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AQUATIC TOXICOLOGY OF TRACE ELEMENTS OF COAL AND FLY ASH

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ABSTRACT

Aquatic bioassays were performed on 22 coal elements, with developmental and juvenile stages of fish and amphibians used as test organisms. For more sensitive test species, LC_{50} values of 0.1 ppm or less were observed for 15 trace elements, and LC_1 values ranged down to 0.1 to 0.2 ppb for mercury and silver. Studies also were performed on the aqueous leaching characteristics and toxicological properties of coal-produced fly ash. A 52-kg sample of precipitator-collected fly ash was subjected to continuous flow-through washing for 2000 consecutive hours in a bench-scale ash-settling pond. Chemical characteristics of the simulated effluent compared closely with those recorded for actual ash-settling ponds. During the first 500 hr of operation, conductivity averaged 690 μmhos/cm, and a mean of 0.56 g/liter was observed for total dissolved solids. Gradual decreases were observed thereafter. Effluent pH averaged 4.3 during the first 500 hr but approached the level of influent water (7.1 to 7.9) by 2000 hr. Maximum effluent concentrations detected for seven selected metals were 126 ppm Al, 766 ppb Zn, 518 ppb Cu, 500 ppb Cd, 370 ppb Ni, 87 ppb Hg, and 8 ppb Ag. Mean concentrations for the first 500 hr of elution were 32.6 ppm Al, 350 ppb Zn, 156 ppb Cd, 155 ppb Ni, 110 ppb Cu, 2.1 ppb Ag, and 1.8 ppb Hg. All metals except mercury reached maximum levels within 500 hr, and concentrations declined thereafter. Mean mercury levels increased to 27 and 15 ppb for the second and third 500-hr elution intervals. After 522 and 1033 hr of elution time, continuous-flow treatment with undiluted ash effluent produced 100% mortality of frog and sunfish eggs. A 0.1 dilution at 1033 hr resulted in 42% hatchability of sunfish eggs. After 1775 hr of continuous leaching, undiluted ash effluent and 0.1 and 0.01 dilutions gave survival frequencies of 57, 76, and 88% for goldfish eggs, compared with 92% for controls. Metals analyzed for undiluted effluent administered to goldfish were well below LC_1 determinations, except aluminum, which was present at the LC_{50} level.

With the increasing dependence on coal as a national energy source, there is a serious need to investigate further the effects of coal production and use on environmental health. Numerous recent studies emphasize the extent to which coal utilization has grown beyond our ability to identify fully the hazardous trace elements in coal, quantify their release rates into the environment, and define their biological and health-related effects (Ayer, 1974; Yavorsky and Akhtar, 1974; Babu, 1975; Vaughan et al., 1975). Approximately two-thirds of the over 60 elements that occur in coal have been detected as environmental pollutants (Vitez, 1976). Although toxicological data are largely incomplete, most of the elements found in coal and other fossil fuels are known to have at least some toxic effects on animal species (National Academy of Sciences—National Academy of Engineering, Committee, 1973; Smith, Ferguson, and Carlson, 1975; Vitez, 1976).

The annual combustion of 600 million tons of coal constitutes the major source of environmental contamination with coal trace elements (Abel and Rancitelli, 1975; Bolton et al., 1975; Sheibley, 1975). The main sources of water pollution are power plants, which dispose of more than 50 million tons/year of bottom ash and precipitated fly ash (Rubin and McMichael, 1974; Chu, Nicholas, and Ruane, 1975). Large quantities of water are used in sluicing ash residues to settling ponds, and pond effluents contain toxic metals that affect the quality of receiving waters (Theis, 1975; Hildebrand, Cushman, and Carter, 1976). For each 1000-MW capacity, sluicing-water requirements for Tennessee Valley Authority (TVA) power stations average 11.5 million gal/day or 4.2 billion gal/year (Environmental Protection Agency, 1974; Chu, Nicholas, and Ruane, 1975). Current projections indicate that the rate of coal combustion will double by the mid 1980s (Vaughan et al., 1975). Therefore, a better understanding of the aquatic toxicology of coal-derived contaminants is essential if we are to maximize coal use and also institute safeguards necessary to maintain reasonable and proper environmental health.

In this study, aquatic bioassays were performed to establish a comparative toxicological ranking for 22 coal elements, identify those which may be particularly hazardous to aquatic ecosystems, and provide quantitative data for use in further evaluations of environmental standards and pollution-abatement technology. In addition, a bench-scale settling pond was developed to simulate fly-ash effluents and to investigate the aqueous leaching of toxic elements. Continuous flow embryo—larval bioassays were used for in situ monitoring of ash effluents to provide direct toxicological evaluations on complex suites of trace elements.

MATERIALS AND METHODS

Aquatic Bioassays

Semistatic embryo—larval bioassays were performed on the goldfish *(Carassius auratus)*, the rainbow trout *(Salmo gairdneri)*, and the narrow-mouthed toad *(Gastrophryne carolinensis)* with rapid-scan procedures previously described (Birge and Just, 1975). Eggs were exposed to coal elements from fertilization through 4 days posthatching, giving treatment periods of 7 days for toads and goldfish and 28 days for trout. Test water and toxicant were renewed at regular 12-hr intervals. Mean water hardness, with standard error, was 195 ± 5.4 ppm $CaCO_3$ for goldfish and toad stages and 104 ± 2.0 for trout. Test water pH averaged 7.4 ± 0.1. Dissolved oxygen was maintained near saturation by continuous, moderate aeration. Other chemical and physical characteristics of the reconstituted test water were described by Birge and Black (1977). Water temperature was 13.0 ± 0.5°C for trout eggs and 22.0 ± 1.0°C for other species.

Test organisms were examined daily to tabulate frequencies of mortality and teratogenesis. Control adjusted LC_1 and LC_{50} values were calculated for combined test responses by log probit analysis (Daum, 1969). Anomalous survivors were counted as lethals. Control eggs were cultured simultaneously with experimentals and under identical conditions, except for omission of toxic coal elements. Minimum sample size was set at 150 eggs per culture.

