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FORMATION AND TRANSFORMATION OF POLYCYCLIC
ORGANIC MATTER FROM COAL COMBUSTION

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BACKGROUND AND SUMMARY OF RESEARCH ACCOMPLISHMENTS

Our original proposal addressed three distinct areas of research to be investigated over a two year period. These were:

1. Formation of POM during carbonaceous fuel combustion
2. Vapor-to-particle conversion of POM
3. Photochemical transformation of particulate POM.

Due to a reduced performance period and level of funding it was decided to emphasize research in areas 2 and 3 above. This course of action has resulted in some 13 publications and some 15 lectures or symposia talks describing our findings. These findings are summarized quite briefly here and further detail is presented in papers already in the literature or in press (8,9).

A. Vapor-Particle Conversion of POM

1. Theoretical Model

The present theoretical treatment is designed to consider the deposition of vapor-phase species (PAHs) onto the surface of particulate material (fly ash) as the two move down a nonuniform temperature gradient (in the stack system). Consideration of the vapor pressure curves of several common PAHs (10) shows that at no stage will the vapor pressures likely to be encountered in emissions from fossil-fueled power plants exceed the saturation vapor pressure. Thus, the process of condensation will not take place. This treatment, therefore, deals specifically with adsorption of PAH onto fly ash as a function of temperature.

The basic assumption is that a given PAH, $P_a$, present in the vapor phase, can adsorb onto the surface, $S$, of particulate material to provide an adsorbed entity, $P_{ads}$, and that the reverse process of desorption can also take place. Thus
where \( k_1 \) and \( k_{-1} \) are the rate constants for adsorption and desorption, respectively. If one assumes, a priori, that \( k_1 \) and \( k_{-1} \) in equation (1) represent first-order processes, then the rate of adsorption of \( P \) can be written

\[
\frac{d[P\cdot S]}{dt} = k_1[P](1-\theta)A - k_{-1}[P\cdot S] .
\]  

In equation (2), \( \theta \) is the fraction of the total available adsorption sites which are occupied and \( A \) is the surface area of the particulate material.

The rate constant for desorption, \( k_{-1} \), is given by

\[
k_{-1} = \frac{kT}{h} \exp \left[ -\frac{E_d}{RT} \right]
\]

where \( E_d \) is the activation energy for desorption, \( T \) is the absolute temperature, and \( k \), \( h \) and \( R \) are Boltzmann's constant, Planck's constant, and the universal gas constant, respectively. The rate constant for adsorption, \( k_1 \), is

\[
k_1 = c \left[ \frac{RT}{2\pi M_a} \right]^{1/2} \exp \left[ -\frac{E_a}{RT} \right]
\]

where \( c \) is the so-called "sticking coefficient" (the probability that the orientation of a molecule with the spherical particle surface will result in adsorption), \( M_a \) is the molecular weight of the adsorbate species, and \( E_a \) is the activation energy for adsorption. A number of assumptions are inherent in equations (3) and (4). These are presented briefly in reference (8) and discussed in detail in a forthcoming publication (11).

In order to evaluate the rate and extent of adsorption as a function of temperature it is convenient to compute the mole fraction, \( X \), of total POM adsorbed and the time taken to achieve one half of the equilibrium
adsorption at a given temperature, $t_\frac{1}{2}$. The equations giving these quantities are: (8,11).

$$1/X = 1 + \frac{(2\pi M_a k)^{\frac{1}{2}}}{6cw_p h} \cdot \frac{d_m^3 \rho T^{\frac{1}{2}} \exp (E_a - E_d)/RT}{d_m^2} \cdot \frac{1-e^{-N_0 t_\frac{1}{2}}}{1-e^{-N_0 t}}$$

(5)

and

$$t_\frac{1}{2} = \frac{-1}{k_1 \gamma + k_2} \ln \frac{(2-X)k_1 \gamma - Xk_2}{2k_1 \gamma}$$

(6)

where

$$\gamma = (1-\theta) \pi \left[ \frac{d_m^3}{d_s^2} \right]^2$$

and $N_0 = 6.02 \times 10^{23}$.

