Published in final edited form as:

Environ Toxicol Chem. 2009 January ; 28(1): 26–35. doi:10.1897/08-050.1.

EVALUATION OF THE EFFECTS OF COAL FLY ASH AMENDMENTS ON THE TOXICITY OF A CONTAMINATED MARINE SEDIMENT

Robert M. Burgess^{†,*}, Monique M. Perron[‡], Carey L. Friedman[§], Eric M. Suuberg^{||}, Kelly G. Pennell^{||}, Mark G. Cantwell[†], Marguerite C. Pelletier[†], Kay T. Ho[†], Jonathan R. Serbst[†], and Stephan A. Ryba[†]

[†]U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, 27 Tarzwell Drive, Narragansett, Rhode Island, 02882 USA

[‡]Harvard School of Public Health, Department of Environmental Health, 665 Huntington Avenue, Boston, Massachusetts, 02115 USA

[§]University of Rhode Island, Graduate School of Oceanography, South Ferry Road, Narragansett, Rhode Island, 02882 USA

^{||}Brown University, Division of Engineering, 182 Hope Street, Providence, Rhode Island, 02912 USA

Abstract

Approaches for cleaning-up contaminated sediments range from dredging to in situ treatment. In the present report, we discuss the effects of amending reference and contaminated sediments with coal fly ash to reduce the bioavailability and toxicity of a field sediment contaminated with polycyclic aromatic hydrocarbons (PAHs). Six fly ashes and a coconut charcoal were evaluated in 7 d whole sediment toxicity tests with a marine amphipod (*Ampelisca abdita*) and mysid (*Americamysis bahia*). Fly ashes with high carbon content and the coconut charcoal showed proficiency at reducing toxicity. Some of the fly ashes demonstrated toxicity in the reference treatments. It is suspected that some of this toxicity is related to the presence of ammonia associated with fly ashes as a result of post-oxidation treatment to reduce nitrous oxides emissions. Relatively simple methods exist to remove ammonia from fly ash prior to use and fly ashes with low ammonia content are available. Fly ashes were also shown to effectively reduce overlying water concentrations of several PAHs. There was no evidence of the release of the metals cadmium, copper, nickel or lead from the fly ashes. A preliminary 28 d polychaete bioaccumulation study with one of the high carbon fly ashes and a reference sediment was also performed. Although preliminary, there was no evidence of adverse effects to worm growth or lipid content, or the accumulation of PAHs or mercury from exposure to the fly ash. These data show fly ashes with high carbon contents may represent viable remedial materials for reducing the bioavailability of organic contaminants in sediments.

*To whom correspondence may be addressed: Robert M. Burgess, U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Atlantic Ecology Division, 27 Tarzwell Drive, Narragansett, Rhode Island, 02882 USA, 401-782-3106 (p), 401-782-3030 (f), burgess.robert@epa.gov.

This is NHEERL-AED, Narragansett Contribution AED-07-107.

Keywords

Marine toxicity; Coal fly ash; Contaminated sediments; Remediation; Polycyclic aromatic hydrocarbons

INTRODUCTION

Contaminated sediments are a global environmental issue known to affect North America, Europe and Australasia [1]. This is because sediments serve as an efficient sink for many anthropogenic contaminants associated with various types of industrial activity including nonionic organic chemicals (NOCs) like polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) and cationic metals like cadmium, copper, nickel and lead. For example, in the United States, the U.S. Environmental Protection Agency's Contaminated Sediment Inventory (CSI) and the National Oceanic and Atmospheric Administration (NOAA) Status and Trends Program have reported large areas of sediments contaminated with anthropogenic chemicals [2,3]. The affected areas have been quantified to represent billions of metric tons of contaminated sediment. The presence of these contaminants can have several adverse effects to the environment ranging from acute and sublethal toxicity to invertebrates and fish to benthic community impairments [4,5]. The implications of these effects are both ecological and economic in nature. For example, severely toxic sediments may significantly impair a benthic invertebrate community fed upon by a commercially important fish. In turn, the lack of the benthic community may result in a nonviable fishery.

The principle approach to clean-up such contaminated sediments is through remediation. Currently, contaminated sediment remediation methods includes environmental dredging in which the contaminated sediments are removed from a site, monitored natural recovery (MNR) where the site is allowed to bury the contaminated sediments naturally through siltation with clean sediments, and in situ capping [6]. Capping is similar to MNR, but is enhanced by placing material on top of the contaminated site. In many instances, capping material is simply sand; however, other more chemically-active capping materials have been investigated including the addition of various forms of activated carbon [6]. The addition of active capping materials seeks to enhance the sequestering of contaminants within the cap and reduce the transport and bioavailability of toxic chemicals associated with the contaminated sediments. Recently, the use of activated carbon as a sediment amendment and potential active capping material has been explored for PCBs, PAHs and pesticides [7–10]. These evaluations have also shown promise for possible field application [11]. For example, for sediments from the Lake Hartwell Superfund site (SC, USA), Werner et al. [12] reported reducing PCB aqueous concentrations by up to 95% and accumulation by semi-permeable membrane devices (SPMDs) by 78% after one month of activated carbon-sediment interaction. Further, in a preliminary field study at Hunter's Point Shipyard (San Francisco, CA, USA), Cho et al. [11] demonstrated activated carbon could be effectively distributed into contaminated sediments and result in evidence of reduced PCB bioavailability to the bivalve *Macoma nasuta* several months following activated carbon deployment.

Coal fly ash, another material that has a long history of use in pollution control [13,14], is now being considered for capping. Coal fly ash is most often formed during the combustion of coal in the production of electricity at power plants. Like activated carbon, fly ash is formed in a process that can produce a type of refractory and highly sorptive black carbon. In recent studies, black carbon has been shown to strongly adsorb many NOCs [15]. Several studies have examined the interaction of NOCs and cationic metals with fly ash demonstrating strong adsorption under some conditions [16–20]. Fly ash is an appealing

remedial material because it is inexpensive, readily available from the very large quantities produced annually from the burning of coal, and reuses a waste substance. For example, according to the American Coal Ash Association and European Coal Combustion Products Association, in 2004 the United States and Europe, generated 64,500 and 43,500 kilotons of fly ash, respectively, of which only approximately 45% was reused (www.ecoba.org, www.ACAA-USA.org). One of the most common uses of coal fly ash is as an additive in making concrete while the remaining ash is often landfilled.