The 22 coal elements and test compounds selected for bioassay analysis are given in Table 1. Depending on the degree of anticipated toxicity, exposure concentrations were initiated at 10 to 100 ppm and continued at two- to tenfold dilutions until survival of experimental animals equaled or approached that observed for controls. Each coal element was administered at 10 to 14 exposure levels. Elemental concentrations of test water were monitored by atomic absorption spectrophotometry with a model 503 Perkin—Elmer unit equipped with an HGA-2100 graphite furnace and a mercury analyzer (Perkin—Elmer Corp., 1973).

Aqueous Leaching of Fly Ash

A bench-scale Plexiglas settling pond was designed to investigate the aqueous leaching characteristics of precipitator-collected fly ash obtained from a local 1000-MW coal-fired power plant. A 52-kg sample of dry ash was deposited in an 88.2-liter settling chamber. A Gilson Minipuls II peristaltic pump (Gilson Medical Electronics, Inc.) provided a continuous flow of water over the ash bed at a rate of 1

TABLE 1

COAL TRACE ELEMENTS SELECTED FOR BIOASSAY EVALUATIONS

Trace element	Bioassay test compound	Concentration* in coal, ppm
Aluminum	$AlCl_3$	10,440—12,900
Antimony	$SbCl_3$	0.50—1.26
Arsenic	$NaAsO_2$	4.45—14.02
Cadmium	$CdCl_2$	0.47—2.52
Cobalt	$Co(NO_3)_2$	2.90—9.57
Chromium	CrO_3	13.75—18.00
Copper	$CuSO_4$	8.30—15.16
Germanium	GeO_2	1.00—6.59
Lanthanum	$LaCl_3$	3.80—10.00
Lead	$PbCl_2$	4.90—34.78
Manganese	$MnCl_2$	33.80—49.40
Mercury	$HgCl_2$	0.12—0.20
Molybdenum	Na_2MoO_4	5.00—7.54
Nickel	$NiCl_2$	16.00—21.07
Silver	$AgNO_3$	0.03—0.12
Selenium	Na_2SeO_4	2.08—2.20
Strontium	$SrCl_2$	10.00—23.00
Thallium	$TlCl_3$	0.29—2.00
Tin	$SnCl_2$	0.03—4.79
Tungsten	Na_2WO_4	0.10—3.00
Vanadium	V_2O_5	28.50—32.71
Zinc	$ZnCl_2$	46—272

*The majority of values are from Ruch, Gluskoter, and Shimp (1974), Fulkerson et al. (1975), and Carter (1975) and represent means for multiple coal samples taken largely from western Kentucky and southern Illinois. Lower means for Ag, Tl, Sn, and W are from Lloyd (1976), and the upper mean for Ag is from Vaughan et al. (1975).

liter/hr, giving a detention time of 42 hr. Water was discharged from the settling chamber into an overflow-equipped effluent reservoir. The ash-to-water ratio and the detention time were calculated to approach conditions observed for a local ash-settling pond (Freeman and Birge, 1978). Also, the detention time was in good agreement with times reported for a number of TVA ash ponds (Chu, Ruane, and Steiner, 1976). Influent and effluent water samples were taken at 1- to 2-day intervals for 2000 hr of continuous operation to observe changes in water-quality parameters. Determinations were made on pH, conductivity, alkalinity, and total dissolved solids, and analyses were performed for seven selected metals (Ag, Al, Cd, Cu, Hg, Ni, and Zn). Alkalinity and total dissolved solids were determined according to standard methods (American Public Health Association, 1975), and metals were analyzed by atomic absorption spectrophotometry. Fly ash displayed good settling characteristics, and effluent water was essentially free of ash particulates. The fly-ash bed compacted sufficiently to impede interstitial percolation, limiting water movement primarily to surface flow. Through the first 770 hr of operation, influent water was distilled and deionized and had a conductivity less than 0.25 μmhos/cm and a pH of 6.8. Total dissolved solids and trace metals were not detectable. During the remainder of the leaching period, the settling chamber was supplied with carbon-filtered tap water, which had a pH of 7.1 to 7.9, conductivity of 141 to 252 μmhos/cm, alkalinity of 54 to 70 ppm $CaCO_3$, and total dissolved solids of 0.19 to 0.24 g/liter. Water temperatures ranged from 24.4 to 26.0°C.

Bioassay Monitoring of Fly-Ash Effluent

Continuous-flow bioassays were performed on the simulated ash effluent to evaluate toxicological properties of the aqueous leachates. Eggs of the goldfish *(Carassius auratus)*, redear sunfish *(Lepomis microlophus)*, leopard frog *(Rana pipiens)*, and Fowler's toad *(Bufo fowleri)* were used as test organisms. Full-strength effluent and serial dilutions thereof were perfused continuously through 300-ml egg chambers at flow rates of 200 to 300 ml/hr. Effluent dilutions of 0.1, 0.01, 0.001, and 0.0001 were achieved with a proportional diluter (Freeman and Birge, 1978). Exposure was maintained from fertilization through hatching, and results were expressed as percent survival (hatchability). Hatching times averaged 1.5 days for Fowler's toad, 2.5 days for the leopard frog, and 3 days for sunfish and goldfish. Minimum sample size was set at 100 eggs. Control egg chambers received the same influent water as that supplied to the simulated ash-settling pond. Bioassays were initiated after 522, 1033, and 1775 hr of continuous aqueous leaching of the original 52-kg fly-ash sample.

RESULTS

Embryo–Larval Bioassays

Fish and amphibian eggs were exposed to each of 22 selecte coal elements (Table 1) from fertilization through 4 days pos hatching, giving treatment periods of 28 days for trout and 7 day for the narrow-mouthed toad and goldfish. Probit-derived LC_{50} an

LC_1 values expressed in parts per million and parts per billion, respectively, are summarized in Table 2. In order of decreasing toxicity, on the basis of LC_{50} determinations, the 12 elements most lethal to trout were Hg, Ag, La, Ge, Ni, Cu, Cd, V, Tl, Pb, Cr, and Sr. The LC_{50} values were 0.005, 0.01, and 0.02 for Hg, Ag, and La, respectively; 0.05 for Ge and Ni; 0.09 for Cu; 0.13 for Cd; and 0.16 to 0.20 for V, Tl, Pb, Cr, and Sr. The calculated LC_1's for the more toxic elements were 0.2 for Hg and Ag, 0.4 for Ge, 0.6 for Ni, 0.8 for La, 1.8 for Cu, 2.5 for Pb, and 6.0 to 6.1 for Sr and Cd (Table 2).

