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Metal Leaching from Experimental Coal Fly-Ash Oyster Cultch

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Coal combustion in electric power generation is predicted to produce 1.8 x 10^8 metric tons of ash annually by the year 2000. Among the numerous uses proposed for incineration residue, two involve placement in the marine environment. Ash-cement aggregates have been used to construct experimental artificial reefs and, more recently, as cultch for oyster (Crassostrea virginica) settlement and cultivation (Parker et al. 1985).

Studies of ash-cement aggregate in the marine environment suggest low metals release rates. Limited studies also suggest there is little accumulation of metals in the tissues of reef-associated marine fauna (see Parker et al. 1985). However, opponents of the use of ash-cement aggregates for artificial reef construction find no conclusive evidence for the long-term environmental safety of the material in the existing data. There are no reports of metal accumulation in oysters grown on ash aggregates, but studies are few and limited in the suite of metals examined (see review in Price et al. 1991). Because oysters accumulate metals far in excess of ambient concentrations (eg. Lytle and Lytle 1982, Eisler 1986), potential leaching and bioaccumulation of metals may be important public health concerns where ash-cement aggregates are being considered for oyster cultivation. This study examined the potential for metal release from an ash-cement aggregate proposed for use in oyster reef construction in Mississippi coastal waters.

MATERIALS AND METHODS

Simple controlled leaching experiments provide an unambiguous chemical test of the biological availability of metals. Such experiments expose the metal-containing material to seawater in a replicated treatment. The concentrations of a suite of metals are then compared, either both before and after exposure in the treatment, to control values or to standards.

A mixture of fly-ash (92.5 %, dry weight) and type II Portland cement (7.5 %) was formed into rough pellets (12.70-19.05 mm diameter) and clusters of fused pellets (up to 30 cm diameter). This material was cured for 48 hr and stored outdoors for 6 mo.

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A strict metals sampling protocol was developed in conjunction with the analytical laboratories responsible for metals analysis. Seven acid-washed aquaria were each filled with 77 L of artificial seawater (Instant Ocean, 1.6% salinity) made up with glass distilled water. These salinity conditions approximate the waters of the major Mississippi oyster grounds. Five randomly selected aquaria each received 8.6 L of aggregate pellets (Treatment). Material volumes were determined by displacement. Two control aquaria were established. One received 8.6 L of unwashed dredged clam shell used in the state oyster reef planting programs (Clam Shell Control). The second contained only 8.6 L of 1.6% salinity artificial seawater (Water Only Control). Limited resources dictated this parsimonious design. Treatment replication improved the accuracy of metals concentration estimates. The two control aquaria were treated as independent standards against which treatment means were statistically compared. Each aquarium was covered with plastic film and aerated using a single airstone. Water samples (500 ml) were collected with acid-washed glassware, sealed, frozen and stored at -25 °C until analysis. Samples were taken from each aquarium one hour after the start of the experiment (January 12, 1989) and at 10-day intervals on six subsequent sampling dates (through March 13, 1989). State authorities required that the trials evaluate leaching of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb) manganese (Mn), mercury (Hg), nickel (Ni), selenium (Se), and zinc (Zn) from the ash aggregate.

Metals analyses were carried out at the School of Veterinary Medicine Analytical Laboratory and, for mercury, at the State Analytical Laboratory. Both are state and federally certified metals analysis facilities. Atomic absorption spectrophotometry (AA), using a Perkin-Elmer AAS-5000, with an acetylene-air flame head, was used to determine the concentrations of arsenic, chromium (total and Cr^{6+}), manganese, iron, zinc, cadmium, nickel, copper and lead in the filtered water (45 micron filter) samples. Arsenic, chromium and manganese were determined by graphite furnace-AAS using a Perkin-Elmer HGA-500 (see Perkin-Elmer Corporation 1978 for analytical procedures). The remainder were read from an acetylene-air flame. Determination of iron, zinc, cadmium, nickel, copper, lead and hexavalent chromium followed procedures described in Perkin-Elmer Corporation (1971). The flameless, cold cell vapor technique, using an IL 351 AAS with the mercury cold vapor generator attachment, was used for the determination of mercury (see Perkin-Elmer Corporation 1971 for analytical procedures). A Perkin-Elmer MPF-44B fluorescence spectrophotometer was used for selenium.

