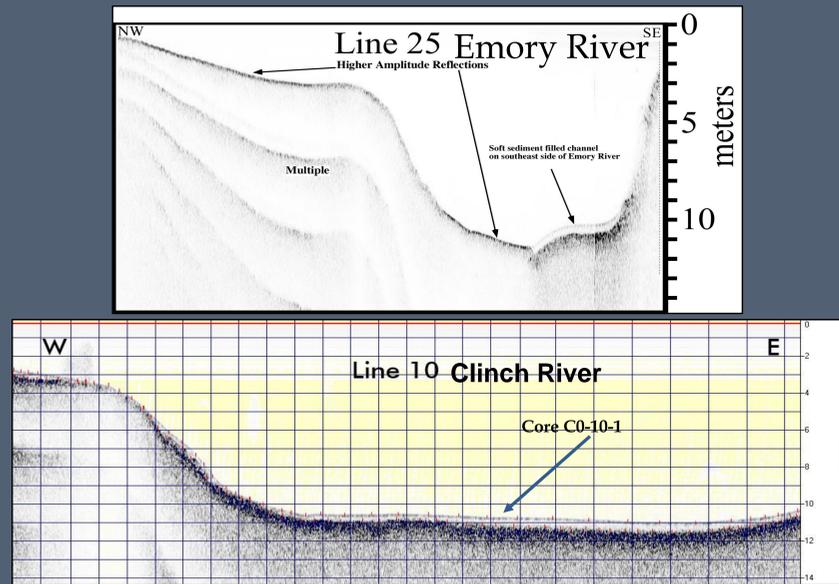
Explanation
 • Sample Location
 • Seismic Lines
 0 300 600 1,200
 Meters
 Appalachian State University

CHEMICAL ANALYSIS OF SEDIMENTS

Individual sediment samples collected for trace element analysis were dried and homogenized prior to a series of sequential extractions. Initially, water extractable trace elements were determined. Next the samples were subjected to three progressive stronger extractions following the Querol et al. (1996) methods to approximate: (1) readily exchangeable ions (Ac-7); (2) carbonate-bound and surface oxide-bound ions; (acid soluble, Ac-5) and (3) ions bound to Fe-Mn oxides (reducible). Similar procedures were used to extract various labile metal fractions from coal fly ash samples from the midwestern US (Landsberger et al., 1995). The nomenclature used in this paper to denote the various extractable fractions is seen to the left.

- **Water** – water extractable fraction
- **Ac-7** – NH₄Ac (1 M), pH = 7 extractable fraction (readily exchangeable)
- **Ac-5** – NH₄Ac (1 M), pH = 5 extractable fraction (carbonate- & surface oxide-bound ions, acid-soluble)
- **Reducible** - 0.1 M NH₂OH·HCl dissolved in 25% acetic acid

SEISMIC REFLECTION PROFILES

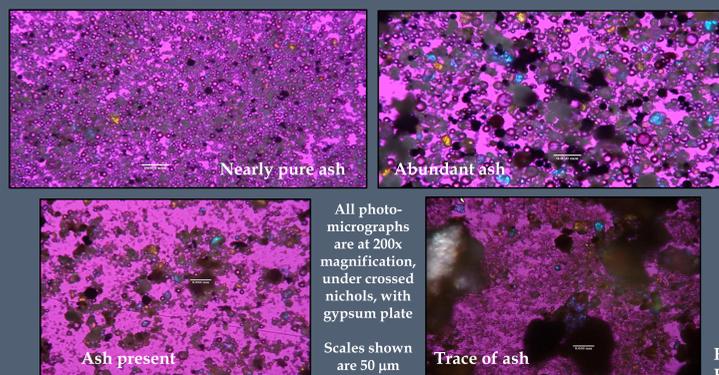


To date we have determined that fly ash from the release forms a discontinuous drape <30 cm thick in the lower 1 km of the Emory River. It appears that the seismic profiler may provide useful information in delineating this rather pure layer of fly ash above river bed sediments. Within the downstream reaches of the Clinch and Tennessee Rivers, the ash is almost exclusively mixed with native sediments. Where such mixtures occur, the seismic profiler was unable to distinguish between the ash/sediment mixture and native sediments. Thus, coring is being used to determine the thickness of this recently deposited layer.

Description of various sampling site locations and relative ash content

Sample	Amount of Ash	Location in channel
E1-3	Present to abundant	Terrace
E2-1	Abundant	Terrace Edge/Top of Slope
E2-2	Present	Slope
E3-3	Present	Slope
C1-1	Abundant	Terrace Edge/Top of Slope
C1-2	Present	Channel Bottom
C1-3	Present to abundant	Slope
C2-1	Present	Slope
C2-2	Present	Channel Bottom
C2-3	Abundant	Channel Bottom
C4-1	Present	Channel Bottom
T1-1	Present to abundant	Channel Bottom
T1-3	Present	Slope
T2-1	Trace	Small Terrace
T2-3	Present to abundant	Terrace
C0-10-1 0-20cm	Trace to present	Channel Bottom
C0-10-1 20-40cm	Trace to present	Channel Bottom
C0-10-1 40-60cm	Present	Channel Bottom
C0-10-1 60-80cm	Present	Channel Bottom
C0-10-1 80-100cm	Trace to present	Channel Bottom
C0-10-1 100-120cm	Present	Channel Bottom
C0-10-1 120-131cm	Present	Channel Bottom