The goldfish was the least sensitive of the three test species. The 12 elements most toxic to goldfish eggs were Ag, Hg, Al, Cd, As, Cr, Co, Pb, Ni, Sn, Zn, and V. The LC_{50} values were 0.03, 0.12, 0.15, 0.17, 0.49, 0.66, 0.81, and 1.66 for the first eight, respectively; 2.14 for Ni and Sn; 2.54 for Zn; and 4.60 for V. The LC_1 values obtained for these metals ranged from as low as 0.4 and 0.6 ppb for Al and Ag to 400 ppb for Zn. Certain coal elements (e.g., Ag and Hg) were more toxic to fish embryos; others (e.g., Al, Cd, Ge, and Pb) exhibited considerable toxicity to posthatched juveniles.

In bioassays with the narrow-mouthed toad, the 12 most lethal elements were Hg, Ag, Zn, Cr, Pb, Cd, Cu, As, Ge, Co, Ni, and Al. The LC_{50} values were 0.001, 0.01, 0.01, and 0.03 ppm for the first four elements, respectively; 0.04 ppm for Pb, Cd, Cu, and As; and 0.05 ppm for Ge, Co, Ni, and Al. The calculated LC_1's ranged only from 0.1 and 0.6 ppb for Hg and Ag to 1.6 and 3.2 ppb for Cd and Pb.

The LC_{50} values were averaged for all animal species (Table 3) to provide a simplified toxicological index for the 22 elements. This mean toxicity index provided a convenient ranking, consisting of three general toxicity groups. Group 1 included ten highly toxic elements with mean LC_{50} values below 1 ppm; group 2 included nine elements with LC_{50} values of 1 to 5 ppm; and group 3 included three elements with an LC_{50} range of 20 to 47 ppm.

The selected coal elements were also ranked according to a most sensitive species index (Table 3) based on median lethal concentrations determined for the animal species exhibiting highest sensitivity to each of the 22 elements. The LC_{50} values ranged from 0.001 ppm Hg to 2.90 ppm W. Elements with approximately the same LC_{50} concentration were further differentiated on the basis of LC_1 values.

Aqueous Leaching of Fly Ash

A 52-kg sample of precipitator-collected fly ash was subjected to continuous washing for 2000 hr at a flow rate of 1 liter/hr.

TABLE 2

COAL-ELEMENT LC_1 AND LC_{50} VALUES WITH 95% CONFIDENCE LIMITS

Element and animal species	LC_{50}, ppm	Confidence limit Lower	Confidence limit Upper	LC_1, ppb	Confidence limit Lower	Confidence limit Upper
Aluminum						
Trout	0.56	0.40	0.70	256	52.7	371
Goldfish	0.15	0.02	0.82	0.4	0.0	5.6
Toad	0.05	0.04	0.08	2.3	0.7	4.8
Antimony						
Trout	0.58	0.34	0.92	28.6	4.6	72.2
Goldfish	11.3	3.99	55.0	111	0.1	663
Toad	0.30	0.18	0.51	3.8	0.7	10.7
Arsenic						
Trout	0.54	0.42	0.67	39.7	15.5	71.6
Goldfish	0.49	0.39	0.61	15.5	7.5	26.6
Toad	0.04	0.02	0.07	1.6	0.2	4.4
Cadmium						
Trout	0.13	0.10	0.18	6.1	1.8	12.9
Goldfish	0.17	0.13	0.21	15.0	4.4	19.2
Toad	0.04	0.03	0.05	1.6	0.9	2.5
Chromium						
Trout	0.18	0.07	0.31	19.1	0.4	56.5
Goldfish	0.66	0.40	1.10	8.1	1.5	22.1
Toad	0.03	0.03	0.04	1.0	0.6	1.5
Cobalt						
Trout	0.47	0.38	0.58	34.2	13.8	60.8
Goldfish	0.81	0.27	2.27	6.8	0.0	42.6
Toad	0.05	0.02	0.08	0.9	0.3	2.0
Copper						
Trout	0.09	0.05	0.15	1.8	1.0	4.5
Goldfish	5.20	4.13	6.41	299	101	571
Toad	0.04	0.03	0.05	1.0	0.3	1.3
Germanium						
Trout	0.05	0.03	0.07	0.4	0.1	0
Goldfish	5.60	1.76	7.84	143	2.7	567
Toad	0.05	0.03	0.08	1.2	0.1	3.8
Lanthanum						
Trout	0.02	0.01	0.04	0.8	0.0	2.7
Goldfish	60.4	30.3	105	1987	136	6503
Toad	0.29	0.19	0.43	7.5	2.3	16.2
Lead						
Trout	0.18	0.10	0.32	2.5	0.2	8.1
Goldfish	1.66	0.85	3.05	14.6	1.4	53.0
Toad	0.04	0.02	0.07	3.2	0.1	9.0
Manganese						
Trout	2.91	1.85	4.37	388	66.2	800
Goldfish	8.22	2.39	24.6	21.5	0.1	182
Toad	1.42	0.84	2.40	3.0	0.5	9.8

TABLE 2 (Continued)