RESULTS AND DISCUSSION

Three metals (cadmium, iron and mercury) were essentially not detected in the treatment aquaria and are not considered further. Except for chromium, the mean concentrations of metals in the treatment samples were generally less than 10 ppb (Table 1). An overall comparison (Friedman's analysis of variance by ranks) of the concentrations of 8 metals among all aquaria and sampling dates (Table 2) detected significant differences in the concentrations of chromium ($p < .001$), manganese ($p < .05$) and selenium ($p < .001$). Treatment aquaria had significantly greater concentrations of chromium and selenium than did either control (nonparametric multiple comparisons, $p < .05$). Most of the chromium found in the treatment aquaria was the hexavalent form (means range from 0.052 to 1.328 ppm). Treatment

Table 1. Mean values ± standard deviations (n = 5), by sampling date, of metals concentrations (ppb) in samples from aquaria containing fly-ash aggregate.

	Metals							
DATE	As	Cr	Cu	Mn	Ni	Pb	Se	Zn
1/12/89	1.00 ±0.71	59.92 ±41.62	4.42 ±3.01	2.10 ±1.73	3.54 ±3.44	1.48 ±0.92	1.32 ±0.40	9.74 ±8.12
1/22/89	1.00 ±1.22	1008.20 ±238.31	5.30 ±2.42	7.74 ±1.24	3.16 ±3.12	1.80 ±1.93	6.09 ±2.03	15.84 ±11.40
2/1/89	1.40 ±1.34	1265.80 ±304.99	4.28 ±3.44	5.90 ±3.55	2.36 ±1.51	2.14 ±1.84	5.31 ±2.32	13.46 ±12.68
2/11/89	2.00 ±1.41	1348.20 ±265.78	7.88 ±1.74	4.10 ±3.78	1.36 ±1.95	2.36 ±3.01	7.05 ±1.97	0.36 ±0.80
2/22/89	3.20 ±2.28	1062.40 ±521.82	8.26 ±4.60	4.46 ±3.94	0.36 ±0.80	3.38 ±2.76	4.41 ±2.23	<0.50*
3/3/89	1.40 ±1.52	1102.60 ±1021.34	3.72 ±2.33	3.26 ±1.65	2.24 ±1.42	0.80 ±1.16	5.46 ±1.29	3.52 ±3.72
3/13/89	2.60 ±2.30	1254.60 ±259.77	7.44 ±3.38	2.82 ±2.52	1.04 ±1.53	1.14 ±1.11	7.63 ±2.34	9.22 ±20.56

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[1] below detection limit; values for Fe, Cd and Hg are not included because these metals were not detected.

hexavalent chromium concentrations increased over time. No hexavalent chromium was detected in either control.

While significant differences between treatment and control manganese concentrations were detected (Table 2), subsequent multiple comparisons did not clearly distinguish treatment from control aquaria. Treatment manganese concentrations were significantly greater than the water only control values (t values > $t_{.05\,(2),\,4}$) on only three of the eight sampling dates (Figure 1). However, treatment manganese concentrations were significantly less than the clam shell control values for the first three sampling dates.

Of the eleven metals we examined, most did not appear to leach from the fly-ash-cement pellets. However, selenium, chromium (primarily hexavalent Cr) and manganese have the potential to leach from the fly-ash-cement aggregate pellets under experimental conditions. With one exception, neither manganese (range below detection limit to 7.74 ppb) nor selenium (range 0.71-10.60 ppb) concentrations in the treatment water samples exceeded EPA drinking water standards (Environmental Protection Agency 1986). Total chromium and hexavalent chromium concentrations in the treatment aquaria were in excess of 10^2-10^3 ppb after only 10 d of leaching, well over EPA drinking water standards (50 ppb, Environmental Protection Agency 1986).

While concentrations of selenium in the treatment water samples were greater than the reported range for Gulf coastal waters (Lytle and Lytle 1982) or U.S. estuaries (Lytle and Lytle 1982, Eisler 1985), they were below recommended levels for the protection of aquatic life. The concentration range of total inorganic selenite currently recommended for protection of aquatic life is 35 ppb in fresh water and 54 ppb in marine waters, below the range of fatal (60-600 ppb) or sublethal concentrations (47-53 ppb) known to affect sensitive aquatic species (Eisler 1985). Treatment selenium concentrations measured in this study suggest this metal may leach from the aggregate but at low levels.