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



Various labile fractions of As, Cd, Cu, & Pb in sediments

As	Water	mg/kg			
		Ac pH 7 extractable	Ac pH 5 extractable	Reducible	Sum of Extractions
E1-1	0.26	BDL	0.92	1.20	2.38
E1-2	0.068	BDL	0.36	0.72	1.14
E1-3	0.14	BDL	0.55	1.16	1.84
E2-1	0.73	0.25	1.22	4.36	6.56
E2-2	0.16	BDL	0.66	1.01	1.83
E3-3	BDL	BDL	0.14	0.16	0.30
C1-1	0.29	0.17	1.07	1.48	3.00
C1-2	BDL	BDL	0.13	BDL	0.13
C1-3	BDL	BDL	0.24	BDL	0.24
C2-1	BDL	BDL	0.12	1.40	1.52
C2-2	0.054	BDL	BDL	1.31	1.36
C2-3	0.10	BDL	0.26	2.22	2.59
C4-1	0.13	BDL	0.22	1.98	2.34
T1-1	0.097	BDL	0.45	0.61	1.16
T1-2	BDL	BDL	0.36	0.29	0.65
T1-3	BDL	BDL	BDL	0.18	0.18
T2-1	BDL	BDL	0.12	BDL	0.12
T2-2	BDL	BDL	0.12	BDL	0.12
T2-3	0.090	BDL	0.64	0.48	1.21

Cd	Water	mg/kg			
		Ac pH 7 extractable	Ac pH 5 extractable	Reducible	Sum of Extractions
E1-1	0.007	0.015	0.11	0.080	0.21
E1-2	0.005	0.059	0.11	0.091	0.27
E1-3	0.007	0.014	0.13	0.092	0.24
E2-1	0.007	0.035	0.057	0.066	0.16
E2-2	0.005	0.015	0.066	0.063	0.15
E3-3	0.005	0.016	0.042	0.049	0.11
C1-1	0.005	0.050	0.10	0.060	0.22
C1-2	0.007	0.078	0.14	0.12	0.34
C1-3	0.006	0.040	0.082	0.083	0.21
C2-1	BDL	0.077	0.13	0.14	0.35
C2-2	BDL	0.083	0.14	0.18	0.41
C2-3	BDL	0.065	0.12	0.14	0.32
C4-1	0.004	0.075	0.13	0.16	0.37
T1-1	0.011	0.058	0.10	0.083	0.25
T1-2	0.009	0.060	0.11	0.083	0.26
T1-3	0.006	0.068	0.11	0.11	0.29
T2-1	BDL	0.013	0.023	0.041	0.076
T2-2	0.005	0.065	0.097	0.093	0.26
T2-3	0.024	0.044	0.070	0.066	0.21

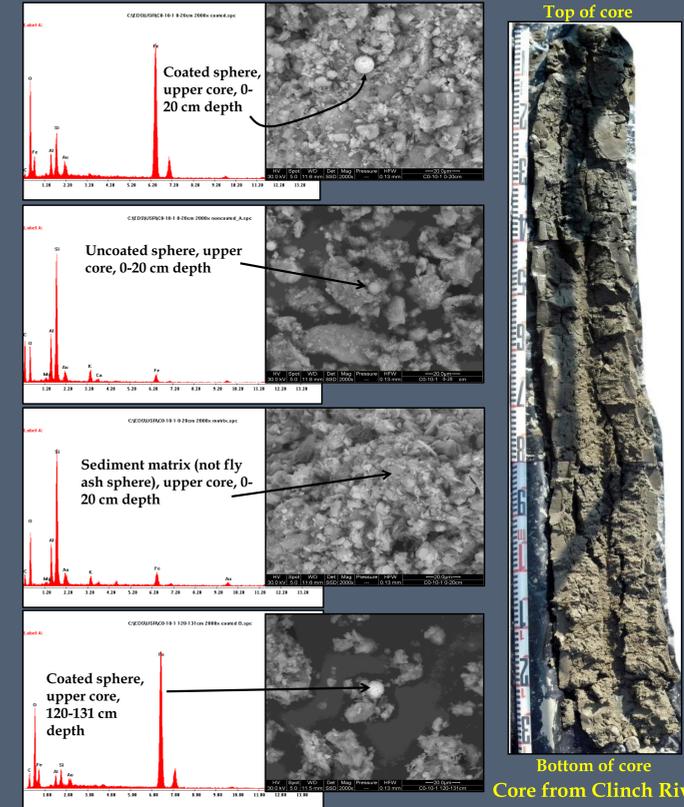
Cu	Water	mg/kg			
		Ac pH 7 extractable	Ac pH 5 extractable	Reducible	Sum of Extractions
E1-1	0.29	0.082	0.69	0.77	1.83
E1-2	0.33	0.25	0.61	1.04	2.24
E1-3	0.15	0.13	0.49	0.99	1.76
E2-1	0.43	0.17	0.76	2.02	3.39
E2-2	0.15	0.069	0.39	0.66	1.27
E3-3	0.11	0.10	0.24	0.29	0.75
C1-1	0.47	0.26	1.27	2.32	4.32
C1-2	0.61	0.57	2.19	1.98	5.35
C1-3	0.28	0.30	1.12	2.95	4.65
C2-1	0.31	0.76	2.90	6.25	10.22
C2-2	0.34	0.70	2.83	4.04	7.91
C2-3	0.34	0.73	2.11	3.97	7.16
C4-1	0.51	2.22	5.26	10.62	18.61
T1-1	0.31	0.27	0.97	1.79	3.33
T1-2	0.37	0.32	0.90	1.07	2.67
T1-3	0.32	0.35	0.96	1.26	2.89
T2-1	0.19	0.084	BDL	0.47	0.74
T2-2	0.29	0.32	0.59	0.42	1.63
T2-3	0.29	0.23	0.79	0.88	2.20