Element and animal species	LC_{50}, ppm	Confidence limit Lower	Confidence limit Upper	LC_1, ppb	Confidence limit Lower	Confidence limit Upper
Mercury						
Trout	0.005	0.004	0.005	0.2	0.1	0.3
Goldfish	0.12	0.10	0.14	14.3	8.2	21.2
Toad	0.001	0.001	0.002	0.1	0.0	0.3
Molybdenum						
Trout	0.73	0.30	1.40	22.3	1.2	83.4
Goldfish	60.0	7.94	92.2	39.3	0.9	261
Toad	0.96	0.58	1.60	3.1	0.6	9.5
Nickel						
Trout	0.05	0.04	0.06	0.6	0.2	1.2
Goldfish	2.14	1.19	3.63	55.8	7.9	160
Toad	0.05	0.03	0.09	0.4	0.0	1.5
Selenium						
Trout	4.18	2.82	5.82	79.5	17.5	202
Goldfish	8.78	7.23	10.6	506	267	805
Toad	0.09	0.08	0.15	5.0	0.7	7.3
Silver						
Trout	0.01	0.01	0.02	0.2	0.1	0.4
Goldfish	0.03	0.02	0.03	0.6	0.4	0.9
Toad	0.01	0.01	0.03	0.6	0.0	2.0
Strontium						
Trout	0.20	0.10	0.38	6.0	0.3	19.9
Goldfish	8.58	2.11	21.2	45.3	0.0	396
Toad	0.16	0.12	0.21	2.4	1.0	4.6
Thallium						
Trout	0.17	0.09	0.30	8.4	0.7	24.8
Goldfish	7.00	1.94	9.96	52.5	1.1	266
Toad	0.11	0.09	0.14	2.4	1.1	4.5
Tin						
Trout	0.40	0.23	0.67	15.5	2.1	42.5
Goldfish	2.14	0.36	3.45	68.8	0.0	390
Toad	0.09	0.08	0.13	1.7	0.3	4.5
Tungsten						
Trout	15.61	6.71	31.98	828	14.2	2810
Goldfish	120	92.3	156	345	4.7	2139
Toad	2.90	2.44	3.50	10.7	4.5	21.2
Vanadium						
Trout	0.16	0.07	0.30	6.9	0.3	22.8
Goldfish	4.60	0.51	9.10	55.2	0.0	116
Toad	0.25	0.13	0.44	7.4	0.6	23.0
Zinc						
Trout	1.06	0.75	1.39	20.0	5.7	33.2
Goldfish	2.54	1.59	4.18	400	26.5	500
Toad	0.01	0.01	0.04	0.6	0.0	2.2

TABLE 3

COMPARATIVE TOXICITY OF COAL ELEMENTS TO FISH AND AMPHIBIAN EMBRYO—LARVAL STAGES

Mean toxicity index*		Most sensitive species index			
Element	LC_{50}, ppm	Element	Species	LC_{50}, ppm	LC_1, ppb
Toxicity group 1		Mercury	Toad	0.001	0.1
Silver	0.02	Silver	Trout	0.01	0.2
Mercury	0.04	Zinc	Toad	0.01	0.6
Cadmium	0.11	Lanthanum	Trout	0.02	0.8
Aluminum	0.25	Chromium	Toad	0.03	1.0
Cobalt	0.29	Copper	Toad	0.04	1.0
Arsenic	0.36	Cadmium	Toad	0.04	1.6
Chromium	0.45	Arsenic	Toad	0.04	1.6
Lead	0.62	Lead	Toad	0.04	3.2
Nickel	0.75	Nickel	Trout	0.05	0.6
Tin	0.88	Cobalt	Toad	0.05	0.9
Toxicity group 2		Germanium	Toad	0.05	1.2
Zinc	1.20	Aluminum	Toad	0.05	2.3
Vanadium	1.67	Tin	Toad	0.09	1.7
Copper	1.78	Selenium	Toad	0.09	5.0
Germanium	1.90	Thallium	Toad	0.11	2.4
Thallium	2.43	Strontium	Toad	0.16	2.4
Strontium	2.98	Vanadium	Trout	0.16	6.9
Antimony	4.07	Antimony	Toad	0.30	3.8
Manganese	4.18	Molybdenum	Trout	0.73	22.3
Selenium	4.35	Manganese	Toad	1.42	3.0
Toxicity group 3		Tungsten	Toad	2.90	10.7
Lanthanum	20.25				
Molybdenum	20.56				
Tungsten	47.17				

*LC_{50} values at 4 days posthatching averaged for three species, narrow-mouthed toad, goldfish, and rainbow trout.

Detention time was 42 hr, and water-quality parameters were plotted and averaged for each of four 500-hr elution intervals. Total dissolved solids, conductivity, and pH showed marked decreases during the first 100 hr of elution time (Fig. 1). Total dissolved solids decreased from 2.2 g/liter at 18 hr to 0.5 g/liter at 94 hr, averaging 0.56 g/liter for the first 500 hr. Conductivity (μmhos) decreased from 2400 at 20 hr to 900 at 94 hr and continued to drop slowly to 200 at 500 hr. The sharpest decline was observed for pH, which decreased from 7.7 at 1 hr to about 4.0 at 18 hr, averaging 4.3

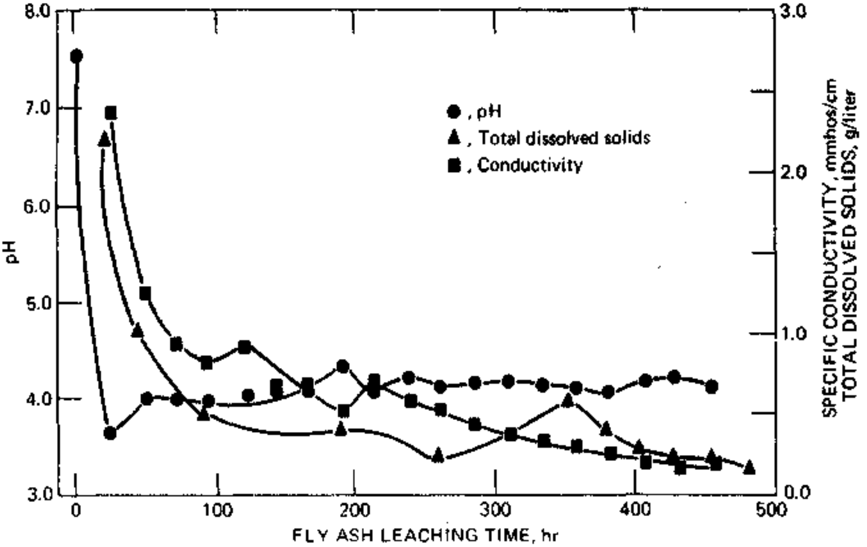

Fig. 1 Changes in fly-ash effluent with leaching time.

for the first elution interval. As seen in Fig. 1, changes in these effluent parameters were most pronounced during the initial 4 days of ash-leaching time, presumably correlating with the period during which leachable components were most rapidly removed from the fly ash. Mean values for the first 500 hr are given in Table 4.

