CHEMICAL AND TOXICOLOGICAL PROPERTIES OF COAL FLY ASH

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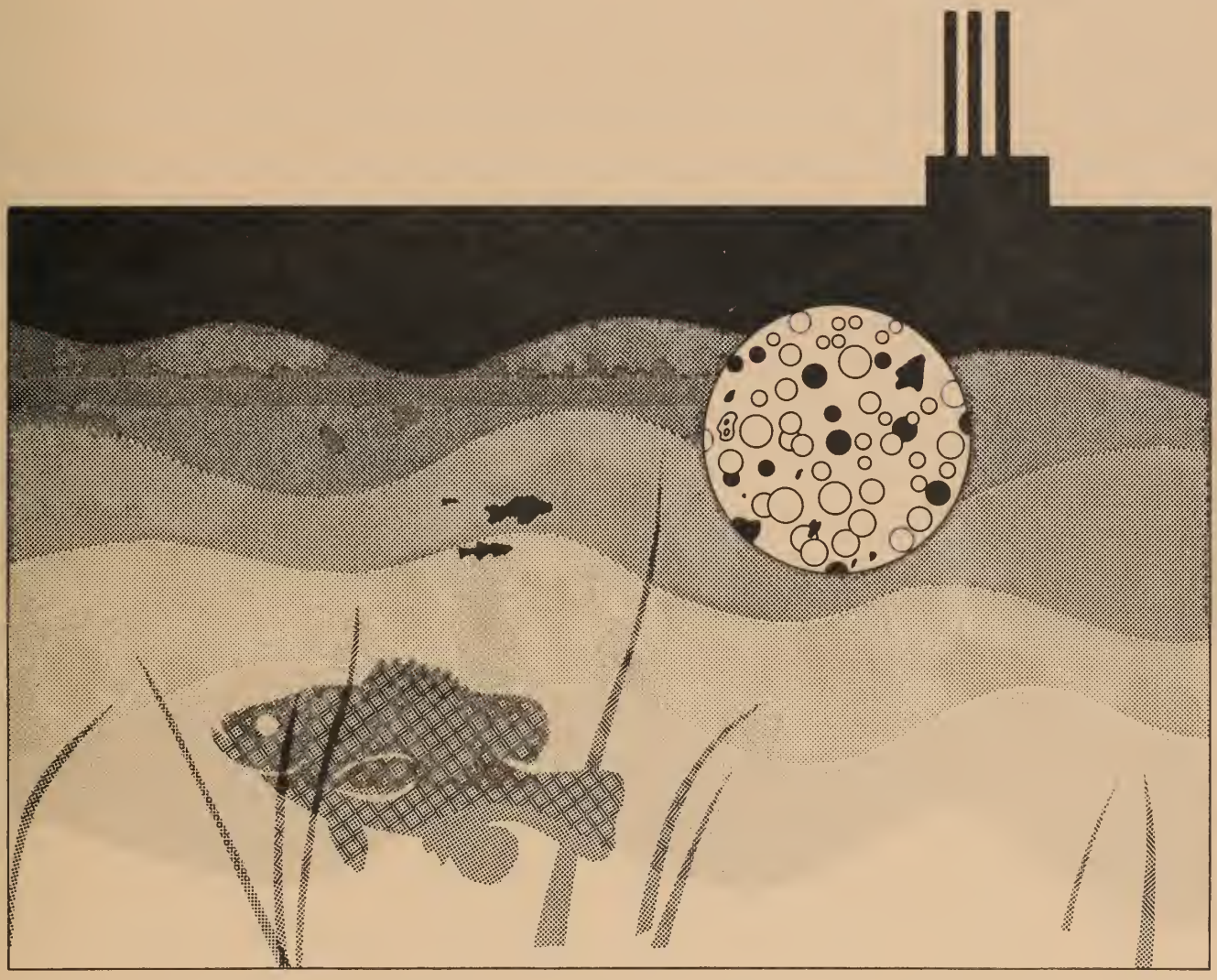

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INTRODUCTION

During the late 1970s shortages of natural gas, fuel oil, and gasoline dramatically demonstrated the need for the increased use of coal by electric utilities. Although predictions vary, the National Coal Association forecasts an increase in coal usage from 787 million metric tons in 1976 to approximately 1.5 billion metric tons by 1985. The combustion of coal produces solid wastes composed primarily of the noncombustible mineral matter (ash) present in the coal. Fly ash is that portion of ash that is small enough, in terms of particle size, to be entrained in the flue gases and carried away from the site of combustion. Of the 67.8 million tons of ash produced in the U.S. in 1977, approximately 48 million tons was fly ash (Faber, 1979). Ash production may reach 125 million tons by 1990 and may increase by a factor of four in the next 20 years (Faber, 1979). In Illinois, the three major electric utilities generated an estimated 1,867,000 tons of fly ash in 1979 (Roy et al., 1981).

The implications of the Resource Conservation and Recovery Act (RCRA) of 1976 have focused attention on coal fly ash and its subsequent disposal problems. The prevalent method of fly ash disposal is by sluicing the ash slurries from the power plants into some type of natural or man-made basin where the ash settles. The resulting supernatant may contain potentially toxic trace constituents, leached from the fly ash, which could pose problems to the aquatic ecosystems into which they eventually flow.

Several studies assessing the environmental impact of coal fly ash have dealt largely with fly ashes generated from coals from the Appalachian region (Chu et al., 1978; Furr et al., 1977; Klein et al., 1975; Plank et al., 1975) and from western bituminous, subbituminous, and lignite coals (Elseewi et al., 1980; Mann et al., 1978; Ondov et al., 1979; Swanson et al., 1976).

Fly ashes produced by the combustion of coals from the Illinois coal basin have also been studied (Cox et al., 1978; Davison et al., 1974; Griffin et al., 1980; Linton et al., 1976; Natusch et al., 1977; Theis and Wirth, 1977). However, as indicated in literature reviews by Adriano et al. (1980), Page et al. (1979), and Roy et al. (1981), the physicochemical properties of fly ash may vary from plant to plant and even from different boilers within a particular plant. Moreover, laboratory leaching and disposal pond studies of the aqueous chemical interactions with fly ashes generated from Illinois Basin coals have also produced varying results. Additional work with Illinois fly ashes is needed in order to assess the possible environmental impacts of coal fly ash disposal.

Elevated pH levels of fly ash leachates have been shown to be toxic to aquatic organisms (Cairns et al., 1972; Wasserman et al., 1974). Other studies (Birge, 1978; Thompson, 1963) have examined the role of trace elements in the aquatic toxicology of leachates from coal and fly ash.

Trace elements leached from fly ash can accumulate in the tissues of fish and fish forage (Cherry et al., 1976; Ryther et al., 1979). Contaminated fish from cooling lakes or other aquatic ecosystems exposed to fly ash effluent may pose potential health hazards to fishermen.

PURPOSE AND OBJECTIVES

The overall purpose of this investigation was to provide information that may be of assistance in predicting the environmental impacts of coal fly ash disposal. Data resulting from this investigation should be useful to utilities, consultants, and state, local, and federal agencies concerned with fly ash and its disposal.

The objectives of the study were to:

- Review the ecological and health literature concerning fly ash.
- Assess the variability in terms of chemical composition and aqueous solubility of fly ashes derived from Illinois Basin coals, and compare these fly ashes to those generated from western U.S. coals.
- Determine if the extracts generated from fly ash were acutely toxic to fishes.
- Determine if the soluble trace metals in the fly ash extracts were accumulated by fishes under laboratory conditions.

SUMMARY OF STUDY FINDINGS

1. Nine fly ash samples generated from Illinois Basin coals--predominantly silts (USDA classification)--varied in color from very dark grayish brown (10YR Munsell soil colors) to gray (2.5Y - 5Y). The average specific gravity of the nine samples was about 2.4. Two fly ashes generated by the combustion of western U.S. lignite coals were lighter in color (light gray) and had greater specific gravities (about 3.05), whereas a western subbituminous coal fly ash had a darker gray (10YR) color and a specific gravity of 2.2.

2. The general mineralogical composition of the Illinois Basin fly ashes was comparable to that of fly ashes generated from eastern U.S. bituminous coals, as reported elsewhere. They were essentially spherical particles composed of an amorphous alumino-silicate glass, quartz, mullite ($Al_6Si_2O_{13}$), and iron oxides. The subbituminous western ash was similar in mineralogical composition to the Illinois samples, except for the presence of calcite in the western ash. The two western lignite samples had higher concentrations of some alkaline metals and matrix sulfur, primarily in the form of anhydrite ($CaSO_4$) and periclase (MgO).

3. Most of the matrix sulfur in all 12 samples existed as sulfate compounds. The average ratio of sulfate S to sulfide S in the Illinois samples was about 5:1.

4. The trace constituent concentrations in the samples were highly variable, but the Illinois fly ash samples generally had greater concentrations of (in decreasing order of concentration) Zn, Ni, Rb, Cs, Cr, Co, U, Ge, Mo, V, Li, Cd, Tl, Sm, Pb, Be, Eu, Tb, Ga, Ce, As,

Cu, Lu, and Sc than did the three western fly ashes. Similar trends for certain transitional metals have been reported elsewhere for ashes from eastern and western coals.

5. Under laboratory conditions, the seven gray samples produced alkaline extracts, whereas the two reddish fly ashes generated acidic extracts. Color may be useful in predicting the initial pH of a fly ash slurry or leachate in the field.

6. The ratio of matrix CaO to SO_3 may influence the pH of extracts during the initial stages. Short-term acidic extracts were associated with samples having a CaO/SO_3 ratio of less than 2; alkaline solutions were produced from samples having matrix CaO/SO_3 ratios exceeding 2.

7. The general trend of EP solubility for the Illinois Basin fly ashes was found to be SO_4-S > Ca, B > Cd > Sb, Mn, Mg > Zn > Na, Mo > K, Ni, Cr, Cu > Be, Ba, Si, Al, Fe. The general pattern of solubility for the subbituminous fly ash was SO_4-S > B > As > Ca > Se > Mg, Zn > Mn > Na > K, Ba, and for the two lignite fly ashes, SO_4-S > B > K, Mo >> Se, Na > Ca > Zn, Mg > Be, Cr > Mn, Si, Ba.

8. Although all fly ashes are currently exempt from the list of hazardous wastes under RCRA, EP data indicated that one of the 12 samples would be classified as a hazardous waste by present criteria. One acidic fly ash contained enough soluble Cd to classify it as a hazardous waste if the status of fly ash as a nonhazardous waste were to be revised.

9. In long-term equilibrations (100-140 days) of five fly ash samples, the concentrations of several potential pollutants began to decrease almost immediately after the first day of extraction, and this decrease continued for 60 to 120 days until steady state conditions developed. The pH of the acidic extracts became neutral after about 3 to 5 weeks and consequently several potential pollutants were less soluble in the resulting nonacidic solution. In all five long-term equilibrations, several constituents reached a metastable equilibrium, persisting at invariant concentrations for the latter part of the extraction interval.

10. The specific concentrations of some of the inorganic constituents in the solutions (prior to equilibration and after steady state conditions developed) exceeded the EPA interim primary or secondary drinking water standards and irrigation water criteria.

11. Organic compounds identified in the fly ashes were only slightly soluble in the aqueous extracts. Although some of the organics present in the samples are on the priority pollutant list, they are present in such low concentrations that it is doubtful that they would pose any significant environmental problems during landfilling operations or ponding.

12. Fly ashes--particularly acidic types--are probably most toxic to aquatic ecosystems when initially slurried to disposal ponds; their toxicity may decrease with time. If the potential contaminants achieve

steady state conditions in the disposal pond, they may have long residence times in the ash effluent, thus increasing the probability of bioaccumulation by aquatic organisms.

13. Of the 12 fly ash samples evaluated, five were selected for toxicity testing on the basis of the diversity of extract pH values observed. All five extracts were acutely toxic to fathead minnow fry.

14. Physicochemical components probably responsible for the acute toxicity of the fly ash extracts to fish were pH, Al, ionic strength, and Zn. Because of the complex composition of some extracts and the unknown synergistic and antagonistic effects of the chemical constituents of the extracts, it was not possible from these experiments to determine which chemical constituents specifically were responsible for the observed mortality.

15. The fly ash extracts were diluted to levels presumed subacutely toxic for use in bioaccumulation experiments. The growth of fathead minnows and green sunfish exposed to these diluted fly ash extracts was not significantly different from that of control test organisms exposed to filtered tap water under similar conditions.

16. The fathead minnows and green sunfish accumulated similar elements from the fly ash extracts; the six chemical constituents most commonly accumulated from fly ash extracts were Al, B, Cd, Mn, Mo, and Ni. Of these six chemical constituents, Cd appeared to be of greatest importance because of its highly toxic nature.

RECOMMENDATIONS

1. An apparent relationship was observed between the initial pH character of a fly ash leachate and its color and the matrix CaO/SO_3 ratio in the solid waste. Further study of the less commonly produced acidic high-iron fly ashes should be done.

2. The long-term equilibration (LTE) extraction procedure was designed to simulate equilibrated ash ponds. Although obtaining representative pond samples is difficult, such field work should be done to assess the accuracy of the LTE procedure.

3. Fly ash laboratory extracts often undergo complex changes in chemistry with time and should be studied to determine which mineral phases control the aqueous solubility of the components. The chemistry of slurry water and disposal ponds should also be studied and modeled to determine whether the same types of changes that occur in laboratory extracts occur in the field.

4. Grab samples were collected from only nine power plants, seven of which were in Illinois. To provide a more complete picture of fly ash composition and variability, samples from other Illinois power plants and from other states should be studied.

5. The scope of the ecological analyses of fly ash in this study consisted of acute static bioassays using fathead minnow fry and bioaccumulation

experiments using fathead minnows and green sunfish. It is appropriate to expand the scope of ecological analysis to a multi-tier approach (Brown and Suloway, 1982; Lee et al., 1979) including bioaccumulation, bioconcentration, and biomagnification experiments. Several species of test organisms representing different trophic levels should be used in chronic or subchronic bioassays.

6. A battery of health effects tests should be conducted to evaluate each fly ash and its extracts. The U.S. EPA has recommended (for a level 1 assessment) that solid wastes be tested for the presence of microbial mutagenicity, rodent acute toxicity, and cytotoxicity. The specific tests include the Ames Test, the Rabbit Alveolar Macrophage (RAM) assay, the Human Lung Fibroblast (WI-38) Assays, and acute toxicity bioassays with rats. With these tests it is possible to screen wastes, including fly ashes and their extracts, for possible carcinogenicity, cytotoxicity, and other detrimental health effects.

METHODS AND MATERIALS

Sample collection and preparation

A summary of the origin and general characteristics of grab samples of 12 fly ashes collected for this study is given in Table 1. All of the samples were collected from the hoppers below the electrostatic precipitators at nine individual power plants. Two samples, each derived from different boilers, were collected at each of three of the facilities.

Nine of the fly ash samples, identified as I1 through I9, were generated by the combustion of Illinois Basin coals (predominantly the Herrin No. 6 coal seam) in Illinois and Indiana. One fly ash (W1) was produced by a power plant in Illinois using a low-sulfur subbituminous coal from Colorado (Fishcreek Seam), and the remaining two fly ashes (W2 and W3) were from plants outside Illinois using lignite from western North Dakota. Figure 1 shows the areal extent of the Illinois Basin and the approximate location of the parent coals of fly ashes I1 through I9 (coals from two mines were used to generate fly ash I5). All chemical and solubility studies were done with the bulk samples as taken from precipitator hoppers. The bulk samples were riffled to insure that representative samples were used for each experiment.

Analytical methods for inorganic, mineralogical, and physical properties

The 12 solid wastes were analyzed both chemically and mineralogically. Chemical analyses of the samples for Si, Al, Mg, Ca, K, Fe, Ti, and P were performed by x-ray fluorescence spectrometry. Arsenic, Ba, Br, Ce, Co, Cr, Cs, Eu, Ga, Hf, La, Lu, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, U, W, Yb, and Zn contents were determined by instrumental neutron activation analysis. Mercury determinations were carried out by neutron activation with radiochemical separation. Boron, Cu, Ge, Li, Mo, Pb, Sn, and V concentrations were measured by optical emission spectrochemical procedures. A detailed discussion of sample preparation, detection limits, and procedures for these techniques can be found in Gluskoter et al. (1977). The sulfur determinations were done by ASTM method D-2492, and

total carbon determinations were carried out by ISO method 609-1975E. The mineralogy of the samples was determined by x-ray diffraction with a Philips Norelco x-ray diffractometer using CuKα radiation (Russell and Rimmer, 1979).

Most of the chemical analyses of the supernatant solutions were determined by inductively coupled argon plasma spectrometry (ICAP) with a Jarrell-Ash

Table 1. Summary of the origin and general characteristics of the 12 fly ash samples.

Fly ash	Color of sample[a]	Location of coal source	Location of power plant	Boiler type
I1	grayish brown 2.5Y 6/2	Illinois	Illinois[b]	cyclone
I2	very dark grayish brown 10YR 3/2	Illinois	Illinois[b]	pulverized
I3	gray 5Y 5/1	Indiana	Illinois[c]	pulverized
I4	gray 5Y 5/1	Indiana	Illinois[c]	pulverized
I5	grayish brown 2.5Y 5.5/2	Illinois	Illinois	pulverized
I6	gray 2.5Y 5/0	Illinois	Illinois	pulverized
I7	very dark grayish brown 10YR 3/2	Illinois	Illinois	cyclone
I8	gray 2.5Y 5/0	Illinois	Illinois[d]	pulverized
I9	gray 2.5Y 5/0	Illinois	Illinois[d]	pulverized
W1	gray 10YR 6/1	Colorado	Illinois	pulverized
W2	light gray 2.5Y 7/2	N. Dakota	Minnesota	pulverized
W3	gray - light gray 2.5Y 6.5/2	N. Dakota	N. Dakota	cyclone

[a]Dry Munsell soil colors
[b,c,d]Samples indicated were taken from same individual power plant but were derived from different boilers.

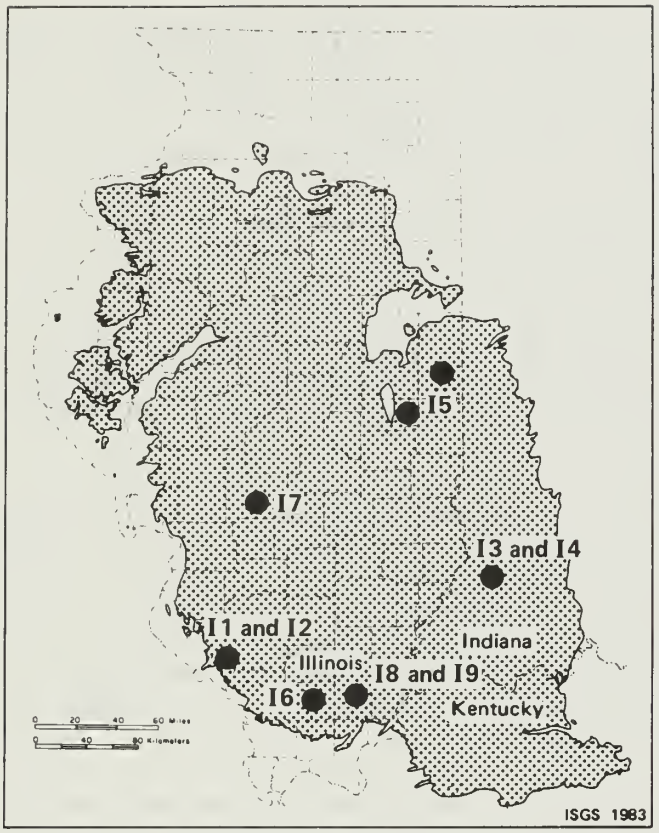

Figure 1. Areal extent of Pennsylvanian strata in which coal resources of the Illinois Basin are found and the approximate location of the parent coals of fly ashes I1 through I9.

Model 975 Plasma AtomComp. The constituents determined by ICAP were Al, As, B, Ba, Be, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, Sn, V, and Zn. The procedures and techniques of this specific instrument are discussed in a Fisher Scientific Company publication by the Jarrell-Ash Division (1978). Sulfate content was measured turbidimetrically (Standard Methods, 1975). Alkalinity was determined by titrations with dilute sulfuric acid, and oxidation-reduction potential (Eh), pH, and electrical conductance were measured by electrodes (U.S. EPA, 1974).

Most of the samples were characterized in terms of particle size distribution by pipet and wet sieving methods (Soil Conservation Service, 1972). Specific gravity determinations were made by ASTM method C128.

Analytical methods for organic matter characterization

Solvent extraction. The organic material in the solid fly ash samples was extracted with benzene, using a large (70-mm x 300-mm body) Soxhlet apparatus. The sample size per Soxhlet varied from 350 to 500 g of fly ash. The volume of benzene used was 1 L and the extraction time was 24 hours. After extraction, the solvent volume was reduced on a rotary evaporator. Elemental sulfur, found to be co-extracted with the organics, was removed

by passing the extract through a column of activated copper according to a method described by Blumer (1957). After removal of the sulfur, the final traces of solvent were removed with gentle heat (50°C) under a stream of dry nitrogen. The benzene-extractable materials, determined gravimetrically, were denoted as "total extractable organics."

The extracts were separated into seven fractions according to the U.S. EPA Level 1 (Revised) Procedure for Organic Analysis (U.S. EPA, 1978). This separation was done by liquid chromatography (LC) on a silica gel column using a gradual gradient of solvents from nonpolar to polar. An infrared spectrum was run on each extract and on each LC fraction. Gas chromatography (GC), high pressure liquid chromatography (HPLC), and gas chromatography-mass spectroscopy (GC-MS) were used to further characterize the organic fractions.

Pyrolysis study. A 5- to 10-gram sample of fly ash was placed in the bottom of a 300-mm x 13-mm-ID Pyrex tube, and a wad of organic-free quartz wool was positioned just above the fly ash to act as a retainer. The diameter of the tube was then constricted by heating with an oxygen-natural gas torch just above the quartz wool retainer. The top of the tube was then sealed with a skirted-septum stopper and the tube was evacuated for several minutes, using a vacuum pump linked to the tube via a hypodermic needle through the septum.

Following the evacuation, the sample end of the tube was heated in a horizontal position at 450°C in a tube furnace while the upper end of the tube was cooled with powdered dry ice. After a 5-minute heating period the tube was immediately sealed and separated at the point of the constriction by melting the glass with an oxygen-natural gas torch. Thus, the volatile organics were condensed and trapped in the upper, cooled portion of the tube.