The quantities $\rho$ and $w_p$ are, respectively, the density and mass per unit volume of the adsorbing particles and $d_m$ and $d_s$ are the mass and surface median diameters, respectively, of the particle size distribution. In the case of a log Gaussian distribution of particle sizes $d_m$ and $d_s$ are related by

$$\ln d_s = \ln d_m - \ln^2 \sigma$$

(7)

where $\sigma$ is the geometric standard deviation of the distribution (16).

The evaluation of equations (5) and (6) requires that realistic values be chosen for the quantities $c$, $M_a$, $w_p$, $\rho$, $d_m^2/d_s^2$, $E_a$, $E_d$, and $0$. In fact, the fractional surface coverage, $e$, is almost certainly dependent on both temperature and the values of $E_a$ and $E_d$; however, it is reasonable to assume that the adsorption process is zeroth order in $e$ so that a constant value can be chosen. Using available literature values for the above parameters (given in figure captions) one can construct the temperature dependent plots of $X$ and $t_\frac{1}{2}$ presented in Figures 1 and 2.

Consideration of the data presented in Figure 1 shows that, over a wide range of conditions, POM present at combustion source temperatures
Figure 1. Dependence of Mole Fraction of PAH Adsorbed on Temperature

Reference values: $c = 1; m_a = 3.360 \ (10^{-22}) \ g/molecule; w_p = 10^6 \ \mu g/m^3 = 10^{-6} \ g/cm^3; p = 3 \ g/cm^3; d_m^3/d_s^2 = 10^{-4} \ cm; E_a = -10 \ kcal/mole; E_d = -30 \ kcal/mole; \theta = \frac{1}{4}$.

(a) Variation of mole fraction of PAH adsorbed as a function of temperature and $C = 0.001, 0.01, 0.1, 1.0$.

(b) Variation of mole fraction of PAH adsorbed as a function of temperature and $d_m^3/d_s^2 = 0.1, 1.0, 10.0 \ \mu m$.

(c) Variation of mole fraction of PAH adsorbed as a function of temperature and $w_p = 10^2, 10^4, 10^6, 10^8 \ \mu g/m$.

(d) Variation of mole fraction of PAH adsorbed as a function of temperature and $E_a - E_d = -15, -20, -25 \ kcal/mole; E_a = -10 \ kcal/mole.$
Figure 1
Figure 2. Dependence of Half-time for Adsorption on Temperature

Reference values: $c = 1; \, m_a = 3.360 \times 10^{-22}$ g/molec; $w_p = 10^6 \mu g/m^3 = 10^{-6}$ g/cm$^3$; $\rho = 3$ g/cm$^3$; $d_m^3/d_s^2 = 10^{-4}$ cm; $E_a = -10$ kcal/mole; $E_d = -30$ kcal/mole; $a = \frac{1}{4}$.

(a) Dependence of half-time for adsorption on temperature and $C = 0.001, 0.01, 0.1, 1.0$.

(b) Dependence of half-time for adsorption on temperature and $d_m^3/d_s^2 = 0.1, 1.0, 10.0$ um.

(c) Dependence of half-time for adsorption on temperature and $w_p = 10^2, 10^4, 10^6, 10^8$, ug/m$^3$.

(d) Dependence of half-time for adsorption on temperature and $E_d = -25, -30, -35$ kcal/mole.
Figure 2
 (>150°C) is predicted to occur mainly in the vapor phase, whereas at the ambient temperatures encountered following emission (<40°C) essentially quantitative adsorption is predicted. Variations from this general behavior are, however, predicted for individual compounds and widely different particle size distributions and mass loadings.