While several studies have examined the chemical interactions of fly ash and contaminants, few studies have investigated the effects of fly ash on the bioavailability and toxicity of NOCs associated with sediments. In the present study, the objective was to evaluate how effectively several samples of coal fly ash affect the toxicity and geochemistry of a marine sediment environmentally contaminated with PAHs. For this evaluation, a marine amphipod (*Ampelisca abdita*) and mysid (*Americamysis bahia*) were used. This study is an evaluation of coal fly ash as a possible remedial substance for capping aquatic contaminated sites. For comparison, a form of activated carbon, powdered coconut charcoal, which has been shown to very effectively reduce the toxicity of NOCs in sediments [21], was included in the study. Finally, to assess the effects of fly ash addition on the nutritional condition of benthic organisms and uptake of possible contaminants, a preliminary 28 d bioaccumulation study with a marine polychaete (*Nereis virens*) was performed using reference sediment amended with fly ash and the effects on organism tissue and lipid mass and PAH and mercury accumulation were evaluated.

MATERIALS AND METHODS

Selection of Fly Ash

Six fly ash samples collected from coal fired power plants in the United States were evaluated. Table 1 presents geochemical characteristics of each fly ash. In general, for the experiments, fly ashes were used in a dry form. In limited cases, fly ashes were treated before use to evaluate effects on performance. Generally, these were fly ashes suspected of being effective at reducing toxicity because of their elevated loss on ignition values. One fly ash was treated by de-aeration. De-aeration was performed to remove air inside the pores of the fly ash and improve the ability for contaminants to interact with the ash when wet. In the procedure, a mass of fly ash was combined with deionized water and mixed. The mixture was placed in a flask under vacuum for approximately 18 h. The fly ash was then separated from the water by centrifugation. Powdered coconut charcoal PCB-G (FC) (90–96% <45 μm) was from Calgon Carbon (Pittsburg, PA, USA) and also de-aerated before use. In some other treatments, before use, a fly ash was rinsed with de-ionized water (DI) three times, the DI decanted, and replaced for storage with reconstituted seawater with a salinity of 30‰ (4°C in the dark). Reconstituted seawater (RS) was made by adding 100‰ brine prepared from Narragansett Bay seawater to DI.

Fly Ash Characterization

The six fly ash samples were evaluated for several geochemical characteristics including loss-on-ignition (LOI), surface area (SA), foam index (FI), and porosity using methods in Kulaots et al. [22]. Fly ashes formed from anthracite or bituminous coals were designated Class F while fly ashes from lignite or subbituminous coals are Class C. For this report, fly ashes are identified by their class and LOI. Unburned residual carbon content (loss on ignition) was performed on one gram samples of pre-dried fly ash (130 °C for 2 h) followed by 740 °C for 2 h. Carbon content (% C) of the coconut charcoal was determined on an elemental analyzer (see description below). Surface area (SA) was determined with nitrogen (N_2) in an automated Quantachrome Corporation Autosorb 1 gas-adsorption instrument

(Boynton Beach, FL, USA) using the standard Brunauer, Emmet and Teller (BET) analysis. Surface area for coconut charcoal was taken from Lebo et al. [23]. Foam index is the commonly used field test for determining the suitability of a particular fly ash as a concrete additive. Generally, the larger the FI, the poorer the fly ash is expected to perform as a concrete additive. Briefly, 2 g of fly ash, eight grams of Portland cement, and 25 ml of de-ionized water were combined in a 70 ml cylindrical jar (40 mm inner diameter), capped, and thoroughly shaken for one minute to completely wet the cement and fly ash. Next, a 10% aqueous solution of commercial surfactant air-entraining admixtures (AEA) (Darex II (W.R. Grace and Company, Cambridge, MA, USA)) was titrated in 0.02 ml increments. Following addition of each increment, the jar was capped and shaken for approximately 15 s, after which the lid was removed, and the liquid surface observed. The visual endpoint was the presence of a stable surface foam lasting at least 45 s. Fly ash porosity was categorized as micropores (<20 Å), mesopores (20–500 Å) and macropores (>500 Å) based upon the International Union of Pure and Applied Chemistry (IUPAC) classification. To determine the porosity of each category, N₂ gas adsorption isotherms were measured at 77 K using the Autosorb-1 instrument described above.

Sediments

For the present study, Long Island Sound (LIS) sediment (New York (NY), USA) was used as the reference. This site is relatively uncontaminated and has been used as a control site for several studies in our laboratory [21]. Surface sediment (top 2 cm) was collected using a Smith MacIntyre grab (0.1 m²) in 2005. Geochemical characteristics of the LIS sediment include approximately 2.0 % organic carbon and 13 µmol acid volatile sulfide (AVS)/g (dry). Contaminated sediment from Elizabeth River (ER)(VA, USA) was collected in 1998. Elizabeth River is highly contaminated with some of the highest PAH concentrations anywhere in the world [24,25]. Geochemical characteristics of the ER sediment include 4.2 % organic carbon and 112 µmol AVS/g (dry). Table 2 shows the concentration of several PAHs and cationic metals associated with the ER sediment [25]. For relative comparison, concentrations of PAHs and cationic metals in a sample of LIS reference sediment collected in February 1998, from the same area as the 2005 collection, are also presented (Table 2).

Sediment and Fly Ash Additions

For toxicity testing, fly ash and coconut charcoal samples were combined with LIS and ER sediments at 20% by weight and for one fly ash also at 5% and 10% (Class F 65.5%). For the preliminary bioaccumulation study, Class F 65.5% fly ash was added to LIS in 5% and 10% by weight amendments. Amendments were prepared by manually homogenizing sediments and fly ash/coconut charcoal with a stainless steel spatula. Amended sediments were then added to toxicity testing or bioaccumulation chambers. Because of the known high toxicity of ER sediment, a dilution effects treatment using beach sand was not included. Previous work with very toxic sediments found dilution of toxicity was minor.

