

CHEMICAL INTERACTIONS OF POLYCYCLIC ORGANIC COMPOUNDS WITH COAL FLY ASH
AND RELATED SOLID SURFACES

Final Report

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I. EXECUTIVE SUMMARY

In this work, the interactions of polycyclic aromatic hydrocarbons (PAHs) with particulate surfaces (especially those of coal fly ash) have been investigated, and the influence of coal ash surface properties on the photochemical transformation of adsorbed PAHs has been studied. The overall objective of the work has been to characterize the effects of adsorption onto atmospheric particulate matter on the chemical behavior of PAHs released into the atmosphere via combustion processes. Progress is reported in the following areas of effort:

(a) Major emphasis has been devoted to the interactions of PAHs with the different particulate phases that are found in heterogeneous coal ash samples. Techniques have been developed and thoroughly characterized for the fractionation of coal ashes into carbonaceous, mineral-magnetic, and mineral-nonmagnetic subfractions. Heats of adsorption for pyrene on such subfractions have been measured by gas-solid chromatography, and the photoreactivity of pyrene and benz[a]anthracene on ash subfractions has been examined. Carbonaceous particles exhibit the highest affinity for vapor-phase PAHs; mineral magnetic particles usually exhibit the smallest tendency to sorb PAHs from the vapor phase. Adsorption of PAHs on carbonaceous particles suppresses, virtually completely, their tendency to undergo photochemical transformation. For coal ashes that contain few carbonaceous particles, the adsorption and photochemical transformation of PAHs tend to be dominated by the mineral nonmagnetic particles; PAHs adsorbed on these particles tend to exhibit relatively efficient phototransformation.

(b) Analyses of adsorbed PAHs deposited on particulate matter generally entail extraction of the PAHs from the adsorbent followed by spectroscopic or chromatographic quantification of the extract. Reports in the literature suggest that extraction using supercritical fluids may produce recoveries that are superior to those obtained via "conventional" extraction techniques. We have compared the extraction efficiency for PAHs adsorbed on a very carbonaceous coal stack ash

subfraction, and find that the use of supercritical fluid extraction does not increase the recoveries of adsorbed PAHs. However, supercritical fluid extraction, in conjunction with on-line gas chromatographic/mass spectrometric techniques, may offer a promising avenue for the detection and identification of small quantities of PAH transformation products. The identification of benz[a]anthracene-7,12-dione as a phototransformation product of benz[a]anthracene adsorbed on a Texas lignite stack ash is reported.

(c) In this work, PAHs are deposited onto particulate matter from the gas phase (in order to mimic, under laboratory conditions, the adsorption phenomena that take place in the atmosphere). Techniques for improving this process, and for measuring the quantity of PAH that adsorbs on a particular sample of particulate matter, have been developed.

II. PROJECT SUMMARY

A. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives, their release into the environment via fossil fuel combustion, and their potentially adverse health effects are subjects of considerable concern. As they enter the atmosphere, semivolatile organic compounds, including PAHs, that are released by combustion processes undergo cooling. As cooling takes place, the compounds may condense onto the surfaces of ambient particles. While "smaller" PAHs (3- and 4-ring compounds) may exist at equilibrium in the atmosphere both as adsorbates on particulate surfaces and in the gas phase, "larger" PAHs (≥ 5 rings) are thought to occur in the atmosphere predominantly as adsorbates on particulate surfaces.

After a PAH is released into the atmosphere, it may be converted chemically to other species. Under many conditions, PAHs undergo photochemical oxidation, producing a variety of oxygen-containing PAH derivatives (e.g., diones, phenols, hydroxyquinones) as products. There is ample evidence (summarized below) that the chemical stability of a particle-bound PAH may be strongly dependent on the physical and chemical properties of the particulate surface on which it is sorbed.

The focus of the research carried out in this project is the interaction of PAHs with particulate surfaces, and the influence of such surfaces on the chemical transformations of adsorbed PAHs. The environmental particulate matter chosen for detailed examination was coal fly ash. Coal ash offers three significant attributes as a "model" adsorbent for such studies. First, in geographical regions in which coal-fired electric generating stations are numerous, coal fly ash is expected to constitute a significant fraction of ambient atmospheric particulate matter. Second, the chemical composition and physical properties of coal fly ash are dependent on the combustion conditions and composition of the feed coal; coal ashes from different power plants exhibit widely varying properties. Hence, the use of coal ash as an adsorbent offers the opportunity to study the effect of particle

composition on the chemistry of adsorbed PAHs. Finally, coal fly ash is a stable material that is relatively easy to study under controlled, but environmentally realistic, conditions in a laboratory setting.

