

University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

US Department of Energy Publications

U.S. Department of Energy

1990

Identification of Solubility-Controlling Solid Phases in a Large Fly Ash Field Lysimeter

Jonathan S. Fruchter

Pacific Northwest National Laboratory

Dhanpat Rai

Pacific Northwest National Laboratory

John M. Zachara

Pacific Northwest National Laboratory, john.zachara@pnl.gov

Follow this and additional works at: <https://digitalcommons.unl.edu/usdoepub>



Part of the [Bioresource and Agricultural Engineering Commons](#)

Fruchter, Jonathan S.; Rai, Dhanpat; and Zachara, John M., "Identification of Solubility-Controlling Solid Phases in a Large Fly Ash Field Lysimeter" (1990). *US Department of Energy Publications*. 206.

<https://digitalcommons.unl.edu/usdoepub/206>

This Article is brought to you for free and open access by the U.S. Department of Energy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in US Department of Energy Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Identification of Solubility-Controlling Solid Phases in a Large Fly Ash Field Lysimeter

Jonathan S. Fruchter,* Dhanpat Rai, and John M. Zachara

Battelle, Pacific Northwest Laboratories, Battelle Boulevard, Richland, Washington 99352

■ Samples of pore fluids and leachates were obtained from a large fly ash field lysimeter in central Pennsylvania. The fly ash in the lysimeter was usually only partially saturated, and only 0.3 pore volumes of water leached through the lysimeter during the 3-year study period. The samples were analyzed for major and trace inorganic anions and cations. The resulting analyses were modeled by using an equilibrium speciation/solubility code to test the hypothesis that the solubilities of at least some species in the fly ash leachate were controlled by solid phases. Potential solubility-controlling solids were identified for Al, Ba, Ca, Cr, Cu, Fe, S, Si, and Sr in the pore waters and leachates. Solid solutions appear to play an important role in controlling the concentrations of Ba, Sr, and Cr. The activity relationships were independent of location within the lysimeter and time of sampling. A laboratory experiment showed that equilibration times between these nine elements and their solubility-controlling solids were on the order of days or less. Geochemical reactions controlling the concentrations of As, B, Cd, Mo, and Se were not identified.

Introduction

The electric utility industry produces approximately 75 million tons of solid waste annually (1). This amount may double by the turn of the century. The vast majority of this waste consists of fly ash and bottom ash produced during the combustion of coal. In the United States, about 80% of these wastes are disposed of on land, either in landfills or ponds. Both the fly ash and the bottom ash are enriched in certain major and trace elements that have the potential to alter nearby groundwater and surface-water quality if released in sufficient concentrations. These elements include arsenic, boron, cadmium, chromium, copper, molybdenum, selenium, sulfur, and zinc. It is, therefore, important to understand those chemical processes in the ash/water system that control the concentrations of these elements in the resulting leachate.

A number of recent studies have concentrated on various aspects of fly ash characterization in the laboratory. These have included leaching studies (2-5) and mineralogical and chemical analyses (6-9). Much of this past work has been summarized in a recent review (10). Several of the leaching studies have documented solubility and adsorption phenomena that control leachate composition and have shown that different mineralogical transformations occur with time and environmental exposure.

Published accounts of fly ash leaching under field conditions are limited. In one such study of a midwestern bituminous fly ash pond, six metals (Cd, Cr, Cu, Ni, Pb, and Zn) were investigated (11). Possible solubility controls were identified for Cr, Cu, and Pb, including $\text{Cr}(\text{OH})_3$, malachite $[\text{Cu}_2(\text{OH})_2\text{CO}_3]$, and $\text{Pb}(\text{OH})_2$. Another study documented the migration of As, Cr, Mo, Pb, and Se from a lignite fly ash landfill in North Dakota (12). This study found elevated concentrations of all of these elements in groundwaters below the landfill.

This paper reports on the characteristics of pore waters and leachates from a large field lysimeter at the Montour

Power Station, Pennsylvania, under natural rainfall conditions. The lysimeter was well instrumented and equipped with several sampling devices. Aqueous samples were obtained from different depths in the field lysimeter over a 3-year period starting in 1985, with the objectives of (1) identifying geochemical reactions controlling pore-water concentration over the study period, (2) determining whether laboratory-derived data were applicable to a field situation, and (3) identifying inadequacies in current understanding of the leaching process and in current descriptive thermodynamic constants for the solubility reactions that were postulated to occur.

A previous study (13) has described leachate concentrations and trends from this lysimeter.

Site Description

The Montour field lysimeter, located in central Pennsylvania, was designed to model a dry coal fly ash disposal facility (14). It was constructed aboveground in the shape of a truncated pyramid, with a 30.5 m \times 30.5 m base and an 18.3 m \times 18.3 m top. The 3.05-m-high lysimeter was constructed of 10 0.305-m layers of compacted fly ash. The fly ash was produced by the combustion of bituminous coal mined in western Pennsylvania. The side slopes were 2:1 horizontal to vertical and vegetated. The top was left bare but covered with a 10-cm layer of bottom ash to prevent wind erosion of the fly ash. A 50-cm layer of bottom ash was also placed at the bottom to facilitate drainage. The lysimeter was equipped with a leachate collection system and a pore-water sampling system, described below.

Because the lysimeter was constructed aboveground and is not irrigated, conditions are only partially saturated except after major precipitation events. Leachate is produced during only part of each year, generally from October to May. The cumulative volume of leachate that exited the base of the lysimeter over the 3-year study period amounted to only 0.3 pore volumes. Thus it seems likely that the ash is still largely unweathered, indicating that the data from the lysimeter should be suitable for comparison with data from laboratory studies performed on freshly collected ash.

Water-Sampling Procedures

Pore-water samples were obtained with ceramic porous cups installed in multiple-instrument installations or nests. In these installations, ceramic porous cups were set into slurried ash to ensure good hydraulic connection between the porous cups and the fly ash at the borehole wall. Samples were taken by first drawing water into the ceramic cups under vacuum and then pressurizing the ceramic cups from the lysimeter surface to force the water out into 1-L polyethylene bottles.

Leachate samples represented lysimeter drainage and were collected directly from a leachate drain located in the southwest corner of the lysimeter. Aliquots of both leachate and pore waters were subsequently sealed in polyethylene vials after appropriate preservation procedures and transferred to the laboratory for analysis. The sam-

pling procedures are described in greater detail elsewhere (14).