Toxicity Testing

Toxicity test methods and acceptability criteria are discussed in detail by Ho et al. [26]. Briefly, testing involved adding ten 48 h old cultured mysids, *Americamysis bahia*, and ten field-collected (0.7– 1.0 mm) amphipods, *Ampelisca abdita*, to each exposure chamber. Tests were performed without seawater renewal (static) with gentle aeration in 100 ml exposure chambers with 60 ml of RS added. Reconstituted seawater was added gently to avoid resuspending the sediments. Organisms were added 24 h later. Mysids were fed daily 100 µl of a solution of 1.4 g (wet) of newly hatched *Artemia* in 10 ml DI while the amphipods were not fed. After 7 d, the tests were terminated, and organisms sieved from the exposure chambers, and assessed for mortality (missing organisms were considered mortalities).

Preliminary Bioaccumulation Study

Exposures using LIS sediment with 5% and 10% additions of Class F 65.5% fly ash were performed based on guidance in U.S. EPA [27]. Exposure chambers were one liter beakers (15 × 12 cm) with a cylindrical coil of 3.0 mm mesh screening (12 cm × 10 cm × 0.1 cm) inserted in the top. Screening allowed for the flow-through seawater to overflow the beaker's edge while stopping organisms from swimming from the chamber. Flow rates during the 28 d exposure was approximately 7 ml/min for approximately 10 volumetric turnovers per day. The flow through exposure system was provided by a siphoning gravity diluter distributing seawater to the chambers. Chambers contained 200 mL of sediment or sediment plus fly ash and one field collected polychaete *Nereis virens* (Aquatic Research Organisms, Hampton, NH, USA). Following addition to the test, animals that had not burrowed after one hour were replaced. During the exposure, the organisms were not fed and new sediment was not added. For each treatment, there were three replicates each containing a worm with an initial weight of 2 to 5 g (wet). Sediments were added to chambers three days (Day -3) prior to the animals and the flow through seawater system started. On Day 0, pre-weighed animals were added to the exposures. Exposures were performed at 20°C, 30‰ under a 12 hours light and 12 hours dark cycle with 30 min brightening and dimming phases, and continuous aeration. On Day 28, animals were removed from the exposure sediment by sieving through a 1 mm stainless steel sieve. Animals were then rinsed with 20°C seawater and placed into 400 ml static depuration chambers containing 40 g of LIS sediment and 150 ml natural seawater. All chambers were aerated with one animal per chamber. After approximately 24 h, the organisms were sieved out of the sediment, rinsed with seawater, weighed, and frozen at -4°C until chemical and lipid determinations. Lipid were determined gravimetrically from 50:50 acetone:hexane mixture extracts of the tissues. Three replicate extractions were performed with sonication on manually homogenized tissues. After the three extracts were composited, a subsample was collected and allowed to evaporate to dryness and the lipid mass determined.

Statistical Analyses

Treatments were performed with two to three replicates and the mean and standard deviation are generally reported. Toxicity testing, polychaete mass and lipid content, and bioaccumulation results were analyzed using analysis of variance (ANOVA) followed by either a Dunnett's test or protected least significant difference test ($p = 0.05$). To normalize for the binomial distribution of percent survival data, the square root of the raw data was arcsin transformed before statistical analysis. For toxicity testing results, comparisons were performed as one-tailed tests to detect only treatments with significantly less survival than the reference (LIS) or greater survival than the toxic sediment (ER). Regression equations, as well as resulting coefficients of determination (r^2) and p -values, were generated on untransformed toxicological and chemical data. Statistical analyses were performed with the SAS System, Release 8.02 (SAS Institute, Cary, NC, USA) and Statistica, Release 6.1 (Statsoft, Tulsa, OK, USA).

Analytical Methods

Chemical analyses were performed on overlying water samples collected on the last day of the toxicity testing exposures (day 7). Because of high flow rates in the bioaccumulation study, overlying water analyses were not conducted. Cationic metal analyses for cadmium, copper, nickel and lead were performed on nitric acid treated water samples using graphite furnace atomic spectroscopy (SIMAA6000, Perkin-Elmer, Wilton, CT, USA). Detection limits for cationic metals were approximately 10, 25, 30 and 25 µg/L for cadmium, copper, nickel and lead, respectively. In water and polychaete tissue samples, 13 PAHs were analyzed including fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, indeno[1,2,3

cd]pyrene, dibenz[*ah*]anthracene and benzo[*ghi*]perylene. In the water samples, PAHs were extracted three times from water samples using acetone partitioned against de-ionized water and one milliliter of heptane. For tissues, PAHs were extracted as described for the lipid analysis, except the extracts for PAH analysis were cleaned-up using a AccuBond II solid phase extraction silica column (500 mg, 6 ml) (Agilent Technologies UK, West Lothian, UK), and then volume reduced to approximately 1 ml. Samples were stored at 4°C in the dark until analysis. Analyses were performed on a Hewlett-Packard® 5890 Series II gas chromatograph with a 5971 mass spectrometer (Hewlett-Packard, Palo Alto, CA, USA) and a 60 m DB-5 fused silica capillary column (J & W Scientific®, Folsom, CA, USA). Detection limits for PAHs were approximately 0.5 ng/L. Fly ash and whole tissue samples were analyzed for mercury using a DMA-80 direct mercury analyzer (Milestone, Shelton, CT, USA). The instrument was calibrated using National Research Council of Canada standard reference materials for trace metals including lobster hepatopancreas (TORT-2) and dogfish muscle (DORM-2) (Institute for National Measurement Standards, Ottawa, ON, Canada). Carbon content of the powdered coconut charcoal was quantified on a ThermoFinnigan FlashEA Series 1112 automated elemental analyzer (ThermoQuest Italia S.p.A, Milan, Italy). Total ammonia (NH_x) was measured using an Orion ion-selective ammonia probe (model 9512BN; Boston, MA, USA) and meter (720A). Detection limits for ammonia were approximately 0.1 mg/L. Along with ammonia, overlying water pH, salinity and temperature were measured to calculate unionized ammonia (NH₃) based on Hampson [28]. For chemical measures, quality assurance included performing analytical and sample blanks, duplicate or triplicate analyses, and where appropriate, internal standard recoveries.