The headspace gas (noncondensable at room temperature) was analyzed by GC, and the components were identified by comparison of retention times with known standards. The condensable portion was taken up in isooctane and analyzed by GC; one sample (derived from fly ash W1) was also analyzed by GC-MS. The major components in the samples were determined by comparison with the GC-MS analysis and with the retention times of reference standards.

The infrared spectra were obtained with a Perkin-Elmer Model 283B Infrared Spectrophotometer. The samples were mounted as neat smears or thin films between sodium chloride prisms. Normally the spectra were obtained by using a 12-minute scan time with response setting 1 and slit program 6. Interpretation of the spectra was made with the help of the following references: Barnes et al. (1944), Bellamy (1958), Nakanishi (1962), Silverstein and Bassler (1963), and Szymanski (1967).

A rough indication of the absorption intensities in the IR spectra obtained from the fly ash samples is reported in the Results Section; the absorption intensities are given as "strong," "medium," and "weak". "Strong" is defined as the strongest absorption in a given spectrum. "Medium" and "weak" designations relative to the strongest absorption within the same spectrum are then determined.

A Perkin-Elmer Sigma 1 gas chromatographic system with a flame ionization detector was used for GC analysis. A 2-m x 3-mm stainless steel column packed with Chromosorb 102 was used for the noncondensable gas analyses. The carrier gas (helium) flow rate was 30 mL/min, the injection port temperature was 125°C, and the detector temperature was 200°C. The column oven temperature was programmed for an initial hold of 50°C for 1 minute, a temperature rise to 170°C at 10°/min, and a final hold at 170°C for 5 minutes.

A 1.25-m X 3-mm stainless steel column packed with 3% SP-2100 on 100/120 mesh Supelcoport (Supelco Inc., Bellefonte, PA) was used for the analysis of the condensables from the pyrolysis study and for the extracts and subfractions of the extracts. The carrier gas (helium) flow rate was 35 mL/min, injection port temperature was 250°C, and the detector (FID) temperature was 315°C. The column oven temperature was programmed for an initial hold at 100°C for 2 minutes, a temperature rise rate of 4°/min to 260°C, with a final hold of 10 minutes. The latter column and conditions were also used for the Level 1 LC fractions.

A Perkin-Elmer Series 3 Liquid Chromatograph with UV detection was used for HPLC determinations. An Altex Ultrasphere® ODS, 5-µm sphere size, 4.6 x 250-mm (Beckman Instruments, Inc., Berkeley, CA) HPLC column was used. A 5-cm guard column with LC-18 pellicular packing (Supelco, Inc., Bellefonte, PA) was placed between the sampling valve and the top of the analytical column. The elution solvent was methanol:water (80:20, v:v) with a 1-mL/min flow rate under isocratic conditions. The order of elution under these parameters was shown to be phenols followed by toluene and then aromatic and polyaromatic hydrocarbons (PAHs) with ascending molecular weights (Fig. 2). Toluene was used as an internal reference standard.

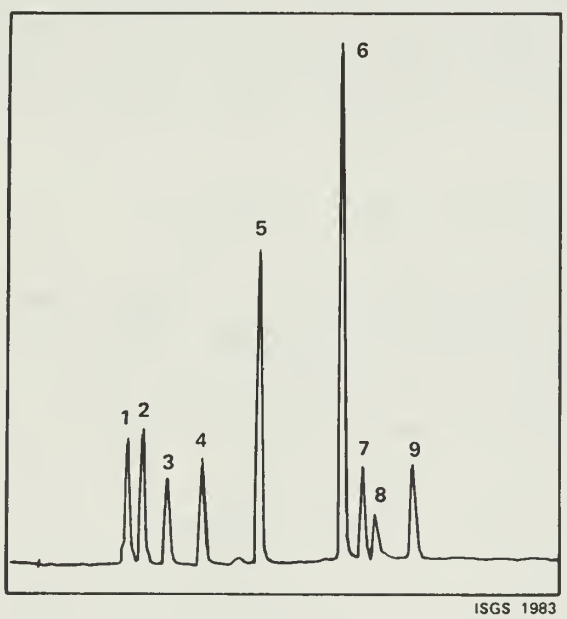

Figure 2. HPLC of a known mixture of phenols and polyaromatic hydrocarbons referenced to toluene. Peak identification: 1. phenol; 2. p-cresol; 3. 2,3-dimethylphenol; 4. 2,4,5-trimethyphenol; 5. toluene; 6. phenanthrene; 7. pyrene; 8. chrysene; 9. benzo (α) pyrene.

The GC-MS analyses were performed by the Institute for Environmental Studies at the University of Illinois, Urbana, using a Hewlett-Packard 5985A GC/MS/data system equipped with a capillary column coated with SP-2100.

Extraction methods

The proposed U.S. EPA Extraction Procedure (EP) (U.S. EPA, 1980) was used to study the solubility of the 12 fly ashes. The EP was intended to serve as a quick test for identifying wastes capable of posing potential pollution hazards when improperly disposed. The EP method calls for mixing 200 g of a solid waste with 3200 mL of deionized water and agitating the mixture by a shaking motion for 24 hours. During the 24-hour solubilization interval, the resulting mixture was acidified to a pH of 5.0 ($\pm$ 0.2) by periodic additions of 0.5N acetic acid if the pH of the aqueous phase was greater than 5. If the pH of the aqueous phase was less than 5, no additions of any kind were made. After the extraction interval, the solid and liquid phases were separated by filtration, and the filtrate was diluted to 4,000 mL with deionized water. In this study, the mixtures were filtered through a 0.45-µm-pore-size Millipore® filter membrane, and the filtrates (extracts) were acidified to a pH <1.5 with nitric acid (HNO_3) prior to ICAP analysis.

A long-term equilibration procedure was also used to assess the solubility of chemical constituents contained in some of the fly ash samples. This procedure involved mixing 3,400 g of fly ash with 17 liters of deionized water in a 19-liter reaction vessel made of Pyrex glass (the large volume was necessary for the bioassays and bioaccumulation studies). These mixtures were stirred for 30 minutes three times a week in order to (as a first approximation) simulate ash ponding environments according to a procedure designed by Griffin et al. (1980). However, this extraction procedure was more specifically oriented toward generating a solution at chemical equilibrium with the solid wastes. This procedure was used to produce a solution that might approximate the aqueous chemistry of pond effluent in settings where metastable chemical equilibrium conditions develop.

Methods for toxicity tests and bioaccumulation experiments

Using procedures outlined by the U.S. EPA (1975), 96-hour static bioassays of extracts generated from fly ash samples were conducted with 1-to-6-day-old fathead minnow fry (*Pimephales promelas*). The acute toxicity testing was divided into two phases: (1) the screening procedure and (2) the LC-50 determination. During the screening procedure the test organisms were exposed to the undiluted extracts; in the LC-50 determinations the organisms were exposed to "full-strength" extract diluted with filtered tap water. The LC-50 is the concentration of extract at which 50% mortality occurs during a bioassay.

Ten 1- to 6-day-old fathead minnows were placed in 250-mL glass beakers containing 200 mL of undiluted or diluted extract. Each bioassay was replicated once.

The acute bioassays were conducted at a constant temperature (21° ± 1°C) and photoperiod (16L-8D) in an environmental chamber. Test organisms were not fed, and the solutions were not aerated during the bioassay. During all bioassays, pH, dissolved oxygen, and temperature were monitored. Mortality data were collected at 24, 48, 72, and 96 hours after the bioassays had begun. Diluted and undiluted extracts were sampled at the conclusion of the bioassays for chemical analyses.

The acute toxicity of the five undiluted LTE extracts was determined with the screening procedure. The LC-50 determinations demonstrated the relative acute toxicities of the solutions and were used to identify the most toxic extracts, to estimate the dilution necessary to eliminate mortality during a 96-hour static bioassay, and to establish extract concentrations for use in the bioaccumulation experiments. LC-50 values were calculated using graphic methods (Litchfield and Wilcoxon, 1949).

In the bioaccumulation experiments for each fly ash extract, five adult fathead minnows were put into each of two 60-liter aquaria containing 40 liters of diluted extract. Control tanks contained aerated, filtered tap water. The five fish from each aquarium jointly constituted a single replicate for tissue analysis. This procedure was repeated using juvenile green sunfish (*Lepomis cyanellus*). Bioaccumulation experiments were conducted at a constant temperature (23° ± 3°C) and photoperiod (16L-8D) in a large environmental chamber.

To insure the size similarity of test organisms used in each bioaccumulation experiment, each fish was weighed and measured before the test. At the conclusion of the experiment or at death if premature mortality occurred, the fish were weighed and measured again, frozen, and stored for chemical analysis. Water samples were analyzed weekly to monitor fluctuations in the chemical composition of the diluted leachates. Temperature was monitored daily and dissolved oxygen and pH were monitored twice per week. The fish were fed frozen brine shrimp daily and excess food was removed each day. Tests were conducted for 30 days. One-way analysis of variance (ANOVA) was used to determine if test organisms used in each replicate were significantly different in size. ANOVA was also used to compare final lengths and weights of fish with initial values to determine if the test organisms exposed to the extracts grew at different rates than those of the controls.

The two replicate frozen green sunfish and fathead minnow groups for each fly ash extract and control were freeze-dried whole, using a Virtis Unitrap 10-100 Freeze Dryer with a Welch Duo-Seal Model 1402 Vacuum Pump, placed into polystyrene bottles with several glass beads, and homogenized using a Spex 8000-11 Mixer Mill. Polyethylene bottles were used to store the homogenized samples.

Total digestion was required to analyze the fish samples for chemical constituents. A 5:1 mixture of HNO_3 and redistilled perchloric ($HClO_4$) acid was added to 1-g subsamples of fish in 150-mL round bottom distillation flasks. Flasks were heated on a Kontes Rotary Kjeldahl Distillation Apparatus until $HClO_4$ fumes began to form. After cooling, the digested samples were transferred to 50-mL volumetric flasks and diluted to volume

with ultrapure water. The final $HClO_4$ concentration (5%) was within the range compatible with ICAP techniques. Diluted solutions were stored in 60-mL polyethylene bottles and refrigerated until analysis.

PHYSICAL AND INORGANIC CHARACTERIZATION OF THE FLY ASH SAMPLES

Particle size and specific gravity

Results for the particle size determinations are presented in Table 2. Most of the samples fell within the silt category (USDA soil classification), predominantly in the 8- to 31-micron range. The silt-sized component of the ashes (less than 62-micron- to 2-micron-diameter particles) ranged from 83 to about 90 percent (Table 2). The particle size distribution of three of the fly ashes is shown in Figure 3; these samples were selected for the illustration as best demonstrating the variability and range of the textural distributions of the samples. Fly ash I2 was a silt loam; I6 and I7 were both loams. The specific gravity of the fly ashes (Table 2) ranged from 2.2 to 3.1 g/cm^3; the Illinois Basin samples averaged about 2.4. Comparable measurements have been reported elsewhere (EPRI, 1979).

Chemical and mineralogical composition

Chemical and mineralogical analyses of the fly ash samples indicated that the ashes generated from Illinois Basin coals (samples I1-I9) consisted

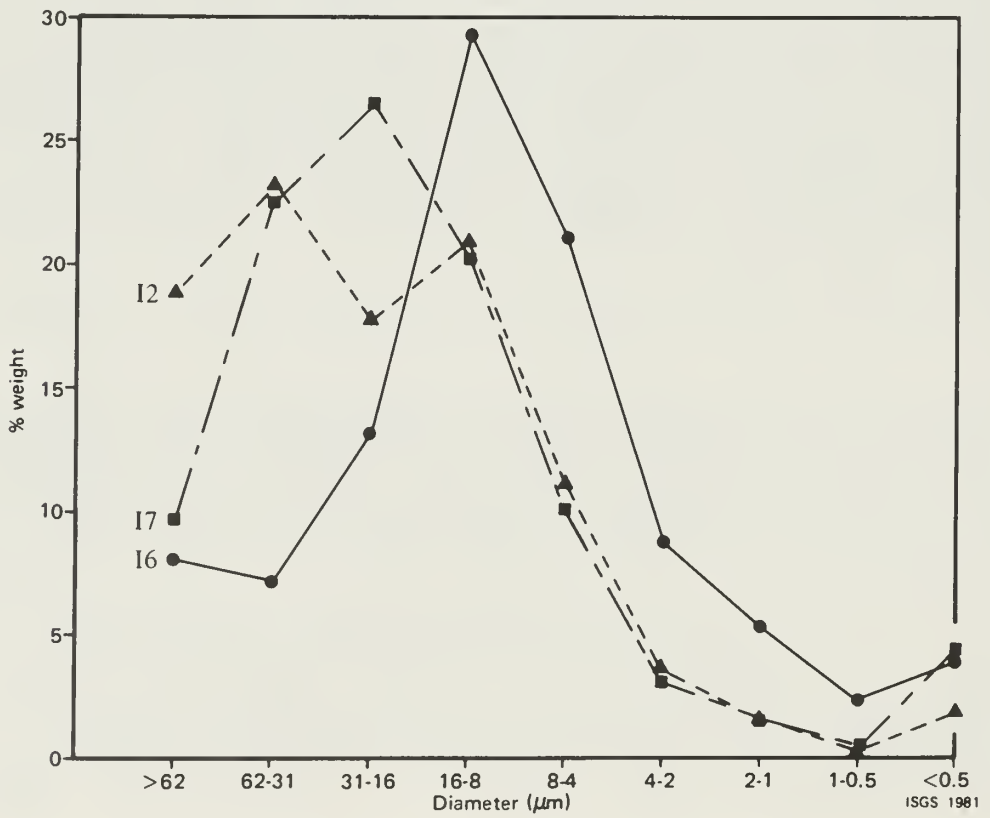

Figure 3. The particle size distribution in fly ashes I2, I6, and I7.

essentially of Si, Al, and Fe as amorphous alumino-silicate glass, quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), and various iron oxide species such as magnetite (Fe_3O_4) and hematite (Fe_2O_3) (Table 3). Comparable results were reported by Natusch et al. (1977) and Griffin et al. (1980) for other Illinois Basin fly ashes. A small amount of lime (CaO) was also detected by x-ray diffractometry in four of the Illinois Basin samples. Silicon, reported as percent silica (SiO_2), ranged from about 43 to 52% (Table 4). Aluminum and Fe, reported in their oxide forms, represented approximately 20% of the material. The reddish-brown colors (10YR, dry Munsell soil colors) associated with I2 and I7 were probably due to the Fe levels, about 2 to 3% greater than the average levels of the seven other Illinois Basin fly ashes lacking the reddish-brown hues and having 2.5Y-5Y colors. The Ca, Mg, Na, Ti, K, and S together (as oxides) constituted about 10% of the samples. Other minor constituents (less than 0.01%) were Ba, Sr, P, and Mn. The total S content of the Illinois Basin samples ranged from 0.32 to 1.06% (Table 5). Most of the total S (62 - 92%) was present as sulfate compounds. The remaining S (8 - 38%) was in sulfide forms. The average ratio of sulfate-S to sulfide-S in the Illinois Basin samples was about 5:1.

In contrast to the Illinois Basin fly ashes, the two lignite-base samples (W2 and W3) consisted of about 30% SiO_2, 25% CaO, and 8% MgO. The mineralogical composition of these samples was predominantly periclase (MgO), quartz (SiO_2), and anhydrite ($CaSO_4$). The lignite-base fly

Table 2. Particle size data for the 12 fly ashes by pipet analysis (percent weight) and specific gravity.

Fly ash	Particle size (μ)									Specific gravity
	>62	31-62	16-31	8-16	4-8	2-4	1-2	0.5-1	<0.5	
I1	11	6	30	23	18	6	4	<1	2	2.4
I2	19	23	17	22	11	4	2	<1	2	2.5
I3	9	12	25	40	9	3	1	<1	<1	2.4
I4	10	8	22	33	16	5	7	<1	<1	2.4
I5	4	8	38	43	4	<1	3	<1	3	2.4
I6	8	7	13	30	21	9	6	2	4	2.3
I7	10	23	27	20	11	3	2	<1	5	2.6
I8	8	15	19	29	16	7	4	<1	3	2.4
I9	7	17	21	27	15	9	3	<1	3	2.4
W1	4	16	29	25	15	6	3	<1	2	2.2
W2	1	(99% <62μ)[a]								3.0
W3	2	(99% <62μ)[a]								3.1

[a]Sample chemistry incompatible with method.

Table 3. Mineralogical composition of the 12 fly ash samples.

Mineral	Fly Ash											
	I1	I2	I3	I4	I5	I6	I7	I8	I9	W1	W2	W3
Quartz (SiO_2)	x	x	x	x	x	x	x	x	x	x	x	x
Mullite ($Al_6Si_2O_{13}$)	x		x	x	x	x		x	x	x		
"Magnetite-maghemite suite" (Fe_3O_4-Fe_2O_3)		x	x	x	x	x	x	x	x	x		
Hematite (Fe_2O_3)	x	x	x	x	x	x	x	x	x	x		
Lime (CaO)	x				x		x		x	x		
Calcite ($CaCO_3$)										x		
Periclase (MgO)											x	x
Anhydrite ($CaSO_4$)							x				x	
Unidentified											x	x

Table 4. Chemical composition of the 12 fly ashes: major and minor constituents (percent weight).

Chemical constituent	Fly ash											
	I1	I2	I3	I4	I5	I6	I7	I8	I9	W1	W2	W3
SiO_2	52.07	48.99	48.71	49.42	48.97	48.11	43.39	52.16	50.85	58.06	35.15	22.98
TiO_2	1.03	1.17	1.08	1.10	1.17	0.98	1.05	1.07	1.05	0.82	0.63	0.45
Al_2O_3	18.93	18.44	22.79	21.92	22.43	18.95	17.16	19.99	19.37	24.34	11.28	13.32
Fe_2O_3	17.06	17.86	16.14	16.37	17.40	16.01	18.49	14.23	14.18	3.29	4.66	7.56
CaO	5.25	3.30	2.52	2.35	2.94	5.11	4.13	4.37	4.10	7.21	23.66	25.38
MgO	0.41	0.20	0.40	0.61	0.60	0.56	0.51	0.75	0.35	1.14	7.91	7.50
MnO	0.04	0.08	0.03	0.05	0.05	0.04	0.05	0.02	0.03	0.02	0.08	0.03
Na_2O	0.63	1.35	0.16	0.22	0.59	0.30	1.75	0.31	0.31	0.30	5.53	9.57
K_2O	3.24	3.58	3.85	3.84	3.82	3.49	4.13	3.85	3.82	1.64	1.09	0.82
P_2O_5	0.09	0.16	0.27	0.18	0.34	0.07	0.39	0.09	0.09	1.05	0.12	0.23
SO_3	1.32	1.80	0.80	0.92	1.20	1.40	2.65	1.75	1.67	0.47	6.27	7.02
Total C	0.64	5.16	4.54	4.41	1.69	4.71	8.18	4.76	4.57	2.06	0.73	0.40
H_2O^-	0.30	0.31	0.31	0.33	0.27	0.39	0.28	0.38	0.33	0.40	0.20	0.20

Table 5. Sulfur species in the 12 fly ashes (percent weight).

Fly ash	Sulfate S	Sulfide S	Total S
I1	0.43	0.10	0.53
I2	0.66	0.06	0.72
I3	0.26	0.06	0.32
I4	0.23	0.14	0.37
I5	0.42	0.06	0.48
I6	0.50	0.06	0.56
I7	0.97	0.09	1.06
I8	0.62	0.08	0.70
I9	0.57	0.10	0.67
W1	0.09	0.10	0.19
W2	2.39	0.12	2.51
W3	2.68	0.13	2.81

ashes were also characterized by greater amounts of Na, Ba, and Sr, while Al and Fe were lower as compared with the amounts in the Illinois Basin samples. These findings are similar to those reported in the coal and fly ash literature, in which higher levels of Ba, Ca, Mg, Na, and Sr have been generally associated with western lignite coals (Abernathy, 1969; Furr et al., 1977; Gluskoter et al., 1977; and Natusch et al., 1977).

The specific gravities reported in Table 2 for the Illinois Basin fly ashes are close to the specific gravity of pure quartz (SiO_2), which is 2.65. The higher specific gravities of the two lignite fly ashes W2 (3.0) and W3 (3.1) were probably due to the low carbon content (Table 4) and the dominant minerals--periclase (MgO), with a density of 3.58 and anhydrite ($CaSO_4$), at about 2.92.

The trace constituent concentrations in the fly ashes (Table 6) were extremely variable. Arsenic in the Illinois Basin samples (I1-I9) ranged from 21 to 360 mg/kg; Co varied from 38 to 88 mg/kg. Zinc was the most variable, ranging from 90 to 2,100 mg/kg. In spite of the variable nature of fly ash, the Illinois Basin samples can be broadly characterized as having greater trace constituent concentrations than the three western samples have. These trace constituents are (in order of decreasing average concentrations in the solid) Zn, Ni, Rb, Cs, Cr, Co, U, Ge, Mo, V, Li, Cd, Tl, Sm, Pb, Be, Eu, Tb, Ga, Ce, As, Cu, Lu, and Sc. Many of these elements have been cited in the literature as generally occurring in greater concentrations in eastern Paleozoic coals and their ashes than in western coals of Mesozoic and Tertiary-age (Abernathy, 1969; Gluskoter et al., 1977; Natusch et al., 1977; and Page et al., 1979). The average concentrations of Hf, Sb, Se, Ta, Th, W, and Yb in the fly ashes were not found to correlate with coal type in this study.

Table 6. Trace constituent concentrations (mg/kg) in the 12 fly ashes.