Solid-Sampling Procedures

Two sets of solid samples were collected. One set consisted of 10 samples from each of the individual lysimeter construction layers that were set aside in 1984 when the test cell was being constructed. These samples were stored in a field-moist condition until they were analyzed.

The second set consisted of samples from three continuous cores collected from the lysimeter in late 1987 after 3 years of exposure. The cores were collected by using a hollow-stem auger with a lined 1.5-m core barrel. Two cores collected fly ash only. The third core collected 3.05 m of fly ash and 0.45 m of the bottom ash drainage blanket at the base of the test cell. All of the core segments contained significant moisture but none were saturated. Visual inspection of these cores did not reveal any horizontal stratification of the ash. The 0.76-m core segments were capped immediately after collection, taped, and coated with paraffin wax to prevent gas or moisture exchange during shipping. The cores were shipped by overnight express in core boxes specially constructed to minimize disturbance. The cores were refrigerated in storage.

Laboratory Procedures

Extraction of Construction-Layer Samples. The 10 construction-layer samples were equilibrated in deionized/distilled water, and the solutions were analyzed for comparison with the compositions of the pore waters. Replicate 100-g samples of each construction-layer composite were placed in 250-mL plastic centrifuge tubes; 100 g of water was then added. The 1:1 mixtures were rotated on a shaker for 4 h at 25 °C, after which pH was measured on the settled suspension over a 15-min time span. The mixtures were returned to the shaker for 1 week at 25 °C and then were centrifuged at 4812g for 30 min. After centrifugation, the pH, Eh and conductivity of the supernatant were measured under air. The supernatant was then filtered through a prewashed 0.1- μ m filter.

Core Subsampling, and Extraction and Analysis of Pore Waters. The three cores were subsampled in a glovebox under N₂ gas within 60 h of collection. Selected subsamples were taken in each core at depths of 2.5–20, 60–90, 135–165, 210–240, and 277.5–297.5 cm. Additional subsamples were taken in the deeper core at 302.5–312.5 and 312.5–327.5 cm. First, small cores of known volume were removed for determination of bulk density and moisture content. Then the rest of the subsample was homogenized, and two 200-g samples were put in individual 250-mL plastic centrifuge tubes. One of these 200-g samples was then freeze-dried, and the other was used in extracting pore water, as described below. The remaining core material was archived.

Freon 113 (200 g) was added to the samples, which were centrifuged for 4 h at 4812g under N₂ atmosphere to displace pore water (15). The displaced water was recovered from the surface of the Freon and its mass recorded.

Analysis of Water Samples. The various types of water samples obtained by the methods described above are summarized in Table I. The samples were analyzed for 23 elements and species by a combination of atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), ion chromatography (IC), and specific ion electrodes (SIE). Ranges of data for each analyte are shown in Table II. The samples represent various types of samples from various locations within the lysimeter taken over a 3-year

Table I. Summary of Aqueous Samples Used in This Study

sample name	sample type	location
AB	pore water	sampler nest AB
CD	pore water	sampler nest CD
composite	pore water	composite of sampler nests AB and CD
leachate	leachate	leachate collection cistern
construction layers	1:1 fly ash/water extract	samples of fly ash layers used in lysimeter construction
extracted pore fluid	pore water extracted by immiscible displacement	fly ash cores taken from the lysimeter 3 years after construction

Table II. Ranges of Concentrations for Montour Lysimeter Aqueous Samples (in mg/L Except pH)^a

analyte	range	analyte	range
Al	0.40–9.8	K	1.4–740
As	0.007–0.78	Mg	0.3–42
B	0.27–31	Mn	0.006–27
Ba	<0.007–0.27	Mo	0.15–48
CO ₃ ²⁻	25–210	Na	0.56–210
Ca	72–800	Se	<0.004–0.79
Cl	1.5–99	Si	0.70–18
Cr	0.041–3.2	SO ₄ ²⁻	140–9600
Cd	<0.004–0.14	Sr	0.55–11
Cu	<0.008–0.50	Zn	<0.002–24
F	0.08–11	pH	6.14–10.2
Fe	<0.01–0.56		

^a For 92 samples.

period. Most of the analytes range over at least 2 orders of magnitude in aqueous concentrations.

Geochemical Calculations

Our first strategy for interpreting the concentration data for the aqueous samples from the lysimeter was to look for evidence of elements whose concentrations appeared to be controlled by solubility reactions. Elements that could not be interpreted in this simple fashion would then be interpreted in terms of adsorption or kinetic controls. To this end, the analytical data defining the chemical composition (pH, major and minor cations and anions) of each individual sample were input to the geochemical code MINTEQA2 (16) for the purpose of calculating ionic strength, ion speciation, single ion activity coefficients, single ion activities for aqueous solute species, and ion activity products and saturation indexes for mineral solids. The use of MINTEQA2 for these purposes as well as other applications is described in two user's manuals (17, 18).

Results

The discussion that follows emphasizes the elements Al, Ba, Ca, Cr, Cu, Fe, S, Si, and Sr, for which the aqueous concentrations can be interpreted or related to specific solubility reactions. Those elements (As, B, Cd, Mo, and Se) for which controlling solubility reactions were not identified are also briefly discussed.

Major Ash Constituents. Aluminum. Measured Al concentrations varied by more than 2 orders of magnitude in the various samples from the large field lysimeter site. Previous laboratory studies (5) implied that in many fly ashes Al is controlled by the solubility of Al(OH)SO₄ when pH values are less than ~6.0, by amorphous Al(OH)₃ when pH is between ~6.0 and 9.0, and by crystalline Al(OH)₃ (gibbsite) when pH is greater than 9.0. Since the pH of all samples from the field lysimeter was above 6.0, it was expected that amorphous Al(OH)₃ and gibbsite would

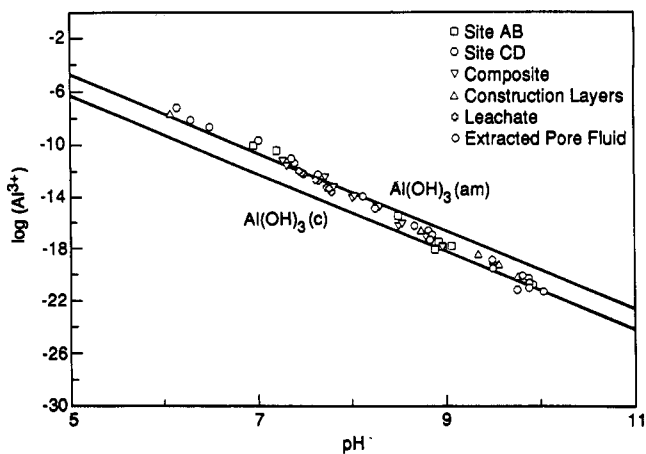


Figure 1. Plot of calculated Al^{3+} activity vs pH for various fly ash lysimeter samples, compared to activities predicted (solid lines) from control by crystalline $\text{Al}(\text{OH})_3$ (gibbsite) and amorphous $\text{Al}(\text{OH})_3$.