Midway in the second elution interval, at 770 hr, the influent source was changed to carbon-filtered tap water. This action was taken to determine whether influent water of higher pH and greater buffering capacity would alter the leaching process. Initially, conductivity and total dissolved solids of the effluent rose proportionately with increases observed for the new influent water, but values for these parameters declined steadily over the third and fourth elution intervals, closely approaching those obtained for influent water by 2000 hr (see Materials and Methods section). After the change to influent tap water, effluent pH for the second elution interval increased steadily from 4.5 to 7.1. A gradual increase continued thereafter, and, during the last two elution intervals, pH ranges of 7.1 to 7.9 and 7.0 to 7.7 were recorded for influent and effluent water, respectively. Although total alkalinity was not determined during the first 1000 hr, ranges for the third and fourth elution intervals were 32 to 55 and 46 to 62 ppm $CaCO_3$, compared with 54 to 69 ppm for influent tap water. After 2000 hr of continuous washing of the original fly-ash sample, influent and

TABLE 4

CHARACTERISTICS OF SIMULATED ASH-POND EFFLUENT

Characteristic	Simulated effluent*	TVA range†
Total dissolved solids, g/liter	0.56 ± 0.17	0.14–0.52
pH	4.3 ± 0.1	4.4–11.3
Conductivity, μmhos/cm	690 ± 80	242–855
Alkalinity,‡ mg/liter $CaCO_3$	43 ± 3	40–154
Ag, μg/liter	2.1 ± 0.9	
Al, mg/liter	32.6 ± 6.1	1.4–7.2
Cd, μg/liter	156 ± 35	1–37
Cu, μg/liter	110 ± 26	10–310
Hg, μg/liter	1.8 ± 0.5	0.2–38
Ni, μg/liter	155 ± 16	31–1100
Zn, μg/liter	350 ± 33	30–1510
Input, ml/hr	969 ± 10	
Output, ml/hr	897 ± 18	
% evaporation	8 ± 2	

*Mean ± standard error for initial 500 hr of continuous operation.

†Range of mean values for 14 TVA ash ponds (Chu, Ruane, and Steiner, 1976).

‡Alkalinity determined for the third 500-hr elution interval.

effluent water did not differ substantially in pH, alkalinity, conductivity, or total dissolved solids.

Effluent concentrations for the seven selected metals monitored through 1500 hr are summarized in Table 5. Maximum concentrations, which in most instances were observed during the first 100 hr of elution time, were 126 ppm Al, 766 ppb Zn, 518 ppb Cu, 500 ppb Cd, 370 ppb Ni, 87 ppb Hg, and 8 ppb Ag. Mean concentrations for the first 500 hours were 32.6 ppm Al, 350 ppb Zn, 156 ppb Cd, 155 ppb Ni, 110 ppb Cu, 2.1 ppb Ag, and 1.8 ppb Hg. The 500-hr elution patterns for Al, Cu, Ni, and Zn are illustrated in Fig. 2. Elevated concentrations observed at about 300 hr correlated with mechanical disturbances that temporarily facilitated water filtration through the fly-ash bed. Concentrations for all metals except mercury continued to decline progressively with further leaching time, resulting in mean values for the third elution interval of 540 ppb Al, 61.4 ppb Zn, 33.6 ppb Ni, 25.7 ppb Cd, 4.1 ppb Cu, and 0.2 ppb Ag (Table 5). Mercury fluctuated from 0.3 to 7.4 ppb during the first 500 hr but increased substantially thereafter, with mean values of 27.4 and 14.9 ppb for the second and third elution intervals. However, the mercury level dropped markedly toward the end of the third elution period, averaging 2.6 ± 0.7 ppb after 1360 hr. Metals were not detected in

TABLE 5

METAL CONCENTRATIONS FOR FLY-ASH EFFLUENT

Element	Maximum concentration, ppb	Mean concentration for three elution intervals, ppb*			Influent concentration, ppb
		0–500 hr	500–1000 hr	1000–1500 hr	
Ag	8	2.1 ± 0.9	0.2 ± 0.2	0.2 ± 0.2	0.0
Al	126,000	32,600 ± 6,100	1,570 ± 260	540 ± 80	230 ± 29
Cd	500	156 ± 35	93.8 ± 24.8	25.7 ± 11.3	1.7 ± 0.8
Cu	518	110 ± 26	14 ± 1.8	4.1 ± 0.8	3.5 ± 0.9
Hg	87	1.8 ± 0.5	27.4 ± 11.7	14.9 ± 5.3	0.0
Ni	370	155 ± 16	58 ± 10	33.6 ± 2.3	3.3 ± 1.4
Zn	766	350 ± 33	106 ± 20	61.4 ± 4.1	4.9 ± 3.1

*Mean values with standard errors were based on analyses taken at 1- to 3-day intervals.

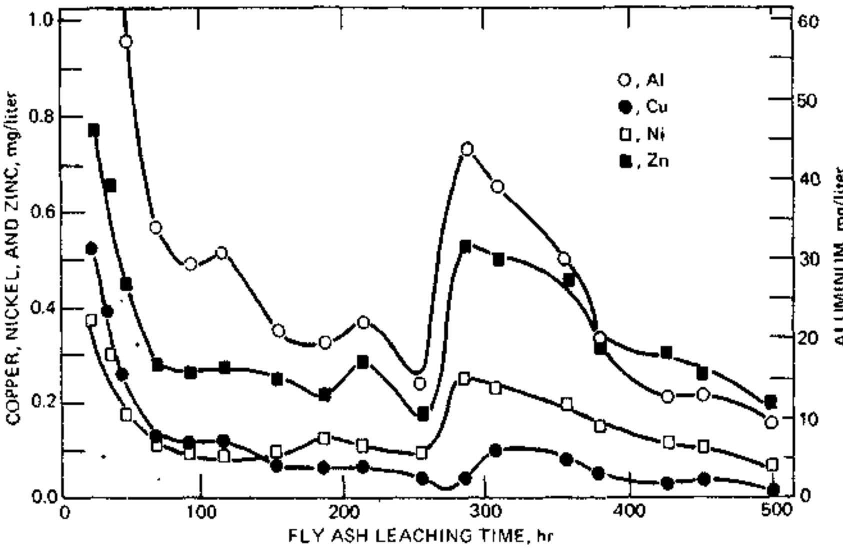

Fig. 2 Leaching patterns for fly-ash metals.

the distilled–deionized influent water used for the first 770 hr, and background values for the carbon-filtered tap water are given in Table 5.