The temperature dependencies shown in Figure 1 are generated with the assumption that adsorption equilibrium is achieved at all temperatures. This requires that the rate of attainment of equilibrium is fast compared with the rate of change of temperature experienced by a given vapor-particle combination. The rate of attainment of equilibrium is indicated in terms of the half-time for reaction in Figure 2. These data show that reaction times depend primarily on the activation energies $E_a$, $E_d$ in equations (3) and (4) and that achievement of sub-second reaction times at both in-stack and ambient temperatures requires activation energy values to be at the lower end of the range investigated. Indeed, reduction of the activation energy for adsorption by only a few kcals results in achievement of equilibrium within a few seconds even at ambient temperatures.

While the foregoing brief discussion is far from rigorous or conclusive, it does validate the possibility of vapor-to-particle conversion of POM occurring via an adsorption mechanism. Further, it points out the very strong temperature dependence of such a process.

2. Field Measurements

In order to investigate the occurrence of vapor-to-particle conversion occurring in a combustion source, measurements were made in the stack system and in the emitted plume of a small coal fired power plant. This plant was specially chosen because it was of obsolete design utilizing a chain grate stoker known to produce high POM emissions (12); it possessed no particle control equipment, thereby facilitating collection of large amounts of
particulate material; and it had a relatively short stack such that sample
collection from the emitted plume was possible.

Fly ash samples were collected during the same time periods both inside
the stack (temp. \(\sim 290°C\)) and from the emitted plume (temp. \(\sim 5°C\)) using both
cascade impaction and total collection on glass fiber filters. Collected
material was extracted with benzene and analyzed for POM using GC, GC-MS,
and fluorimetry. All necessary analytical precautions were taken and it was
established that material collected from the plume was derived exclusively
from the power plant.

The results of these analyses are presented in Tables 1 and 2 which
list the individual compounds uniquely identified and provide a quantitative
measure of the specific concentrations (\(\mu g/g\)) of several compounds associated
with fly ash at the two sampling points. Preliminary identification was
established using GC retention time data and in many cases was confirmed
using either a single-ion mass chromatogram or a mass spectrum from a GC
peak. Only crude vapor traps were employed during sample collection so no
quantitative measure of vapor phase POM was obtained. Fluorescence measure-
ment of condensation trap residues did, however, indicate that a considerable
quantity of POM was present from in-stack sampling but none was in residues
from plume sampling.

These results establish quite firmly that, in this power plant, consider-
sably more POM is associated with fly ash collected from the plume at
a temperature of 5°C than with that collected from the same stream at a
temperature of 290°C. This behavior is in exact accord with that predicted
in Figure 1. Furthermore, since the two collection points were only \(\sim 100\) ft
apart, quite rapid vapor-to-particle conversion is indicated. Unfortunately
while the full range of aerodynamic equivalent particle sizes accessible to
Anderson Stack and Hi Vol samplers was collected, this only represented a
small range of specific surface area due to the considerable particle
irregularity encountered. Nevertheless correspondence between specific
concentration of POM and specific surface area of fly ash fractions was
noted. This further suggests the operation of a surface adsorption mechanism.

3. Laboratory Simulation

In an attempt to obtain direct measurements of the rate and extent of
POM adsorption and to evaluate the quantities $c, E_a, E_d$ in equations (3)
and (4), a series of laboratory simulation experiments were set up. Fresh
coal fly ash which had previously been shown to contain no detectable POM
was presented in an expanded bed through which a stream of air containing
pyrene vapor (13) was passed. The objective was to expose all particles to
the same constant concentration of pyrene for different times and to deter-
mine the specific concentrations of pyrene as a function of time at differ-
ent temperatures.

The experiments showed that the uptake of pyrene was so rapid that a
uniform vapor phase concentration could not be achieved. The amount of pyrene
required to saturate the fly ash was, however, shown to increase significantly
with decreasing temperature. Furthermore, attempts to remove adsorbed pyrene
by heating in a stream of clean air were unsuccessful (14).