RESULTS AND DISCUSSION

Fly Ash Characteristics

Fly ashes varied in LOI with values ranging from 0.84% for a Class C fly ash to 65.5% for a Class F fly ash (Table 1). Surface areas for the fly ashes followed the trend set with LOI: fly ashes with low LOI values had low surface areas (0.84% and 3.46 m²/g) while the fly ashes with large LOI also had large surface area values (65.5% and 35.3 m²/g). As expected, the foam index mirrored the LOI and SA relationships; the fly ashes with the greatest LOIs also had elevated FI values indicating poor fly ash for making concrete. In almost every case, the fly ashes had more micropore capacity than either mesopore or macropore volume. Further, low LOI fly ashes had much greater porosity than the high LOI fly ashes with values ranging from seven to ten times greater depending upon the pore size (Table 1). Powdered coconut charcoal carbon content was approximately 73% with a very large surface area of 1100 m²/g (Table 1).

Finally, the Class C fly ashes when added to the sediments were observed to cause them to solidify in their consistency. This quality of a fly ash, called pozzolanicity (ability to react with calcium hydroxide to form solid-phase calcium silicate hydrates), is an advantage as a cement additive, but not necessarily desirable in an environmental remediation method.

Effects of Fly Ashes on Sediment Toxicity

Mysid survival in the LIS reference sediments without any fly ash added ranged from 87 to 97% (Table 3). Conversely, in some cases, mysid survival in LIS sediment amended with fly ashes showed significant toxicity. For example, exposure to Class C 0.84% and 1.3%, as well as the Class F 33.6% and Class F 35% fly ashes, resulted in statistically significant reductions in survival in LIS. Both of the Class C fly ashes were toxic suggesting some characteristic of this type of ash, possibly related to pozzolanicity, causes toxicity. Both of these organisms interact with sediment surfaces, anything that reduces that interaction, like the sediment hardening caused by fly ash pozzolanicity, may result in additional stress. The

Class F 6.1%, Class F 33.6% de-aerated, and all doses of the Class F 65.5% fly ash (5, 10 and 20%) showed no significant toxicity. The coconut charcoal treatment demonstrated nearly 100% survival. Exposure of the mysid to ER and ER with fly ash amendments resulted in significant toxicity in many treatments (Table 3). However, the presence of fly ash with the ER sediment reduced toxicity in all doses of the Class F 35% and 65.5% fly ashes and coconut charcoal treatments. Toxicity reductions in the rinsed Class F 65.5% treatments were only marginal. In contrast, in the 5% and 10% (non-rinsed) and 20% Class F 65.5%, 20% Class F 35%, and coconut charcoal amendments, toxicity reductions were significant as compared to the ER non-amended treatments. In all other treatments, the fly ash did not significantly reduce toxicity to the mysid including in the rinsed treatments.

Amphipod survival in the LIS sediment was between 97% and 100% (Table 3). Adverse effects of the fly ashes on amphipod survival in LIS sediment were less severe than on the mysid. When compared to the LIS treatments, the only statistically significantly toxic fly ashes were the Class F 33.6% and Class F 65.5% (20% amendment only). However, the deaerated form of Class F 33.6% was not toxic (as also observed with the mysid). As with the mysid, the coconut charcoal did not cause any significant toxicity to the amphipod. In contrast, exposure of the amphipod to ER and ER with fly ash amendments caused significant toxicity in several treatments (Table 3). Presence of three fly ashes, including Class F 33.6%, Class F 35%, and all doses of Class F 65.5% (except 5% rinsed treatment), resulted in a significant decrease in toxicity as compared to the non-amended ER sediments. The coconut charcoal also removed a significant portion of observed toxicity caused by ER sediment.

Despite the observed mortality associated with some of the fly ashes as compared to LIS, when the survival data for both species in the Elizabeth River treatments are presented versus the amount of carbon added to each exposure chamber (using LOI or elemental analysis data), a linear relationship is found (Fig. 1). The relationship is significant with an r^2 of 0.56 and $p \ll 0.05$. These data, along with the research of others discussed earlier, suggest the carbon associated with the fly ash is acting as a form of highly adsorbent black carbon which sequesters the PAHs to the sediment-fly ash mixture and reduces bioavailability as manifested here by toxicity. Consequently, considerations for using fly ash as a contaminated sediment remediation amendment, should involve ashes with the higher carbon contents. However, the high carbon fly ashes were often toxic when tested with our reference sediment. Understanding the potential causes of this toxicity will be needed to use fly ash in a viable remedial application.

Finally, the amendment of fly ash to the LIS and ER sediments did result in an increase in overlying water pH in the toxicity testing chambers. In the LIS sediments, the increase in pH averaged 0.17, 0.59 and 0.93 for the 5%, 10% and 20% additions of the Class F 65.5% fly ash, respectively. In the ER sediment, the increases were smaller with changes of 0.24, 0.42 and 0.34 for the 5%, 10% and 20% additions of Class F 65.5% fly ash, respectively. For the other fly ashes added at 20%, the mean pH increase in the overlying waters of the LIS treatments was 1.17 ± 0.15 and the increase in the ER treatments was 0.16 ± 0.22 . While these changes in pH are unlikely to be toxic by themselves to the mysid and amphipod used in the present study, the increases in pH may have implications for the toxicity of any pH-dependent toxicants, like ammonia, associated with the fly ashes. This may contribute to understanding the causes of apparent fly ash toxicity observed in the LIS reference sediment amendments.

Suspected Effects of Ammonia on Toxicity

The presence of ammonia may explain the toxicity observed with some of the fly ashes when added to the LIS reference sediment. Two fly ashes were from coal fired power plants

that use selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) technologies to control acid rain causing nitric oxide (NO_x) emissions. These technologies can also result in ammonia residues, including ammonium sulfates, associated with the organic and inorganic components of the fly ash [29]. Class F fly ashes with 33.6% and 65.5% LOI were treated with these technologies (Table 1). In general, the amount of total ammonia (NH_x) measured in the overlying waters of the exposure chambers on the last day of the test increased with increasing LOI values (Table 3). For example, in the LIS treatments, the Class F fly ashes 33.6% and 65.5% have total ammonia concentrations of 12.8 mg/L and 15 mg/L, respectively. Both of these were treated with SCR or SNCR and are among the more toxic fly ashes when added to the LIS sediment (Table 3). Although the mysids found the Class C fly ashes just as toxic. In contrast, the Class F 35% fly ash was not treated with SCR or SNCR and had relatively low toxicity and total ammonia concentrations in the LIS treatment despite having high LOI (Tables 1, 3). This fly ash was also effective at reducing the toxicity of the ER sediment (Table 3). Interestingly, the de-aeration process resulted in the Class F 33.6% sediment having greatly reduced overlying water ammonia concentrations and being less toxic to both species (Table 3).