Constituent	Fly ash I1	I2	I3	I4	I5	I6	I7	I8	I9	W1	W2	W3
Ag	0.2	0.5	0.2	0.1	0.4	0.2	1	0.4	0.4	0.1	0.5	0.1
As	21	59	150	200	360	23	60	44	45	8	27	89
B	1700	1600	940	920	1300	1500	870	910	890	800	5000	2300
Ba	580	660	840	900	780	480	2000	730	600	3000	6300	13800
Be	11	14	28	29	15	13	9	11	9	7	4	7
Br	<5	<5	<5	<5	<5	<5	<5	4	4	<3	<7	<6
Cd	1.3	2.7	2.6	2.3	2.5	<1.0	37.8	5.1	4.7	<1.2	<1.1	<1.1
Ce	130	130	270	210	196	152	120	153	172	187	100	95
Co	38	47	88	82	63	42	41	45	46	11	10	13
Cr	222	284	172	172	172	176	310	232	225	43	45	47
Cs	12	15	13	13	14	13	17	14	14	5	3	2
Cu	79	126	125	115	97	70	189	78	78	47	96	50
Eu	2	3	3	4	3	2	2	2	2	2	<1	2
Ga	36	100	27	45	45	30	74	39	40	35	22	35
Ge	27	51	80	72	41	55	15	17	16	<9	<11	<11
Hf	6	7	7	7	6	6	6	6	6	14	8	7
Hg	<0.02	0.06	0.15	0.11	<0.09	0.23	<0.02	0.24	0.22	0.03	0.36	0.10
La	41	84	65	91	95	66	43	64	70	85	30	30
Li	105	82	117	105	324	120	95	110	110	88	110	53
Lu	1	1	2	1	1	1	1	1	1	1	1	1
Mo	56	99	56	44	43	100	70	91	91	14	20	27
Ni	106	153	253	241	174	97	155	121	116	<15	<14	17
Pb	116	145	224	184	450	200	149	249	252	81	104	72
Rb	157	176	200	164	182	164	246	167	167	50	35	24
Sb	3	5	17	14	12	4	10	9	8	2	7	5
Sc	26	24	10	35	7	13	15	27	28	6	12	17
Se	19	24	10	8	7	13	15	12	15	6	19	10
Sm	11	20	14	20	14	13	12	13	13	13	4	5
Sr	430	<60	810	850	1140	390	510	470	420	1900	5500	7600
Ta	2	2	2	2	2	1	2	2	1	2	2	1
Tb	2	2	3	2	2	2	1	2	2	1	1	1
Th	22	26	31	27	25	22	23	25	24	33	24	21
Tl	16	19	11	12	16	11	42	18	19	<5	<7	<7
U	20	43	6	12	7	23	<6	26	31	4	<10	<10
W	2	7	1	2	3	3	<4	4	4	2	<5	<6
V	270	370	330	270	250	380	270	370	360	120	80	93
Yb	5	6	7	7	6	5	6	6	6	5	4	5
Zn	630	90	720	760	870	340	2100	950	880	60	43	30
Zr	270	312	380	320	290	280	310	280	290	<15	460	350

Fly ash classifications

The 12 fly ashes were classified by a system developed by Roy et al. (1981) and Roy and Griffin (1982). This system is based on the chemical composition of the solid waste and the pH of an ash:distilled water mixture (1:1). Seven of the nine Illinois Basin fly ashes were alkaline Modic silts (Fig. 4). Fly ashes fitting into the Modic field have a sialic component (% weight of SiO_2 + Al_2O_3 + TiO_2), which indicates that these elements consist of a combination of from >48% to 88% of the total mass. The ferric component (% weight of Fe_2O_3 + SO_3) is from 0 to 23%, and the Calcic component (CaO + MgO + Na_2O + K_2O) is from 0 to 29%. These seven

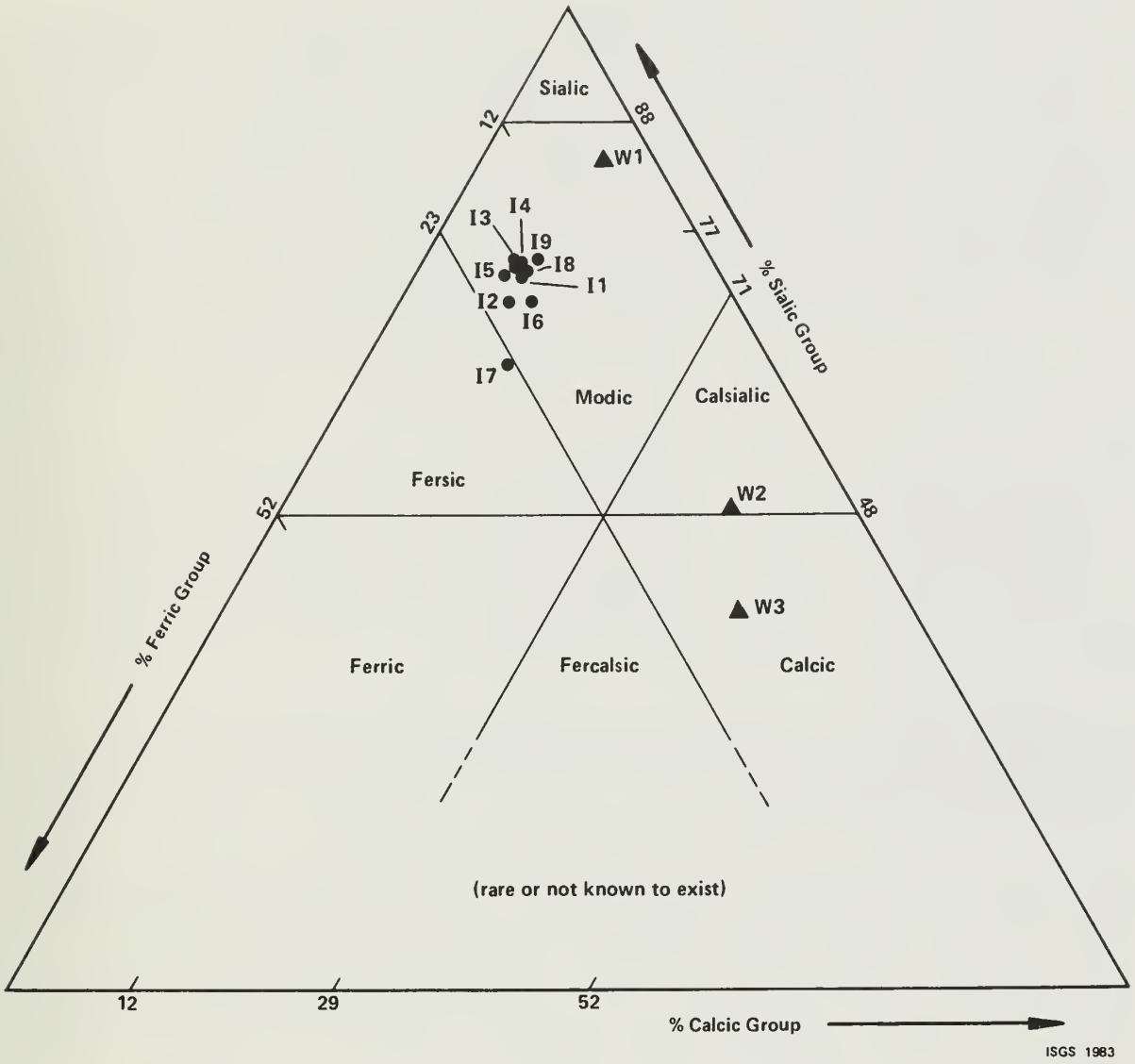

Figure 4. The 12 fly ashes plotted on the Sialic-Ferric-Calcic diagram for classification.

fly ashes produced alkaline leachates with pH values greater than 9.0 and had silt textures. The other two Illinois Basin samples differed in chemical composition: I2 was an acid C-Modic silt loam, and I7 was an acid C,Zn-Fersic silt. These two fly ashes produced acidic extracts. Both fly ashes had total C levels exceeding 5% and I2 was characterized by a high ferric component (Fig. 4) and Zn content (>0.2%). The two lignite-base fly ashes (W2 and W3) plotted more toward the Calcic end member than did the Illinois Basin samples. Fly ash W2 was an alkaline B,Ba,Sr-Calsialic, and W3 was classified as an alkaline B,Ba,Sr-Calcic. The subbituminous fly ash (W1) was an alkaline Ba-Modic silt. A summation of the classifications of all 12 fly ashes is given in Table 7.

Figure 5 shows the positions of the fly ashes in this study and 27 other fly ashes on the sialic-ferric-calcic compositional field diagram. Twenty-one of the samples were fly ashes generated from eastern U.S.

Table 7. Fly ash sample classifications.

Sample	Type
I1	alkaline Modic silt
I2	acid C-Modic silt loam
I3	alkaline Modic silt
I4	alkaline Modic silt
I5	alkaline Modic silt
I6	alkaline Modic silt
I7	acid C, Zn-Fersic silt
I8	alkaline Modic silt
I9	alkaline Modic silt
W1	alkaline Ba-Modic silt
W2	alkaline B, Ba, Sr-Calsialic[a]
W3	alkaline B, Ba, Sr-Calcic[a]

[a]Texture was not determined

bituminous coals, one from a German bituminous coal and the other 17 samples were derived from subbituminous and lignite coals from the western U.S., India, and Australia.

Fly ashes from eastern U.S. bituminous coals tended to fall on the left side of the diagram in the Modic and Fersic fields (Fig. 5): this pattern is reasonable, because the eastern U.S. coals generally have higher concentrations of Fe than do western coals (Gluskoter et al., 1977). Fly ashes from western U.S. lignite and subbituminous coals tended to plot on the right side of the diagram in the Modic, Calsialic, and Calcic fields. Western U.S. coals are generally associated with higher levels of Ca, Mg, and Na than are eastern coals (Abernathy, 1969; Furr et al., 1977; Gluskoter et al., 1977). Near the Sialic-Modic boundary are three fly ashes generated from lignite coals in India. Indian lignite coal is characteristically low in Ca (Chopra et al., 1979); therefore, these fly ashes did not fit the general pattern for the U.S. ashes. Additional work with high-iron fly ashes is needed to provide a clearer indication of the distribution of Ferrics and Fercalcics; few such fly ashes are completely characterized in the literature. However, the magnetic fractions of some Fersics and Modics can be classified as Ferrics, as shown in Figure 5.

ORGANIC MATTER CHARACTERIZATION OF SELECTED FLY ASH SAMPLES

Solvent extraction

Five fly ashes were extracted with benzene. An amount of elemental sulfur equivalent to about 10% of the total extractable material in each ash was co-extracted with the organic matter and interfered with the quantification

of the total extractable organics. The elemental sulfur was removed by passing the extract through activated copper powder following the first concentration step. The amount of the benzene-extractable organic matter in each fly ash sample is reported as mg/kg of fly ash and as a percent weight of the organic C contained in the sample (Table 8). The C and S values for each fly ash sample are also reported in Table 8. In two western fly ashes (W1 and W2), less than 1% of the total organic C was benzene-extractable; in two other fly ashes (I6 and I8), less than 0.1% of the C was extracted into benzene. The unburned and partly burned coal particles in the fly ashes are presumed to be the source of most of the organic C. These coal particles would be only slightly soluble in benzene.

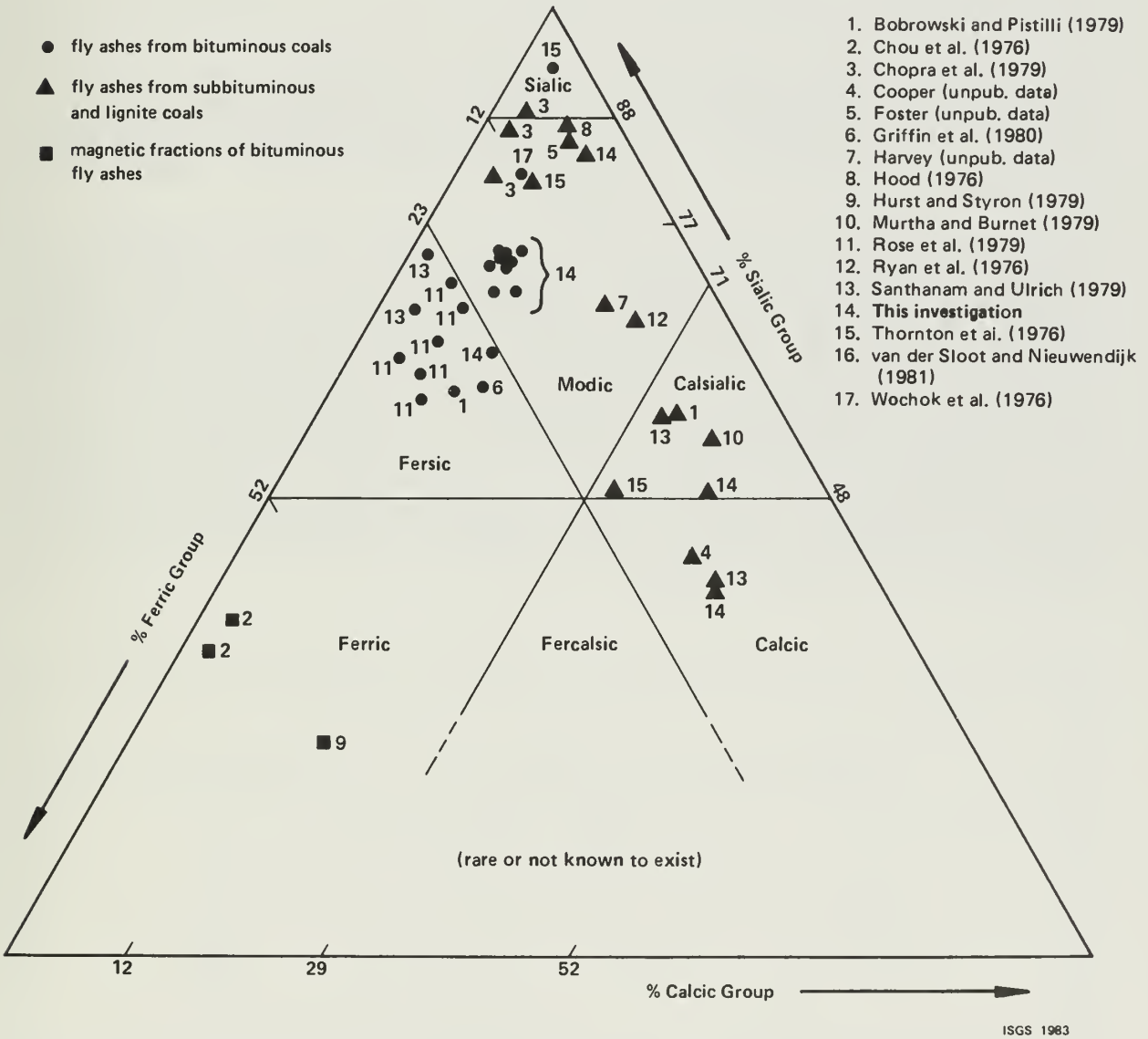

Figure 5. The 12 fly ash samples and 27 other fly ash samples from the literature plotted on the Sialic-Ferric-Calcic diagram for classification.

Table 8. Carbon, sulfur, and benzene-extractable organic matter of selected fly ashes.

Fly Ash	Total C (%)	Inorganic C (%)	Organic C (%)	Total S (%)	Benzene Extractable (mg/kg)	Benzene Extractable Organic C (%)
I5	1.69	<0.02	1.69	0.48	38.0	0.22
I6	4.71	<0.02	4.71	0.56	17.1	0.04
I8	4.76	<0.02	4.76	0.70	37.4	0.08
W1	2.06	1.33	0.73	0.19	60.6	0.83
W2	0.73	<0.02	0.73	2.51	57.5	0.78

The infrared spectrum (Fig. 6, for example) of the benzene extracts was used for comparison with the infrared spectra of the corresponding LC fractions of the extracts. Absorption peaks due to aliphatic and aromatic structures and from hydroxyl, carbonyl, ether, and nitrogen containing groups were evident in all the extracts.

The benzene extracts of four of the fly ashes were separated into seven LC fractions according to the Level 1 procedure. Only 11 mg of extract was obtained from fly ash I6; because the LC separation could not be done with this small amount of extract, the analysis of this sample was discontinued. The results from LC fractionation are expressed gravimetrically as milligrams of solvent-free LC fraction per kilogram of fly ash (Table 9). Except for the extract from W1, the major portions of the organics in the extracts were found in fractions LC-1 and LC-6. The LC fractions of the W1 extract were more evenly distributed on a weight percent basis than were those of the other fly ashes. The IR spectrum indicated that the W1 extract had a somewhat different distribution of compounds (Fig. 7) than did the other fly ashes examined.

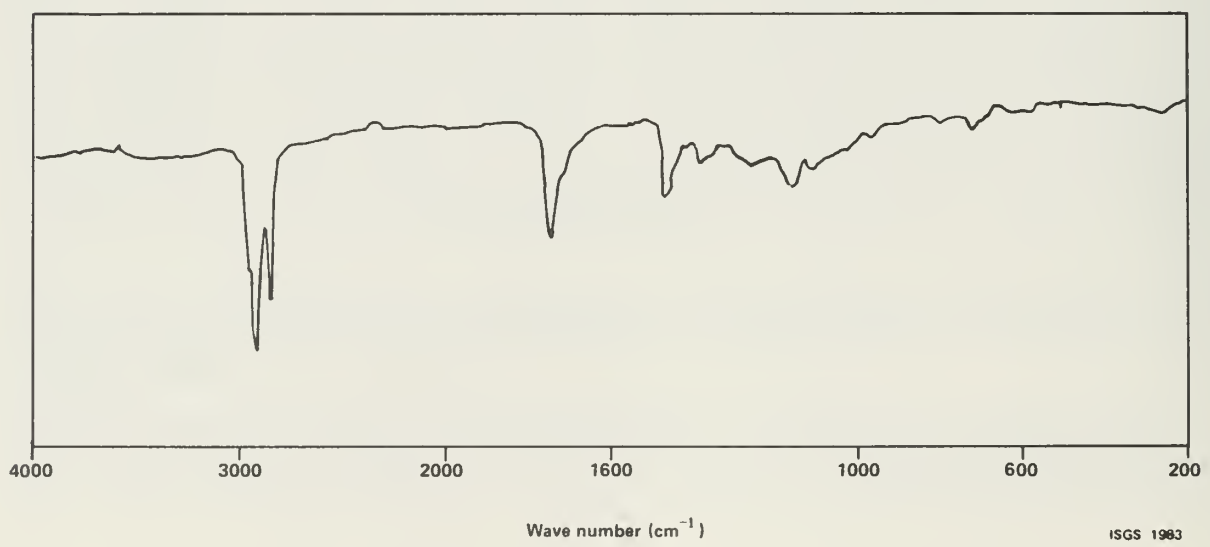

Figure 6. Infrared spectrum of the benzene-extractable organic material in fly ash I8.

Table 9. Liquid chromatographic fractionation of the benzene extracts of four fly ashes.

Fly Ash	mg LC fraction per kg fly ash						
	LC-1	LC-2	LC-3	LC-4	LC-5	LC-6	LC-7
I5	16.0	0.1	1.3	1.8	2.3	9.3	1.2
I8	16.0	0.1	1.8	2.1	1.8	8.7	1.6
W1	13.0	1.3	8.2	3.9	2.6	6.0	1.9
W2	29.1	1.7	2.3	2.8	2.2	4.7	1.1

The infrared spectra of the LC-1 fractions of all the fly ash samples were very similar and were typical of aliphatic hydrocarbons showing strong $-CH_3$ and $-CH_2$ stretching absorptions, medium $-CH_2-C(CH_3)_2$, and symmetrical $-C-CH_3$ deformation absorptions (Fig. 8). Gas chromatograms of these fractions contained peaks for all n-paraffins from C_{11} through approximately C_{36}, and numerous peaks due to much smaller concentrations of branched-chain aliphatics.

The infrared spectra of the LC-2 fractions showed that the fractions were highly aliphatic, with very weak aromatic absorptions, indicating alkyl-substituted and/or fused-ring aromatics. The gas chromatograms of these fractions indicated that the major constituents were n-paraffins. The HPLC chromatogram of the LC-2 fraction of fly ash W1 (Fig. 9) had nine major peaks including phenanthrene, pyrene, and chrysene. Phenanthrene and pyrene were also detected in coal ash in a study discussed in EPRI (1978). Numerous smaller peaks, most of which were eluted prior to chrysene, appeared in the HPLC chromatogram. This fact indicated that smaller quantities of polynuclear aromatic hydrocarbons other than chrysene (of lower molecular weight than chrysene and phenols) were possibly present in the fly ash.

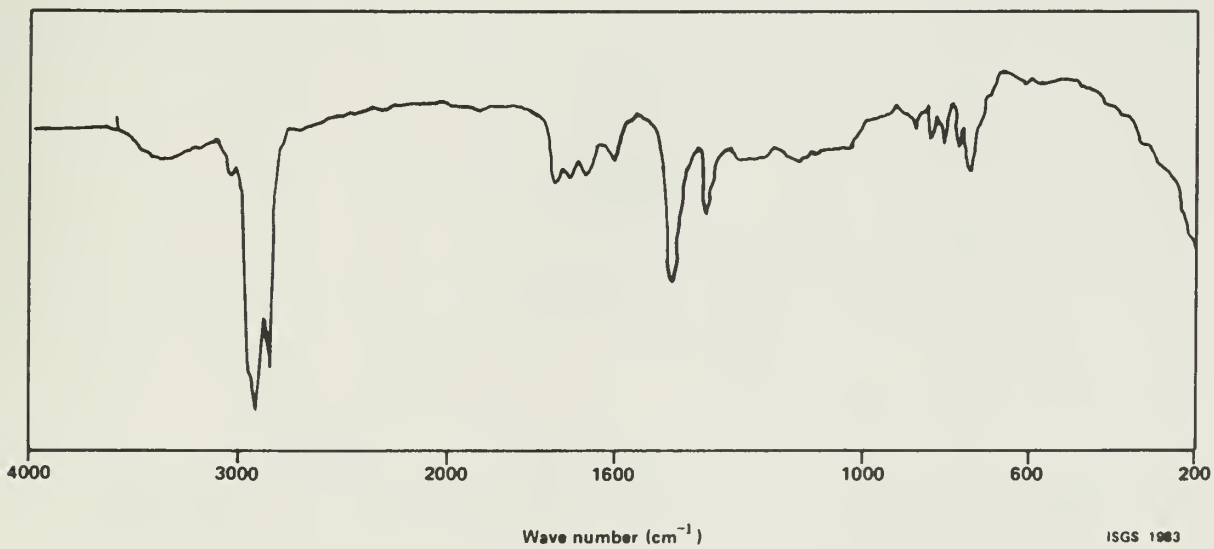

Figure 7. Infrared spectrum of the benzene-extractable organic material in fly ash W1.