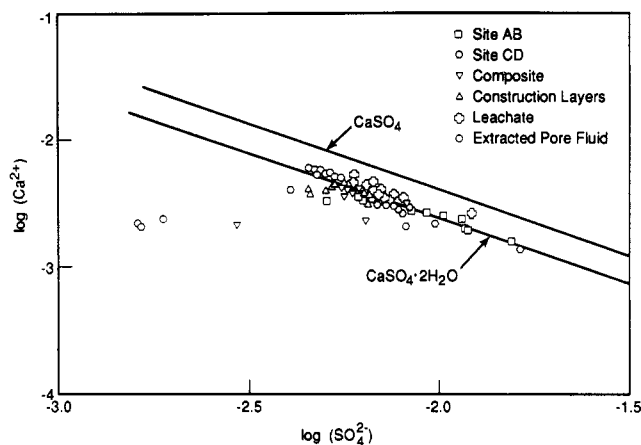


Figure 2. Plot of calculated $\log \text{Ca}^{2+}$ activity vs calculated $\log \text{SO}_4^{2-}$ activity for various fly ash lysimeter samples, compared to activities predicted (solid line) from control by CaSO_4 (anhydrite) and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum).

control the solubility of Al. The computed Al^{3+} activities (Figure 1) varied as a smooth function of pH, regardless of the origin of samples. Comparison of the observed Al^{3+} activities with those predicted to be in equilibrium with the $\text{Al}(\text{OH})_3(\text{am})$ and $\text{Al}(\text{OH})_3(\text{c})$ (Figure 1) indicated that the activities observed at pH values of less than ~ 8.5 and greater than 9 were similar to those in equilibrium with $\text{Al}(\text{OH})_3(\text{am})$ and $\text{Al}(\text{OH})_3(\text{c})$, respectively. These results were consistent with the experimental data for fly ashes reported by several authors (5, 19, 20).

Calcium and Sulfur. Ca and S were the major soluble elements in the pore waters and leachates. Analytical measurements showed that reduced S species (SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$) were present in negligible quantities and that SO_4^{2-} was the dominant species. The presence of SO_4^{2-} as the dominant species was consistent with the oxidizing redox potentials and the presence of other highly oxidized aqueous species, such as CrO_4^{2-} . Concentrations of SO_4^{2-} were high, with an average concentration of ~ 0.02 M, commensurate with the high S concentrations typically present in bituminous coals and their ashes. Calcium concentrations in fly ashes may be controlled by $\text{CaSO}_4/\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3 , or $\text{Ca}(\text{OH})_2$ (10). Among these compounds, $\text{Ca}(\text{OH})_2$ is expected only at very high pH values (greater than ~ 12). Calcium activities were essentially independent of pH in the measured pH range (6–10), suggesting that CaCO_3 and $\text{Ca}(\text{OH})_2$ are not the solubility-controlling solids. The plot of Ca^{2+} activity as a function of SO_4^{2-} activity (Figure 2) shows that Ca^{2+}

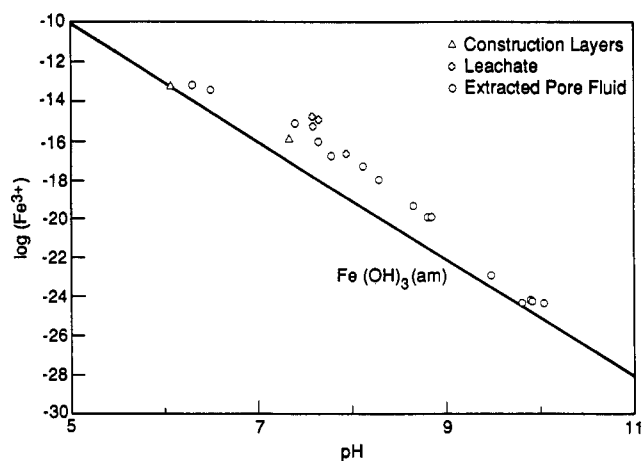


Figure 3. Plot of calculated $\log \text{Fe}^{3+}$ activity vs pH for various fly ash lysimeter samples, compared to activities predicted (solid line) from control by amorphous $\text{Fe}(\text{OH})_3$.

activity decreased as sulfate activity increased, as would be expected if Ca concentrations were controlled by calcium sulfate. Both CaSO_4 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ have been identified in fly ashes by many researchers (6, 10, 21, 22). The Ca^{2+} activities observed were similar to those predicted from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Figure 2). Because $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) rather than CaSO_4 (anhydrite) usually precipitates below 42°C from aqueous solutions of an ionic strength less than that of seawater (23), this result was expected.

Iron. Aqueous Fe was present in measurable quantities only in the leachate, construction layers, and extracted pore water; it was below detection limits in all other samples. Speciation measurements made by ion chromatography indicated that all of the detectable Fe in these samples was in the Fe(III) state. The similarity of the measured Fe^{3+} activities to those calculated in equilibrium with $\text{Fe}(\text{OH})_3(\text{am})$ (Figure 3) in some of the samples and the reported presence of amorphous $\text{Fe}(\text{OH})_3(\text{am})$ in other fly ashes (6) together suggest that Fe concentrations may be controlled by $\text{Fe}(\text{OH})_3(\text{am})$. However, between pH 7 and 9, the calculated iron activities are almost 2 orders of magnitude higher than those expected from reported values for $\text{Fe}(\text{OH})_3(\text{am})$. Possible explanations for this discrepancy are (1) that despite the fact that $0.0030\text{-}\mu\text{m}$ filters were used on the construction layer and extracted fluid samples ($0.1\ \mu\text{m}$ was used on the leachate sample), some colloidal iron still remained in the filtrates, and (2) that the published thermochemical data for amorphous iron hydroxides are not accurate.