While these experiments were essentially qualitative, they do establish
the facts that coal fly ash will strongly adsorb pyrene (and probably other
POM) and that the saturation capacity is a strong inverse function of tem-
perature.

Overall, therefore, the results of these three studies point strongly
towards the idea that POM, formed initially as vapor, is adsorbed onto co-
entrained particulate material as the temperature falls. There is some
doubt about the rate at which this process takes place but the evidence is
in favor of rapid (on the order of seconds) adsorption, even at ambient
temperatures, under most conditions encountered in or near combustion sources.
B. Oxidative Transformation of POM

Information about the fate of particulate polynuclear aromatic hydrocarbon's (PAH) released to the atmosphere is presently fragmentary and unclear, however, it is widely accepted that POM present in atmospheric aerosols is highly susceptible to photochemical transformation in the presence of sunlight. Certainly, there is ample evidence that most PAH's will undergo photo-oxidation in solution, as the pure solid, and when adsorbed onto certain solid substrates such as alumina (1) and it has been inferred that similar processes take place when the compounds are adsorbed on airborne particulates (1,15,16). Indeed, it has been suggested that the half-lives of such PAH's in the presence of sunlight may be "only hours or days" (1).

Contrary to this expectation, we now report that the rate and extent of photodecomposition of PAH's may be decreased substantially by adsorption onto coal fly ash particles. Certain PAH's are, however, found to undergo rapid oxidation in the dark when adsorbed onto fly ash.

Studies were conducted using a model system in which individual PAH's were adsorbed onto the surface of fly ash collected from the electrostatic precipitators of several coal fired power plants. Known gas phase concentrations of individual PAH's were generated using a simple diffusion cell (13,14) and passed through an expanded bed (4,17) of fly ash. Regulation of the bed temperature and the time of exposure provided a means of controlling the amount of a PAH adsorbed. All fly ash samples were size fractionated by sieving the 44-74 μm physical size range utilized. Exhaustive pre-extraction with several solvents (cyclohexane, benzene, methanol) showed that none of the fly ashes employed contained more than 50 ng/g of total PAH.

Sample irradiation was achieved using outdoor sunlight and several artificial light sources (150W Xenon arc lamp, 275W commercial sunlamp,
5-OT3/C1 General Electric "quartz line" lamps; all unfiltered). The fly ash was tumbled in a quartz container to provide equal exposure of all surfaces and radiant fluxes were estimated to be equal to or greater than that of midday summer sunlight (45°N lat.) over the wavelength range 300 to 800 nm. Portions of each fly ash sample were exhaustively extracted directly following exposure to gaseous PAH and then after irradiation or dark storage. Analyses for the original PAH and for degradation products were performed by high performance liquid chromatography (UV absorbance detection) and by UV absorption and fluorescence spectrometry. The extent of decomposition was determined both from the disappearance of the original PAH and from the appearance of its reaction products. (Reproducibility of multiple analyses was established to be ±8% RSD.) Individual experiments were conducted to determine the influence of PAH type and concentration, irradiation time, intensity, and wavelength distribution, dark stability, and the nature of the adsorbing substrate on the rate and extent of PAH decomposition.

Rather unexpectedly none of the PAH's which were irradiated following adsorption onto fly ash exhibited appreciable photodegradation (Table 1, Class I). Such degradation as did occur took place very rapidly and did not proceed thereafter with time up to 100 hours (Figure 3A). Furthermore, no significant dependence on irradiation intensity nor amount of PAH adsorbed was observed. Under similar illumination conditions, however, extensive photodecomposition was observed for all PAH's irradiated in solution (Figure 3A) and for both anthracene and benzo[a]pyrene adsorbed onto alumina from methanolic solution. Additional evidence for the apparent influence of adsorbent substrate on photodecomposition was obtained by adsorbing anthracene and benzo[a]pyrene vapors onto both fly ash and alumina which were then coated on thin layer chromatographic plates and
### Table 1
Decomposition of Polycyclic Aromatic Hydrocarbons Absorbed on Coal Fly Ash