In aqueous solution, the toxic component of total ammonia (NH_x) is ammonia (NH_3), a non-ionic substance toxic to both the mysid and amphipod [30–32] with the median lethal concentration (LC_{50} s) ranging from approximately 0.5 to 5.0 mg/L. Long Island Sound reference sediment overlying water NH_3 concentrations for fly ash treatments with LOI of 33.6% and 65.5% easily extended into this range with values from 0.9 to 1.1 mg/L. Figure 2 reports survival versus overlying water NH_3 concentrations, with a strong and significant relationship between amphipod survival and NH_3 ($r^2 = 0.91$; $p = \ll 0.05$). The relationship for mysids was less strong with a r^2 of only 0.23 and an insignificant p value (0.07). This apparent disagreement between the species' responses may reflect the amphipod's exposure via the sediments, where the fly ash ammonia is present at the greatest concentrations, and the mysid's exposure via the water column where the NH_3 concentrations may be, by comparison, diluted. Further, the mysids may be responding to an unidentified toxicant.

The de-aeration process used in the present study involved placing the fly ash, or coconut charcoal, in a de-ionized water solution under a vacuum for approximately 18 h. It would appear that the vacuum treatment effectively removes toxic NH_3 from the fly ash. Gao et al. [29] evaluated several other dry and semi-dry methods for removing ammonia from fly ash including static and flowing humid air, water aerosols (fog), and ozonation with and without chemical oxidation. Methods using flowing humid air and water aerosols showed the most promise in reducing ammonia concentrations [29]. In the present study, use of water to simply rinse the fly ash also appeared to reduce ammonia concentrations (Table 3). Unfortunately, both the de-aeration and rinsing processes appeared to limit the effectiveness of the fly ashes at reducing the toxicity of the contaminated sediment (Table 3). Toxicity data from the current study indicates using fly ashes, especially SCR and SNCR treated, as capping material at contaminated sites would require the ash be cleaned of ammonia in some fashion not affecting its ability to reduce contaminant bioavailability before application. However, higher LOI fly ashes not SCR or SNCR treated, like the Class F 35% used in the present study, are also available.

Finally, despite the suggested relationship between observed toxicity and the presence of ammonia in some fly ash treatments, other toxicants could be active. Specifically, these other toxicants could include water soluble organic contaminants and/or metals (see discussion of metals below). Further, the vacuum de-aeration process used to wet the fly ash along with the DI water rinsing would, in principle, also remove potentially toxic volatile

organic contaminants. The roles of volatile organic contaminants and other toxicants in causing fly ash related toxicity need to be examined further.

Effects of Fly Ashes on Overlying Water PAHs and Cationic Metals

Addition of fly ash nearly universally reduced the concentrations of PAHs measured in the overlying water of the exposure chambers after seven days. In the LIS reference sediment treatments (data not shown), the sediment alone resulted in very low levels of five PAHs being detected in the overlying waters, with all at concentrations less than 4 µg/L. In the Class C 1.3% treatment, three PAHs were measured in the overlying water but at concentrations equal to or less than 1 µg/L. In the other treatments, overlying water PAH concentrations were below detection. Given the relatively low concentrations of PAHs typically found in LIS sediment (Table 2), these overlying water concentrations were expected. Overall, in the ER treatments with fly ash present (Table 4), as the PAHs increased in molecular weight, the amount present in the overlying water decreased as compared to the ER treatment without fly ash (or coconut charcoal). More specifically, in the ER treatments, the observed trend was that as LOI values increase, the concentration of PAHs in the overlying water decreases. Consequently, in the Class F 35% and 65.5% fly ashes, few PAHs were detected in the overlying water and at levels less than 1 µg/L. Similarly, concentrations of PAHs in the overlying water of Class F 33.6% fly ash (regular and de-aerated) were relatively low compared to the low LOI fly ashes. Figure 3 reports the overlying water concentration of total PAHs (sum of the 13 PAHs measured) versus the amount of carbon added to the exposure chambers. As in Figure 1 for toxicity, the concentration of total PAHs is shown to decrease as the amount of carbon increases resulting in a strong correlation ($r^2 = 0.88$) and significant relationship ($p \ll 0.05$). The Class C fly ashes demonstrated, in some cases, elevated concentrations of low and medium molecular weight PAHs in the overlying water especially fluoranthene and pyrene (Table 4). This may indicate Class C fly ash is releasing PAHs. However, previous analysis of Class C fly ashes in our laboratory found very little or no PAHs to be extractable [19]. This type of possible release was not observed with any of the Class F fly ashes or in the LIS treatments. It may also be possible that the ER water extracts from treatments amended with Class C fly ashes were contaminated with small sediment particles, artificially elevating the overlying water concentrations. However, the concentrations of the higher molecular weight PAHs in these samples do not follow the trend expected if this were the case when compared to the treatment containing only ER sediments.

Unlike the PAHs, the cationic metals cadmium, copper, nickel and lead were not detected in the overlying water of any sediment treatments. Given the relatively low concentrations of cationic metals associated with both LIS and ER, the lack of elevated concentrations in the overlying water was expected (Table 2). Further, leaching of cationic metals into the overlying water from the fly ash treated samples was not observed, suggesting, at least preliminarily, that the fly ashes did not represent a risk of toxic exposure for these metals. Other metals associated with fly ash include mercury, arsenic and selenium, when evaluating the possible adverse effects of fly ash further research on the release of these metals is recommended [33].

Effects of Fly Ash on Polychaete Mass, Lipid Content and Contaminant Accumulation

There has been some concern expressed about the implications of adding carbon-rich materials to environmental sediments because of possible adverse effects to indigenous organisms. For example, Jonker et al. [34] reported reductions in the lipid mass of oligochaete worms (*Limnodrilus sp.*) exposed to PCB contaminated sediments amended with anthracite coal and charcoal. Further, research by Millward et al. [8] showed that despite reductions in PCB bioaccumulation by the polychaete *Neanthes arenaceodentata*

when activated carbon was amended into contaminated field sediments, the worm demonstrated reduced growth rates. Finally, McLeod et al. [9] reported that bivalves (*Macoma balthica*) showed lower condition indices when exposed to PCB contaminated field sediments amended with activated carbon. These findings suggest the addition of certain carbon-rich materials may have adverse ecological effects.