Silicon. Si was one of the major matrix elements of the fly ash. Aqueous Si concentrations were measured in selected samples only (composite pore-water samples, extracted pore water, leachate, and construction-layer samples). The computed aqueous activities of H_4SiO_4 (Figure 4) indicated that SiO_2 (amorphous or quartz) was not controlling the Si concentrations in the test-cell pore waters. The similarity of the measured activities to those predicted in equilibrium with wairakite (Figure 5) suggested that wairakite might be the solubility-controlling aluminosilicate. Wairakite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$) is the Ca analogue of the more common sodium zeolite, analcite. It has been reported in altered/weathered volcanic tuff. Whether this solid can or will form in utility fly ash is not known at present. Other studies have suggested other aluminosilicates, such as proto-imogolite (6), laumontite (10), or mullite (11).

Minor Ash Constituents. Barium and Strontium. Ba and Sr form sparingly soluble compounds with carbo-

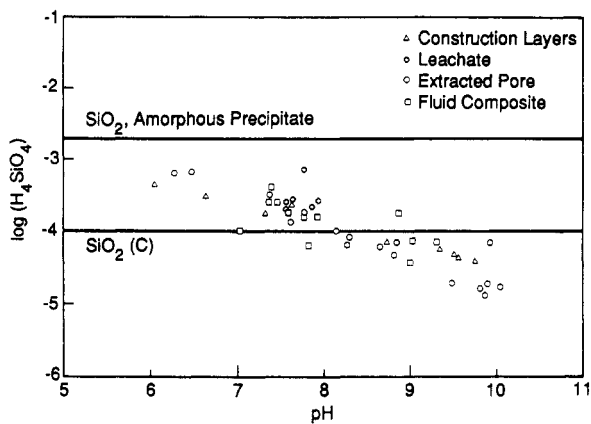


Figure 4. Plot of calculated $\log H_4SiO_4$ activity for various fly ash lysimeter samples, compared to activities predicted (solid line) from control by $SiO_2(c)$ (quartz) and amorphous SiO_2 .

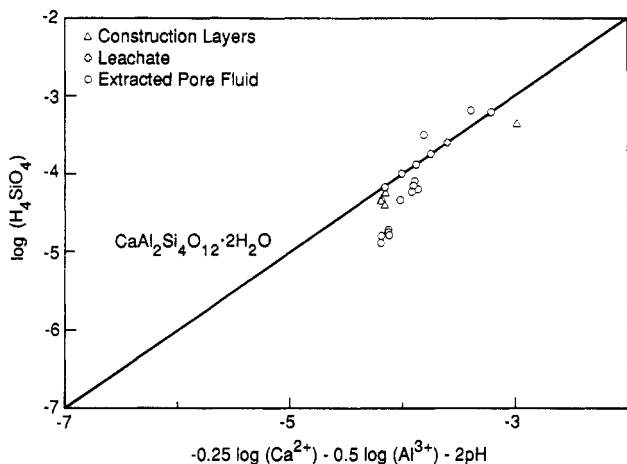


Figure 5. Plot of $\log H_4SiO_4$ activity of various fly ash lysimeter samples vs the logarithm of the equilibrium expression for the formation of $CaAl_2Si_4O_{12} \cdot 2H_2O$ (wairakite). Only those samples from Figure 4 that had measured Al^{3+} concentrations above the detection limit are included in this figure.

nates and sulfates. The total concentrations of Ba varied by about an order of magnitude, while those of Sr were nearly constant in the pore waters and leachates. The concentrations of Ba and Sr were essentially independent of pH throughout the measured pH range, suggesting that $BaCO_3$ and $SrCO_3$ were not the solubility-controlling solids. Because the dominant pore-water anion was SO_4^{2-} , the activities of Ba^{2+} and Sr^{2+} were plotted as a function of the activity of SO_4^{2-} (Figure 6) to determine if celestite ($SrSO_4$) and barite ($BaSO_4$) control pore-water concentrations. The results for Ba showed that Ba^{2+} activities were up to an order of magnitude higher than those in equilibrium with $BaSO_4(c)$. In addition, the results for Sr^{2+} in Figure 6 showed that Sr^{2+} was slightly undersaturated with respect to celestite ($SrSO_4$). These results for Ba and Sr are similar to those reported for a large number of unweathered fly ashes (5).

Recent experiments in our laboratory with the freshly coprecipitated $(Ba,Sr)SO_4$ also showed a similar behavior. This laboratory-observed behavior was found to be not the result of thermodynamic equilibrium with a $(Ba,Sr)SO_4$ solid solution, but instead a result of perhaps a stronger interaction between Ba and SO_4 than between Sr and SO_4 . In the Ba-substituted $SrSO_4$, this stronger interaction would reduce the solubility of $SrSO_4$, and in Sr-substituted $BaSO_4$, it would increase the solubility of $BaSO_4$. With aging of the coprecipitates, however, the Ba and Sr activities were seen to approach that of the pure end mem-

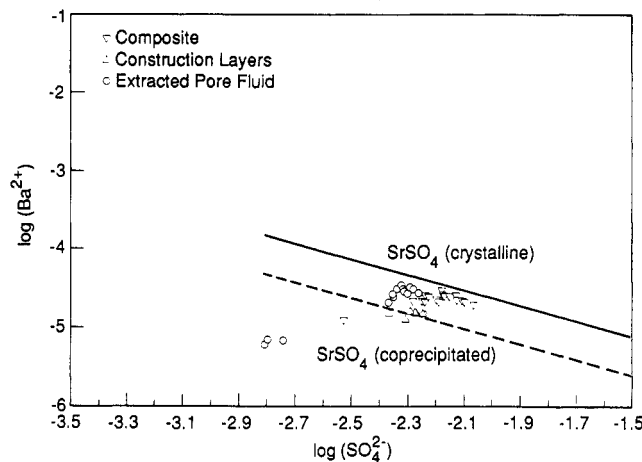
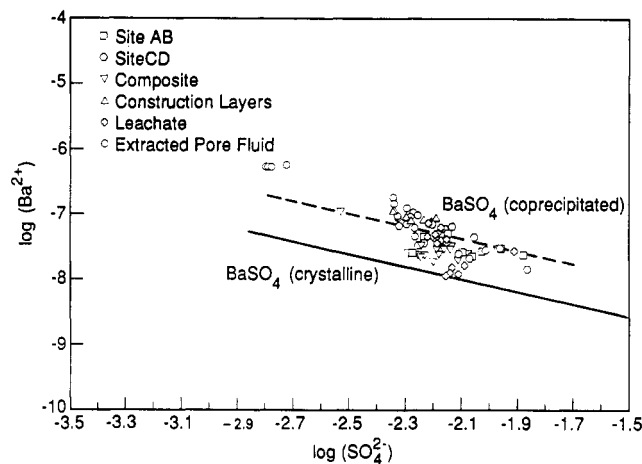