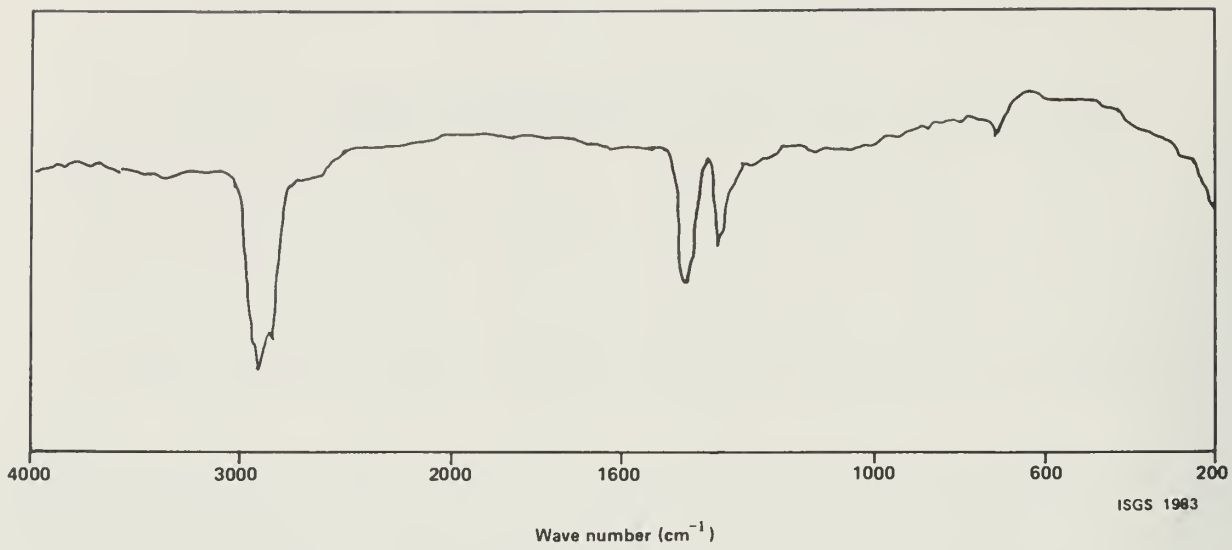

Figure 8. Infrared spectrum of the LC-1 fraction from the benzene extract of fly ash W1.

The infrared spectra of the LC-3 samples exhibited strong aliphatic absorption peaks and weak aromatic peaks except for the W1 LC-3 fraction (Fig. 10), which appeared to have more aromatic compounds than the remaining three LC-3 fractions. There were also strong absorptions in the carbonyl (1750-1700 cm^{-1}) regions of the W1 LC-3 spectrum. Because these appeared in fraction LC-3, they were likely due to long-chain aliphatic esters or aryl esters. The aryl esters were first thought to be contaminants of plasticizers introduced during sample handling. Plastic bags were used as storage containers prior to organic analysis (both ethyl and diethyl phthalate were identified by GC-MS in the 450°C pyrolysate of fly ash W1). However, aryl esters have been recently indicated in a char

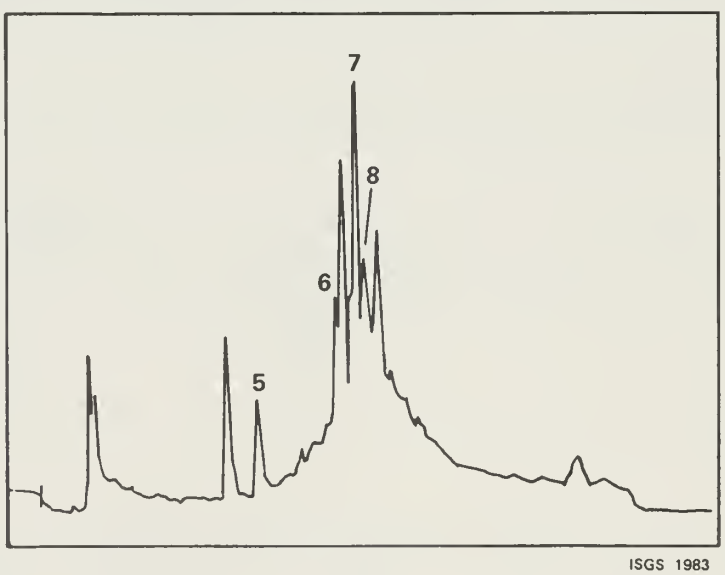

Figure 9. HPLC chromatogram of the LC-2 fraction from the benzene extract of fly ash W1. See Figure 2 for identification of the numbered peaks.

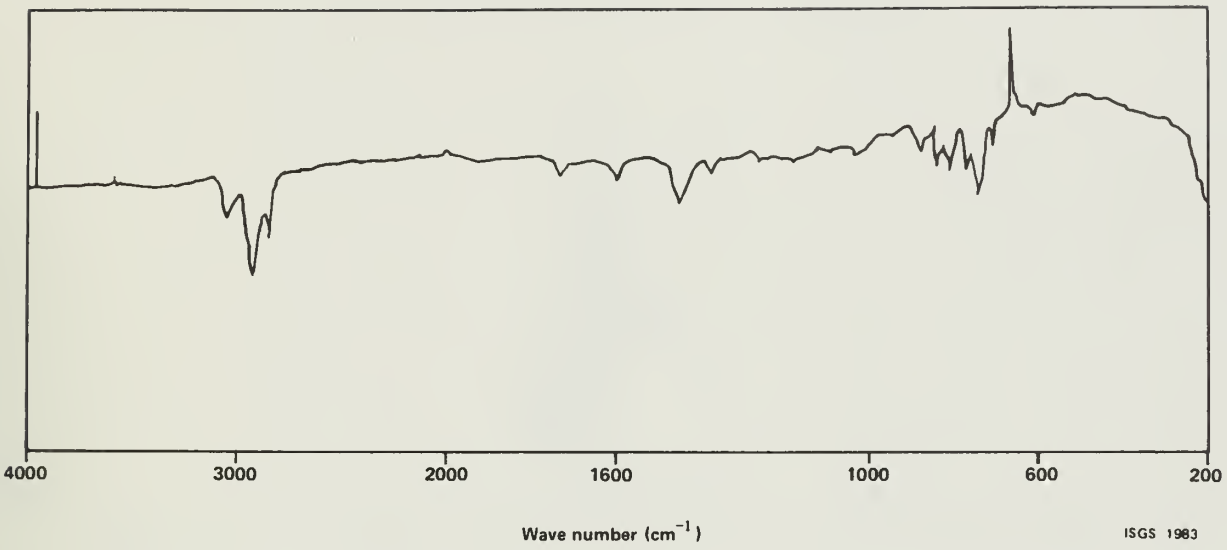

Figure 10. Infrared spectrum of the LC-3 fraction from the benzene-extractable organic matter in fly ash W1.

prepared by heating coal at 350°C in a fluidized bed (Fuller et al., 1982). Also, aryl esters were inexplicably found in the fly ash wash water from a power plant (F. Harrison, Lawrence Livermore National Laboratory, personal communication, 1982). The gas chromatograms of the LC-3 samples showed the presence of eight to ten dominant components, which are as yet unidentified (Fig. 11).

The PAHs (phenanthrene, pyrene, and chrysene) were identified in the LC-3 samples using HPLC. Numerous other smaller peaks due to aromatics having molecular weights higher than chrysene were also detected. The HPLC chromatogram of W1 LC-3 is shown in Figure 12.

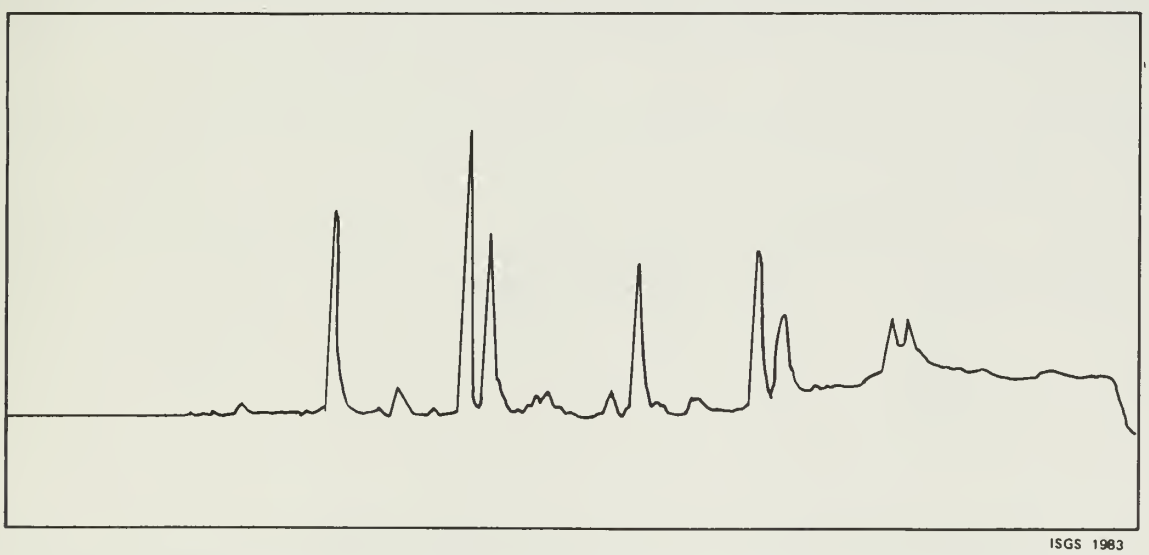

Figure 11. Gas chromatogram of the LC-3 fraction from the benzene-extractable organic matter in fly ash W1.

Figure 12. HPLC chromatogram of the LC-3 fraction from the benzene extract of fly ash W1. See Figure 2 for identification of the numbered peaks.

The infrared spectra of the LC-4 fractions showed the beginning of major differences in the compositions of the organics derived from the various fly ashes. The LC-4 fraction of W1 (like the LC-3 fraction) contained more aromatic compounds and was more complex in composition than were the organics in the other fly ashes. The peaks due to carbonyl absorption were resolved into at least two distinct peaks (Fig. 13), indicating the presence of both aliphatic and aryl esters or long-chain aldehydes and ketones. Phenanthrene and pyrene were again identified by HPLC (Fig. 14). Other smaller peaks eluted earlier than pyrene; this was interpreted to indicate that polar compounds were beginning to be eluted. There were no major peaks later than that of pyrene.

Figure 13. Infrared spectrum of the LC-4 fraction from the benzene extract of fly ash W1.

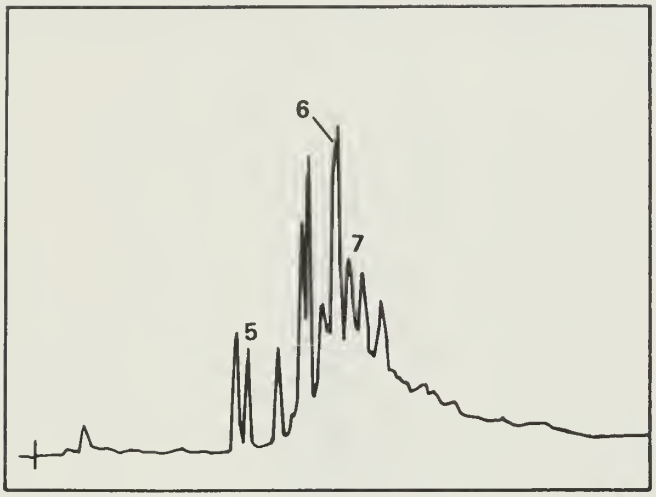

Figure 14. HPLC chromatogram of the LC-4 fraction from the benzene extract of fly ash W1. See Figure 2 for identification of the numbered peaks.

The infrared spectra of the LC-5 fractions were similar to the spectra of the LC-4 samples, except that the LC-5 fraction from I8 had anomalous and unassigned peaks at 2340 and 1690 cm^{-1} (Fig. 15). The W1 sample had more carbonyl peaks than the other fly ash samples (such as the peak at 1630 cm^{-1}) indicating the possible presence of additional aldehydes and ketones. The 1675 cm^{-1} peak may be due to hydroxyl overtones.

The HPLC chromatogram of the LC-5 fraction from the W1 fly ash extract (Fig. 16) showed numerous peaks with retention times in the same range as those of PAHs. According to the Level 1 scheme, this fraction contains aromatics with polar functional groups.

The infrared spectra of the LC-6 fractions for I5, I8, and W2 were quite similar, with strong hydroxyl, carboxyl, and carbonyl absorptions. The infrared spectrum of the LC-6 fraction from W1 (Fig. 17) had well-resolved

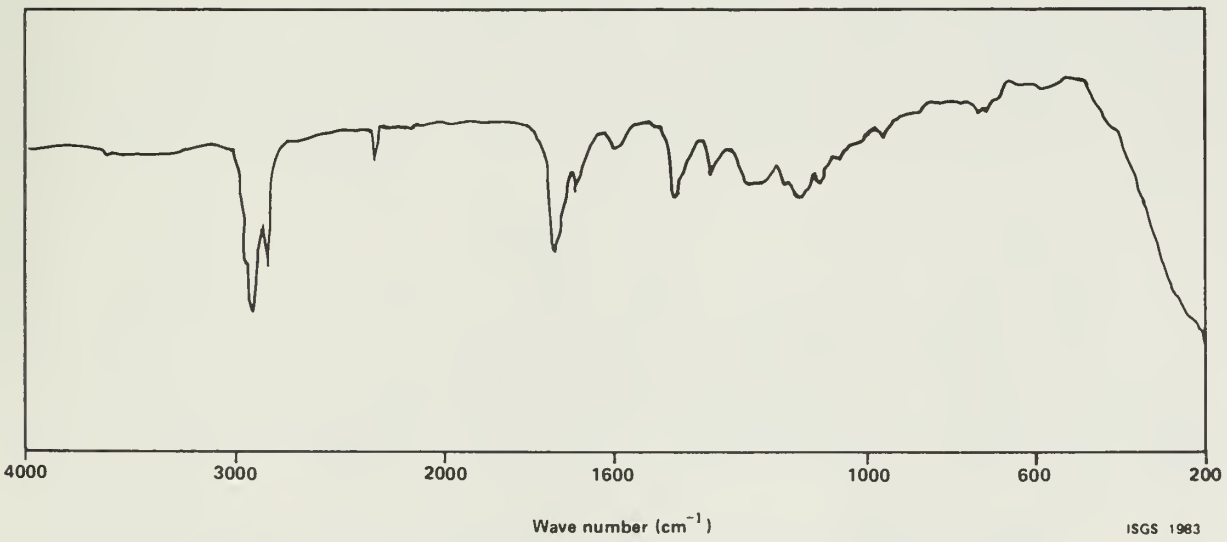

Figure 15. Infrared spectrum of the LC-5 fraction from the benzene extract of fly ash I8.

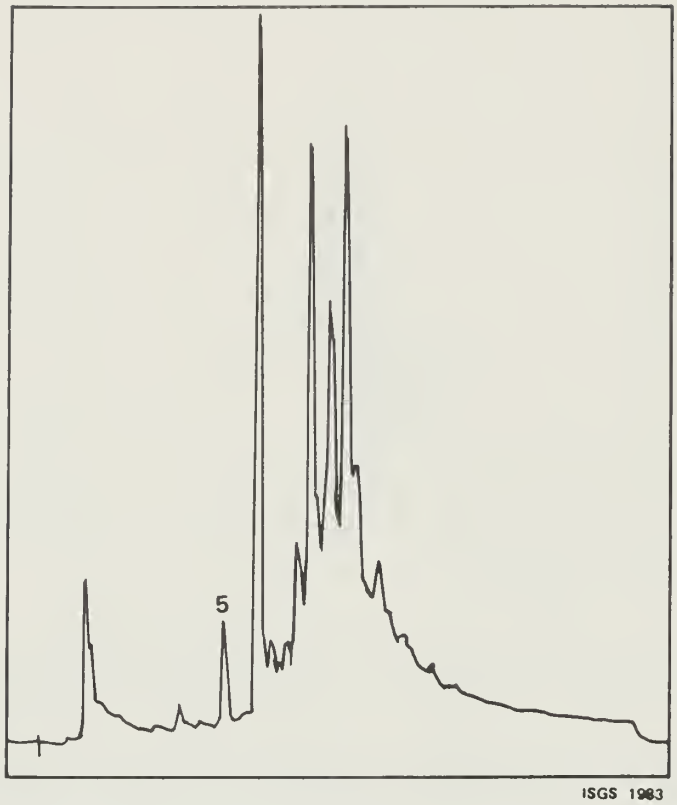

Figure 16. HPLC chromatogram of the LC-5 fraction from the benzene extract of fly ash W1. Peak 5 is toluene, the internal standard.

absorptions at 3190 and 3355 cm^{-1}, overriding a broad hydroxyl peak and the peaks indicating aromatic character. These latter peaks were probably amino-nitrogen peaks. HPLC analysis showed that the sample probably contained a large number of phenolic compounds as well as other polar aromatics (Fig. 18).

Figure 17. Infrared spectrum of the LC-6 fraction from the benzene extract of fly ash W1.

Figure 18. HPLC chromatogram of the LC-6 fraction from the benzene extract of fly ash W1. Peak 5 is toluene, the internal standard.

The LC-7 fractions were quite small and appeared to be contaminated with silica gel from the column. Infrared intensities were weak, but the absorptions were essentially comparable to the absorptions in the respective LC-6 fractions. The HPLC results showed only one major peak, which eluted earlier than toluene and was assumed to be a strongly polar compound.

Some of the organics identified with these fly ashes are on the priority pollutant list; however, they are present in very small quantities (ppb levels at most), which are comparable to results reported elsewhere (EPRI, 1979). However, the organics associated with these fly ash samples do not appear to be present in concentrations that would pose any significant environmental hazard during landfilling operations or to the aquatic environment during ponding.

Pyrolysis studies

The noncondensable gas in the headspace was analyzed by gas chromatography. The results of these analyses are given in Table 10. The detection of a particular component is indicated by an "x" in the appropriate column. Because the headspace was still at a reduced pressure at the time of analysis, no attempt was made to quantify the amount of any of the individual components. Only saturated and unsaturated hydrocarbons of low molecular weight--typically found in the pyrolysates of higher hydrocarbons--were detected. In the W1 pyrolysate, carbon dioxide accounted for more than 50% of the total chromatographable gases.

Table 10. Hydrocarbons detected in the noncondensable pyrolysates (pyrolysis at 450°C except where indicated).

Hydrocarbon	Fly Ash								W1			W2	W3
	I2	I3	I4	I5	I6	I7	I8	I9	300°C	400°C	450°C		
methane	x	x	x	x	x	x	x	x	x	x	x	x	x
ethylene	x	x	x	x	x		x	x	x	x	x	x	x
ethane	x	x	x	x	x	x	x	x		x	x	x	x
propylene	x	x	x	x	x		x	x	x	x	x	x	x
propane	x	x		x	x	x	x			x	x	x	x
iso-butane	x	x	x	x	x	x	x	x	x	x	x	x	x
2-methyl propene				x						x	x	x	x
1-butene	x	x	x	x	x	x	x	x	x		x	x	x
n-butane	x	x	x	x	x	x	x	x		x	x	x	x
2-methyl butene				x						x	x	x	x
iso-pentane		x	x	x	x	x	x	x	x	x	x	x	x
1-pentene	x	x		x							x	x	x
3-methyl butene				x								x	x
n-pentane	x	x		x	x	x	x	x	x	x	x	x	x
2-methyl pentene												x	x
4-methyl pentene												x	x
1-hexene						?						x	x
n-hexene		x	x			?		x			x	x	x

Table 11. Organic components in the condensable pyrolysates of the fly ashes: (x) detected; (xx) detected in larger quantity; (t) trace; (?) retention time does not match.

Organic Component	Fly Ash										
	I2	I3	I4	I5	I6	I7	I8	I9	W1	W2	W3
toluene									x		
ethyl phthalate	x	xx	x	xx	x			xx	x		t
n-C_{14}	x	x	x		x	x					t
n-C_{15}	x	x	x	t	x	x					t
n-C_{16}	x	x	x	t	xx	x	x	x	xx		t
i-C_{17}	x			t	x		x		x	x	
n-C_{17}	x	x	x	t	x	x	x	x	x	x	t
i-C_{18}	x		x	t	x		x	x	x		
n-C_{18}	x		x	t	x	x	x	x	x	x	t
n-C_{19}	x	x	x	x	x	x	x	x	x	x	t
diethyl phthalate	x	xx	xx	xx	xx		xx	xx	x	xx	t
n-C_{20}	x			x	x	x	x		x		t
i-C_{21}					x						
n-C_{21}	x	?	x	x	x	x	x	?		x	
i-C_{22}				x	x				x		
n-C_{22}	x		xx	x	x	x			x	x	t
n-C_{23}				xx	x	t					
n-C_{24}	x		x	t	xx	x	x	x	x	x	t
n-C_{25}	x		x	t			x	x		x	
n-C_{26}	xx			xx		x				x	
n-C_{27}											
C_{28}?	x		x				xx	x	xx	xx	
C_{28}?	x		x			xx	xx	x		xx	

The "GC-fingerprints" of the noncondensable gas produced from the I1, I2, I3, I4, and I7 samples were similar in the kind and quantity of any given component (Figs. 19, 20; Table 11). The I5, W1, W2, and W3 condensates were also similar to each other (Figs. 21, 22); however, the two groups were quite dissimilar in that the non-condensables from the latter four ashes contained major components that were present in much lower quantities or did not appear in the former group.

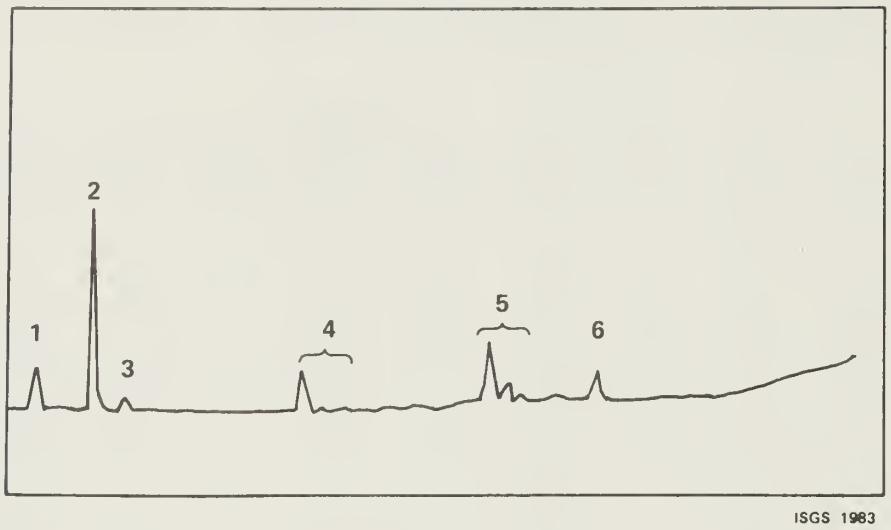

Figure 19. Gas chromatogram of the noncondensable hydrocarbons produced by pyrolysis at 450°C of fly ash I2. Peak identification: 1. methane; 2. ethylene; 3. ethane; 4. C_3's; 5. C_4's; 6. C_5's.