Bioassay Analysis of Fly-Ash Effluent

Four sets of embryo–larval bioassays were performed on fly-ash effluent by use of a continuous-flow system. Tests were initiated after 522, 1033, and 1775 hr of continuous aqueous leaching of the original 52-kg sample of precipitator-collected fly ash. At 522 hr tests were conducted on eggs of the leopard frog and Fowler's toad with undiluted ash effluent. Frog eggs suffered rapid and complete mortality, and a hatching frequency of 46% was observed for Fowler's toad. Survival was 97 to 99% for control populations treated with the same influent water source used to supply the fly-ash leaching chamber (Table 6). Bioassays were initiated at 1033 hr on eggs of the redear sunfish. Undiluted effluent produced complete mortality, and 0.1 and 0.01 dilutions gave survival frequencies of 42 and 90%, which closely approached control survival. In tests with goldfish eggs conducted at 1775 hr, survival averaged 57, 76, and 88% for undiluted effluent and 0.1 and 0.01 dilutions, respectively. Control survival was 92%.

Effluent metal concentrations observed for the amphibian bioassays approximated mean values given for the second elution interval (Table 5). Although ash toxicants produced a near-LC_{50} response for toad eggs, the exposure period was limited to only 1.5 days. In addition, developmental stages of Fowler's toad are highly resistant to trace metals, compared with other amphibian and piscine species (Birge, 1976). Animal species used for the initial toxicological

TABLE 6

EMBRYO—LARVAL BIOASSAYS ON FLY-ASH EFFLUENT

Species	Elution interval, hr	Exposure time, days	Bioassay solution	Percent survival at hatching
Leopard frog	522—582	2.5	Ash effluent	0
(Rana pipiens)			Control	97
Fowler's toad	522—558	1.5	Ash effluent	46
(Bufo fowleri)			Control	99
Redear sunfish	1033—1105	3.0	Ash effluent	0
(Lepomis			Diluted effluent	
microlophus)			0.1	42
			0.01	90
			0.001	93
			0.0001	95
			Control	89
Goldfish	1775—1847	3.0	Ash effluent	57
(Carassius			Diluted effluent	
auratus)			0.1	76
			0.01	88
			Control	92

characterization of coal elements were not available for the first two sets of effluent bioassays. Sunfish eggs, however, have the same hatching time (exposure period) as goldfish and generally exhibit similar sensitivity when used in aquatic bioassays (Birge, Black, and Westerman, 1978). During the exposure period for sunfish eggs, mean effluent metal concentrations, with standard errors, were 0.4 ± 0.2 ppb Ag, 1070 ± 230 ppb Al, 72.0 ± 43.0 ppb Cd, 5.5 ± 1.8 ppb Cu, 20.6 ± 4.8 ppb Hg, 31.5 ± 1.4 ppb Ni, and 70.0 ± 6.7 ppb Zn. At the 0.1 dilution, which gave 42% survival for sunfish eggs (Table 6), all analyzed metals except aluminum were well below goldfish LC_1 values. Aluminum was present at approximately two-thirds of the LC_{50} value. Although the effluent was not analyzed for all possible toxicants, this correlation tends to support application of the toxicological index given for coal elements (Tables 2 and 3). Before the goldfish bioassays were initiated, effluent metal concentrations had dropped to 0 ppb Ag, 160 ± 10 ppb Al, 1.5 ± 1.5 ppb Cd, 4.5 ± 1.8 ppb Cu, 3.8 ± 0.7 ppb Hg, 23.0 ± 3.0 ppb Ni, and 44.5 ± 8.0 ppb Zn. These values were all below LC_1's calculated for goldfish, except aluminum, which was present at about the LC_{50} level (Table 2). The undiluted effluent gave 57% survival.

DISCUSSION

The embryo–larval bioassays reported in Table 2 demonstrate the high toxicity of numerous inorganic coal elements to aquatic biota. Depending on the animal species, LC_{50} values of 0.1 ppm or less were observed for 15 coal elements, and calculated LC_1's ranged down to 0.1 to 0.2 ppb for mercury and silver. Tungsten was the least toxic element in all cases, with LC_{50} values ranging from 2.90 ppm for the toad to 120 ppm for the goldfish. When the test data were averaged, the increasing order of sensitivity of animal species was goldfish, trout, and toad.

The order of toxicity of the 22 elements, as determined by LC_{50} values, varied somewhat for embryo–larval stages of the three species. Only Ag, Cd, Cr, Hg, Ni, and Pb occurred among the 12 most toxic elements for all three, but Al, As, Co, Cu, Ge, V, and Zn were included in this group for two species (Table 2). Of particular interest were the consistent extreme toxicity of mercury and silver to developmental stages of all species and certain selective responses, such as the high relative toxicity of aluminum to goldfish, germanium and lanthanum to trout, and selenium and zinc to the toad.

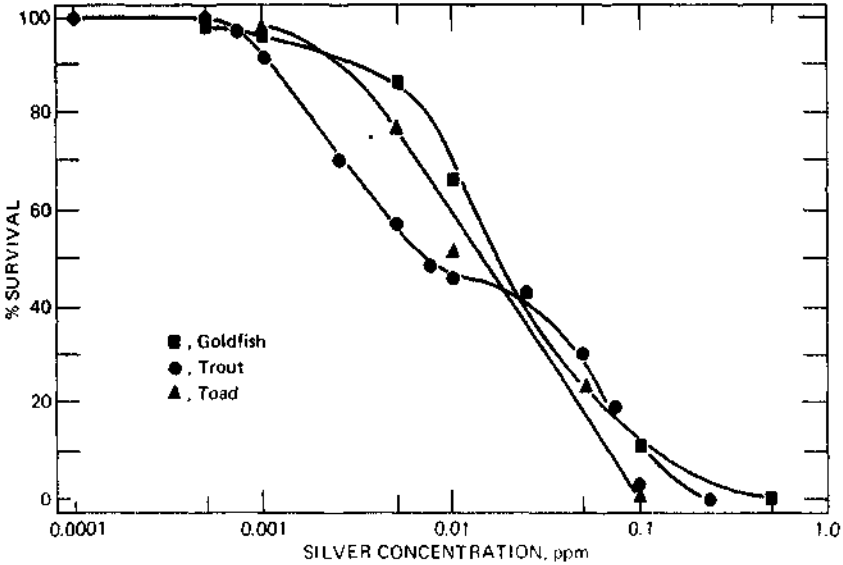

Fig. 3 Effects of silver on embryo—larval stages.