Figure 6. Plots of calculated $\log Ba^{2+}$ activity and calculated $\log Sr^{2+}$ activity vs calculated $\log SO_4^{2-}$ activity for various fly ash lysimeter samples, compared to activities predicted (solid lines) from control by $BaSO_4(c)$ (barite) and $SrSO_4(c)$ (celestite).

bers. Total Ba and Sr were present in equimolar ratios in the ash. The fact that the observed Ba and Sr behavior in lysimeter samples was similar to the 14-day equilibrated-coprecipitated $(Ba_{0.5}Sr_{0.5})SO_4$ (Figure 6) indicates that the lysimeter fly ash was relatively unweathered. The results collectively show that Ba and Sr concentrations are controlled by their sulfate solids, currently more likely by coprecipitated $(Ba,Sr)SO_4$ than by $BaSO_4$ or $SrSO_4$.

Chromium. Oxidation-state analyses of the samples showed that the soluble Cr was present as Cr(VI). Because of the very high sulfate concentrations and near-neutral to alkaline pH values, adsorption was not expected to control Cr concentrations. Studies have shown that CrO_4^{2-} adsorption is significantly depressed in the presence of SO_4 (24). It has also been shown that $BaCrO_4$ and $Ba(S,Cr)O_4$ have relatively low solubilities and rapid precipitation/dissolution kinetics, and that they could form and control Cr(VI) concentrations in geologic environments (25). These solids may be important in the large field lysimeter, where there are significant total concentrations of Ba and SO_4^{2-} . A comparison of measured CrO_4^{2-} activity with that in equilibrium with $BaCrO_4$ (Figure 7) showed that $BaCrO_4$ was not the solubility-controlling solid. The reported results (25) demonstrated that $Ba(S,Cr)O_4$ was more stable than $BaCrO_4$. Additionally, this solid solution was found to control Cr(VI) levels in an oxidizing SO_4^{2-} -containing soil. To evaluate whether $Ba(S,Cr)O_4$ is the solubility-controlling solid, the specific composition of the $Ba(S,Cr)O_4$ in the ash must be known. At present, techniques are not available to characterize the small quantities of $Ba(S,Cr)O_4$ in the fly ash.

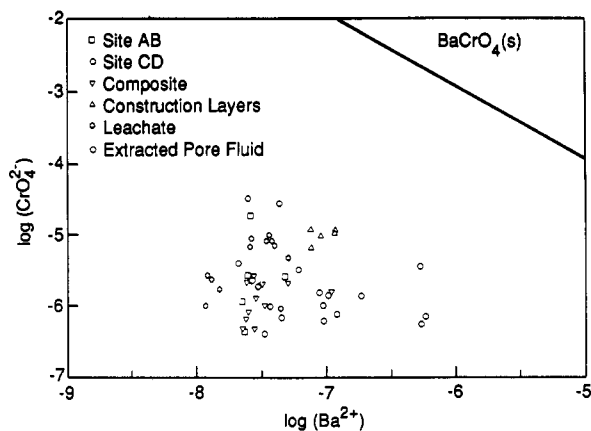


Figure 7. Plot of calculated $\log \text{CrO}_4^{2-}$ activity vs calculated $\log \text{Ba}^{2+}$ activity for various fly ash lysimeter samples, compared to activities predicted (solid line) from control by $\text{BaCrO}_4(\text{s})$.

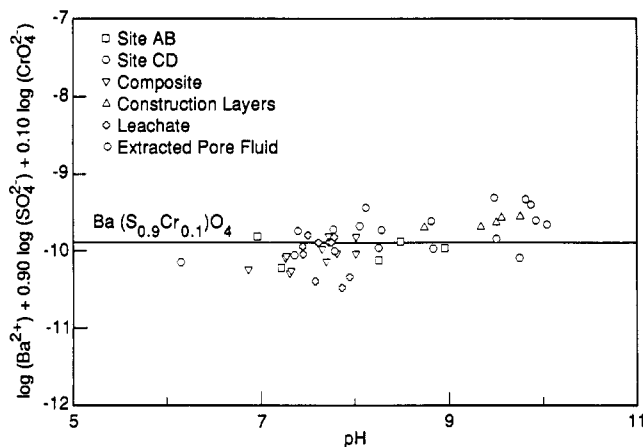


Figure 8. Plot of $[\log (\text{Ba}^{2+}) + 0.9 \log (\text{SO}_4^{2-}) + 0.1 \log (\text{CrO}_4^{2-})]$ vs pH observed in different solutions. The solid line is based on activities in equilibrium with $\text{Ba}(\text{S}_{0.9}\text{Cr}_{0.1})\text{O}_4$ reported by Rai et al. (25).

Figure 8 shows a $\text{Ba}(\text{S},\text{Cr})\text{O}_4$ solid solution that, if present, could be controlling the chromate concentrations. The various aqueous analyses could be fit by solid-solution composition of $\text{Ba}(\text{S}_{0.9}\text{Cr}_{0.1})\text{O}_4$. Whether this solid solution in fact controlled the aqueous Cr(VI) concentrations in Montour samples could not be definitely assessed with this set of data. The $\text{Ba}(\text{S}_{0.9}\text{Cr}_{0.1})\text{O}_4$ solid solution is a plausible solubility control because the large variability in Cr(VI) concentrations as a function of depth, time, and pH is well explained by this single hypothesized solid phase (Figure 8). There was also enough Ba, Cr, and SO_4^{2-} present in the ash that $\text{Ba}(\text{S}_{0.9}\text{Cr}_{0.1})\text{O}_4$ could form.