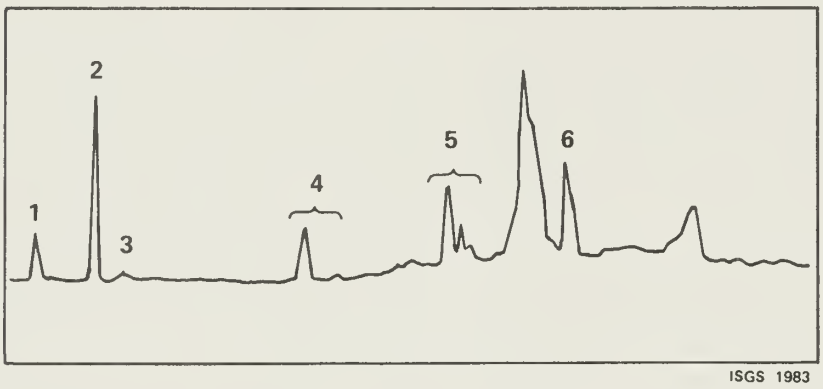

Figure 20. Gas chromatogram of the noncondensable hydrocarbons produced by pyrolysis at 450°C of fly ash I3. See Figure 19 for identification of the numbered peaks.

The condensable fraction from the pyrolysis of the W1 sample was analyzed by GC-MS. The major components detected were the n-paraffins with 13 to 28 carbon atoms per molecule. The compounds present in the largest quantities were n-C_{13}, n-C_{18}, n-C_{20}, n-C_{22}, n-C_{24}, and n-C_{28} (Fig. 23). In a study discussed in EPRI (1978), n-C_{17}, n-C_{18}, n-C_{21}, n-C_{22}, and n-C_{27-31} were the dominant hydrocarbons in an ash sample, existing in the 516 to 816 µg/kg concentration range. This range is consistent with the semiquantitative analysis reported here.

The results from this study are typical of results obtained when coal char is pyrolyzed under similar conditions. These results lead to the conclusion that a probable source of these hydrocarbons was the coal particles present in the ash. However, aryl esters, especially ethyl- and diethyl phthalate were detected in significant quantities. Diethyl phthalate appeared to be the major component in the condensates of the other fly ashes used in this study. The source of these phthalates in the condensates may have been the plastic bags used to store the samples. A

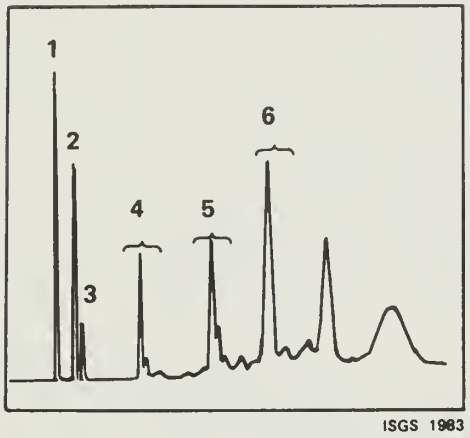

Figure 21. Gas chromatogram of the noncondensable hydrocarbons produced by pyrolysis at 450°C of fly ash W2. See Figure 19 for identification of the numbered peaks.

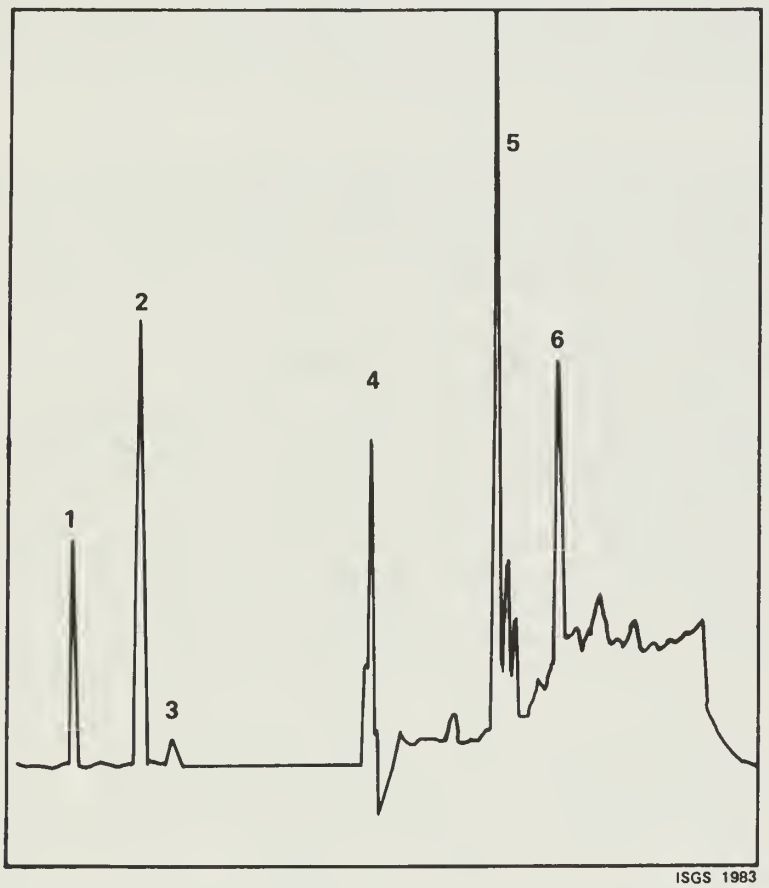

Figure 22. Gas chromatogram of the noncondensable hydrocarbons produced by pyrolysis at 450°C of fly ash I5. See Figure 19 for identification of the numbered peaks.

similar result was observed from benzene extracts of these ashes. However, others (Fuller et al., 1982; Harrison, personal communication, 1982) have reported aryl esters in char prepared in a manner that would preclude aryl ester contamination and in fly ash wash water.

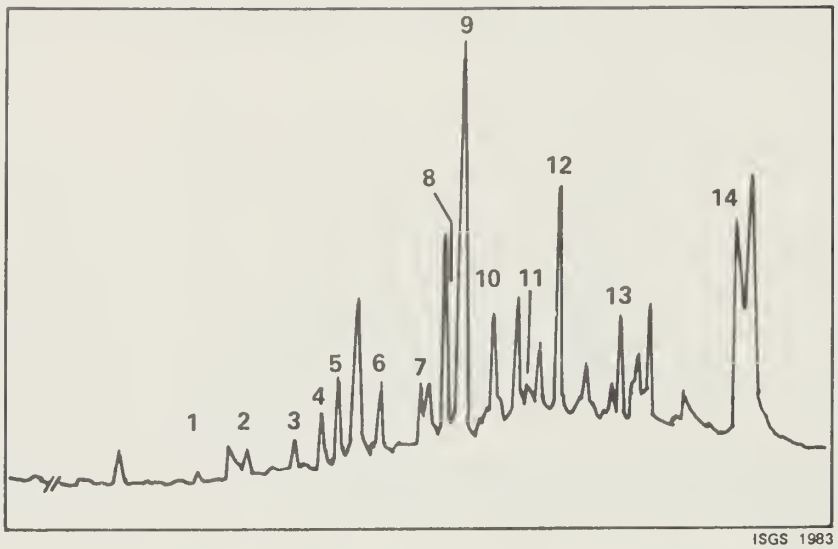

Figura 23. Gas chromatogram of the condensable organics produced by pyrolysis at 300°C of fly ash W1. Peak identification: 1. n-tridecane; 2. n-tetradecane; 3. n-pentadecane; 4. ethyl phthalate; 5. n-hexadecane; 6. n-heptadecane; 7. n-octadecane; 8. n-nondecane; 9. diethyl phthalate; 10. n-eicosane; 11. n-heneicosane; 12. n-docosane; 13. n-tetracosane; 14. n-octacosane.

Identification of the major condensable components derived from the other fly ash samples was accomplished by making comparisons to the W1 GC-MS data and to the GC retention times of standards. Many other components were also detected; however, they were not sufficiently well-resolved nor present in large enough concentrations to permit identification.

CHARACTERIZATION OF THE FLY ASH EXTRACTS

Conventional chemical analysis of fly ash cannot presently be used to determine the mobility of potentially toxic trace constituents in aquatic ecosystems. Most fly ashes are composed primarily of aluminosilicate glass spheres that are only slightly soluble; however, the surfaces of the glassy spheres of the individual fly ash particles may contain adsorbed molecules of potentially toxic constituents that may be desorbed into water. The toxicity of leachates to aquatic organisms may be due partly to the release of some trace constituents that are absorbed on the surfaces of the particles rather than bound up in the insoluble glassy matrix.

To evaluate the potential for water and soil contamination from the leaching of fly ash, several laboratory extraction methods have been proposed. Several leaching procedures and solubility studies were reviewed by Roy et al. (1981). The overall indication of these studies was that field leachates or laboratory extracts from fly ashes were extremely variable, as were the solid wastes. The variable nature of an ash and its leachate was directly related to the operating conditions of the individual power plants, the composition of the coals being used, and the leaching or extraction procedures employed.

The pH of fly ash leachate may range from 4 to more than 12; alkaline solutions were more commonly reported (Roy et al., 1981). Short-term extracts generated by the two reddish-brown samples (I2 and I7, Table 1) were acidic (about pH 4.2), whereas the grayer samples (Table 1) were all alkaline (pH >11). The color of fly ashes may be useful in predicting the initial pH of a leachate. The ratio of matrix CaO to SO_3 may

influence the pH of the leachates. For the 12 samples in this study and the acid Fersic (an acidic high-iron fly ash) studied by Griffin et al. (1980), short-term (24-hour) extracts that were acidic were associated with samples having a CaO/SO_3 ratio of less than two. Alkaline extracts were produced from samples having a matrix CaO/SO_3 ratio exceeding two. This observation may reinforce an observation by Swaine (1977) that H_2SO_4 exists on some fly ash particle surfaces. The presence of H_2SO_4 could result in acidic extracts from some ashes while the resulting pH is influenced by the dissolution of matrix lime in systems.

U.S. EPA Extraction Procedure (EP)

The results of the application of the proposed U.S. EPA Extraction Procedure (EP) are given in Table 12. The pH of all the extracts associated with the Illinois Basin samples was approximately 5.0, because the procedure calls for adjusting the pHs of the solutions to this value. However, the two lignite-base samples W2 and W3 still retained their alkaline character after the addition of the maximum allowable amount of acetic acid (800 mL of 0.5N). The extreme buffering capacity of these two samples could produce very alkaline leachates in improper disposal schemes.

Results (Table 12) indicated that, while the major constituents of the solid waste (Al, Si, and Fe) were only slightly soluble in this leaching environment, some trace and minor constituents were very soluble. Most of the S (90.0 $\pm$ 16.6%) in the Illinois fly ashes was soluble, whereas about 18 to 75% of the matrix Ca went into solution. The amount of soluble B ranged from about 24 to 56% of the total, averaging about 44%, comparable to the amount of soluble B (about 50%) observed by Cox et al. (1978) in a short-term extraction procedure with an Illinois Basin fly ash. Calcium, S, and B were consistently the most soluble major constituents in the western ashes. Calcium was found to be among the most soluble constituents in lignite fly ashes by other investigators (Churey et al., 1979). The most soluble trace metal in the Illinois fly ashes was Zn; Ba was the most soluble trace metal in the subbituminous fly ash (W1). The concentration of 0.16 mg/L As in the W1 solution indicated that about 40% of the available As was soluble. About 20% of the matrix Se in W1 was soluble, and Se concentrations were below detection limits in the Illinois fly ash extracts. Nearly 37% of the total Se in the W2 fly ash was solubilized, producing a solution with 0.35 mg Se/L. Churey et al. (1979) also found Se very soluble in ashes from lignite coals. Chromium and Zn concentrations did not exhibit any discernible pattern; the amount of soluble Zn varied from 1.65 percent in I3 to nearly 29% in I1. The EP test may not have been conducive to Zn extraction, or these results may indicate that most of the Zn in some samples was bound in the glassy matrix and did not exist as an adsorbed surface constituent or a soluble salt such as $ZnSO_4 \cdot H_2O$ as proposed by Henry and Knapp (1980).

In reporting on leachability trends, Natusch et al. generalized that Fe, Si, Ba, Ca, and Mg were among the least soluble constituents. This study indicates that Ca and Mg may be more soluble when fly ash is subjected to the leaching conditions of the proposed EP procedure. Natusch et al. (1977) also concluded that Mn and Zn exhibited substantial extractability. In the present study, Mn and Zn were also among the more soluble

Table 12. Chemical constituent concentrations obtained by the proposed U.S. EPA Extraction Procedure (EP) performed on the 12 fly ashes (concentrations in mg/L).

	Fly ash											
	I1	I2	I3	I4	I5	I6	I7	I8	I9	W1	W2	W3
pH	4.9	5.2	5.2	5.1	5.2	5.1	5.0	5.0	4.9	5.2	9.4	10.8
Total alkalinity[a]	—	—	—	—	—	—	—	—	—	—	5266	5250
phenolphthalein alk.[a]	—	—	—	—	—	—	—	—	—	—	350	202
E.C. in mmhos/cm	1.53	2.99	2.25	1.17	2.39	4.11	2.23	3.08	3.13	2.46	9.51	10.70
Eh in mV[b]	+403	+450	+450	+484	+446	+446	+427	+433	+442	+456	+282	+212
Al	3.84	5.55	1.19	1.54	0.71	14.7	0.61	19.2	20.1	<0.13	<0.13	14.4
As	<0.08	<0.08	0.13	0.14	0.12	<0.08	<0.08	<0.08	0.10	0.16	<0.08	<0.08
B	20.6	39.1	21.2	18.0	32.5	25.4	24.3	22.3	23.6	17.1	104	35.2
Ba	0.06	0.20	0.13	0.13	0.13	0.21	0.05	0.10	0.10	0.49	0.39	0.36
Be	0.01	0.003	0.004	0.004	<0.002	0.01	0.002	0.01	0.01	<0.002	0.004	0.003
Ca	337	881	542	507	662	1344	563	847	878	662	2352	1619
Cd	0.12	0.04	0.07	0.06	0.05	0.03	1.38	0.13	0.14	<0.01	<0.01	<0.01
Cr	<0.02	0.36	<0.02	<0.02	<0.02	0.19	<0.02	0.32	0.38	<0.02	0.04	<0.02
Cu	0.28	0.09	0.17	0.09	<0.02	0.03	0.32	0.04	0.06	<0.02	<0.02	<0.02
Fe	0.77	0.17	0.05	<0.05	<0.05	0.45	0.11	0.38	0.43	<0.05	<0.05	<0.05
K	19.1	14.0	21.5	17.2	22.5	13.6	58.9	35.1	27.4	2.50	62.8	85.4
Mg	9.43	9.61	7.96	6.62	9.44	15.8	23.1	15.7	14.9	43.6	244	1.08
Mn	1.04	1.30	1.59	1.19	2.43	3.99	2.61	1.70	1.66	0.47	0.15	<0.004
Mo	0.01	0.47	0.27	0.22	0.16	0.29	0.12	0.33	0.36	0.08	0.51	0.38
Na	17.9	6.52	5.09	5.41	19.2	4.38	111	4.35	3.66	1.77	700	2082
Ni	0.28	0.09	0.16	0.13	0.18	0.15	0.61	0.22	0.21	<0.02	<0.02	<0.02
Pb	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.08	<0.04
Sb	<0.05	<0.05	0.11	0.10	0.06	0.07	<0.05	0.05	0.06	<0.05	0.08	<0.05
Se	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.04	<0.04	0.06	0.35	0.13
Si	11.9	24.8	15.2	15.3	20.8	33.3	16.9	21.6	25.9	37.3	24.7	0.61
Sn	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
V	<0.08	<0.08	<0.08	<0.08	<0.08	<0.04	<0.08	<0.08	<0.08	<0.08	0.11	<0.08
Zn	4.23	6.80	1.20	0.76	1.21	1.65	12.6	3.20	3.32	0.28	0.28	0.44
SO_4	927	719	436	349	714	783	1591	932	909	161	1566	1744

[a] As mg/L $CaCO_3$

[b] Relative to a normal hydrogen electrode

constituents. The amount of soluble Mn averaged 12.88 ± 6.29% in the Illinois Basin samples.

The general trend of EP solubility for the Illinois Basin fly ashes was: SO_4-S > Ca, B > Cd > Sb, Mn, Mg > Zn, Na, Mo > K, Ni, Cr, Cu > Be, Ba, Si, Al, and Fe. The general pattern of EP solubility for the subbituminous fly ash W1 was: SO_4-S > B, As > Ca > Se > Mg, Zn > Mn > Na > K, and Ba; SO_4-S > B > K > Mo >> Se, Na > Ca > Zn, Mg > Be, Cr > Mn, Si, and Ba was the order for the lignite fly ashes W2 and W3. However, these solubility trends apply only to EP extracts; in dissimilar leaching environments, different extractability trends may be observed. In solubility or leaching experiments in which extraction takes place in alkaline conditions (as typical with many fly ash leachates), different solubility regimes in the resulting alkaline solutions may take place, since the pH of the extract is often the dominant factor controlling the solubility of many inorganic constituents.

The Cd level in the EP extract from I7 exceeded the recommended level outlined by the proposed U.S. EPA Resource Conservation and Recovery Act (RCRA) (Table 13). The concentrations listed are 100 times the EPA's National Interim Primary Drinking Water Standards (U.S. EPA, 1976).

If the EP extract contains any constituent exceeding the maximum allowable level for that given contaminant in an EP aqueous extract, the parent waste may be classified as a hazardous waste. The classification of a waste as potentially hazardous may also be based on criteria other than the EP data (U.S. EPA, 1980). Fly ash was recently removed from the list of Subtitle C in Section 3001 of RCRA. Therefore, all fly ashes are classified as

Table 13. Contaminant concentrations (mg/L) in EP extracts qualifying for hazardous waste classification (U.S. EPA, 1980).

Constituent	Concentration (mg/L)
Arsenic	5.0
Barium	100
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0
Endrin	0.02
Lindane	0.40
Methoxychlor	10.0
Toxaphene	0.50
2,4-D	10.0
2,4,5-TP Silvex	1.00

nonhazardous wastes under present criteria. However, these guidelines are still in a period of revision, and the status of fly ash as a nonhazardous waste may be modified.

If the status of power plant by-products were to be revised, one fly ash (I7) would fall into the hazardous waste classification. There was about 73.0% soluble Cd in this sample, releasing 1.38 mg Cd/L in solution; the maximum allowable extract level for Cd is 1.00 mg/L. On the basis of these data, the parent ashes of the other 11 EP extracts would not be classified as hazardous wastes under the present criteria.

LONG-TERM EQUILIBRATION EXTRACTION

Most aqueous systems of fly ash do not reach equilibrium in most short-term (24-hour) extraction tests (Elseewi et al., 1980). Short-term extraction procedures will leach out the more soluble salts, but other elements such as Sb, As, Ba, and Se (James et al., 1977), and Ca, Cu, Fe, and Zn (Natusch et al., 1977) may be continuously leached into solution for periods longer than 24 hours. Therefore, as a first approximation in predicting the water quality of ponded fly ash leachate, a long-term equilibration extraction procedure was designed to produce a solution potentially equilibrated with the solid waste. Fly ash ponds may reach metastable equilibrium conditions if the rates of the chemical reactions controlling the solubility of the particular mineral phases involved are slow in comparison with the retention times of the water in the ponds.

Five of the 12 fly ash samples were chosen for solubility studies by this long-term equilibration (LTE) procedure to suggest the general chemical character of disposal ponds that may develop after these ashes have been slurried. In the LTE procedure (in contrast to the EP method), the pH of the solutions was not adjusted, and a greater solid-to-liquid ratio (a 20% slurry wt/vol) was used. These solutions were periodically sampled during the extraction period. Results for the two acidic fly ashes (I2, I7), two alkaline samples (I3, I8), and one of the western samples (W2) are presented in Tables 14, 15, 16, 17, and 18.

It is difficult to make direct comparisons between the LTE data and those from the EP because of the different pHs of the extractants, the length of the solubilization period, the method of agitation, and the ratios of solid to liquid used in each procedure. After 24 hours (the duration of the EP method), the two LTE solutions generated from the Illinois Basin fly ashes (I2 and I7) were acidic (pH 4.1), while the other two (I3 and I8) were alkaline (about pH 11). The western fly ash extract, W2, was highly alkaline (pH 12.4).

As suggested by the data in Tables 14-18, the solutions were probably not in chemical equilibrium with the solid phase after the first 24 hours of solubilization, because the concentrations of many aqueous species continued to change for several weeks. Figures 24, 25, and 26 graphically demonstrate the changes in concentrations of selected constituents for three of the samples.

Table 14. Change in chemical composition as a function of time of fly ash 12 extract generated by long-term (142 days) equilibration procedure (concentrations in mg/L).

	1 hour	24 hours	48 hours	7 days	21 days	36 days	65 days	95 days	108 days	124 days	142 days
pH	4.1	4.1	4.1	4.6	5.6	6.3	6.6	6.3	6.7	6.7	6.4
Total alkalinity[a]	8.0	8.0	8.0	8.1	8.8	10.0	8.8	10.0	15.0	12.1	14.2
E.C. in mmhos/cm	3.80	3.67	3.54	2.74	2.78	2.81	2.84	2.83	2.79	2.80	2.94
Eh in mV[b]	+665	+664	+662	+645	+652	+638	+554	+640	+585	+576	+572
Al	195	190	191	9.21	<0.11	0.34	<0.13	<0.13	<0.13	<0.13	<0.06
As	<0.05	<0.05	0.39	<0.05	<0.05	<0.08	<0.08	<0.08	<0.08	<0.08	<0.05
B	65.2	68.8	73.0	83.3	93.2	85.2	89.5	85.4	89.5	81.9	88.3
Ba	0.10	0.24	0.22	0.12	0.07	0.03	0.03	0.02	0.04	0.04	0.04
Be	0.09	0.09	0.13	0.02	<0.001	<0.002	<0.002	<0.002	<0.002	<0.002	<0.001
Ca	630	626	621	600	558	546	575	547	514	492	607
Cd	0.44	0.44	0.48	0.40	0.23	0.10	0.08	0.06	0.04	0.04	0.05
Cr	1.00	0.88	1.16	<0.01	<0.01	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cu	2.13	2.07	2.22	0.63	<0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Fe	18.6	17.3	16.6	4.56	<0.04	<0.05	<0.05	<0.05	<0.05	<0.05	0.02
K	99.9	99.2	100	106	105	84.9	81.8	73.0	89.9	85.4	77.8
Mg	29.9	30.9	33.3	36.6	42.4	40.7	43.1	41.4	38.6	37.7	42.7
Mn	2.65	2.78	2.99	4.24	5.03	4.60	4.67	4.24	3.90	3.61	3.99
Mo	0.02	0.02	0.04	0.08	0.57	1.22	1.70	1.94	2.11	2.09	2.61
Na	70.4	69.0	75.8	79.1	99.9	94.6	95.4	90.7	101	96.2	95.9
Ni	0.94	0.96	1.03	0.96	0.86	0.56	0.41	0.30	0.23	0.23	0.20
Pb	<0.03	<0.03	<0.04	<0.03	<0.03	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Sb	<0.05	<0.05	0.08	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.02
Se	<0.05	<0.05	0.06	<0.05	<0.05	0.10	0.15	0.06	0.17	0.15	0.19
Si	34.8	36.8	36.9	40.5	16.1	7.53	6.70	6.31	6.18	5.97	6.71
Sn	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
V	<0.06	<0.06	<0.08	<0.06	<0.06	<0.08	<0.08	<0.08	<0.08	<0.08	<0.01
Zn	14.0	14.5	13.6	13.1	6.90	2.09	2.25	0.88	0.53	0.52	0.55
SO_4	2972	3271	3121	1876	1827	1770	1876	1621	1765	1741	1630

[a] As mg/L $CaCO_3$

[b] Relative to a normal hydrogen electrode.