In the current study, addition of fly ash at 5% and 10% doses did not significantly affect worm growth during the 28 d exposures (Table 5). The reference sediment showed a larger change in growth but not significantly. Interestingly, the presence of fly ash resulted in an increasing trend in lipid content in the polychaetes as fly ash dose increased but the trend was not significant despite the tripling of lipid mass in the 10% fly ash treatment as compared to the reference sediments. These preliminary data suggest that the presence of coal fly ash does not significantly reduce growth or lipid content in worms. As the bioaccumulation data are preliminary, further evaluation of the effects of coal fly ash on organism growth and lipid content are necessary to definitively address this question.

Fly ash may contain several potentially toxic contaminants as residues resulting from the burning of coal. These contaminants may include PAHs and mercury [19,35]. The presence or possible presence of these contaminants has generated concerns about use of fly ashes for environmental remediation. Analysis of the worm tissues for PAHs in the current study found none were detectable (Table 5). This finding is not unexpected for at least two reasons. First, several studies have shown that polychaetes, like *N. virens*, have the capability to efficiently metabolize PAHs [36]. In future research, to get a better assessment of the bioavailability of PAHs from a fly ash exposure, use of a non-PAH metabolizing species is recommended. Second, PAHs, when associated with fly ash, are extremely difficult to remove even using laboratory solvent extraction techniques [19]. In addition, Vaporil et al. [37] reported the results of using the gut juice of the estuarine lug worm *Arenicola marina* to extract PAHs from several forms of black carbon including diesel soot, coal dust and a Class F fly ash. Gut juice was unable to extract any PAHs from the fly ash whereas several of the other forms of black carbon did release PAHs.

For the fly ashes evaluated in the current study, concentrations of mercury ranged from approximately 4 to 1500 µg/Kg (Table 1). However, analysis of mercury in worm tissues resulted in a range of 175 to 271 µg/Kg (dry) with the LIS sediments having the greatest concentrations followed by the 10% fly ash addition (Table 5). Although published mercury bioaccumulation data for polychaetes is limited, these values are similar to those reported in the polychaete *Maldanes sarsi* collected from relatively pristine waters of the Barents Sea: 130 to 450 µg/Kg (dry) [38]. Overall, despite the elevated levels of mercury in the Class F 65.5% fly ash, the data suggested mercury was not readily released during the 28 d bioaccumulation study. These data, while preliminary, agree with leaching studies in which mercury was not shown to readily release from fly ash into the aqueous phase even when very high concentrations of ammonia (1000 mg NH₃/L) were used to enhance mercury dissolution from the ash [33,35,39].

Finally, by comparison to the static toxicity testing chambers discussed above, in the flow through bioaccumulation chambers, water column pHs in both the 5% and 10% fly ash treatments increased by only 0.02 and ammonia concentrations were below detection limits.

SUMMARY

In the present study, fly ashes with elevated LOI values (greater than 30%) showed promise for reducing the toxicity of a PAH contaminated sediment. Further, these fly ashes also reduced concentrations of PAHs in the overlying water. The presence of ammonia associated with some of the fly ashes may have contributed to toxicity in the LIS reference

treatments. Future potential use of fly ash as a remedial tool will require research to confirm the role of ammonia and determine the most effective way to reduce stress caused by ammonia while not hindering the effectiveness of fly ash in reducing toxicity caused by NOCs. Methods discussed by Goa et al. [29] show promise as simple techniques for addressing elevated levels of ammonia associated with some fly ashes. It is again worth noting that the 35% LOI Class F fly ash was not treated to reduce NO_x emissions and demonstrated relatively low toxicity to the mysid and no toxicity to the amphipod in the reference sediments. Further, this fly ash effectively reduced the toxicity of the contaminated sediment to both species. While toxic cationic metals were not observed to leach from the fly ash into the overlying water of the exposure chambers, the possible involvement of volatile organic contaminants in observed toxicity in the reference sediment needs to be investigated further. Preliminary bioaccumulation results suggest high LOI fly ash does not adversely affect polychaete growth or lipid content. Further, neither PAHs nor mercury were found to accumulate in exposed animals. However, these findings are preliminary and would need to be investigated further preferably in very long-term bioaccumulation studies (greater than 28 d).

Interestingly, the most effective fly ashes samples for reducing toxicity and PAH concentrations were the poorest candidates for use in making concrete (based on high foam indices (Table 1)). This observation suggests the potential use of fly ash for remediation would not compete with uses in concrete manufacturing. If coal fly ash is demonstrated to be environmentally safe, given its' wide availability and low costs, especially compared to more expensive sediment amendments, it may prove to be a very cost-effective remedial method. However, before use in the environment, further research is needed to fully assess potential ammonia or other contaminant toxicity from fly ash (volatile organics, arsenic, selenium, boron), possible ecological effects of fly ash amendments in the field, mercury bioavailability, and importance of carbon in fly ash performance.

Acknowledgments

We thank Denise Champlin, Anne Kuhn, Joseph LiVolsi, Wayne Munns and Steven Rego for internal review comments.

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Figure 1.

Effects of fly ash and coconut charcoal carbon amendments on mean test species survival in the Elizabeth River treatments. Linear regression shown for all data with both species (including coconut charcoal). Note: fly ash carbon is semi-quantitatively based on loss on ignition (LOI) measurements.

Figure 2. Relationship between mean overlying water unionized ammonia (NH₃) concentrations and mean test species' survival in the Long Island Sound reference sediment. Regression lines are solid and dashed for the amphipod *Ampelisca abdita* and mysid *Americamysis bahia*, respectively.

Figure 3. Effects of fly ash and coconut charcoal carbon addition on mean overlying water total polycyclic aromatic hydrocarbon (PAH) concentrations. Note: fly ash carbon is semi-quantitatively based on loss on ignition (LOI) measurements.

Table 1

Characteristics of fly ashes and coconut charcoal amended into sediments in this study. See text for analysis descriptions. Mean values are reported with variability associated with characterizations approximately 5–20%.