In our studies, PAHs are deposited, in known quantity, from the vapor phase onto coal ash (or other particulate solids) so as to mimic, under laboratory conditions, the process whereby PAHs generated in the vapor phase by combustion sources subsequently deposit onto atmospheric particulate matter.

Previous investigations in this and other laboratories [1-9] have shown that coal ash surfaces tend to stabilize PAHs to photodecomposition. Those coal ashes highest in carbon and/or iron content usually are most effective in stabilizing PAHs to phototransformation. These observations imply that PAHs present in the atmosphere as adsorbates on particulate surfaces have significantly greater residence times than had previously been assumed.

Progress during the full project period (July 1, 1987-December 31, 1989) is summarized below.

B. FRACTIONATION OF COAL ASHES

Most coal ashes are extremely heterogeneous, comprising a wide variety of different particle shapes, sizes and compositions. By means of differences in particle size distribution, magnetism, and particle density, it is possible to separate most coal ashes into four distinct types of particles: carbonaceous, magnetic, light mineral (non-magnetic), and heavy mineral (non-magnetic). By carrying out such fractionation procedures, and examining the interactions of PAHs with each of the individual subfractions, it is possible directly to elucidate the relative affinities of PAHs (or other adsorbates) for the different particle types that comprise coal ashes. It is also possible to establish the influence of each particle type on the chemical behavior of adsorbed PAHs.

We have carried out such a separation for two ashes, derived from Kaneb (KA)

coal and Texas (TX) lignite. KA ash has a relatively high carbon content (5.5% C for the unfractionated ash); many PAHs adsorbed on this ash fail to undergo measurable photochemical transformation, even under prolonged illumination. In contrast, TX ash is relatively low in carbon (0.64%) and PAHs adsorbed on it undergo photodecomposition. We have examined the photochemical decomposition of pyrene adsorbed on the four major subfractions of both ashes, and have measured the heats of adsorption of pyrene on the subfractions by gas-solid chromatography.

These results have been published [10]; a copy of this paper is included as Appendix I to this report. The major conclusions of this study are listed below.

(1) Pyrene adsorbed on graphitic carbon, or particles high in carbon content, is extremely resistant to photochemical transformation. Pyrene has a much greater affinity for carbonaceous particles than for the other constituent phases of coal ash. Hence, for coal ashes relatively high in carbon, pyrene preferentially adsorbs on the carbonaceous particles, and is very resistant to photodecomposition. The presence of even a small quantity of carbon in stack ash leads to stabilization of adsorbed pyrene, when compared with data for adsorbents that do not contain carbon. Note, however, that the largest ash particles tend to contain the highest concentrations of carbon, but it is the smaller (respirable) ash particles that are most likely to escape stack collection devices and be released into the atmosphere.

(2) For ashes that are very low in carbon but contain both magnetic and non-magnetic mineral particles, pyrene preferentially adsorbs on the non-magnetic particles. Pyrene adsorbed on non-magnetic mineral particles is relatively susceptible to photodegradation. Hence, pyrene adsorbed on a coal ash that is low both in carbon and magnetic mineral phases will exhibit relatively efficient photodegradation.

(3) The magnetic subfraction of coal ash is the weakest adsorbent for pyrene. However, pyrene adsorbed on magnetic particles is very resistant to phototransformation. Hence, for ashes that are low in carbon but high in iron content, the

magnetic subfraction may play a minor role in stabilizing adsorbed pyrene toward photodegradation.

(4) Particles that exhibit very low affinity for pyrene but are dark in color (such as the magnetic fractions of some ashes) may act to suppress the photodegradation of pyrene adsorbed on nonmagnetic mineral particles, via the "inner-filter effect" (shielding pyrene molecules adsorbed on the nonmagnetic phases from the incident light).