One study of fly ash disposal in a marine environment showed the Cr to be present in that system largely as Cr(III) (26). Studies have shown (25) that Cr(III) in fly ash systems generally forms solid solutions with iron hydroxides $[(\text{Fe},\text{Cr})(\text{OH})_3]$. These solid solutions show very low solubilities ($<10^{-7}$ M) at the pH levels of the samples used in this study. Therefore, very low leachate Cr concentrations can be expected in those fly ash systems where Cr(III) is the major redox species.

Copper. Detectable aqueous Cu concentrations were observed in the pore-water sampler nest composite samples, the construction-layer samples, and pore waters from the ash cores. Tenorite (CuO) and malachite $[\text{Cu}_2(\text{O}-\text{H})_2\text{CO}_3]$ have been predicted to be present in fly ash samples (20, 27). It has been reported (10) that under oxidizing conditions, like those present in the field lysimeter, and in the pH range measured at the test cell, CuO is the most likely solubility-controlling phase among the

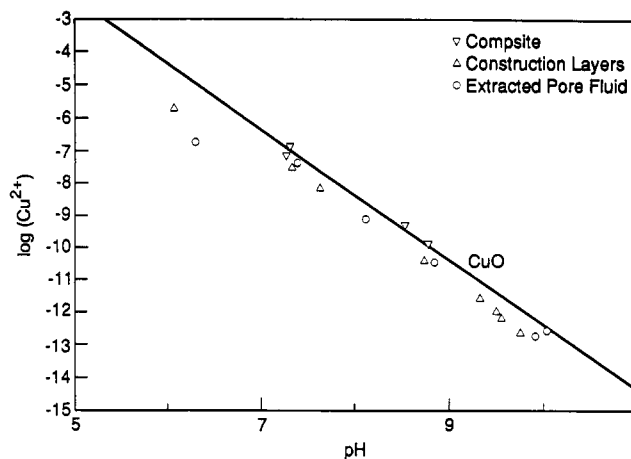


Figure 9. Plot of calculated $\log \text{Cu}^{2+}$ activity vs pH for various fly ash lysimeter samples, compared to activities predicted (solid line) from control by CuO (tenorite).

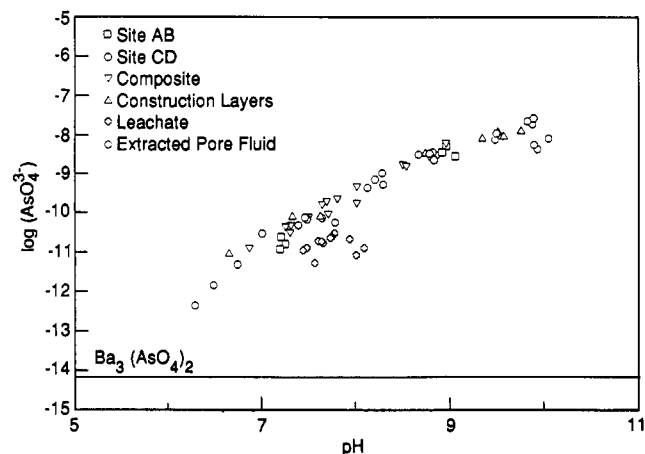


Figure 10. Plot of calculated $\log \text{AsO}_4^{3-}$ activity vs pH for various fly ash lysimeter samples, compared to activities predicted (solid line) from control by $\text{Ba}_3(\text{AsO}_4)_2$ when Ba^{2+} is fixed at $10^{-7.5}$ M.

solids that may be present in near-surface geologic environments [the others are $\text{Cu}_4\text{SO}_4(\text{OH})_6$, $\text{Cu}_2(\text{OH})_2\text{CO}_3$, and $\text{Cu}(\text{OH})_2$]. CuO has also been reported as a common ore mineral in oxidized systems (23). These findings, along with the fact that measured Cu^{2+} activities are similar to those predicted from CuO (Figure 9), indicate that the aqueous Cu concentrations in the field lysimeter samples were controlled by CuO (tenorite). Our extensive laboratory studies (unpublished results) with four different fly ashes that were equilibrated at different pH values with and without the addition of CuO and Cu^{2+} also indicate that CuO is the solubility-controlling solid.

Other Trace Elements. In addition to the elements discussed above, aqueous concentrations of several other trace elements (As, B, Cd, Mo, and Se) were also measured. Using the existing thermochemical data, attempts were made to determine whether their concentrations could be related to precipitation/dissolution reactions. These attempts were unsuccessful. Therefore, it was not clear whether the aqueous concentrations of these elements were controlled by precipitation/dissolution, adsorption/desorption, or rates of dissolution of fly ash matrix.

Calculations using the standard redox potentials for As(III) and As(V) suggested that As should be in the As(V) state at the Eh levels found in the test cell solutions. Speciation measurements have not been performed to test this hypothesis. Barium arsenate $[\text{Ba}_3(\text{AsO}_4)_2]$ has been proposed as a solubility-controlling phase for As(V) (28). However, the plots of AsO_4^{3-} activity against pH in Figure

Table III. Summary of Inferred Solubility-Controlling Solids

element	solubility-controlling solid	
	formula	name
Al	Al(OH) ₃ (am) (pH 6-9)	amorphous aluminum hydroxide
	Al(OH) ₃ (c) (pH >9)	gibbsite
Fe	Fe(OH) ₃ (am)	amorphous ferric hydroxide
Ca,S	CaSO ₄ ·2H ₂ O	gypsum
Ba,Sr	(Ba,Sr)SO ₄	barium and strontium coprecipitates
Cu	CuO(c)	tenorite
Cr	Ba(S,Cr)O ₄	barium sulfate/barium chromate solid solution

10 do not appear to support that hypothesis for these samples. Similar results were reported by another study (29).

No conclusive statements regarding the mechanisms that control Cd behavior can be made. The observed aqueous concentrations of Cd were near their detection limits and were similar to those reported in a previous study of a large number of fly ashes (5).