Fly Ash or Sample Designation	Loss on Ignition (%)	Class	Surface Area (m ² /g)	Foam Index (ml/2 g fly ash)	Micropores (mL/g-carbon)	Mesopores (mL/g-carbon)	Macropores (mL/g-carbon)	Nitric oxides (NO _x) Treated ?	Mercury (µg/Kg dry)
68	0.84	C	3.46 ^b	0.057	0.171	0.117	0.082	No	3.76 ± 0.33
75	1.3	C	5.68 ^b	0.096	0.183	0.104	0.031	No	10.7 ± 0.95
21	6.1	F	3.8 ^b	0.3	0.025	0.026	0.013	No	186 ± 8.62
22	33.6	F	17.7 ^b	1.2	0.025	0.016	0.009	Yes	461 ± 45.7
30	35	F	15.2 ^b	1.46	0.020	0.024	0.021	No	1190 ± 126
23	65.5	F	35.3 ^b	2.42	0.025	0.015	0.008	Yes	1470 ± 450
Coconut Charcoal	73.4 ^a	-	1100 ^c	-	-	-	-	-	-

^a % carbon.

^b Values reported after removing minor inorganic contributions (0.7 to 0.8 m²/g).

^c From Lebo et al. [23].

- Not available.

Table 2

Representative concentrations of polycyclic aromatic hydrocarbons (PAHs) and cationic metals in sediments from Long Island Sound (LIS) and Elizabeth River (ER). From Ho et al. [25].

Contaminant	Sediment	
	Long Island Sound (LIS) ^a	Elizabeth River (ER)
Polycyclic Aromatic Hydrocarbon (µg/Kg dry)		
Fluorene	-	210000
Phenanthrene	120	560000
Anthracene	-	67000
Fluoranthene	320	280000
Pyrene	380	190000
Benz[<i>a</i>]anthracene	140	42000
Chrysene	300	41000
Benzo[<i>e</i>]Pyrene	280	14000
Benzo[<i>a</i>]Pyrene	190	18000
Perylene	-	4900
Indeno[1,2,3- <i>cd</i>]Pyrene	-	4900
Dibenz[<i>ah</i>]Anthracene	-	1700
Benzo[<i>ghi</i>]perylene	210	4700
Metals (mg/Kg dry)		
Cadmium	<0.6	<0.6
Copper	47.7	93.8
Nickel	29.8	23.6
Lead	40.0	72.1

^a 1998 LIS sampling.

- Not detected.

Table 3

Mysid (*Americanysis bahia*) and amphipod (*Ampelisca abdita*) survival after exposure for seven days to reference and contaminated sediments amended with fly ash.

Treatment (Loss on Ignition (LOI))	Survival (%)		Ammonia (mg/L)	
	<i>A. bahia</i>	<i>A. abdita</i>	NH _x	NH ₃
<i>Long Island Sound (LIS)</i>				
<i>5 % Fly Ash Addition</i>				
LIS	97 ± 6	97 ± 6	<1.4 ± 0.0	<0.1 ± 0.0
LIS + Class F 65.5%	90 ± 14	95 ± 7	1.5 ± 0.1	<0.1 ± 0.1
LIS + Class F 65.5% (rinsed)	100 ± 0	95 ± 7	<1.4 ± 0.0	<0.1 ± 0.0
<i>10 % Fly Ash Addition</i>				
LIS	97 ± 6	100 ± 0	< 1.0 ± 0.3	<0.1 ± 0.0
LIS + Class F 65.5%	95 ± 7	100 ± 0	6.8 ± 0.7	0.1 ± 0.0
LIS + Class F 65.5% (rinsed)	100 ± 0	100 ± 0	1.2 ± 0.3	<0.1 ± 0.0
<i>20 % Fly Ash Addition</i>				
LIS	87 ± 15	100 ± 0	< 1.4 ± 0.3	<0.1 ± 0.1
LIS + Class C 0.84%	30 ± 30 [*]	90 ± 0	4.4 ± 0.4	0.3 ± 0.0
LIS + Class C 1.3%	13 ± 15 [*]	73 ± 29	4.7 ± 0.2	0.3 ± 0.0
LIS + Class F 6.1%	93 ± 6	73 ± 31	<1.0	0.1 ± 0.1
LIS + Class F 33.6%	33 ± 21 [*]	27 ± 29 [*]	12.8 ± 2.2	0.9 ± 0.1
LIS + Class F 33.6% (de-aerated)	93 ± 6	93 ± 12	< 1.7 ± 0.7	<0.1 ± 0.1
LIS + Class F 35%	55 ± 7 [*]	95 ± 7	5.2 ± 0.5	0.1 ± 0.0
LIS + Class F 65.5%	73 ± 15	23 ± 25 [*]	15 ± 0.1	1.1 ± 0.1
LIS + Coconut Charcoal	97 ± 6	93 ± 12	< 1.4 ± 0.3	<0.1 ± 0.1
<i>Elizabeth River (ER)</i>				
<i>5 % Fly Ash Addition</i>				
ER	0 ± 0 [*]	0 ± 0 [*]	3.9 ± 0.1	<0.1 ± 0.0
ER + Class F 65.5%	40 ± 0 ^{##}	50 ± 28 ^{##}	3.3 ± 0.5	<0.1 ± 0.1

Treatment (Loss on Ignition (LOI))	Survival (%)		Ammonia (mg/L)	
	<i>A. bahia</i>	<i>A. abdita</i>	NH _x	NH ₃
ER + Class F 65.5% (rinsed)	5 ± 7 [*]	0 ± 0 [*]	3.3 ± 0.5	<0.1 ± 0.0
10 % Fly Ash Addition				
ER	0 ± 0 [*]	0 ± 0 [*]	3.6 ± 0.2	<0.1 ± 0.0
ER + Class F 65.5%	100 ± 0 [#]	70 ± 14 ^{**#}	4.8 ± 0.2	0.1 ± 0.0
ER + Class F 65.5% (rinsed)	5 ± 7 [*]	20 ± 14 ^{**#}	3.6 ± 0.1	0.1 ± 0.0
20% Fly Ash Addition				
ER	0 ± 0 [*]	0 ± 0 [*]	5.3 ± 0.7	0.2 ± 0.1
ER + Class C 0.84%	0 ± 0 [*]	0 ± 0 [*]	4.8 ± 0.1	0.3 ± 0.1
ER + Class C 1.3%	0 ± 0 [*]	0 ± 0 [*]	4.5 ± 0.5	0.3 ± 0.1
ER + Class F 6.1%	0 ± 0 [*]	3 ± 6 [*]	4.4 ± 0.2	0.1 ± 0.1
ER + Class F 33.6%	0 ± 0 [*]	37 ± 25 ^{**#}	15 ± 0.3	0.9 ± 0.1
ER + Class F 33.6% (de-aerated)	0 ± 0 [*]	0 ± 0 [*]	5.4 ± 0.6	0.3 ± 0.1
ER + Class F 35%	70 ± 14 ^{**#}	85 ± 7 ^{**#}	3.0 ± 0.1	<0.1 ± 0.0
ER + Class F 65.5%	60 ± 17 [#]	73 ± 12 [#]	15 ± 0.5	0.8 ± 0.1
ER + Coconut Charcoal	100 ± 0 [#]	83 ± 15 [#]	3.1 ± 0.1	0.1 ± 0.1