The coal fly ash fractionation scheme described in Appendix I [10] is useful for many coal ashes. For some ashes, however, the chemical composition of the particles is a much more complex function of particle size and density, and, with careful effort, a considerably greater variety of fractions can be prepared.

For example, we have carried out a fractionation of a coal stack ash that is unusually high in carbon content (22.5% by weight in the unfractionated ash). The results of this study are in press in Environmental Toxicology and Chemistry [11]; a copy of this manuscript is included as Appendix II to this report. In this ash, the demarcation between "magnetic" and "nonmagnetic" mineral particles is not well-defined; a variety of subfractions having different magnetic properties can be isolated.

The photochemical reactivity of pyrene adsorbed on subfractions of this ash very clearly demonstrates the importance of the carbon content of the adsorbent. For all subfractions having bulk carbon percentages $\geq 4\%$ and specific surface areas $\geq 2.85 \text{ m}^2/\text{g}$, minimal phototransformation ($\leq 6\%$) of adsorbed pyrene is detected upon 24-hr illumination. However, for subfractions containing lower weight percentages of carbon (ranging from 0.47-0.69 %C) and having smaller specific surface areas ($0.50\text{-}0.68 \text{ m}^2/\text{g}$), the photochemical behavior of adsorbed pyrene is dramatically different, with extensive photodecomposition (35-45 %) of adsorbed pyrene being observed for 24-hr illumination. For subfractions of this ash, the only parameters that exhibit correlations with the photoreactivity of pyrene are carbon content and

specific surface area. The iron content of the fractions (which has tended to correlate with low photoreactivity of adsorbed PAHs in previous studies) appears in this case to be irrelevant. Additional details and a complete compilation of the data are presented in Appendix II.

C. QUANTIFICATION OF VAPOR DEPOSITION

Our original apparatus for depositing PAHs from the vapor phase onto adsorbents [12] provided no means for accurately measuring the quantity of PAH vapor deposited per unit weight of adsorbent. This deficiency has been remedied by incorporation of a gas chromatographic flame-ionization detector in the PAH vapor stream. The apparatus, and techniques for its use, have been published [13]; a reprint is attached as Appendix III to this report.

Many studies of the chemistry of adsorbed PAHs performed in other laboratories have employed "solution deposition", rather than "vapor deposition", of the PAH on the adsorbent [4,5,14-16]. In "solution deposition", the adsorbent is contacted with a liquid solution of the PAH in an organic solvent. For some time, we have been concerned with the influence of such solvents on the adsorptive properties of coal ashes, and the possibility that results of phototransformation studies involving "solution-deposited" PAHs may not be directly comparable with those obtained by vapor deposition. Indeed, preliminary studies have shown that pyrene adsorbed from solution onto coal ashes tends to be more photoreactive than pyrene deposited from the vapor phase [17]. In this context, Table III in Appendix III, comparing the solvent-extraction recoveries of vapor- and solution-deposited pyrene from various coal ashes and other adsorbents, is interesting. Extraction recoveries for pyrene from some adsorbents (including graphite and two coal ashes that are relatively high in carbon) are much lower for vapor-deposited than for solution-deposited pyrene. The opposite is true for pyrene adsorbed on silica gel and on one coal ash that is relatively low in carbon.

Interpretation of these results, and their relevance (if any) to the chemical stability of adsorbed PAHs, requires further study. However, the results have an important implication for the chemical analysis of adsorbed PAHs on atmospheric particles. It may be quite inaccurate to use standards, prepared by deposition from solution, to infer the extraction recovery of a PAH from sampled atmospheric particles (in which the PAH was deposited from the vapor phase).

D. EXTRACTION OF PAHs FROM COAL FLY ASH

Ideally, it would be possible to quantify the amount of each PAH adsorbed on a particulate surface, and to identify PAH phototransformation products, by "in situ" analytical determinations directly on the adsorbent surface (i.e., without extraction). Unfortunately, all efforts to accomplish this objective for PAHs adsorbed on coal ash surfaces (both in this and other laboratories) have, to date, been unsuccessful. At present, for analyses of the quantity of PAH present on an adsorbent, and identification of chemical transformation products of PAHs, it is necessary that the compounds in question be removed from the ash by extraction, followed by analysis of the resulting solution by spectroscopic or chromatographic means. It has long been known that such extractions may produce adsorbate recoveries substantially smaller than 100 %, particularly for adsorbents that are relatively high in bulk carbon content and/or PAH adsorbates containing 5 or more rings). [18,19]. Achieving improved extraction recoveries is accordingly a matter of high priority, both in the chemical analysis of particle-bound PAHs and in environmentally-oriented studies such as ours.

