# Evaluation of potential toxicity of fly ash released to the Emory River, TN, to benthic invertebrates in whole-sediment and elutriate exposures

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## ABSTRACT

The objective of this study was to evaluate the potential toxicity of fly ash in whole-sediment or fly ash in elutriate toxicity tests conducted with benthic invertebrates. A preliminary 10-d whole-sediment toxicity test was conducted at the US Army Corps of Engineers (USACE) Engineer Research and Development Center with amphipods (*Hyalella azteca*) exposed to two ash samples collected from the Emory River and a control sediment (Browns Lake, MS). Mean 10-d survival and growth of amphipods in the ash samples were significantly reduced relative to the control. Concentrations of arsenic, copper, cadmium, and nickel in the ash samples were at or above the threshold effect levels for amphipods. Longer-term whole-sediment toxicity tests were conducted at the US Geological Survey (USGS) Columbia Environmental Research Center with amphipods (*H. azteca*) and two juvenile mussels (rainbow mussel, *Villosa iris* and wavy-rayed lampmussel, *Lampsilis fasciola*) for 28 d, and midge (*Chironomus dilutus*) for 10 d. Organisms were exposed to one ash sample and a control sediment (West Bearskin Lake, MN). Mean survival or growth of amphipods and mean growth of wavy-rayed lampmussels and mdige in the ash sample was significantly lower than the control, whereas the survival and growth of rainbow mussels were not significantly different between the control and ash samples. The concentration of arsenic in the ash sample was above the empirically based sediment probable effect concentration. Additionally, two elutriate samples were prepared to simulate an extreme re-suspension event of fly ash in the Emory River and the sluice channel during dredging to remove fly ash, and used to conduct a 10-d elutriate toxicity test with 5-month-old rainbow mussels at USGS. The elutriates contained elevated concentrations of arsenic, selenium, and barium relative to local soil and sediment. Mean 10-d survival of the mussel (based on foot movement or heartbeat) ranged from 90 to 100% and was not significantly different among reference site water (0% elutriate), 10%, 50%, and 100% elutriate concentrations for both elutriate samples. However, a significantly lower percentage of mussels moved their foot with exposure to 100% elutriate from sluice channel compared to mussels in reference site water. These results indicate that fly ash can be chronically toxic to some sediment-dwelling organisms possibly due to elevated metal concentrations. However, the short-term release of contaminants during re-suspension of fly ash may not adversely affect the survival of juvenile rainbow mussels.

## Background

Fly ash was released to the Emory River, TN from the Tennessee Valley Authority Kingston Fossil Plant in December 2008 (USEPA 2009, TVA 2009). The environmental cleanup of this spill will most likely result in the removal of over 5 million cubic yards of fly ash from the river and surrounding areas in connection with recovery and remediation efforts. The impact of this release on the river ecosystem is under investigation.

**U.S. Department of the Interior**

**U.S. Geological Survey**

## Objective

Evaluate the potential toxicity of fly ash in whole-sediment toxicity tests and fly ash in elutriate toxicity tests conducted with benthic invertebrates.

## MATERIALS AND METHODS

Two fly ash samples were collected in December 2008 from the Emory River near Kingston and used to conduct a preliminary 10-d whole-sediment test with amphipods (*Hyalella azteca*) at USACE (Table 1). Another ash sample was collected in July 2009 and used to conduct chronic whole-sediment test with amphipods, two juvenile mussels (rainbow mussel, *Villosa iris* and wavy-rayed lampmussel, *Lampsilis fasciola*), and midge (*Chironomus dilutus*) at USGS (Table 1).

Two elutriate samples were prepared by USACE to simulate an extreme re-suspension event of fly ash in the Emory River and the sluice channel during dredging to remove fly ash (see the poster by Stanley et al. in this session for detail), and were provided to USGS to conduct a 10-d elutriate test with rainbow mussel (Table 1).