#### Class I  Irradiated PAH

<table>
<thead>
<tr>
<th>Compound</th>
<th>Irradiation Time (hrs.)</th>
<th>Conc. PAH adsorbed (µg/g)</th>
<th>No. of Samples</th>
<th>Average Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrene</td>
<td>5-126</td>
<td>67-291</td>
<td>19</td>
<td>-6.3(±14.7)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>2-113</td>
<td>129-186</td>
<td>5</td>
<td>+10. (±12.3)</td>
</tr>
<tr>
<td>Fluorantheine</td>
<td>2.5-18</td>
<td>49,115</td>
<td>2</td>
<td>-7.2(±2.0)</td>
</tr>
<tr>
<td>Anthracene</td>
<td>3-24</td>
<td>300</td>
<td>3</td>
<td>-11.0(±7.0)</td>
</tr>
<tr>
<td>Benzo[a]pyrene*</td>
<td>2.5-36.5</td>
<td>44-110</td>
<td>5</td>
<td>-8. (±8.)</td>
</tr>
<tr>
<td>Benzo[a]pyrene**</td>
<td>21-100</td>
<td>15-44</td>
<td>4</td>
<td>-14. (±7.)</td>
</tr>
</tbody>
</table>

*quartzline lamp
**xenon arc lamp

#### Class II  Non-irradiated PAH

<table>
<thead>
<tr>
<th>Compound</th>
<th>Change</th>
<th>Compound</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acenaphtene</td>
<td>None</td>
<td>Fluorene</td>
<td>Decomposed</td>
</tr>
<tr>
<td>7,12 Dimethylbenz[a]anthracene</td>
<td>None</td>
<td>Benzo[b]fluorene</td>
<td>Decomposed</td>
</tr>
<tr>
<td>Carbazole</td>
<td>None</td>
<td>Benzo[a]fluorene</td>
<td>Decomposed</td>
</tr>
<tr>
<td>Acridine</td>
<td>None</td>
<td>9,10 Dimethylnaphthalene</td>
<td>Decomposed</td>
</tr>
<tr>
<td>Phenazine</td>
<td>None</td>
<td>9,10 Dihydroanthracene</td>
<td>Decomposed</td>
</tr>
<tr>
<td>Fluorantheine</td>
<td>None</td>
<td>4-Aza fluorene</td>
<td>Decomposed</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>None</td>
<td>Anthracene</td>
<td>Decomposed</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>None</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3. [A] Percent conversion of irradiated Benzo[a]pyrene compared to nonirradiated sample as a function of time adsorbed onto fly ash solution. [B] Percent conversion of fluorene adsorbed on coal fly ash as a function of time.
Figure 3

A

PERCENTAGE CHANGE

IRRADIATION TIME (HOURS)

B

% CONVERSION

TIME, HOURS

○ = DARK
○ = LIGHT
exposed to identical irradiation. In a typical experiment of this type benzo[a]pyrene present on the alumina surface underwent 50 per cent decomposition upon exposure for 80 minutes to an unfiltered 150W Xenon arc lamp. By contrast, only 15 per cent decomposition was observed for the benzo[a]pyrene adsorbed on fly ash and irradiated under identical conditions.