Table 15. Change in chemical composition as a function of time of fly ash I3 extract generated by long-term (141 days) equilibration procedure (concentrations in mg/L).

	1 hour	24 hours	48 hours	7 days	21 days	36 days	64 days	94 days	107 days	123 days	141 days
pH	11.7	11.6	11.5	12.3	12.8	12.1	11.5	11.2	11.4	11.4	11.1
Total alkalinity[a]	406	457	457	1530	1043	526	283	256	238	232	231
phenolphthalein alk.[a]	350	398	398	1403	950	497	213	213	187	183	183
E.C. in mmhos/cm	2.38	2.17	2.07	4.96	4.17	2.29	1.43	1.15	1.11	0.91	0.89
Eh in mV[b]	+435	+430	+422	+385	+303	+339	+320	+408	+336	+354	+381
Al	27.1	18.1	13.1	<0.06	0.69	0.63	1.95	2.50	2.62	2.45	2.54
As	0.13	0.11	0.08	0.15	0.11	0.10	0.09	0.13	0.12	0.08	0.16
B	34.3	33.2	38.5	29.9	30.2	17.7	15.5	14.7	14.9	13.7	14.1
Ba	0.12	0.21	0.38	0.55	0.56	0.58	0.37	0.27	0.20	0.13	0.17
Be	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.001
Ca	537	456	392	699	660	249	124	88.8	72.9	67.3	64.4
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	0.08	0.09	0.10	0.08	0.07	0.04	0.02	<0.02	<0.02	<0.02	<0.02
Cu	<0.02	<0.02	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.001
Fe	<0.05	<0.05	<0.05	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.01
K	74.0	71.2	70.3	69.5	85.6	88.1	96.2	100	99.7	98.1	105
Mg	<1.42	<1.42	<1.42	0.11	0.08	<0.08	<0.08	<0.08	<0.08	<0.08	0.04
Mn	<0.004	<0.004	<0.004	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.01
Mo	3.02	3.00	3.09	3.90	4.52	4.74	4.73	4.77	4.79	4.63	4.75
Na	27.7	24.7	24.5	23.8	27.2	24.8	25.8	28.1	28.8	28.4	29.5
Ni	<0.02	<0.02	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02
Pb	<0.04	<0.04	<0.04	<0.03	<0.03	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Sb	0.05	<0.05	<0.05	0.06	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.04
Se	0.15	0.13	0.14	0.08	0.05	<0.04	<0.04	<0.04	<0.04	<0.04	0.09
Si	0.30	0.30	0.32	1.14	1.77	5.95	10.7	10.8	10.5	9.71	10.3
Sn	<0.03	<0.03	<0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.03
V	0.08	0.08	0.08	0.06	0.06	0.06	0.06	0.06	0.48	0.44	0.54
Zn	0.01	0.09	0.04	0.53	1.02	1.03	0.16	0.19	<0.01	0.22	0.01
SO_4	1000	980	919	746	491	246	175	157	152	143	164

[a] As mg/L $CaCO_3$

[b] Relative to a normal hydrogen electrode.

Table 16. Change in chemical composition as a function of time of fly ash I7 extract generated by long-term (106 days) equilibration procedure (concentrations in mg/L).

	1 hour	24 hours	48 hours	7 days	21 days	36 days	76 days	95 days	106 days
pH	4.1	4.1	4.1	4.7	7.4	7.5	7.6	7.5	7.5
Total alkalinity[a]	—	—	—	—	13.6	8.0	32.0	41.0	33.0
E.C. in mmhos/cm	5.29	5.39	5.16	4.79	4.49	4.51	4.43	4.20	4.10
Eh in mV[b]	+574	+572	+569	+567	+531	+581	+557	+544	+552
Al	158	163	133	3.46	0.13	0.14	0.22	0.12	0.13
As	0.17	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.05	<0.05
B	66.5	72.0	80.6	90.0	87.1	84.6	84.5	82.8	85.3
Ba	0.07	0.13	0.13	0.08	0.04	0.03	0.03	0.03	0.04
Be	0.10	0.09	0.09	0.01	<0.002	<0.002	<0.002	<0.001	<0.001
Ca	670	561	546	483	475	472	449	465	500
Cd	3.88	3.21	2.68	1.97	0.09	0.04	0.03	0.05	0.04
Cr	2.36	1.89	1.55	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cu	5.21	5.65	6.01	0.85	<0.02	<0.02	<0.02	<0.01	<0.01
Fe	49.5	43.1	39.7	11.5	<0.05	<0.05	<0.05	<0.05	<0.05
K	244	285	312	288	241	225	229	216	215
Mg	73.1	77.2	85.2	82.7	80.9	76.7	78.6	77.9	80.1
Mn	6.99	6.34	6.24	6.42	3.50	2.25	1.84	2.21	2.02
Mo	0.01	0.01	0.01	0.85	7.15	8.03	9.05	9.03	10.3
Na	396	447	485	493	490	467	477	462	471
Ni	2.01	1.75	1.57	1.26	0.35	0.12	0.06	0.10	0.08
Pb	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Sb	<0.05	0.09	<0.05	<0.05	0.05	0.07	0.10	0.10	0.10
Se	<0.04	<0.094	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Si	46.9	44.5	45.0	32.9	7.61	4.19	3.40	4.17	3.84
Sn	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.01	<0.01
V	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.08	<0.01	<0.01
Zn	36.2	27.5	20.3	15.1	1.32	0.56	0.03	0.03	0.09
SO_4	4316	3968	4067	2922	2723	2823	2637	2603	2683

[a] As mg/L $CaCO_3$

[b] Relative to a normal hydrogen electrode.

Table 17. Change in chemical composition as a function of time of fly ash I8 extract generated by long-term (140 days) equilibration procedure (concentrations in mg/L).

	1 hour	24 hour	48 hour	7 days	21 days	37 days	63 days	93 days	106 days	122 days	140 days
pH	10.9	10.8	10.6	11.5	11.1	10.8	10.5	10.4	10.4	10.3	10.1
Total alkalinity[a]	239	238	237	283	181	162	146	140	140	140	141
phenolphthalein alk.[a]	174	173	174	208	129	122	85	90	91	86	88
E.C. in mmhos/cm	2.48	3.09	2.97	2.69	2.66	2.72	2.68	2.80	2.56	2.49	2.56
Eh in mV[b]	+433	+399	+449	+377	+364	+363	+362	+422	+380	+394	+426
Al	63.2	59.6	48.3	0.44	0.42	0.51	0.45	0.44	0.57	0.38	0.31
As	<0.05	<0.05	<0.05	<0.05	<0.05	<0.08	<0.08	<0.08	<0.08	<0.08	<0.05
B	39.8	40.4	35.4	23.7	18.0	17.5	16.1	16.3	17.2	15.7	16.8
Ba	0.30	0.30	0.25	0.28	0.22	0.13	0.14	0.12	0.11	0.11	0.11
Be	<0.002	<0.002	<0.002	<0.002	<0.002	0.005	0.005	0.005	0.002	0.009	0.009
Ca	804	796	713	768	719	656	610	618	601	565	657
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	0.34	0.38	0.37	0.65	0.77	1.19	1.24	1.32	1.29	1.24	1.32
Cu	<0.03	<0.03	<0.03	<0.03	<0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Fe	<0.08	<0.08	<0.08	<0.08	<0.08	<0.05	<0.05	<0.05	0.06	<0.05	0.04
K	110	107	91	161	164	131	115	116	139	129	133
Mg	0.76	0.59	0.44	<0.09	0.43	0.91	1.20	1.58	1.75	1.69	1.92
Mn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.004	<0.004	<0.004	<0.004	<0.004	<0.01
Mo	10.5	10.5	9.83	17.5	18.6	15.1	14.5	14.9	14.5	13.7	14.5
Na	28.2	24.6	22.6	28.6	31.8	43.8	37.8	37.5	39.1	38.9	39.0
Ni	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pb	<0.03	<0.03	<0.03	<0.03	<0.03	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Sb	0.05	<0.05	<0.05	0.07	0.07	0.12	0.12	0.14	0.13	0.17	0.13
Se	0.21	0.23	0.19	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Si	<0.21	<0.21	<0.21	12.5	18.3	12.9	9.41	7.70	7.23	6.45	7.03
Sn	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
V	0.11	0.11	0.10	0.60	0.99	1.14	1.10	1.14	1.10	1.05	1.12
Zn	0.24	<0.01	0.16	0.59	0.23	0.48	0.43	0.04	0.02	0.02	0.10
SO_4	1879	2083	1940	1512	1572	1634	1614	1636	1636	1568	1601

[a] As mg/L $CaCO_3$

[b] Relative to a normal hydrogen electrode.

Table 18. Change in chemical composition as a function of time of fly ash W2 extract generated by long-term (140 days) equilibration procedure (concentrations in mg/L).

	1 hour	24 hour	48 hour	7 days	21 days	37 days	63 days	93 days	106 days	122 days	140 days
pH	12.4	12.4	12.2	12.4	12.9	12.7	12.5	12.8	12.7	12.7	12.8
Total alkalinity[a]	2191	2078	2417	2120	2759	3380	3486	3187	3360	3175	3445
phenolphthalein alk.[a]	2022	1948	2168	1924	2403	2969	2552	2870	2750	2630	2858
E.C. in mmhos/cm	8.82	12.2	11.3	11.1	13.2	14.5	16.4	16.6	15.5	14.8	15.7
Eh in mV[b]	+349	+430	+377	+392	+321	+313	+284	+261	+299	+279	+271
Al	1.38	0.58	0.40	1.59	20.8	33.0	44.0	50.3	54.8	55.8	56.7
As	0.05	0.05	0.05	0.05	0.21	0.41	0.48	0.46	0.47	0.44	0.52
B	120	109	98.3	51.1	52.9	51.4	56.5	56.4	57.4	56.0	63.1
Ba	0.10	0.06	0.09	0.16	0.26	0.05	0.07	0.12	0.20	0.20	0.14
Be	<0.002	<0.002	<0.002	<0.002	<0.001	0.004	0.003	0.003	0.003	0.008	0.005
Ca	869	778	701	121	11.3	9.26	8.40	8.20	8.70	9.01	7.80
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	0.15	0.16	0.15	0.19	0.20	0.28	0.28	0.25	0.26	0.23	0.24
Cu	<0.03	<0.03	<0.03	<0.03	<0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.01
Fe	<0.08	<0.08	<0.08	<0.08	<0.08	0.06	<0.05	<0.05	<0.05	<0.05	<0.01
K	294	260	243	301	317	253	248	233	239	255	220
Mg	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<1.54	<1.54	<1.54	0.17	0.01
Mn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.005	<0.004	<0.004	<0.004	<0.01
Mo	1.60	1.61	1.54	2.54	2.87	2.69	2.67	2.56	2.58	2.40	2.27
Na	2681	2332	2220	2643	2905	2757	2771	2676	2816	2834	2856
Ni	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pb	<0.03	<0.03	<0.03	<0.03	<0.03	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Sb	<0.02	<0.02	<0.02	<0.02	<0.02	<0.05	<0.05	<0.05	<0.05	<0.05	0.03
Se	0.03	0.28	0.26	0.19	0.24	0.35	0.35	0.35	0.34	0.31	0.36
Si	3.48	3.80	3.84	20.3	56.3	61.9	57.9	48.0	44.6	40.7	42.7
Sn	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
V	<0.06	<0.06	<0.06	<0.06	0.46	0.60	0.65	0.63	0.62	0.60	0.60
Zn	0.11	0.12	<0.01	0.21	0.05	0.64	0.35	0.24	0.73	1.24	0.49
SO_4	5461	5362	5063	4764	4067	3669	3619	3799	3606	3557	3514

[a] As mg/L $CaCO_3$

[b] Relative to a normal hydrogen electrode.

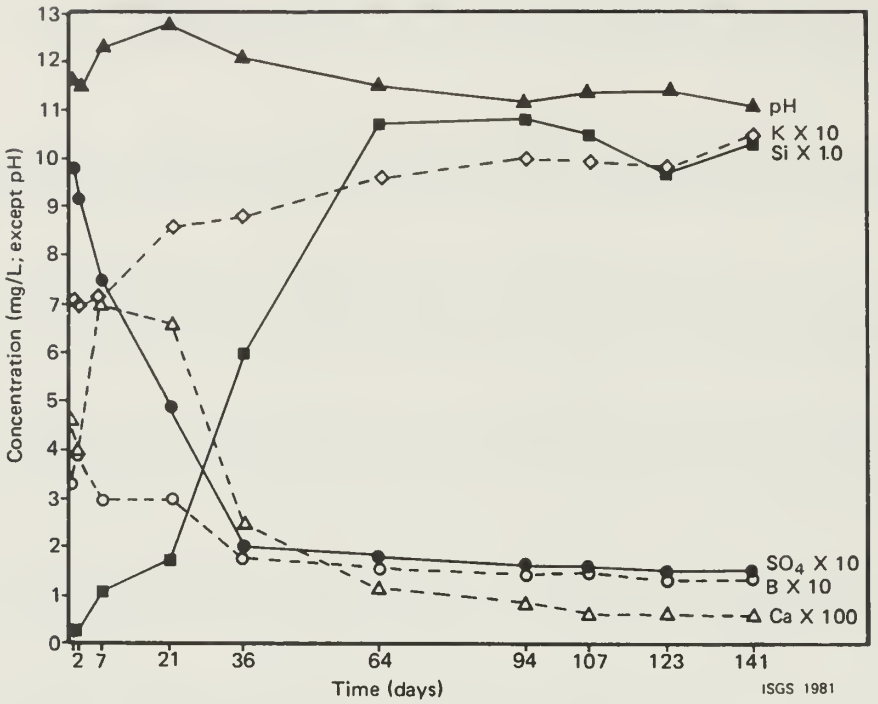

Figure 24. Changes in the concentrations of selected aqueous constituents in the LTE extract of fly ash I3 with time.

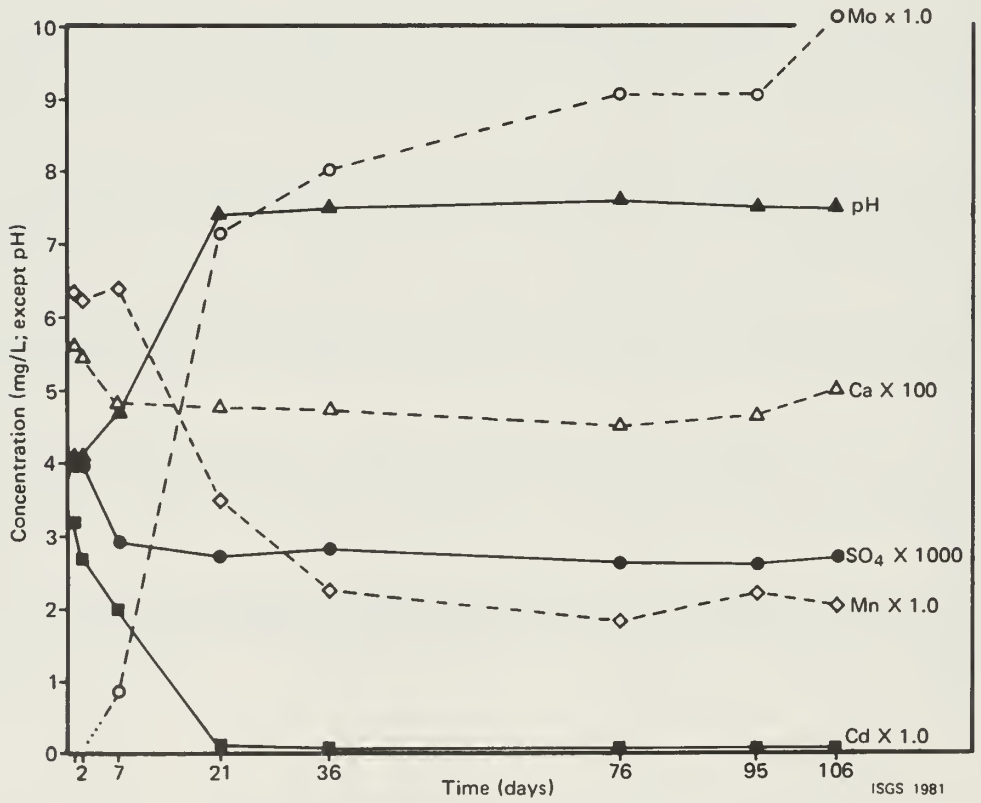

Figure 25. Changes in the concentrations of selected aqueous constituents in the LTE extract of fly ash I7 with time.

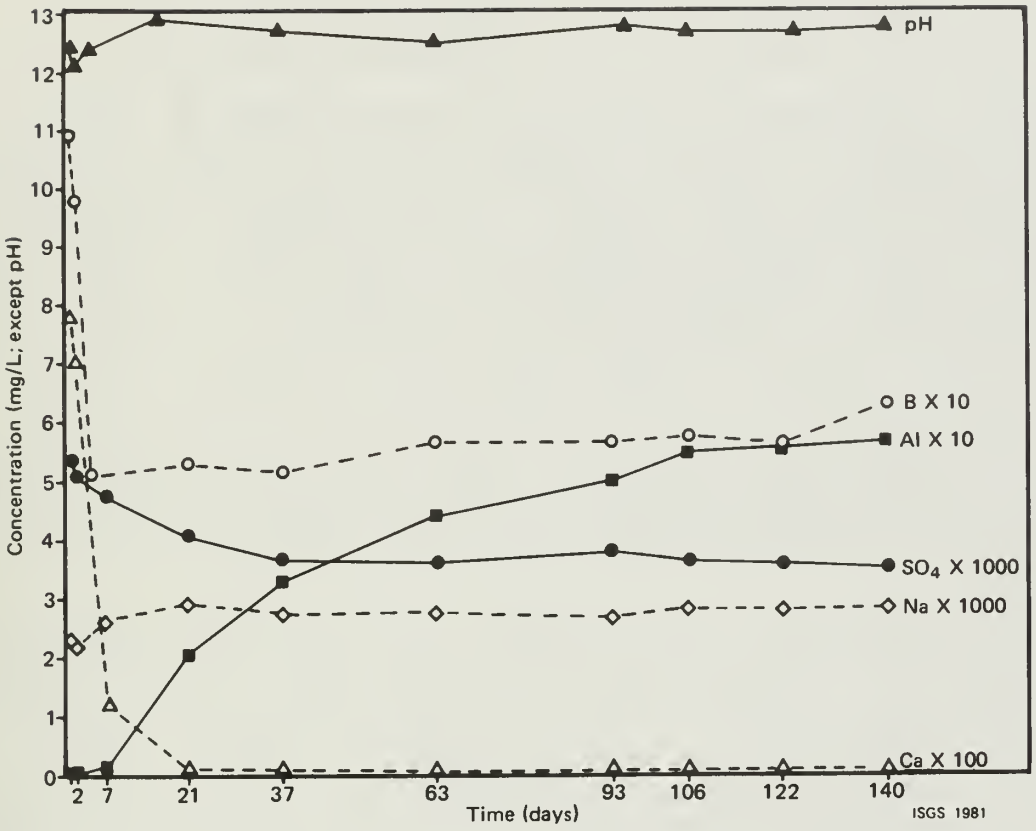

Figure 26. Changes in the concentrations of selected aqueous constituents in the LTE extract of fly ash W2 with time.

In each solution, most of the constituents were in greater concentrations during the first week of extraction than they were later. Beginning almost immediately after the first day, these same constituents decreased in concentration, and this trend prevailed for about 60 to 120 days. After that interval, the concentrations of these constituents no longer changed significantly, having reached relatively steady state conditions.

In both the initially acidic solutions (I2 and I7) the concentrations of B, Ba, Ca, Cd, Mg, Mn, Na, Ni, Si, SO_4, and Zn as well as pH became constant in 3 to 5 weeks (Tables 14, 16). The dominant factor controlling the solubility of many metals is pH. Both acidic extracts became neutral in pH and, as a consequence, several constituents were less soluble in the resulting nonacidic solution. Therefore, Al, Be, Cd, Cr, Cu, Fe, and Ni were in greater concentrations during the early phase of the extractions. Molybdenum steadily increased during the entire extraction interval of the acidic fly ashes and had not reached a steady state when the LTEs were terminated.

These changes in solubility over time make generalized solubility trends difficult to predict with certainty. For example, the ranking of the amount in solution versus the total amount in the solid for fly ash I2 after 24 hours of extraction was Cd, Zn > SO_4-S > B > Ca, Mg > Cu > Na, Be, Ni, K > Mn > Cr > Al > Ba, Si, Mo, Pb, and Fe. After 142 days, the relative solubilities were: SO_4-S > B > Mg > Mo, Ca > Cd > Na > Se > Mn > Zn > Sb, K > Ni > Ba > Cu, Cr, Pb, and Si. The change in solubility

trends is a reflection of the shifts in equilibria controlling the solubility of the constituents during the extraction interval.

In contrast, the pH of the two alkaline solutions (I3 and I8) remained above pH 10 during the entire extraction interval (140 days), and slowly decreased thereafter. In both the acidic and alkaline solutions, Al was more soluble during the early phases of the procedure but significantly decreased in concentration with time. In contrast to the two alkaline solutions produced by the Illinois Basin fly ashes, the pH of the solution generated by the lignite fly ash (W2) was essentially invariant for the entire solubilization-equilibration interval (140 days). Moreover, the solubility of Al from the lignite sample steadily increased with time.