Sediment samples were collected on test day 0 for whole-sediment characterization (grain size, total organic carbon, percent water, total recoverable metals, and total polycyclic aromatic hydrocarbons (PAHs)). A diffusion sampler (peeper) was inserted on day 0 and collected on day 7 for pore-water metal analysis. Subsamples of sediment were also collected on day 7 for analysis of simultaneously extracted metal (SEM) and acid-volatile sulfide (AVS).

Table 1. Conditions of toxicity tests with amphipods (*Hyalella azteca*), midge (*Chironomus dilutus*), rainbow mussels (*Villosa iris*), and wavy-rayed lampmussels (*Lampsilis fasciola*) in whole-sediment or in elutriate exposures conducted in basic accordance with standard methods (ASTM 2009a,b)

| Parameter | Whole-sediment testing at USACE | Whole-sediment testing at USGS | Elutriate testing at USGS |
|---|---|---|---|
| **Test species** | Amphipod | Amphipod, midge, rainbow mussel, wavy-rayed lampmussel | Rainbow mussel |
| **Test type** | Static-renewal | Flow-through | Static-renewal |
| **Test material** | Fly ash collected from Emory River | Fly ash collected by USFWS from Emory River | Two ash elutriates (from Emory River and sluice channel) prepared by USACE (see posters by Stanley et al. and Chappell et al. in this session) |
| **Test duration** | 10 d | 28 d | 10 d |
| **Temperature** | 23°C | 23°C | 20°C |
| **Light** | Ambient laboratory light, 200 lux, 16L:8D | | |
| **Water or sediment volume** | 100 ml of sediment with 175 ml of overlying water | 100 ml of sediment with 175 ml of overlying water | 200 ml |
| **Water renewal** | 2 volume additions daily | 2.7 volume additions daily | Monday, Wednesday, Friday |
| **Age of test organisms** | 7- to 14-d-old amphipods | About 7-d-old amphipods and midge<br>About 3-month-old mussels | About 5-month-old mussels |
| **# organisms/chamber** | 10 | 10 | 10 |
| **# replicate chambers** | 8 | 4 | 4 |
| **Feeding** | 1 ml of YCT | Amphipods: 1 ml of YCT<br>Midge:1.5 ml of flake fish food<br>Mussels: 2 ml of algal mixture twice daily | 2 ml of algal mixture twice daily |
| **Chamber cleaning** | None | None | New test chamber after 7 d |
| **Test water** | Dechlorinated tap (Vicksburg municipal; hardness 75 mg/L as $CaCO_3$) | Diluted well water (hardness 100 mg/L as $CaCO_3$) | Reference site water |
| **Test concentration** | Ash sample from Emory River, control sediment from Browns Lake, MS | Ash sample from Emory River, control sediment from West Bearskin Lake, MN | 100%, 50%, 10%, 0% (dilutions prepared with site water) |
| **Water quality** | Dissolved oxygen, pH, hardness, alkalinity, and ammonia were measured weekly | | |
| **Endpoint** | Survival, biomass | Survival, biomass (amphipod and midge), length (mussels) | Survival, length |
| **Test acceptability** | ≥80% control survival | | |
| **Data analysis** | Following the guidance outlined in USEPA 2002 with TOXSTAT® software (WEST 1996) | | |

## Results and Discussion

- Concentrations of arsenic, copper, cadmium, and nickel in the ash samples used for the test at USACE were at or above the threshold effect level for amphipods (Table 2).
- Concentrations of arsenic in the ash sample used for the tests at USGS were above the empirically based sediment probable effect concentration (PEC) and U.S. EPA chronic water quality criterion (WQC) for arsenic (Table 3). Concentrations of other metals and total PAHs were below their respective PEC and WQC.