Measured B, Mo, and Se concentrations were well above detection limits, varied widely, and were essentially independent of pH. The estimated thermochemical data for several borate minerals (pinnoite, inderite, inyoite, colemanite, inderborite, hungchaoite, borax, sborgite, McAllisterite, kaliborite, and nobleite) has shown that these B minerals are very soluble and could not control B concentrations in the field lysimeter (30). The observed B concentrations fell within the range of values for B reported for a large number of fly ash extracts (5). In the case of Mo, powellite (CaMoO₄) appears to control Mo concentrations in hot-water extracts of many fly ashes (5). However, the observed activities of MoO₄²⁻ in the large field lysimeter samples were about an order of magnitude higher than the activities in equilibrium with CaMoO₄, suggesting that CaMoO₄ was not the solubility-controlling solid. The mechanisms that may control B, Mo, and Se concentrations are not understood.

Summary of Results. Collectively, these results indicate that the observed aqueous concentrations of Al, Ba, Ca, Cr, Cu, Fe, S, Si, and Sr were controlled by solubility phenomena. Regardless of the origin of the aqueous samples (i.e., their location, depth, and when they were taken at the large field lysimeter site), the aqueous concentrations of these elements in all of these samples were explained by specific solubility reactions. The solubility-controlling solids for different elements are listed in Table III. To draw definite conclusions regarding these inferred solid phases, further experiments must demonstrate their existence. Plausible geochemical reactions that could control the aqueous concentrations of As, B, Cd, Mo, and Se were not identified.

Discussion

The solubility controls identified in this paper for various elements were based on matching calculated single ion activities for elements with activities expected in equilibrium with different solid phases. Such evidence is by its nature circumstantial. Therefore, this type of analysis should be considered as a guide to further experimentation to confirm the presence of these solid phases, rather than as a definitive proof. This confirmation can be done by either direct or indirect methods. Direct methods include X-ray diffraction and various electron spectroscopies. Indirect methods include observing the

pH behavior of the element over a wider pH range or approaching equilibrium for the proposed solid in the sample from both oversaturation and undersaturation. In most cases, indirect methods will be most applicable because trace-element solids are present in low concentrations.

Hypothesized reactions pertaining to the solubility-controlling solids have been discussed in the previous section. In inferring that the concentrations of several elements (e.g., Al, Ba, Ca, Cu, Fe, S, Sr) are controlled by solubility limits, it was assumed that the observed elemental concentrations were governed by equilibrium reactions and that the solubility-controlling solids were present in the ash. Before the conclusions can be relied upon, the validity of these assumptions must be ascertained.

Most of the solubility-controlling solids expected to be present in the Montour ash are sulfate and hydroxide compounds (Table III), which are known to have rapid precipitation/dissolution kinetics. Most environmentally important aqueous complexation reactions that would affect the final concentrations in equilibrium with solubility-controlling solids are also rapid. Therefore, it is reasonable to hypothesize that equilibrium reactions control the aqueous concentrations of elements contained in sulfate and hydroxide compounds. The validity of this equilibrium assumption was tested through laboratory batch equilibration experiments of the construction-layer samples. As can be seen by examination of Figures 1-10, solubility reactions that controlled aqueous concentrations in the lysimeter pore waters developed in the laboratory in 7 days or less.

Conclusions

A variety of solid and aqueous samples from a large field lysimeter site were analyzed, and the resulting data were modeled by using an equilibrium geochemical code (MINTEQ). Despite the caveats discussed in the preceding section, several conclusions are supported by the results of these studies.

The concentrations of Al, Fe, Cu, S, Ba, Sr, Cu, and Cr appear to be determined by solubility-controlling solids. Solid solutions appear to play an important role in controlling the concentrations of Ba, Cr, and Sr. Geochemical reactions controlling the aqueous concentrations of As, B, Cd, Mo, and Se were not identified. For elements for which a solubility control is hypothesized, the different types of aqueous samples all show similar activity relationships, regardless of location, depth, time of sampling, or equilibration time.

Registry No. Al, 7429-90-5; As, 7440-38-2; B, 7440-42-8; Ba, 7440-39-3; Zn, 7440-66-6; Ca, 7440-70-2; Cl, 7782-50-5; Cr, 7440-47-3; Cd, 7440-43-9; Cu, 7440-50-8; F, 7782-41-4; Fe, 7439-89-6; K, 7440-09-7; Mg, 7439-95-4; Mn, 7439-96-5; Mo, 7439-98-7; Na, 7440-23-5; Se, 7782-49-2; Si, 7440-21-3; Sr, 7440-24-6.

Literature Cited

- (1) Murarka, I. P.; McIntosh, D. A. *Solid Waste Environmental Studies (SWES): Description, Status, and Available Results*; EPRI EA-5322-SR; Electric Power Research Institute: Palo Alto, CA, 1987.
- (2) Warren, C. J.; Dudas, M. J. *J. Environ. Qual.* **1984**, *13*, 530-538.
- (3) Theis, T. L.; Wirth, J. L. *Environ. Sci. Technol.* **1977**, *11*, 1096-1100.
- (4) Roy, W. R.; Griffin, R. A.; Dickerson, D. R.; Schuller, R. M. *Environ. Sci. Technol.* **1984**, *18*, 734-739.
- (5) Ainsworth, C. C.; Rai, D. *Chemical Characterization of Fossil Fuel Wastes*; EPRI EA-5321; Electric Power Re-