Other studies dealing with fly ash extracts have also noted analogous changes in concentrations with time. Talbot et al. (1978) equilibrated a western U.S. fly ash for 6 months in an open system. The pH of the alkaline extract decreased from 11 to 8.8 after 1 month, having reached a steady state.

Townsend and Hodgson (1973) equilibrated an alkaline fly ash generated from British coals in a closed system. They observed that the pH and the OH and Ca concentrations increased initially, and then became invariant, whereas the B and SO_4 concentrations decreased during the extraction interval. Helm et al. (1976) also noted that concentrations of SO_4 and B decreased with time in solutions generated from shake tests with an alkaline fly ash produced from eastern bituminous coals. Page et al. (1979) equilibrated a 1:1 fly ash-water mixture for 30 days. In the resulting alkaline solution, Ca and OH concentrations steadily decreased, whereas the pH remained constant.

The present study may have several implications concerning the water quality of ash disposal ponds in a chronological framework. The two fly ashes that formed acidic extracts initially contained potentially toxic trace metals, such as Cd. With time, these acidic solutions became neutral, and several such trace constituents were no longer soluble, although other potential pollutants persisted in solution for longer periods. The fly ashes that produced alkaline extracts generated solutions that remained alkaline, and similarly, several potential pollutants also persisted in solution.

These results indicate that fly ash, particularly acidic samples, are most toxic to aquatic ecosystems when initially slurried to disposal ponds and that their toxicity may decrease with time. However, if potential pollutants are in metastable equilibrium in the pond, they may have long residence times in the ash effluent, increasing the probability of bioaccumulation by aquatic organisms. Excessive levels of Se have been detected in various species of fish inhabiting a cooling lake associated with a coal-fired power plant in Illinois (Larimore and Tranquilli, 1979). Intermittent overflow of a nearby ash pond into the cooling lake may have been the source of the Se.

The specific concentrations of the constituents exceeding EPA interim primary or secondary drinking water standards or irrigation water criteria are listed in Table 19. Depending on the solid waste, As, Cd, Cr, and Se

Table 19. Constituents in the long-term equilibrations exceeding EPA interim primary or secondary drinking water standards or irrigation water criteria as a function of time (concentrations in mg/L).

Constituent		Fly ash									
		I2		I3		I7		I8		W2	
		1 hour	142 days	1 hour	141 days	1 hour	106 days	1 hour	140 days	1 hour	140 days
Primary drinking water											
Arsenic	0.05			0.13	0.16	0.17					0.52
Cadmium	0.01	0.44	0.05			3.88	0.04				
Chromium	0.05	1.00		0.08		2.36		0.34	1.32	0.15	0.24
Selenium	0.01		0.19	0.15	0.09			0.21		0.03	0.36
Secondary drinking water											
Copper	1.0	2.13				5.21					
Iron	0.30	18.6				49.5					
Manganese	0.05	2.65	3.99			6.99	2.02				
Sulfate	250	2972	1630	1000	164	4316	2683	1879	1601	5461	3514
Zinc	5.0	14.0				36.2					
pH (units)	5.5 - 9.5	4.1		11.7	11.1	4.1		10.9	10.1	12.4	12.8
Irrigation water											
Aluminum	20.0	196				158		63.2			56.7
Boron	2.0	65.2	88.3	34.3	14.1	66.5	85.3	39.8	16.8	120	63.1
Molybdenum	0.05		2.61	3.02	4.75		10.3	10.5	14.5	1.60	2.27
Nickel	2.0					2.01					

were in concentrations exceeding the primary standards after 1 hour in the LTE solutions. After 106 to 140 days of extraction, the concentrations of these constituents changed, but the levels of some of the potential pollutants still remained above recommended levels. In each solution, other constituents exceeded the secondary standards and the recommended levels for irrigation water (U.S. EPA, 1976). As with the primary standards, certain potential pollutants remained in solution in excessive levels. Boron, Mo, and SO_4 were constituents common to all five extracts that remained above recommended levels during the entire extraction interval.

TOXICITY TESTS

All five undiluted fly ash LTE extracts were acutely toxic to fathead minnows, causing total mortality (Table 20). Three of the extracts (W2, I3, and I8) were very alkaline (pH >10.0), and mortality due to ionic shock was expected. In a previous study (Suloway, et al., 1981), test solutions in which the pH was greater than 9.2 were acutely toxic to fathead minnow fry. However, two of the samples in the present study (I2 and I7) were relatively neutral in pH and were not expected to cause total mortality. All extracts were then tested with LC-50 determinations.

The concentration of dissolved oxygen in all the screening procedures was more than 60% of saturation. The pHs of the extracts remained relatively stable during the bioassays with the exception of I8, in which the pH decreased almost an entire pH unit. There was a 5% mortality in the controls.

LC-50 determinations (Table 21) were made to measure the relative toxicities of the extracts and to determine the dilutions necessary to ensure survival during a 96-hour bioassay of the toxic extracts. An inverse relationship existed between toxicity and the LC-50 value for an extract. The LC-50 values for W2 and I3 were 2.8 and 63.0 (Table 21), respectively. Sixty-three mL of I3, diluted with 37.0 mL of dilution water, was just as toxic as only 2.8 mL of W2 diluted with 97.2 mL of dilution water. Therefore, with an increase in toxicity, there was a decrease in the LC-50 value.

TABLE 20. The percentage of mortality of 1-to-6 day-old fathead minnow fry (*Pimephales promelas*) resulting from 96-hour exposures to full-strength extracts generated from five fly ashes. Initial and final pHs and concentrations of dissolved oxygen (mg/L) are listed.

Sample	pH_i	pH_f	$D.O._i$	$D.O._f$	Mortality (%)
W2	12.816	12.733	8.75	8.59	100.0
I3	11.498	11.171	8.80	8.74	100.0
I8	10.260	9.314	8.87	8.40	100.0
I2	7.559	7.225	8.79	7.87	100.0
I7	6.40	6.758	8.77	8.24	100.0

Table 21. The LC-50 values, amount of dilution necessary to eliminate mortality, and the initial pH values for extracts generated from five fly ashes.

Fly ash sample	pH_i	LC-50 mL/100mL	Confidence intervals[a] mL/100mL	Dilution for zero percent mortality
W2	12.816	2.8	2.5 - 3.1	1:1000
I3	11.498	63.0	58 - 68	1:2.5
I8	10.260	84.0	80 - 88	1:1.4
I2	7.559	82.0	78 - 86	1:2
I7	6.40	82.0	79 - 85	>1:1.25

[a]There is a 95 percent probability that the LC-50 falls within the confidence interval listed.

The results of the LC-50 determinations indicate that W2 was the fly ash extract most toxic to young fathead minnows; it required as much as a 1:1000 dilution to eliminate mortality. The I3 ash produced the second most toxic extract; the remaining three extracts had similar LC-50 values.

The acute toxicity of a leachate should be partly a function of its chemical composition. Simple linear and multiple regression analyses were used to determine, for each extract, the relationship between the mortality data and the chemical data collected during the LC-50 determinations (Tables 22-25). The I8 test solutions were not chemically analyzed. The range of concentrations for each chemical constituent, the recommended water quality level for each chemical constituent, the change in r^2 for the multiple regression, and the r value for the simple linear regression are listed in each table. In statistical analysis, the values for r and r^2 will vary from <0.001 to 1.000. The closer the value is to 1.000, the stronger the relationship between mortality and a particular chemical constituent: for example, for the extract from W2 the strongest relationship detected by the multiple regression analysis (Table 22) was between mortality and initial pH (r^2 = 0.519). The concentrations of several chemical constituents (B, Mo, SO_4, pH, and pH_f) were highly correlated with mortality (r >0.70). When the results of these statistical analyses are considered with the levels of various chemical constituents present in the test solutions, the importance of various chemical constituents with respect to acute toxicity of a particular fly ash extract can be assessed.

A strong relationship existed between the acute toxicity of the W2 leachate and its pH. Alkaline (pH > 9.2) solutions have been shown to be acutely toxic to young fathead minnows (Suloway et al., 1981). Cairns et al. (1972) described the effects of a fly ash pond spill on a small river and suggested that the principal lethal agent was the high pH level. Wasserman et al. (1974) reported that runoff from alkaline ash ponds was lethal to catfish because the increased pH caused the precipitation of ferric hydroxide, which might have clogged the gill apparatus, causing asphyxiation.

Table 22. The range of concentrations and recommended water quality levels for chemical constituents measured in test solutions of W2.

Chemical constituent	Range of concentrations (mg/L)[a]	Recommended water quality levels (mg/L)[b]	r^2 Change[c]	r[c]
Al	<0.33 - 0.68	1.0	0.118	-0.20
As	<0.07	0.05	-	-
B	1.23 - 5.72	25	0.003	0.89
Ba	0.049- 0.088	2.5	0.020	-0.82
Be	<0.001- 0.009	0.055	0.019	0.23
Ca	6.69 - 17.4	16	-	-
Cd	<0.04	0.001	-	-
Co	<0.01	0.25	<0.001	-0.12
Cr	<0.01 - 0.02	0.25	0.140	0.69
Cu	<0.004- 0.014	0.05	0.001	-0.21
Fe	<0.04	0.25	-	-
Mg	5.57 - 17.2	87	0.010	-0.88
Mn	<0.008	0.1	<0.001	0.04
Mo	0.03 - 0.19	7	<0.001	0.89
Ni	<0.03	0.01	-	-
Pb	<0.05	0.05	-	-
Sb	<0.04	0.2	<0.001	0.05
Se	<0.07	0.25	0.040	0.26
Si	4.34 - 5.54	-	0.053	0.35
Sn	<0.03 - 0.17	-		
SO_4	74 -328	250	0.006	0.89
V	<0.08	-	0.008	0.24
Zn	<0.005- 0.147	0.1	0.004	0.05
pH_i	8.4 - 10.4	6.5-9.0[d]	0.519	0.72
pH_f	8.4 - 8.9	6.5-9.0[d]	0.003	0.84

[a]All values in mg/L except pH.
[b]Values are MATES cited from Cleland and Kingsbury (1977) unless another source is indicated.
[c]Values of r^2 and r represent the results from multiple and simple linear regression analyses of the relationship between mortality observed in the test solutions of the extract and the concentrations of each chemical constituent measured in those test solutions.
[d]From Quality Criteria for Water 1976 (U.S. EPA, 1976).

The extract of I3, like that generated from W2, was very alkaline and relatively toxic. The regression analyses indicated strong relationships between the final and initial pH and fish mortality (Table 23). Although the range of values for the final pH regression was rather narrow, there were 16 data points between the minimum and maximum pH values. The initial pH values were also elevated enough to cause mortality. Aluminum, As, and Ca were present in concentrations that exceeded recommended values; however, probably only Al was present at sufficient levels to be acutely toxic.

The extract generated from I7 was slightly acidic (pH < 6.7) when the LC-50 determinations were calculated (Table 24). The extract was much less toxic than those of W2 and I3; therefore, test solutions used to determine the LC-50 value did not require large dilutions. The high percentage of extract in the test solutions (75 to 100%) and the lower pH resulted in

Table 23. The range of concentrations and recommended water quality levels for chemical constituents measured in test solutions of I3.

Chemical constituent	Range of concentrations (mg/L)[a]	Recommended water quality levels (mg/L)[b]	r^2 (d) Change[c]	r[c]
Al	0.27 - 1.94	1.0	<0.001	0.31
As	<0.07 - 0.14	0.05	0.034	0.16
B	3.99 - 12.7	25	0.011	0.31
Ba	0.075- 0.1	2.5	<0.001	-0.66
Be	<0.009	0.055	0.002	-0.27
Ca	18.1 - 21.1	16	-	-
Cd	<0.01	0.001	-	-
Co	<0.004	0.25	-	-
Cr	<0.01 - 0.03	0.25	0.008	0.12
Cu	<0.006	0.05	0.019	-0.30
Fe	<0.04	0.25	-	-
Mg	7.64 - 18.7	87	0.033	-0.66
Mn	<0.009	0.1		
Mo	0.01 - 4.18	7	0.007	0.31
Na	<2.73	-	-	-
Ni	<0.03	0.01	-	-
Pb	<0.05	0.05	-	-
Sb	<0.03 - 0.05	0.2	0.005	0.30
Se	<0.07 - 0.08	0.25	0.023	-0.08
Si	4.74 - 10.3	-	<0.001	0.03
Sn	<0.04	-	0.002	-0.26
SO_4	50 -161	250	<.001	0.16
V	<0.08 - 0.46	-	0.031	0.35
Zn	<0.02	0.1	0.016	-0.02
pH_i	8.3 - 10.3	6.5-9.0[d]	0.246	0.50
pH_f	8.3 - 8.5	6.5-9.0[d]	0.469	0.84

[a]All values in mg/L except pH.
[b]Values are MATES cited from Cleland and Kingsbury (1977) unless another source is indicated.
[c]Values of r^2 and r represent the results from multiple and simple linear regression analyses of the relationship between mortality observed in the test solutions of the extract and the concentrations of each chemical constituent measured in those test solutions.
[d]From Quality Criteria for Water 1976 (U.S. EPA, 1976).

higher concentrations of various chemical constituents in the test solutions of I7 than were found for I3 or W2. The concentrations of B, Cd, Mn, Ni, SO_4, and Zn exceeded recommended levels in the test solutions (Table 24). However, B, Cd, Mn, Ni, and SO_4 were probably not present in sufficient concentrations by themselves to cause mortality according to toxicity data available in the literature (Cardwell, 1976; Cleland and Kingsbury, 1977; Pickering and Gast, 1972; Pickering, 1974; Pickering and Henderson, 1966).

Zinc concentrations ranged from 0.21 mg/L to 0.63 mg/L in the I7 test solutions (Table 24). Toxic effects of Zn on fathead minnows having mean 96-hour LC-50 values of 0.6 mg/L Zn in duplicate flow-through acute bioassays included mortality at concentrations as low as 0.294 mg/L of Zn (Benoit and Holcombe, 1978). However, 8-week-old fathead minnows and soft water (46 mg/L as $CaCO_3$) were used in their experiments. Chapman (1978) reported that

Table 24. The range of concentrations and recommended water quality levels for chemical constituents measured in test solutions of I7.

Chemical constituent	Range of concentrations (mg/L)[a]	Recommended water quality levels (mg/L)[b]	r^2 Change[c]	r[c]
Al	<0.08 - 0.30	1.0	-	-
As	<0.07	0.05	-	-
B	66.5 - 90.1	25	0.025	0.78
Ba	0.31 - 0.078	2.5	-	-
Be	<0.001- 0.012	0.055	-	-
Ca	<0.004	16	-	-
Cd	<0.01 - 0.04	0.001	0.012	0.68
Co	<0.004- 0.05	0.25	0.092	0.58
Cr	<0.02	0.25	-	-
Cu	<0.004- 0.016	0.05	-	-
Fe	<0.05	0.25	-	-
Mg	13.1 - 41.7	87	0.047	0.79
Mn	<0.008- 3.88	0.1	0.084	0.78
Mo	<0.01 - 2.37	7	-	-
Na	<2.73	-	-	-
Ni	<0.03 - 0.22	0.01	0.019	0.82
Pb	<0.05 - 0.06	0.05		
Sb	0.03 - 0.06	0.2	<0.001	0.59
Se	<0.07 - 0.18	0.25	0.002	0.67
Si	3.44 - 6.89	-	0.003	0.78
Sn	<0.04	-	-	-
SO_4	0 -1786	250	0.050	0.74
V	<0.08	-	-	-
Zn	0.21 - 0.63	0.1	0.002	0.74
pH_i	6.6 - 8.0	6.5-9.0[d]	0.645	-0.80
pH_f	6.8 - 8.2	6.5-9.0[d]	0.018	-0.79

[a]All values in mg/L except pH.
[b]Values are MATES cited from Cleland and Kingsbury (1977) unless another source is indicated.
[c]Values of r^2 and r represent the results from multiple and simple linear regression analyses of the relationship between mortality observed in the test solutions of the extract and the concentrations of each chemical constituent measured in those test solutions.
[d]From Quality Criteria for Water 1976 (U.S. EPA, 1976).

96-hour LC-50s for Zn for steelhead trout varied, depending on which life stage was exposed. Mount (1966) found an inverse relationship between Zn toxicity and water hardness for fathead minnows. Mount tested the acute toxicity of Zn under various pH and hardness conditions, making direct correlations of Zn and toxicity difficult. Using hard (200 mg/L as $CaCO_3$) and alkaline (nominal pH = 8.0) dilution water, the LC-50 was approximately 8.2 mg/L of Zn. These data suggest that Zn might be partly responsible for the mortality caused by I7 test solutions.

Sulfate and other ions were present in relatively high concentrations, contributing to the electrical conductivity (EC), which varied between 4.1 and 5.29 mmhos/cm (Table 16) in the undiluted extract of I7. Significant mortality of fathead minnow fry has been observed in reconstituted water in

Table 25. The range of concentrations and recommended water quality levels for chemical constituents measured in test solutions of I2.

Chemical constituent	Range of concentrations (mg/L)[a]	Recommended water quality levels (mg/L)[b]	r^2 Change[c]	r^c
Al	<0.07 - 0.33	1.0	0.075	0.61
As	<0.07	0.05	-	-
B	72.8 - 91.7	25	<0.001	0.70
Ba	0.021- 0.049	2.5	0.286	-0.67
Be	<0.001- 0 .008	0.055	0.083	-0.29
Ca	<0.004	16		
Cd	<0.04	0.001	0.022	0.48
Co	<0.004	0.25	<0.001	-0.24
Cr	<0.01	0.25	0.002	-0.39
Cu	<0.004- 0.014	0.05	-	-
Fe	<0.04	0.25	-	-
Mg	<0.001	87	-	-
Mn	1.54 - 2.01	0.1	0.020	0.70
Mo	7.45 - 9.96	7	0.011	0.71
Na	<2.73	-	-	-
Ni	0.04 - 0.07	0.01	0.020	0.57
Pb	<0.05 - 0.07	0.05	-	-
Sb	0.09 - 0.11	0.2	0.003	0.50
Se	0.07	0.25	-	-
Si	3.74 - 5.17	-	0.145	0.28
Sn	<0.04	-	-	-
SO_4	33 -3036	250	0.026	0.75
V	<0.08	-	-	-
Zn	0.09 - 0.27	0.1	0.019	0.33
pH_i	7.6 - 7.6	6.5-9.0[d]	0.246	-0.49
pH_f	7.6 - 7.7	6.5-9.0[d]	0.016	-0.72

[a]All values in mg/L except pH.
[b]Values are MATES cited from Cleland and Kingsbury (1977) unless another source is indicated.
[c]Values of r^2 and r represent the results from multiple and simple linear regression analyses of the relationship between mortality observed in the test solutions of the extract and the concentrations of each chemical constituent measured in those test solutions.
[d]From Quality Criteria for Water 1976 (U.S. EPA, 1976).

which the EC exceeded 4.0 mmhos/cm (Suloway et al., 1981). Thus, the total ionic strength of the test solutions of I7 also probably contributed to the acute toxicity of this fly ash extract.

The extract generated from I2 was nearly neutral in pH when the LC-50 determinations were made (Table 24). This extract was much less toxic than were the W2 and I3 extracts (Table 21); therefore, test solutions used to determine the LC-50 value were comprised of 50 to 100% extract. Because of the high percentage of extract used in the test solutions, concentrations of various chemical constituents were higher in the test solutions of I2 than in I3 and W2. The concentrations of B, Mn, Mo, Ni, SO_4, and Zn in test solutions of I2 exceeded recommended water quality levels and correlated well with mortality data based on the simple linear regressions.

Boron concentrations were high, but extremely high concentrations of B are required to produce toxic effects in aquatic life (Becker and Thatcher, 1973). For example, the minimum lethal dose for minnows exposed to boric acid at 20° C for 6 hours was reported to be 18,000 to 19,000 mg/L in distilled water and 19,000 to 19,500 mg/L in hard water (Le Clerc and Devlaminck, 1955; Le Clerc, 1960). According to toxicity data available in the literature (Cardwell, 1976; Cleland and Kingsbury, 1977; Mount, 1966; Pickering, 1974; Pickering and Gast, 1972; Pickering and Henderson, 1966). The individual concentrations of Mn, Mo, Ni, SO_4, and Zn were probably not high enough to cause the mortality observed in the test solutions of I2. The total ionic strength of the I2 extract as measured by EC was less than that of the I7 extract (Tables 14 and 16). The EC of the undiluted I2 extract ranged from 2.74 to 3.80. Insignificant mortality was observed in reconstituted water in which the EC was less than 3.0 (Suloway et al., 1981). Because of the complex chemical composition of the I2 fly ash extract and the unknown synergistic and antagonistic effects of the chemical constituents composing the extract, it is not possible from these experiments to determine specifically which chemical constituents were directly responsible for the observed mortality.

BIOACCUMULATION EXPERIMENTS

Analyses of variance of fish lengths and weights (Tables 26 and 27) showed that only the fathead minnows were different in weight for sample I3, and so all duplicates were combined for each organism for each sample. The mean initial length and weight of fathead minnows used in the bioaccumulation experiments were approximately 50 mm and 1 g, respectively (Table 28). The mean initial length and weight of the green sunfish used

Table 26. The mean initial lengths and weights of adult fathead minnows used in the bioaccumulation experiments.

Sample	N	Mean length (mm)	F value[a]	Mean weight (g)	F value[a]
W2-A	5	50.4		1.106	
W2-B	5	49.2	0.176	1.164	0.008
I3-A	5	53.4		1.334	
I3-B	5	50.6	1.252	1.012	4.207
I8-A	5	49.2		1.102	
I8-B	5	49.4	0.004	1.118	0.003
I7-A	5	49.0		1.064	
I7-B	5	49.4	0.069	1.204	0.350
I2-A	5	46.8		1.008	
I2-B	5	48.8	0.361	1.256	0.724
Control-A	5	47.8		0.994	
Control-B	5	48.2	0.060	1.002	0.002

[a]Results of the analysis of variance indicate that if $F_{(1,8)}$ is greater than 3.46, the replicates are significantly different.

Table 27. The mean initial lengths and weights of juvenile green sunfish used in the bioaccumulation experiments.

Sample	N	Mean length (mm)	F value[a]	Mean weight (g)	F value[a]
W2-A	5	50.2		1.376	
W2-B	5	46.0	0.859	1.012	1.709
I3-A	5	48.6		1.304	
I3-B	5	49.2	0.292	1.344	0.030
I8-A	5	49.0		1.278	
I8-B	5	48.6	0.020	1.202	0.083
I7-A	5	51.4		1.498	
I7-B	5	50.8	0.044	1.484	0.002
I2-A	5	51.0		1.578	
I2-B	5	50.8	0.098	1.568	0.012
Control-A	5	47.8		1.356	
Control-B	5	48.6	0.133	1.326	0.013

[a]Results of the analysis of variance indicate that if $F_{(1,8)}$ is greater than 3.46, replicates are significantly different.

were 50 mm and 1.3 g, respectively (Table 29). Fathead minnows and green sunfish in the control solutions were essentially the same size as those exposed to the fly ash extracts (Table 30).