Table 2. Measured metal concentrations in two ash samples tested by USACE. Red font indicates a level exceeding the threshold

| Metal | Ash 1 (mg/kg) | Ash 2 (mg/kg) | Threshold[a] (mg/kg) |
|---|---|---|---|
| Antimony | <0.5 | <0.5 | NA |
| Arsenic | 97 | 101 | 11 |
| Barium | 296 | 328 | NA |
| Beryllium | 3.5 | 4.1 | NA |
| Cadmium | 0.5 | 0.6 | 0.6 |
| Chromium | 30 | 34.5 | 36 |
| Cobalt | 14 | 15.6 | NA |
| Copper | 59 | 65 | 28 |
| Iron | 13420 | 13300 | NA |
| Lead | 25 | 31 | 37 |
| Manganese | 87 | 97 | 630 |
| Mercury | 0.162 | 0.122 | NA |
| Molybdenum | 4.4 | 4.3 | NA |
| Nickel | 31 | 34 | 20 |
| Selenium | 6.6 | 7.3 | NA |
| Silver | <0.5 | <0.5 | NA |
| Thallium | 1.8 | 2.1 | NA |
| Vanadium | 80 | 91 | NA |
| Zinc | 54 | 61 | 98 |

[a] Threshold effect level for amphipods (*Hyalella azteca*; Buchman 2008).

- The survival or growth of amphipods and the growth of wavy-rayed lampmussel and midge exposed to ash samples were reduced significantly relative to the controls (Table 4). The differences in the survival or growth of rainbow mussel were not significant between the ash and control sediment samples (Table 4).
- The elutriates contained elevated concentrations of arsenic, selenium, and barium relative to local soil and sediment (see the poster by Chappell et al. in this session for details). Mean survival of rainbow mussels (based on foot movement or heartbeat) was not significantly different among reference site water (0% elutriate), 10%, 50%, and 100% elutriate concentrations for both elutriate samples (Table 5). However, a significantly lower percentage of mussels (35%) moved their foot mussels in 100% elutriate from sluice channel, compared to mussels in reference site water (88%).

Table 3. Physical and chemical data for the ash sample and a control sediment (West Bearskin Lake) tested by USGS. Red font indicates a level exceeding the threshold

| Analyte | Unit | Ash | Control | Threshold |
|---|---|---|---|---|
| Moisture | % | 38.4 | 39.6 | NA |
| Grain Size-Clay | % | 7.0 | 6.0 | NA |
| Grain Size-Sand | % | 13 | 81.6 | NA |
| Grain Size-Silt | % | 80 | 12.4 | NA |
| Total Organic Carbon | % | 0.2 | 2.1 | NA |
| *Sediment metals* | | | | |
| Arsenic | mg/kg dry | 71 | <3.7 | 33 [a] |
| Cadmium | mg/kg dry | 0.59 | <1.7 | 4.98 [a] |
| Chromium | mg/kg dry | 29 | 23 | 111 [a] |
| Copper | mg/kg dry | 62 | 20 | 149 [a] |
| Lead | mg/kg dry | 25 | 16 | 128 [a] |
| Nickel | mg/kg dry | 32 | 26 | 48.6 [a] |
| Zinc | mg/kg dry | 57 | 60 | 459 [a] |
| Mercury | mg/kg dry | 0.079 | <0.23 | 1.06 [a] |
| Average metal PEC-Q | | 0.5 | 0.18 | 1.0 [a] |
| ΣSEM - AVS | µmol/g dry | 0.69 | -0.58 | 1.7 [b] |
| *Peeper pore water metals* | | | | |
| Arsenic | µg/L | 184 | 15.4 | 150 [c] |
| Cadmium | µg/L | < 0.30 | < 0.30 | 0.25 [c] |
| Copper | µg/L | 1.01 | < 0.58 | 9.0 [c] |
| Lead | µg/L | < 0.56 | < 0.56 | 2.5 [c] |
| Nickel | µg/L | < 0.73 | 2.54 | 52 [c] |
| Zinc | µg/L | < 16 | < 16 | 120 [c] |
| Total PAH | mg/kg dry | 0.3931 | 0.285 | 22.8 [a] |

[a] Probable effect concentration (MacDonald et al. 2000).
[b] USEPA 2005.
[c] USEPA chronic water quality criterion at 100 mg/L hardness (USGS 2006).