While the extent of photodegradation of PAH's adsorbed on fly ash is apparently small, a number of the compounds studied (Table 1, Class II) were found to undergo quite extensive oxidation in the absence of light. In particular, different fly ashes were found to give different oxidation rates. In all cases, however, the major oxidation product was the same ketone or quinone as obtained from the photo-oxidation process. As illustrated in Figure 3B for fluorene, which oxidizes to 9-fluorenone, considerable conversion occurs during the actual PAH adsorption step but subsequent irradiation has no effect upon the rate or extent of further reaction. The extent of initial reaction, which occurs at the elevated adsorption temperature, varies from 7 to 90 percent decomposition depending on the type of fly ash used as the adsorbent substrate and was shown not to be due simply to passage of a PAH through the adsorption apparatus. It is apparent, therefore, that the nature of the adsorbent is an important factor in determining the rate of this dark reaction. This observation is borne out by the findings that non-photochemical conversion does not occur for solid fluorene, for fluorene dissolved in methanol or cyclohexane, nor for fluorene adsorbed onto alumina, silica gel, Linde 13X molecular sieve, glass and Ambersorb XE-340 adsorbent resin. However, fluorene adsorbed onto activated carbon and graphite was observed to decompose in a similar manner to that adsorbed on coal fly ash.
Finally, it is noteworthy that all of the compounds which undergo spontaneous oxidation as a result of adsorption onto coal fly ash (Table 1, Class II) contain a benzylic carbon atom indicating that this structure is especially susceptible to non-photochemical oxidative attack. Possible exceptions to this rule are afforded by anthracene and benzo[a]pyrene which exhibit very slow non-photochemical oxidation when adsorbed onto fly ash.

It is apparent from the foregoing results that PAH adsorbed onto the surface of coal fly ash exhibits quite different chemical behavior from that adsorbed onto other solid substrates, or present either as the pure solid or in solution. The net result is stabilization of PAH against photochemical oxidation on the one hand, but promotion of spontaneous non-photochemical oxidation for a limited class of compounds on the other. The reasons for this behavior are not clear. It is conceivable that the limited photochemical decomposition is due either to efficient competitive absorbance of radiation by the fly ash matrix (18), or to the PAH being largely present in pores where light cannot penetrate. A more convincing suggestion, however, is that energetic adsorption, such as apparently occurs on fly ash, activated carbon and graphite surfaces, effectively stabilizes PAH's against photo-oxidation by molecular orbital rearrangement which either increases the electronic excitation energy or decreases the lifetime of the excited state (18). The small amount of rapid photo-oxidation which is observed (Table 1, Class I) could then be due to a fraction of the PAH which is not directly bonded to the active surface but rather to another PAH molecule or to a weakly adsorbing mineral impurity. The promotion of non-photochemical oxidation could, in turn, be due either to extensive molecular orbital rearrangement or simply to the ready availability of active oxygen on strongly adsorbing surfaces (19). Not unexpectedly the points of highest Bronsted acidity (e.g. position 9 in fluorene) are most susceptible to oxidative attack.
C. Ramifications of POM Transformation

The types of transformation discussed above, while far from definitive, do point out several important considerations which should be borne in mind in assessing the environmental/health impact and methodology for the measurement and control of POM. These may be categorized as follows:

1. Environmental Considerations

From the standpoint of the environmental and potential human health impact of POM two main points are important. The first is that adsorption of vapor phase POM onto particulate matter will result in the predominance of POM on small particles which provide the largest available surface area per unit mass. Thus, POM will be preferentially concentrated in particles whose aerodynamic size falls in the range which can remain airborne for several days and which is capable of being deposited in the pulmonary region of the human respiratory system when inhaled.(20,21). This prediction is in accord with the results of measurements of the atmospheric aerosol size distribution of POM (21).

Secondly, the findings concerning the demonstrated photochemical and nonphotochemical transformation of POM suggest three important environmental considerations. These are:

a. The adsorptive association of PAH's with coal fly ash stabilizes these compounds against photochemical degradation on the one hand, thereby preserving their potentially carcinogenic properties. On the other hand, however, a limited number of PAH's are quite rapidly converted to their corresponding ketones or quinones whose toxic and carcinogenic potential is largely unknown (22,23). In this regard it is noteworthy that fluorene is normally encountered at much higher levels in the atmosphere than is fluorene (24).
b. Based on the evidence presented herein, one would not expect to find diurnal variations in the concentration of PAH's present in plumes emitted from coal fired power plants. One would, however, expect to find significant differences between PAH transformation rates in plumes derived from different power plants due to the different surface characteristics of the fly ashes emitted.

c. If, in fact, all PAH's containing a benzylic carbon atom are susceptible to non-photochemical oxidation, as suggested herein, then the probable oxidative behavior of a large number of PAH's can be predicted (17,22). For example, one would expect several strongly carcinogenic compounds such as di-methyl benz[a]anthracene and 3-methyl chloranthene (3) to be rapidly oxidized and thus detoxified. Possible evidence for this prediction is afforded by the fact that neither of these compounds has been found in atmospheric particulate samples (1,24).