^{*} indicates a significant decrease in survival as compared to the reference Long Island Sound treatment ($p = 0.05$) and

[#] indicates a significant increase in survival as compared to the Elizabeth River non-amended treatment ($p = 0.05$).

Concentrations of total ammonia (NH_x) and unionized ammonia (NH₃) in overlying waters after seven days of exposure. Initial water concentrations were < 1.0 mg NH_x/L. Shown is the mean ± standard deviation ($n = 2$ or 3).

Table 4

Concentration of polycyclic aromatic hydrocarbons (PAHs) released into overlying waters from Elizabeth River sediment in the 20% addition treatments after seven days of exposure. Shown is the mean $\pm$ standard deviation ($n = 2$).

	Polycyclic Aromatic Hydrocarbons (µg/L)												
Treatment	Flu ^a	Ph ^b	Ant ^c	Flu ^d	Py ^e	BaA ^f	Chr ^g	BeP ^h	BaP ⁱ	P ^j	IP ^k	DahA ^l	BghiP ^m
Elizabeth River (ER) only	1.0 ± 0.2	1.5 ± 0.2	2.7 ± 0.1	3.6 ± 1.2	2.7 ± 0.3	1.6 ± 0.6	2.7 ± 0.8	5.4 ± 1.1	2.5 ± 1.0	2.0 ± 0.8	2.1 ± 0.1	1.7 ± 0.2	2.1 ± 0.1
ER + Class C 0.84%	2.9 ± 2.2	0.7 ± 0.1	3.0 ± 0.6	20 ± 0.9	12 ± 0.4	1.3 ± 0.1	1.7 ± 0.1	0.3 ± 0.4	0.3 ± 0.4	-	0.6 ± 0.1	0.5 ± 0.1	0.6 ± 0.1
ER + Class C 1.3%	2.1 ± 0.8	1.6 ± 0.3	3.2 ± 0.4	18 ± 2.8	9.9 ± 0.7	1.8 ± 0.4	2.4 ± 0.9	2.2 ± 1.1	1.6 ± 0.7	1.4 ± 0.7	1.5 ± 0.5	1.4 ± 0.6	1.5 ± 0.4
ER + Class F 6.1%	1.1 ± 0.1	1.2 ± 0.1	1.5 ± 0.2	1.6 ± 0.1	1.9 ± 0.1	0.8 ± 0.1	1.1 ± 0.1	1.1 ± 0.2	0.9 ± 0.2	0.7 ± 0.2	1.3 ± 0.2	1.2 ± 0.2	1.4 ± 0.1
ER + Class F 33.6%	0.6 ± 0.1	0.7 ± 0.1	1.1 ± 0.1	1.3 ± 0.1	1.6 ± 0.1	0.6 ± 0.1	1.8 ± 0.2	2.2 ± 0.6	0.3 ± 0.4	0.7 ± 0.1	1.0 ± 0.1	0.6 ± 0.1	1.0 ± 0.1
ER + Class F 33.6% (de-aerated)	-	0.8 ± 0.2	0.4 ± 0.6	1.6 ± 0.1	1.3 ± 0.3	0.6 ± 0.1	1.0 ± 0.1	1.3 ± 0.1	0.3 ± 0.4	-	0.4 ± 0.5	-	0.9 ± 0.1
ER + Class F 35%	-	-	-	0.1 ± 0.2	-	-	-	-	-	-	-	-	-
ER + Class F 65.5%	-	-	-	0.6 ± 0.1	0.7 ± 0.1	-	0.7 ± 0.1	0.6 ± 0.1	-	-	-	-	-
ER + Coconut Charcoal	-	0.9 ± 0.1	0.6 ± 0.1	0.8 ± 0.2	0.9 ± 0.2	-	0.8 ± 0.3	-	-	-	-	-	-

^aFluorene,

^bPhenanthrene,

^cAnthracene,

^dFluoranthene,

^ePyrene,

^fBenz[*a*]anthracene,

^gChrysene,

^hBenz[*e*]pyrene,

ⁱBenz[*a*]pyrene,

^jPerylene,

^kIndeno[1,2,3-*cd*]pyrene,

^lDibenz[*ah*]anthracene,

^mBenz[*ghi*]perylene

- Not detected

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Change in wet tissue mass, lipid content, tissue polycyclic aromatic hydrocarbon (PAH) concentrations, and tissue mercury concentrations during preliminary 28 day bioaccumulation study with Long Island Sound reference sediment amended with 65.5% loss on ignition (LOI) Class F fly ash in 5% and 10% additions. Shown is the mean $\pm$ standard deviation ($n = 3$).

Table 5

Treatment	Fly ash Addition (%)	Change in Mass (mg wet) ^a	Lipid (% organism dry)	Total PAH (mg/Kg dry)	Mercury (µg/Kg dry)
Long Island Sound (LIS)	0	546 $\pm$ 388	7.6 $\pm$ 4.5	-	271 $\pm$ 47.1
LIS + 65.5%	5	319 $\pm$ 33	11 $\pm$ 4.2	-	175 $\pm$ 15.7
LIS + 65.5%	10	450 $\pm$ 279	25 $\pm$ 16	-	238 $\pm$ 77.9

^aDay 28 mass (wet) – initial mass (wet).

- Not detected.