Several patterns of response were discernible concerning the differential sensitivity of the three test organisms. Highest uniformity was obtained for silver, which gave an exceptionally narrow range of LC_{50} values (0.01 to 0.03 ppm). As seen in Fig. 3, this relationship held for the full range of exposure concentrations. Germanium produced similar effects on the two most sensitive test animals, trout and toads, but was substantially less toxic to the goldfish (Fig. 4). This same pattern was given by Cu, Mo, Ni, Sb, Sr, Tl, and V. A still more heterogeneous response occurred for Pb (Fig. 5), Hg, and certain other elements (e.g., La, Sn, and W). Considering the response patterns summarized in Figs. 3 to 5, it is probable that the diversity of aquatic species affected by pollution would increase in the order of Pb, Ge, and Ag. Although elements such as Pb and Ge likely would affect fewer species, these toxicants probably would contribute to an ecological imbalance of aquatic biota. As noted, Se, Zn, and certain other elements (e.g., As and Co) were more selective for the toad, and, on the basis of LC_{50} values, the toad was the most sensitive species for 17 of the 22 elements. This suggests that amphibians may constitute particularly sensitive target sites for coal contaminants. For example, goldfish LC_{50} determinations for selenium and zinc exceeded those for the toad about 100 and 250 times, respectively.

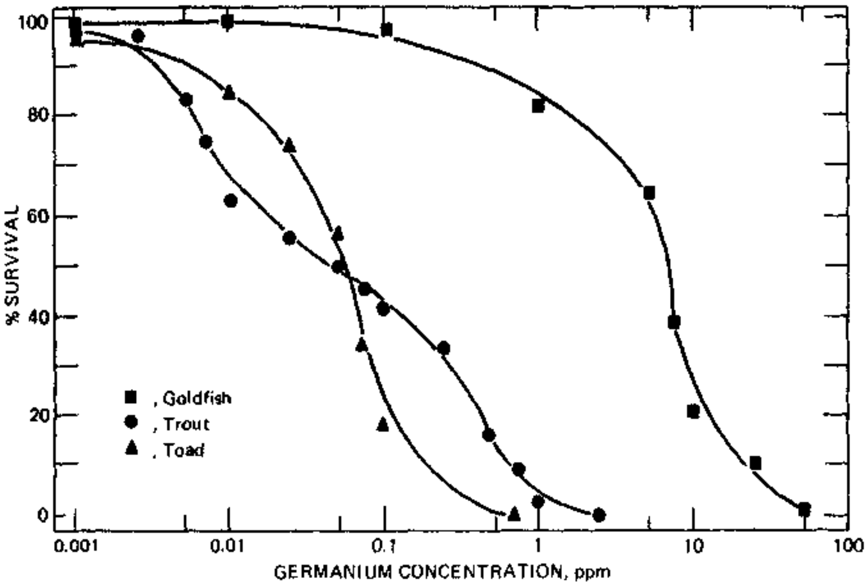

Fig. 4 Effects of germanium on embryo—larval stages.

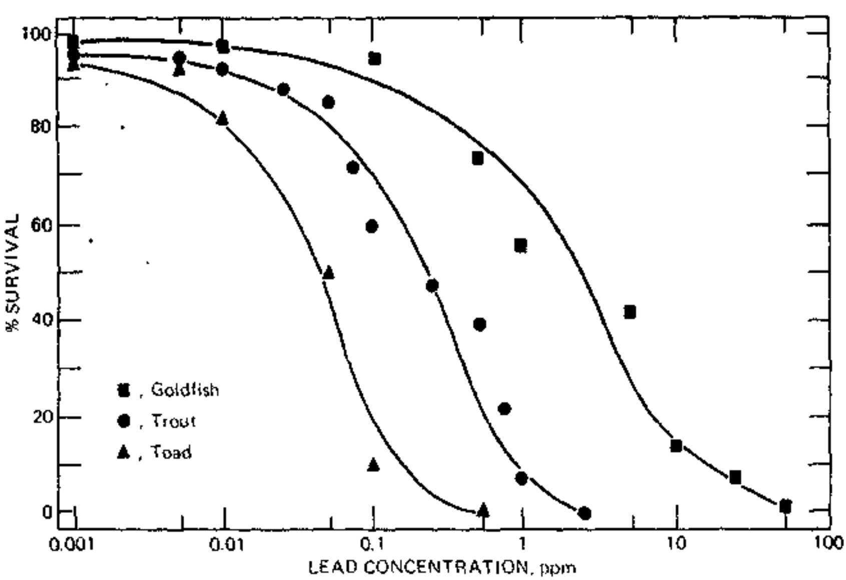

Fig. 5 Effects of lead on embryo—larval stages.

The heterogeneity of response observed for the three animal species somewhat complicates application of the bioassay data on coal elements to impact assessment and pollution-abatement technology. Therefore, the mean LC_{50} and sensitive species indexes (Table 3) were developed to provide a simplified data base for energy and environmental engineers. The sensitive-species ranking for coal elements was used to delineate upper limits of toxicity observed for the 66 independent bioassays, and the mean index summarized average test responses. Despite some notable exceptions (e.g., Al and La), the toxicological orders given in the two indexes were generally similar. Principal differences in relative order were attributed to elements exhibiting disproportionate selective toxicity for a particular animal species. The only extreme disparity involved lanthanum, for which mean and sensitive species LC_{50} values differed by three orders of magnitude. We should note that several recent publications review additional bioassay data for some of the trace metals found in coal (National Academy of Sciences—National Academy of Engineering, Committee, 1973; Vaughan et al., 1975; Environmental Protection Agency, 1976).

In the fly-ash leaching study, characteristics of the simulated effluent were compared with those recorded for 14 TVA ash ponds. As seen in Table 4, good agreement was obtained for all test parameters except aluminum and cadmium, but concentrations for these metals were within TVA ranges early in the third elution interval. The high initial values for aluminum and cadmium may have resulted from use of distilled influent water, which contributed to low pH in the simulated ash pond. These and other results indicate that the quality of effluent water may be improved somewhat by regulating certain parameters (e.g., pH and alkalinity) of influent water used for ash sluicing.