The effects of manganese leaching into the marine environment at the low levels found in this study are not well known, but are probably not of concern. Calabrese et al. (1973) report no toxic effects on oyster embryos at 5 ppm magnesium chloride, much greater levels than detected in this study. Manganese may accumulate at low rates the tissues of striped bass and white perch larvae (Wright 1987) but does not appear to affect survival of larval and yearling fish (Hall et al. 1986). Manganese does not accumulate in oysters or other benthic organisms (Guthrie et al. 1979, Wright 1987) or adult fish (Hall et al. 1978). However, it is interesting to note that manganese concentrations in the early treatment samples were significantly less than levels reported for the clam shell control. This suggests that planting fly-ash aggregate pellets may introduce less manganese into the marine environment than planting dredged clam shells.

The source fly-ash material contained high levels of chromium (37 ± 14 ppm by X-ray fluorescence, Battelle Pacific Northwest Laboratories communication to Mississippi Power Co.). Both mean and maximum chromium concentrations in the treatment aquaria were two to three orders of magnitude greater than either control and much greater than reported ambient seawater chromium concentrations in either Mississippi

Table 2. Results of tests for differences in concentrations of selected metals among all aquaria on all sampling dates (Friedman's Analysis of Variance by Ranks procedure). Asterisks indicate a significant difference (* = P<.05, ** = P<.01, *** = P<.001, N = 7).

Metal	As	Cr	Cu	Mn	Ni	Pb	Se	Zn
Chi-squared value	5.81	27.12***	10.49	15.08*	10.03	11.16	28.78***	8.68

Non-parametric multiple comparisons of mean metal concentration ranks (descending rank order from left). Similar means are underlined.

Manganese	A4	A7[1]	A2	A5	A1	A6	A3[1]
	—	—	—	—	—	—	
		—	—	—	—	—	—
Selenium	A5	A1	A4	A6	A2	A7[1]	A3[2]
	—	—	—	—	—		
				—	—	—	
					—	—	—
Chromium	A5	A4	A6	A1	A2	A7[1]	A3[2]
	—	—	—	—	—		
						—	—
		—	—	—	—	—	

[1] clam shell control.
[2] water only control.