Table 4. Mean survival and growth ($n$ =4 or 8) of benthic species in 10- or 28-d whole-sediment toxicity tests with fly ash sample and a control sediment

| Test organism | Test Lab | Test duration (d) | % Survival (SD) Control | % Survival (SD) Ash | Growth[a] (SD) Control | Growth[a] (SD) Ash |
|---|---|---|---|---|---|---|
| Amphipod | USACE | 10 | 99 (4.0) | 78 (10)*/78 (15)*[b] | 0.17 (0.03) | 0.12 (0.03)*/0.12 (0.03)* |
| Amphipod | USGS | 28 | 98 (5.0) | 68 (5.0)* | 0.50 (0.06) | 0.37 (0.03)* |
| Midge | USGS | 10 | 88 (15) | 95 (5.8) | 0.80 (0.13) | 0.57 (0.04)* |
| Rainbow mussel | USGS | 28 | 100 (0) | 100 (0) | 56 (20) | 44 (16) |
| Wavy-rayed lampmussel | USGS | 28 | 100 (0) | 100 (0) | 81 (14) | 38 (13)* |

[a] Biomass (mg, total dry weight of surviving organisms divided by the number of original organisms) for amphipod and midge; shell length increase (%) for mussels.
[b] Values for two ash samples.
* significant reduction relative to the control ($p$ <0.05; t-test or Kruskal-Wallis test).

Table 5. Mean water quality characteristics ($n$ =2) and mean survival of 5-month-old rainbow mussel ($n$=4) in 10-d static-renewal tests with two ash elutriate samples diluted by reference site water (0%) tested by USGS

| Treatment | Concentration | pH | Conductivity (µS/cm) | Alkalinity (mg/L as $CaCO_3$) | Hardness (mg/L as $CaCO_3$) | Ammonia (mg N/L) | % Survival (SD) (foot movement) | % Survival (SD) (heartbeat) |
|---|---|---|---|---|---|---|---|---|
| EMR-EL-MS (Emory River) | 0% | 7.6 | 96 | 31 | 36 | 0.12 | 88 (15) | 100 (0) |
| | 10% | 7.5 | 118 | 38 | 37 | 0.14 | 78 (21) | 100 (0) |
| | 50% | 7.6 | 122 | 41 | 42 | 0.11 | 85 (19) | 95 (10) |
| | 100% | 7.8 | 165 | 51 | 63 | 0.13 | 83 (10) | 90 (0) |
| SLC-EL-MS (Sluice channel) | 0% | 7.6 | 96 | 31 | 36 | 0.12 | 88 (15) | 100 (0) |
| | 10% | 7.6 | 124 | 34 | 45 | 0.13 | 68 (10) | 98 (5.0) |
| | 50% | 7.7 | 172 | 42 | 65 | 0.10 | 70 (20) | 90 (14) |
| | 100% | 7.8 | 272 | 69 | 106 | 0.13 | 35 (17)* | 98 (5.0) |

* Significant reduction relative to the reference site water ($p$ <0.05; one-tailed Dunnett's test).

## Conclusions

- Fly ash might be chronically toxic to some sediment-dwelling organisms.
- Elevated concentrations of metals (e.g., arsenic) and/or physical characteristics of the fly ash might contribute to this observed sediment toxicity.
- A short-term (e.g., <10 d) release of contaminants during re-suspension of fly ash may not adversely affect the survival of juvenile mussels.

## ACKNOWLEDGEMENTS

We thank Eric Brunson, Doug Hardesty, Jamie Hughes, Tom May, Jingjing Miao, and David Whites for technical assistance.

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