Appreciable metal leaching continued, however, even after 770 hr, when the change was made in influent water (Table 5). The resulting suite of toxic metals produced lethality of test organisms through 1775 to 1847 hr of continuous elution time (Table 6). Effluent metal concentrations (Table 5) were compared to freshwater guidelines (National Academy of Sciences—National Academy of Engineering, Committee, 1973; Environmental Protection Agency, 1976) to further evaluate potential effects of fly-ash leaching on aquatic biota. Through 1775 hr, mercury remained well above the limit of 0.05 ppb, and aluminum exceeded the 100-ppb level considered deleterious to growth and survival of fish. Cadmium was over the trout standard of 0.4 to 1.2 ppb for 1775 hr and exceeded the maximum limit for other aquatic species (4 to 12 ppb) for 1050 to 1435 hr. On the basis of the Environmental Protection Agency's (EPA) application factor (0.01) and the trout, toad, and goldfish embryo–larval LC_{50} values, nickel and zinc concentrations exceeded recommended levels for all test species through 1775 hr, and silver was above acceptable limits for 1050 to 1266 hr. Copper, with an application factor of 0.1, exceeded calculated concentrations for trout and toad through 1000 to 1500 hr but was over the goldfish limit for only 22 hr. Using embryo–larval rather than adult LC_{50} values resulted in more stringent limits for Ag, Cu, Ni, and Zn. However, freshwater standards should permit adequate protection for sensitive life-cycle stages. Except for copper, the suggested EPA application factors appeared acceptable for embryo–larval stages. On the basis of data in Table 2, 0.01 to 0.05 of LC_{50} determinations gave values that generally fell within or near 95% confidence limits for LC_1's. In comparison with the EPA value of 0.1, a more suitable application factor for copper was found to be 0.05 for goldfish and trout and 0.01 for the toad.

Since combined toxicological effects of complex suites of trace metals are difficult to quantify by existing hazard-assessment criteria, direct bioassay monitoring was used to provide further characterization of ash effluent. As noted, after 1033 hr of continuous elution, undiluted ash effluent produced 100% mortality of sunfish eggs, and survival of goldfish eggs was reduced to 57% when exposure was initiated at 1775 hr. A 0.1 dilution produced an approximate LC_{50} for sunfish, and 0.01 gave essentially control-level survival for both species. When median survival was obtained, concentrations of all monitored metals except aluminum were at or below goldfish LC_1 values, and aluminum was present at about the LC_{50} level (Table 2). Effluent dilutions that gave control-level survival did not contain any monitored metals at concentrations exceeding goldfish LC_1 values. Although ash effluent was not analyzed for all possible toxicants, results obtained by direct effluent monitoring were in good agreement with the independent embryo–larval bioassays for coal elements. Also, trace metals present at or below the probit LC_1's did not exert any overt synergistic effects. In addition, results indicate that continuous-flow embryo–larval test systems are highly suitable for in situ toxicological monitoring of complex coal effluents.

Although not intended to serve in lieu of actual field studies, simulated ash ponds can be used to characterize aqueous leaching processes and to evaluate ash effluents for potential environmental hazards. Test parameters can be manipulated individually to determine effects on metal elution rates, and such model systems can be particularly useful in comparing ash residues of coal from different formations. The chemical composition of bottom and fly ash is highly variable, depending on the source of the coal used, combustion conditions, and such factors as the efficiency of emission-control equipment (Moulton, 1973; Chu, Nicholas, and Ruane, 1975; Cooper, 1975). In addition to differences in ash composition, numerous physical and chemical factors may affect the leaching of trace elements and the final composition of ash-pond water. These factors include the quantity of water used for sluicing; its temperature, pH, and hardness; and various performance characteristics of the settling pond. As noted by Chu, Nicholas, and Ruane (1975), the effects of such variables on the quality of ash-pond effluents are not sufficiently understood. It is known, however, that a number of coal-derived inorganic elements reach appreciable concentrations in ash-pond waters. Since 1973, TVA has analyzed for 17 trace elements in quarterly grab samples from bottom ash, fly ash, and combined ash ponds, and the results have been summarized by Chu and co-workers (Chu, Nicholas, and Ruane, 1975; Chu, Krenkel, and Ruane, 1976). Discharges from fly-ash ponds were reported to contain up to 7.3 ppm Al, 0.3 ppm Ba, 0.04 ppm Cd, 0.1 ppm Cr, 0.3 ppm Cu, 0.08 ppm Pb, 13.4 ppm Mn, 1.1 ppm Ni, and 1.5 ppm Zn. Ranges for a number of these metals are summarized in Table 4.

Other investigators also have considered various problems associated with fly-ash disposal (Guthrie, Cherry, and Rodgers, 1974; Theis, 1975; Holland et al., 1975). Theis (1975) indicated that the production of metal leachates and alterations of pH and dissolved oxygen may affect receiving waters. He also demonstrated significant release rates for trace metals when fly ash was dispersed in distilled water. Holland et al. (1975) investigated the environmental effects of trace elements in the pond disposal of ash and flue-gas desulfurization sludge. Samples of ash and sludge from five generating stations were studied by simulated ponding. In general, concentrations of aqueous leachates were low, but Ba, B, Cr, Hg, and Se exceeded EPA guidelines for public water supplies. However, these investigators did not compare their findings with EPA standards for freshwater biota, which generally are more stringent, and they did not consider the combined toxic effects of the resulting metal mixtures. Guthrie, Cherry, and Rodgers (1974) evaluated the impact on biota in waters receiving ash-basin effluent from a coal-fired power plant. Bacterial, plant, and animal diversities were reduced at sites affected by ash effluents. Abiotic water parameters affected by ash-basin effluents included temperature, turbidity, dissolved oxygen, and pH. Concentrations of coal-ash leachates (e.g., Cd, Cr, Cu, Hg, and Zn) were lowest in effluent water, somewhat greater in aquatic biota, and highest in benthos. This indicated accumulation of these toxicants in biomass and bottom sediment.

The results given here show clearly that a substantial number of minor and trace elements of coal and fly ash are highly toxic to aquatic organisms. Many are leachable from ash residues at concentrations that prove lethal to fish and amphibian embryo—larval stages and other organisms. Since annual coal utilization in the United States may reach 1 billion tons or more in the near future (Vaughan et al., 1975), it remains essential to characterize more fully the toxic properties of coal-derived contaminants, ascertain their release rates, and determine their pathways of exchange within and ultimate effects upon aquatic ecosystems.

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