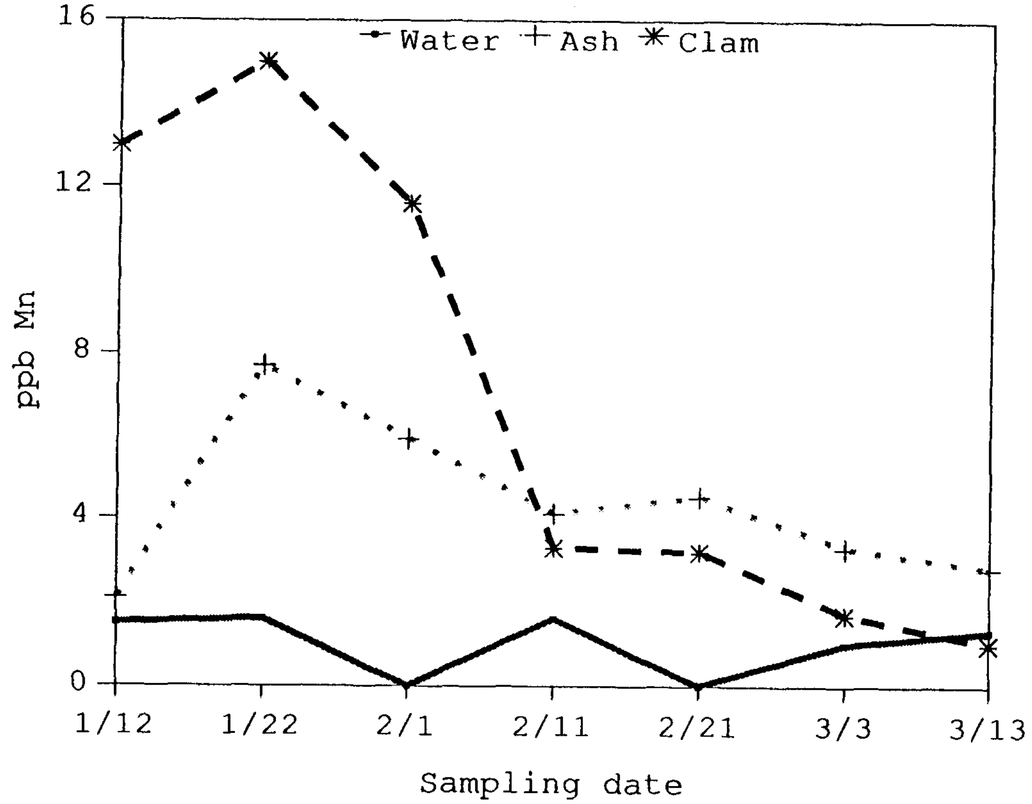

Figure 1. Concentrations (in ppb) of manganese (Mn) in water control, clam shell, and fly-ash treatment by sampling date. Value for fly-ash aquaria is the mean of 5 aquaria. Values for water only and clam shell are from single aquaria.

estuaries (<100 ppb, Lytle and Lytle 1982) or in other coastal waters (Lytle and Lytle 1982, Eisler 1986).

Hexavalent chromium, the major chromium species in the treatment aquaria (means range from 0.052 to 1.328 ppm), is considered toxic to aquatic and marine biota (Eisler 1986, U.S. Environmental Protection Agency 1986). Adverse effects of chromium to sensitive species have been documented at 10.0 ppb of hexavalent chromium in fresh water and 5.0 ppb in seawater (see review in Eisler 1986), much less than the concentrations found in the treatment aquaria. The hexavalent chromium concentrations reported in this study exceed reported acute and chronic toxicity values for many aquatic and seawater fish and invertebrate species (Eisler 1986, Environmental Protection Agency 1986).

Oysters accumulate chromium from seawater at relatively low concentrations (e.g. Shuster and Pringle 1969). Hall et al. (1978) and Eisler (1981) found that edible tissues of oysters (C. virginica) contained 0.1 to 0.6 mg/kg wet weight of chromium (100-600 ppb). Shuster and Pringle (1969) reported chromium concentrations as high as 3.4 mg Cr/kg wet weight in oysters from uncontaminated waters. While a number of studies have reported no accumulation of chromium in the tissues of oysters experimentally grown on fly-ash (see reviews in Parker et al 1985, Price et al 1991), these results remain open to interpretation. The chromium content of the fly-ash aggregate used in these studies was not reported. Chromium is difficult to analyze and may be underestimated in high salt matrices such as oyster tissues (Eisler 1986). Environmental and metabolic factors may also significantly affect accumulation rates, but in poorly understood ways (Eisler 1981, 1986).

In contrast with the findings of other studies (see reviews in Parker et al 1985, Price et al 1991), these results suggest that, under certain conditions, fly-ash cement aggregate pellets in seawater may leach metals, particularly hexavalent chromium. This raises a number of concerns. Criteria for the protection of the environment and food against chromium are numerous, disparate and often contradictory (Eisler 1986). The roles of environmental and metabolic factors that affect sensitivity and accumulation rates of chromium are also unknown. As a result, established Cr criteria should be applied conservatively in evaluating chromium threats to aquatic organisms. Potential sublethal effects, especially of hexavalent chromium, on phytoplankton (Sanders and Cibik 1988), fishes, oysters and other benthic invertebrates (Eisler 1981, 1986) at the levels detected in this study are not known.

Chromium, the most active metal in this study, is a recognized hazard to aquatic organisms and to food and water (Eisler 1986, Environmental Protection Agency 1986), and reportedly accumulates in the tissues of oysters, fishes and other organisms (Hall et al. 1978, Eisler 1986). Because leaching rates may vary with environmental conditions (particularly salinity), ash characteristics, particle size and composition, and accumulation rates also vary in response to a variety of factors (Eisler 1986), detailed site specific studies to determine the potential environmental effects of metals leaching into the environment should be conducted before any placement of fly-ash aggregate for oyster culture.

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