At the conclusion of the experiments, all the duplicates that could be analyzed proved to be homogeneous (Tables 31 and 32). The mean final lengths and weights of the fathead minnows and green sunfish between replicates were not significantly different from each other (Tables 33 and 34). Although the concentrations of the extracts to which the organisms were exposed should not have caused mortality, it was hypothesized that the toxic components may have been of sufficient concentration to cause sublethal, physiological perturbations resulting in decreased growth. The results of the ANOVA demonstrated that at the termination of the bioaccumulation experiments the green sunfish and fathead minnows in the

Table 28. Initial mean total lengths and weights of adult fathead minnows exposed to extracts from five fly ashes and a control.

Sample	N	Mean length (mm)	Standard deviation	Mean weight (g)	Standard deviation
Control	10	47.9	3.33	0.998	0.230
W2	10	49.8	4.09	1.135	0.300
I3	10	52.0	3.66	1.160	0.252
I8	10	49.3	4.76	1.110	0.389
I7	10	49.4	4.34	1.134	0.334
I2	10	47.8	4.81	1.132	0.432

Table 29. Initial mean total lengths and weights of juvenile green sunfish exposed to extracts from five fly ashes and a control.

Sample	N	Mean length (mm)	Standard deviation	Mean weight (g)	Standard deviation
Control	10	48.2	3.1	1.341	0.379
W2	10	48.1	5.1	1.194	0.433
I3	10	48.9	3.0	1.324	0.328
I8	10	48.8	4.0	1.240	0.374
I7	10	51.1	4.0	1.491	0.431
I2	10	50.9	3.9	1.573	0.366

Table 30. Comparison of the mean initial lengths and weights between the control test organisms and the organisms exposed to fly ash extracts.

	Green sunfish[a]		Fathead minnow[a]	
	length	weight	length	weight
Control vs W2[b]	0.002	0.585	1.167	1.178
Control vs I3	0.229	0.010	2.618	0.748
Control vs I8	0.124	0.322	0.242	0.551
Control vs I7	0.613	2.883	0.677	1.001
Control vs I2	2.619	1.738	0.003	0.673

[a]The values listed are $F_{(1,18)}$ values generated by one-way analysis of variance. If the F value is greater than 3.01, the means are significantly different.
[b]N = 10 for each test and control group.

Table 31. The mean final lengths and weights of juvenile green sunfish used in the bioaccumulation experiments.

Sample	N	Mean length (mm)	F value[a]	Mean weight (g)	F value[a]
W2-A	5	56.2		2.912	
W2-B	5	52.4	0.789	2.362	0.529
I3-A	5	54.4		2.700	
I3-B	5	54.4	0.000	2.478	0.167
I8-A	5	55.6		2.711	
I8-B	5	54.6	0.058	2.614	0.027
I7-A	5	59.2		3.594	
I7-B	5	60.6	0.177	3.798	0.049
I2-A	5	58.2		3.280	
I2-B	5	58.8	0.020	3.480	0.055
Control-A	5	54.0		2.933	
Control-B	5	56.8	0.119	3.068	0.021

[a]Results of the analysis of variance indicate that if $F_{(1,8)}$ is greater than 3.46, the replicates are significantly different.

Table 32. The mean final lengths and weights of adult fathead minnows used in the bioaccumulation experiments.

Sample	Mean length (mm)	F value[a]	Mean weight (g)	F value[a]
W2-A	53.2		1.500	
W2-B	50.1	0.829	1.530	0.009
I3-A	54.5		1.710	
I3-B	50.2	b	1.322	b
I8-A	52.4		1.554	
I8-B	50.0	0.486	1.242	0.825
I7-A	43.0		0.900	
I7-B	53.4	b	1.646	b
I2-A	47.2		0.958	
I2-B	48.6	0.190	1.312	1.435
Control-A	50.2		1.392	
Control-B	49.6	0.045	1.218	0.459

[a]Results of the analysis of variance indicate that if $F_{(1,8)}$ is greater than 3.46, the replicates are significantly different.
[b]Insufficient data for statistical analysis.

Table 33. Final mean total lengths and weights of adult fathead minnows exposed to extracts from five fly ashes and a control.

Sample	N	Mean length (mm)	Standard deviation	Mean weight (g)	Standard deviation
Control	10	49.9	4.0	1.305	0.373
W2	10	52.1	3.6	1.515	0.456
I3	7	51.4	3.5	1.433	0.123
I8	10	51.2	5.0	1.398	0.510
I7	6	51.7	8.2	1.522	0.563
I2	10	47.9	4.6	1.135	0.453

Table 34. Final mean total lengths and weights of juvenile green sunfish exposed to extracts from five fly ashes and a control.

Sample	N	Mean length (mm)	Standard deviation	Mean weight (g)	Standard deviation
Control	10	56.0	6.6	2.997	1.155
W2	10	54.3	6.3	2.637	1.104
I3	10	54.4	4.4	2.589	0.777
I8	10	55.1	6.1	2.661	0.815
I7	10	59.9	7.1	3.696	1.305
I2	10	58.5	6.3	3.380	1.213

controls were essentially the same length and weight as those exposed to the extracts (Table 35). Furthermore, when the differences between initial and final mean lengths and weights for fathead minnows (Table 36) and green sunfish (Table 37) were compared, the growth of the control and experimental animals was approximately the same. Only the fathead minnows exposed to I3 and I2 extracts grew appreciably less than the controls, but the differences were not significant.

Table 35. Comparison of the mean final lengths and weights between the control test organisms and the organisms exposed to fly ash extracts.

	Green sunfish[a]		Fathead minnow[a]	
	length	weight	length	weight
Control vs W2[b]	0.313	0.457	1.503	1.141
Control vs I3	0.368	0.773	0.585	0.446
Control vs I8	0.091	0.508	0.369	0.195
Control vs I7	1.467	1.447	0.291	0.516
Control vs I2	2.676	0.470	0.968	0.753

[a]The values listed are $F_{(1,18)}$ values generated by one-way analysis of variance. If the F value is greater then 3.01, the means are significantly different.
[b]N = 10 for each test and control group, except for I3 fathead minnows, N = 7, and for I7 fathead minnows, N = 6.

Table 36. Differences between initial and final mean lengths and weights of adult fathead minnows exposed to extracts from five fly ashes and a control.

	Difference in mean length (mm)	Percent increase in mean length	Difference in mean weight (g)	Percent increase in mean weight
Control	+2.0	4.2	+0.307	30.8
W2	+2.3	4.6	+0.380	33.5
I3	+0.6	1.2	+0.273	23.5
I8	+1.9	3.9	+0.288	25.9
I7	+2.3	4.7	+0.388	34.2
I2	+0.1	0.2	+0.003	0.3

Table 37. Differences between initial and final mean lengths and weights of juvenile green sunfish exposed to extracts from five fly ashes and a control.

	Differences in mean length (mm)	Percent increase in mean length	Differences in mean weight (g)	Percent increase in mean weight
Control	+7.8	16.2	+1.656	123.5
W2	+6.2	12.9	+1.443	120.9
I3	+5.5	11.2	+1.265	95.6
I8	+6.3	12.9	+1.421	114.6
I7	+8.8	17.2	+2.205	147.9
I2	+7.6	14.9	+1.807	114.9

Several of the extracts generated from the fly ash samples contained relatively elevated concentrations of trace elements. The bioaccumulation experiments were designed to determine if fathead minnows or green sunfish would concentrate these chemical constituents directly from the diluted leachates. Ryther et al. (1979) demonstrated in laboratory experiments that many elements, including As, Co, I, Se, V, and Zn were concentrated from fly ash by sandworms (*Nereis vivens*) and three species of marine bivalves (*Mya arenaria, Mercenaria mercenaria,* and *Crassostrea virginica*). Depending on the organism and the constituent, these elements were concentrated by factors ranging from 1.2 to nearly 14. Typical enrichment was in the range of 1.2 to 1.6. Cherry et al. (1976) noted that Se, Br, Zn, Cl, and Ca were concentrated in mosquito fish, *Gambusia affinis*. The constituent most concentrated was Se (9.4 mg/kg in mosquito fish muscle). Excessive levels of Se were found in fish in an Illinois cooling lake (Larimore and Tranquilli, 1981). Magnuson et al. (1980) found that crayfish accumulated Ba, Cr, Fe, Se, and Zn from a fly ash pit effluent.

Concentrations of 24 elements (mg/kg) were measured in the fish tissues from the bioaccumulation experiments of the present study (Tables 38 and 39). Fathead minnows exposed to diluted W2 extract contained at least twice as much Al, As, and Ni as the controls. The level of Ni (0.944 mg/kg) was more than five times that found in the control fish. Similar accumulations were found in the green sunfish. The concentrations of Al, As, and Ni in green sunfish exposed to W2 were 1.5, 1.3, and 4.6 times, respectively, those found in the controls.

Concentration factor is defined by Phillips and Russo (1978) as the ratio of the concentration (wt/wt) of a substance in an organism (or a particular tissue or organ) to the concentration (wt/vol) of that substance in the water in which that organism had been living. For example, an organism containing 10 µg Cu/g tissue taken from a lake containing 1 µg Cu/L has concentrated Cu 10,000 times; thus, by definition, the concentration factor is 10,000.

The mean final concentrations of Al, As, and Ni in the diluted W2 extract in which the fathead minnows were placed were 0.39, <0.05, and <0.02 ppm, respectively. The concentration factors for As and Ni cannot be calculated, but they would be high (>20). The concentration factor for Al in W2 by fathead minnows was 37.2. The concentration factor for Al in W2 by green sunfish was 40.8. The concentration factors for As and Ni in W2 by green sunfish were both greater than 15.

Both green sunfish and fathead minnows concentrated Mo from I3 extract. The concentration of Mo present in the I3 extract did not exceed primary or secondary drinking water standards (Table 19), nor did it exceed the level recommended by the EPA to protect aquatic life (Table 23). Yet the green sunfish exposed to the I3 extract had 10 times more Mo than did the control fish. The difference between the levels of Mo in fathead minnows exposed to the control solution and to the I3 extract was almost a factor of 6. The concentration factors of Mo for green sunfish and fathead minnows exposed to I3 fly ash extract were 1.4 and 1.6, respectively.

Fathead minnows accumulated Al from the I3 extract. The concentration factor for Al from I3 by fathead minnows was 253.6; the level of Al present

Table 38. The mean concentrations of various chemical constituents measured in adult fathead minnows exposed to extracts from five fly ashes and a control.

	Control	Fly ash W2	Fly ash I3	Fly ash I8	Fly ash I7	Fly ash I2
Al	6.34	14.5	27.9	7.66	13.0	3.62
As	<0.498	0.939	0.562	0.689	<.498	<0.498
B	0.994	1.16	1.27	2.42	4.15	3.99
Ba	10.3	11.4	11.9	8.84	10.1	8.32
Be	<0.012	<0.012	<0.012	<0.012	<0.012	0.012
Ca	7000	10700	8380	9080	8310	7930
Cd	0.051	0.062	0.033	0.044	0.422	0.125
Co	0.555	0.477	0.653	0.487	1.00	0.473
Cr	0.983	1.16	0.597	1.76	0.887	0.691
Cu	1.78	1.46	1.36	1.26	0.849	0.809
Fe	21.5	21.6	26.9	21.1	26.1	18.2
K	11700	13400	14400	12200	14300	13200
Mg	282	371	295	322	293	291
Mn	1.55	2.00	1.70	2.67	25.2	638
Mo	<0.050	0.062	0.290	1.06	0.315	0.324
Na	845	1120	1090	950	945	876
Ni	0.161	0.944	0.162	0.268	0.969	0.442
P	2092	2870	2340	2560	2380	2350
Pb	2.99	2.26	2.26	1.70	1.16	0.796
Sb	0.207	0.348	0.251	0.220	0.201	0.324
Se	0.397	0.609	0.330	0.422	0.328	0.566
Si	0.677	0.857	1.80	0.778	0.749	0.641
Sn	0.651	0.299	<0.187	0.315	0.371	<0.187
Zn	47.0	51.7	41.0	43.2	38.3	36.0
% Extract	0.0	1.0	10.0	15.0	15.0	15.0

in the fathead minnows exposed to the I3 extract was four times greater than the level measured in the control fish (Table 38). Green sunfish did not accumulate Al from I3, but they did accumulate Pb. The concentration of Pb in the tissues of green sunfish exposed to the I3 extract was twice that present in the controls. The concentration factor for Pb was greater than 25. Neither the concentration of Al nor of Pb exceeded primary or secondary drinking water standards in the I3 extract (Table 19). The results of the LC-50 determinations gave some indications of a problem with Al in the I3 extract, because the level of Al exceeded the recommended level for the protection of aquatic life (Table 23).

As occurred with the extract from I3, Mo was accumulated from the I8 extract by both the fathead minnows and the green sunfish. Molybdenum levels in the green sunfish tissue exposed to the I8 extract were almost 40 times greater than those in the control fish. The level of Mo accumulated in fathead minnows exposed to I8 extract was more than 20 times that found

Table 39. The mean concentrations of various chemical constituents measured in juvenile green sunfish exposed to extracts from five fly ashes and a control.

	Control	Fly ash W2	Fly ash I3	Fly ash I8	Fly ash I7	Fly ash I2
Al	6.96	10.6	4.56	2.00	11.3	10.2
As	0.587	0.784	<0.498	0.478	0.543	0.499
B	1.62	1.89	1.08	1.56	4.16	4.62
Ba	1.28	1.52	1.20	0.894	0.949	0.867
Be	<0.012	<0.012	<0.012	0.012	<0.012	<0.012
Ca	10400	14400	11100	11300	10600	9780
Cd	0.038	0.043	0.045	0.042	0.056	0.049
Co	0.520	0.530	0.381	0.364	0.600	0.504
Cr	1.04	1.42	1.01	1.32	0.944	0.841
Cu	0.325	0.335	0.464	0.304	0.344	0.336
Fe	20.8	25.7	15.2	15.0	23.2	19.6
K	12600	10600	14300	12700	13500	12300
Mg	350	434	363	378	344	326
Mn	3.55	4.13	3.18	3.44	4.61	2.78
Mo	<0.064	0.080	0.628	2.38	0.435	1.04
Na	986	1020	1060	981	1040	9720
Ni	0.146	0.668	0.263	0.370	0.308	0.228
P	2780	3310	2920	2980	2600	2630
Pb	0.511	0.457	1.03	0.510	0.748	0.367
Sb	0.289	0.342	0.243	0.381	0.233	0.252
Se	0.351	0.425	0.538	0.370	0.435	0.480
Si	0.892	1.73	0.716	0.625	0.855	0.759
Sn	0.190	0.357	0.261	0.213	0.279	0.246
Zn	32.1	43.5	34.5	39.4	34.2	28.6
% Extract	0.0	1.0	10.0	15.0	15.0	15.0

in the controls. The concentration factors of Mo for green sunfish and fathead minnows exposed to I8 extract were 1.1 and 0.50, respectively. These relatively low concentration factors indicate that there were high levels of Mo in the I8 extract and that the level of Mo in the fish tissue might increase further with longer exposure.

Fathead minnows exposed to extract generated from I7 accumulated Al, B, Cd, Mn, and Ni. The level of Cd in the I7 extract exceeded the primary drinking water standard, and the level of Mn exceeded the secondary drinking water standard (Table 19). The bioconcentration factors of Al, B, Cd, Mn, Mo, and Ni by fathead minnows exposed to the I7 extract were >162, 0.3, 21.1, 68.8, 0.8, and 38.8, respectively. The levels of these elements in the fathead minnows exposed to the I7 extract were at least twice those found in the control fathead minnows. In fact, the levels of five of these six elements (all but Al) were 5 times those found in the controls.

The green sunfish exposed to the I7 extract accumulated the same elements as the fathead minnows although some of these constituents accumulated to a lesser degree. The levels of B, Mo, and Ni present in the green sunfish exposed to the I7 extract were at least twice those measured in the controls. The concentration factors for B, Mo, and Ni in green sunfish exposed to the I7 extract were 0.29, 1.1, and 12.3, respectively.

Finally, the composition of the extracts generated from samples I7 and I2 were similar. The accumulation of elements from the I2 extract by the test organisms also was similar to that observed in test organisms exposed to I7. The chemical constituents accumulated to the greatest degree by the fathead minnows were B, Cd, Mn, Mo, and Ni (Table 38). The concentration factors for B, Cd, Mn, Mo, and Ni in fathead minnows exposed to the I2 extract were 0.3, >6.3, 81.8, 0.2, and >22.1, respectively.

The green sunfish exposed to the I2 extract accumulated the same chemical constituents as did the fathead minnows, although some of these elements were accumulated to a lesser degree. The levels of B and Mo in the green sunfish exposed to the I2 extract were almost 2.9 and 17.0 times, respectively, those measured in the controls. The concentration factors for B and Mo in green sunfish exposed to the I2 leachate were 0.3 and 0.5.

The six most frequently accumulated chemical constituents from the fly ash extracts were Al, B, Cd, Mn, Mo, and Ni. Other chemical constituents were accumulated, but these elements were accumulated to the greatest extent. In most situations, the results of the chemical analyses of the extracts and the LC-50 determinations did not indicate which chemical constituents would be accumulated. The United States Food and Drug Administration (FDA) currently lists Hg, Pb, Cd, As, Se, and Zn at the top of the priority list in its program concerning toxic elements in food (Jelinek and Corneliussen, 1977). Of these, only Hg has an FDA-specified regulatory limit for fish and shellfish (Anonymous, 1974); FDA guidelines for other metals in foods have not been established (Phillips and Russo, 1978).

Aluminum is an element which is relatively inert on biological processes, and it rarely presents a human health hazard (Schroeder and Darrow, 1973). Aluminum has a relatively high bioaccumulative tendency in freshwater fish muscle. Consumption of seafoods containing Al presents little risk due to the low toxicity of Al to human beings (Phillips and Russo, 1978).

Boron is used in a process for bleaching pulverized wood by the pulp and paper industry (Thompson et al., 1976), as a hardener for other metals (Phillips and Russo, 1978), and as a neutron absorber in nuclear installations (National Academy of Science, 1973). It becomes enriched in fly ash from fossil fuels. Boron generally has a low bioaccumulative tendency in freshwater fish and a low toxicity to aquatic organisms and to humans (Phillips and Russo, 1978).

Cadmium is rare in nature, but is highly toxic (National Academy of Science, 1973). Inhalation or ingestion of Cd produces both acute and chronic health effects. Cadmium poisonings in humans resulting from oral consumption or inhalation are well documented (Fassett, 1975; Flick et al., 1971; Voors and Shuman, 1977; American Conference of Governmental and Industrial Hygientists, 1974; Stokinger, 1963; World Health Organization,

1972). Cadmium is a dangerous cumulative poison. A concentration factor of up to 1,000 has been reported (National Academy of Science, 1973). Several authors have measured Cd uptake by freshwater organisms. The accumulation of Cd by freshwater fish has been studied in white catfish, *Ictalurus catus* (Rowe and Massaro, 1974); goldfish, *Carassius auratus* (Marafante, 1976); bluegill, *Lepomis macrochirus* (Mount and Stephan, 1967; Eaton, 1974); zebra fish, *Brachydanio rerio* (Rehwolt and Karimian-Teherani, 1976); stickleback, *Gasterosteus aculeatus* (Pascoe and Mattey, 1977); guppy, *Poecilia reticulata* (Kinkade and Erdman, 1975); brook trout, *Salvelinus fontinalis* (Benoit et al., 1976); rainbow trout, *Salmo gairdneri* (Kumada et al., 1973); and largemouth bass, *Micropterus salmoides* (Cearley and Coleman, 1974). Very little Cd is accumulated in the edible portions of fishes; it is usually concentrated in the gills, liver, and kidneys. Cadmium in fishes, therefore, does not appear to represent a hazard to human consumers. However, oysters, abalone, and mussels are capable of accumulating extremely high levels of Cd in edible portions (Phillips and Russo, 1978).

Manganese has a relatively low tendency for bioaccumulation in freshwater fishes. Manganese has a low toxicity to humans, but poisonings have occurred from excessive exposures to Mn in plants (Berry et al., 1974). Chronic poisoning may result from the inhalation of Mn compounds (Sullivan, 1969). Manganese has been detected in marine and freshwater fishes and has been shown to be accumulated via the food chain in marine and freshwater invertebrates. However, Mn appears to be a relatively nonhazardous element in most waters due to the low toxicity of Mn to humans and aquatic life (Phillips and Russo, 1978).

Molybdenum has a low bioaccumulative tendency in fish. Bioaccumulation of Mo by lake trout, *Salvelinus namaycush*, was studied by Tong et al. (1974). Molybdenum compounds exhibit a low order of toxicity for exposed workers (American Conference of Governmental and Industrial Hygienists, 1974). Molybdenum does not tend to accumulate in the edible portions of fish and has a relatively low toxicity to humans (Phillips and Russo, 1978).

Although Ni is present in considerable amounts in plant and animal tissues, dietary intake of Ni is not harmful to humans. Workers exposed to Ni may develop a sensitivity to it and even dermatitis. Because of Ni's low toxicity to humans, almost no information is available on the accumulation of Ni by aquatic organisms (Phillips and Russo, 1978).

In industrial situations Ni dust has been shown to cause lung and nasal cancers in exposed workers (Doll, 1958), and Ni metal can cause eczema in sensitized workers (Browning, 1969). Nickel carbonyl, an intermediate in the nickel refining process (also found in cigarette smoke and a possible product of the incomplete combustion of coal), can cause cancer in rats and humans and represents the primary nickel related hazard to human health (Sunderman and Donnelly, 1965; Schroeder, 1970). The low toxicity of nickel when orally ingested has been demonstrated for several animals (Underwood, 1971). Nickel constantly occurs in food, many waters, and all forms of life, both marine and terrestrial (Bowen, 1966).

The results of this study demonstrated that fly ash extracts were acutely toxic to fathead minnows and that various trace elements are accumlated in both

fathead minnows and green sunfish. Of the six chemical constituents most commonly accumulated in the fish, Cd appears to be the most toxic. Neither the bioaccumulation and biomagnification of trace elements in fish of various trophic levels nor the health effects from the human consumption of those fish are well understood; both subjects warrant additional study.

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