- search Institute: Palo Alto, CA, 1987.
- (6) Warren, C. J.; Dudas, M. J. *J. Environ. Qual.* **1985**, *14*, 405-410.
 - (7) Bauer, C. F.; Natusch, D. F. S. *Environ. Sci. Technol.* **1981**, *15*, 783-788.
 - (8) Hansen, L. D.; Silberman, D.; Fisher, G. L. *Environ. Sci. Technol.* **1981**, *15*, 1057-1062.
 - (9) Mattigod, S. V.; Ervin, J. O. *Fuel* **1983**, *62*, 927-931.
 - (10) Rai, Dhanpat; Ainsworth, C. C.; Eary, L. E.; Mattigod, S. V.; Jackson, D. R. *Inorganic and Organic Constituents in Fossil Fuel Combustion Residues. A Critical Review*; EPRI EA-5176; Electric Power Research Institute: Palo Alto, CA, 1987; Vol. 1.
 - (11) Theis, T. L.; Richter, R. O. *Environ. Sci. Technol.* **1979**, *13*, 219-224.
 - (12) Groenewald, G. H.; Hassett, D. J.; Koob, R. D.; Manz, O. E. In *Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal I*; McCarthy, G. J., Lauf, R. J., Eds.; Materials Research Society: Pittsburgh, PA, 1985; Vol. 43, pp 213-226.
 - (13) Villame, J. F.; Bell, J. W.; LaBuz, L. L. In *Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal IV*; McCarthy, G. J., Glasser, F. P., Roy, D. M., Hemmings, R. T., Eds.; Materials Research Society: Pittsburgh, PA, 1988; Vol. 133, pp 325-332.
 - (14) Rehm, B. W.; Christel, B. J.; Stolzenburg, T. R.; Nichols, D. G. *Field Evaluation of Instruments for the Measurement of Unsaturated Hydraulic Properties of Fly Ash*; EPRI EA-5011; Electric Power Research Institute: Palo Alto, CA, 1987.
 - (15) Kinniburgh, D. G.; Miles, D. L. *Environ. Sci. Technol.* **1983**, *17*, 362-368.
 - (16) Felmy, A. R.; Girvin, D. C.; Jenne, E. A. *MINTEQA—A Computer Program for Calculating Aqueous Geochemical Equilibria*; EPA 600/3/84/032; U.S. Environmental Protection Agency, Office of Research and Development: Athens, GA, 1984.
 - (17) Brown, D. S.; Allison, J. D. *MINTEQA A1, An Equilibrium Metal Speciation Model: User's Manual*; EPA 600/3-87/012; U.S. Environmental Protection Agency, Athens Environmental Research Laboratory: Athens, GA, 1987.
 - (18) Peterson, S. R.; Hostetler, C. J.; Deutsch, W. J.; Cowan, C. E. *MINTEQA User's Manual*; NUREG/CR-4808 (PNL-6101); U.S. Nuclear Regulatory Commission: Washington, DC, 1987.
 - (19) Roy, W. R.; Griffin, R. A. *Environ. Sci. Technol.* **1984**, *18*, 739-742.
 - (20) Talbot, R. W.; Anderson, M. A.; Andren, A. W. *Environ. Sci. Technol.* **1978**, *12*, 1056-1062.
 - (21) Simons, H. S.; Jeffery, J. W. *J. Appl. Chem.* **1960**, *10*, 328-336.
 - (22) Scheetz, B. E.; White, W. B. In *Fly Ash and Coal Conversion By-Products: Characterization, Utilization, and Disposal I*; McCarthy, G. J., Lauf, R. J., Eds.; Materials Research Society: Pittsburgh, PA, 1985; Vol. 43, pp 53-60.
 - (23) Mason, B.; Berry, L. G. *Elements of Mineralogy*; W. H. Freeman & Co.: New York, 1968.
 - (24) Zachara, J. M.; Girvin, D. C.; Schmidt, R. L.; Resch, C. T. *Environ. Sci. Technol.* **1987**, *21*, 589-594.
 - (25) Rai, D.; Zachara, J. M.; Eary, L. E.; Ainsworth, C. C.; Amonette, J. E.; Cowan, C. E.; Szelmeczka, R. W.; Resch, C. T.; Schmidt, R. L.; Girvin, D. C.; Smith, S. C. *Chromium Reactions in Geologic Materials*; EPRI EA-5741; Electric Power Research Institute: Palo Alto, CA, 1988.
 - (26) Hjelmar, O. In *Proceedings of the International Conference on Coal Fired Power Plants and the Aquatic Environment Copenhagen, Denmark*; International Association of Water Pollution Research: London, 1982.
 - (27) Theis, T. L.; Halvorsen, M.; Levein, A.; Stankunas, A.; Unites, D. Fly Ash Leachate Attenuation Mechanisms. Draft report; TRC Environmental Consultants, Inc: East Hartford, CN, 1982.
 - (28) Wageman, R. *Water Res.* **1978**, *12*, 139-145.
 - (29) Turner, R. R. *Environ. Sci. Technol.* **1981**, *15*, 1062-1066.
 - (30) Mattigod, S. V. *Soil Sci. Soc. Am. J.* **1983**, *47*, 654-655.

Received for review October 31, 1989. Accepted March 19, 1990. We gratefully acknowledge the Pennsylvania Power and Light Co. for their cooperation and assistance throughout this project. The research was funded by the Electric Power Research Institute, Inc. (EPRI) under Contract RP2485-08, "Leaching Chemistry".

Determination of Polycyclic Aromatic Hydrocarbons in Urban Street Dusts and Their Source Materials by Capillary Gas Chromatography

Hideshige Takada,* Tomoko Onda, and Norio Ogura

Department of Environmental Science and Conservation, Faculty of Agriculture, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183, Japan

■ Molecular distributions of polycyclic aromatic hydrocarbons (PAHs) in street dust samples collected from the Tokyo metropolitan area were determined by capillary gas chromatography following HPLC fractionation. Sixty-four compounds including three- to six-ring PAHs and sulfur heterocyclics were identified by capillary GC/MS. Total PAH concentrations were in the range of a few micrograms per gram of dust. The source materials (automobile exhaust, asphalt, fuel-oil combustion products) were also analyzed. The PAH profile, especially relative abundance of alkyl-PAHs and sulfur-containing heterocyclics, indicated that PAHs in the street dusts on the heavily trafficked streets are strongly affected by automobile exhausts and those in the residential area have a somewhat more significant contribution from combustion products in stationary sources. With both types of dusts, asphalt is thought to contribute only a minor part of their PAHs.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) have long been recognized as hazardous environmental chemicals.

Some PAHs are known to be carcinogenic to man (1). PAHs are mainly formed during the combustion of coal and petroleum (2) and are widely distributed in soils and sediments throughout the world (3-9). Their sources and transport mechanisms have been the subject of a number of recent investigations (10-19). On urban street surfaces, PAHs of various origins (e.g., weathered materials of street surfaces, automobile exhaust, lubricating oils, gasoline, diesel fuel, tire particles, and atmospherically deposited materials) are present as street dust. The street dust material is washed from roads during heavy rain storms and transported to rivers, wastewater treatment plants, and estuaries (17, 18). Therefore, street dust is considered to be one of the important sources of PAHs in the aquatic environment, but the data available on PAHs in street dusts are limited (14, 20, 21). In particular, their detailed molecular compositions were rarely given (14, 20), although PAH profiles are useful to estimate their sources and fates. For example, Wakeham et al. (14) extensively characterized PAH profiles for lacustrine sediments, street dust, and plausible source materials (asphalt, automobile exhaust,