It has recently been reported that extraction using supercritical fluids may produce significantly higher recoveries (than conventional liquid-phase extractions) of PAHs adsorbed on a wide variety of particulate solids, including coal ashes [20-22]. We therefore have conducted a thorough comparison of liquid and supercritical fluid extraction techniques for pyrene adsorbed on a very demanding, high-carbon,

adsorbent--a high-carbon ash subfraction (ash subfraction "HC3" described in Appendix II), the bulk carbon content of which is 66.4 %. The results of this study show that supercritical fluid extraction produces equal (but not higher) recoveries of pyrene to those obtained by "conventional" liquid extraction techniques. Thus, at least for this sample (and, by inference, for high-carbon adsorbents in general), supercritical fluid extraction offers no "recovery" advantage over more conventional (and more rapid and inexpensive) extraction techniques. These results have been submitted for publication to Talanta; cf. Appendix IV for a copy of the manuscript.

Irrespective of its capability (or lack thereof) to produce enhanced recoveries of adsorbed PAHs, supercritical fluid extraction may play a key role in the identification of transformation products of PAHs; see Section E immediately following for more detail.

E. IDENTIFICATION OF PRODUCTS PRODUCED BY PHOTOTRANSFORMATION OF ADSORBED PAHs

Identification and quantification of chemical transformation products of PAHs adsorbed on coal fly ash is very difficult, for several reasons. First, the quantities of such products formed may be extremely small (≤ 1 ng). The quantity of parent PAH initially present may be very small and, as noted above, many PAHs are stabilized with respect to chemical transformation by adsorption on coal ash (thus, the percentage conversion of PAH to products may be very small). Second, some PAH transformation products may be less stable than the PAH precursor; this is a particular problem in photochemical studies, in which the initial PAH photoproduct may undergo rapid photodegradation to secondary products. Finally, analytical procedures that rely on extraction of PAHs from the adsorbent surface (Section D) may cause difficulty, either because the product of interest cannot be extracted efficiently from the ash or because the product(s) undergo additional chemical transformation at the elevated temperatures used in most extraction systems.

One important advantage of supercritical fluid extraction is that it offers a

possibility for efficient introduction of the extract as a "plug" onto the head of a gas chromatography (GC) column [23]. Gas chromatography/mass spectrometry (GC/MS) can then be used in an attempt to identify and quantify PAH transformation products. The "preconcentration" achieved by inserting the supercritical fluid onto the GC column is not readily achieved by analytical procedures that involve use of conventional liquid extractants. Hence, supercritical fluid extraction, combined with GC/MS, may play an important role in the identification of PAH transformation products.

An example system that has been examined in this laboratory is the phototransformation of benz[a]anthracene (BaA) adsorbed on a nonmagnetic mineral fraction derived from a Texas lignite stack ash. Using supercritical fluid extraction, followed by GC/MS, it has been shown unambiguously that benz[a]anthracene-7,12-dione is a significant phototransformation product of BaA. Because the BaA dione product is less photosensitive than the parent compound, it can be detected even when the percentage conversion of adsorbed BaA to the dione is relatively small. These preliminary results imply that this procedure for PAH transformation products may have broad utility.

As noted above, the need for solvent (or supercritical fluid) extraction of adsorbed PAHs or their transformation products would be obviated if the adsorbed organic compounds could be detected and quantified in the adsorbed state. We have attempted the use of several optical spectroscopic techniques for this purpose in the past, without appreciable success. During this project period, we examined the potential utility of secondary ion mass spectrometry (SIMS), using concentrated sulfuric acid as the matrix, for this purpose. SIMS, performed under these conditions, is capable of detecting certain polar organic compounds adsorbed on particulate solids [24]. However, a study of the utility of this technique for detection of PAHs adsorbed on coal ash failed to demonstrate sufficient sensitivity for the technique to be of practical value. At present, therefore, there is still

no alternative to extraction of adsorbed PAHs and photoproducts prior to identification or quantification.

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