Pb	Water	mg/kg			
		Ac pH 7 extractable	Ac pH 5 extractable	Reducible	Sum of Extractions
E1-1	0.19	0.21	0.55	1.46	2.41
E1-2	0.17	0.099	0.57	2.56	3.41
E1-3	0.17	0.12	0.80	1.92	3.01
E2-1	0.20	BDL	0.36	1.45	2.01
E2-2	0.26	0.12	0.57	1.28	2.23
E3-3	0.20	0.20	0.46	1.15	2.00
C1-1	0.20	BDL	0.37	1.41	1.99
C1-2	0.28	0.077	0.37	4.49	5.22
C1-3	0.24	BDL	0.19	2.71	3.14
C2-1	BDL	BDL	0.52	7.62	8.15
C2-2	BDL	0.096	0.34	8.33	8.76
C2-3	BDL	BDL	0.30	5.33	5.63
C4-1	BDL	BDL	0.33	5.82	6.14
T1-1	0.36	BDL	0.25	2.67	3.28
T1-2	0.30	BDL	0.27	3.42	3.99
T1-3	0.21	BDL	0.23	3.97	4.41
T2-1	BDL	BDL	0.13	1.44	1.57
T2-2	BDL	0.074	0.26	3.97	4.30
T2-3	1.16	BDL	0.21	2.54	3.90

BDL denotes 'below detection limits'

Funding for this study has been provided by the National Science Foundation's Rapid Response Program and Tennessee Valley Authority.

SEM and EDAX findings



- Ash spheres with metallic coatings could easily be detected on SEM images
- Ash spheres were present on both the upper (recently deposited) and lower (deposited years ago) portions of the cores taken from the Clinch River downstream of the spill
- EDAX analysis showed that coated spheres contained mostly iron oxides; but detectable levels of trace elements (> 10,000 mg/kg) were absent on metallic sphere coatings
- Uncoated spheres and the sediment matrix were largely aluminosilicates (clay minerals); no trace elements were detected

Extractable fractions of all trace elements were compared (as ratios) with the sum of all extractable fractions (Σ_{ext}) as follows: (1) Water : Σ_{ext} ; (2) Water + Ac-7 : Σ_{ext} ; (3) Water + Ac-7 + Ac-5 : Σ_{ext} . Findings showed:

- None of these ratios for any of the trace elements exhibited any trends across the continuum from "trace" to "abundant" amounts of fly ash present in sediments
- As and Cd tended to be less mobile (H₂O soluble) compared to Cu and Pb for "trace" and "present" levels of ash; water solubility (relative to Σ_{ext}) was similar for all trace elements for 'present to abundant' and 'abundant' levels of ash
- Almost no additional As was released from sediment in the Ac-7 readily extractable fraction, whereas Cd and Cu increased by several fold; only modest increases were noted for Pb
- The ratio of the sum of the first three extractions to Σ_{ext} varied greatly, but was generally lower for Pb compared with other trace elements.

CONCLUSIONS:

1. Relatively pure ash deposits from the recent spill are mostly confined to the Emory River.
2. Within the Clinch and Tennessee Rivers, the recent fly ash is mostly mixed with native sediments in the upper 30 cm of the river bed; evidence of older fly ash was found in deeper sediments (120 - 131 cm depths).
3. Total extractable concentrations of Cd, Cu, and Pb were highest in sediments from the Clinch River and showed no relationship with ash content. Arsenic concentrations were slightly higher in the Emory River compared to the Clinch River and appeared to be related to ash content.
4. EDAX analysis of metallic coatings on recently deposited ash spheres showed that these were primarily Fe oxides with no detectable trace elements (detection limit \approx 10,000 mg/kg); the sediment matrix was largely aluminosilicates with no detectable trace elements.
5. The ratio of the trace element concentration extracted in each step of the sequential extraction to the sum of the concentrations from all of the steps in the extraction was independent of ash abundance for all trace metals.

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