2. Sample Collection

If POM is capable of converting rapidly from vapor to particulate form then the relative amounts of each would be expected to vary with the position (i.e. temperature and particle surface density) in a combustion system. Consequently, measurements of separate vapor and particulate POM will apply only to a specific point in a specific plant operate under specific conditions and cannot be extended to other power plants in general. Furthermore, the predictions of Figures 1 and 2 suggest that considerable vapor-to-particle conversion may actually occur within the sampling device - especially when it is maintained at a temperature which is different from that of the stream being sampled. As a result measurements of the particle size distribution of POM and of the ratio of particulate to vapor phase POM will not represent true quantities but rather sampling artefacts.
Of more practical importance, however, is the very clear need to collect both vapor and particulate POM in order to establish total POM emission factors. Current methodology for sampling emission sources does employ vapor collection devices; however, some doubt has been expressed concerning their collection efficiency (25), and it seems likely that present POM emission estimates may be low where measurements are made at elevated temperatures. Certainly emission estimates based on analyses of particulate material alone, when it is collected from within an emission source, are likely to be grossly in error (26).

Finally, it will be noted that the non-photochemical oxidation observed for POM adsorbed on fly ash is unlikely to occur to the same degree in adsorbent vapor phase POM collectors. Consequently the compounds identified in vapor collection devices may differ considerably from those emitted from a source - certainly the relative concentrations may differ. In short, the material collected may differ qualitatively and quantitatively from that emitted.

Overall, therefore, it seems that the transformation processes discussed herein may result in extremely poor representation of emitted POM unless special sampling precautions are taken. Indeed, the only bona fide way of characterizing POM emissions would be to collect material directly from the emitted plume. Since this is unrealistic for routine measurements, it is recommended that emphasis be placed on the determination of total POM under conditions which promote particle association prior to sample collection. For this purpose it is suggested that the sampling train be operated at or below ambient temperatures (27).

3. Emission Control

The vapor-to-particle transformation behavior of POM has two important consequences in terms of emission control. First, the fraction of the
total POM which is in the vapor phase during passage through particle control devices will not be collected. Secondly, the effect of adsorption is to move the aerodynamic equivalent mass median diameter of the adsorbed species to a value which is significantly smaller than that of the substrate particle mass as described by equation (7). Just as this enhances the ability of POM to penetrate the human respiratory system so it will also increase the difficulty of controlling POM emissions since small particles in the range of interest (0.1 to 5.0 μm aerodynamic diameter) are collected with reduced efficiency by most particle control devices (28).

One positive point which can be made is that collection of POM vapor by scrubbers may be quite efficient insofar as the low temperatures encountered in liquid systems may promote adsorption and at least partial collection of vapor species.

It is apparent from the foregoing discussions that transformation of POM from vapor to particulate form and to different molecular forms can take place within a combustion source, during sampling, and following sample collection. Indeed a number of chemical transformation processes in addition to those discussed have been reported (1). It is also apparent that such transformations can profoundly influence the meaning and validity of POM measurements, the environmental impact of POM, and the applicable control technology.

Finally, it is important to recognize that the processes described herein, although presented in terms of a coal-fired power plant, will occur quite generally. They must, therefore, be taken into account when considering any combustion source.

D. Attainment of Objectives

The objectives of our original proposal were as follows:

1. Investigation of the characteristics of coal combustion which
influence the formation of polynuclear aromatic species.

2. Investigation of the mechanism(s) of conversion of polynuclear aromatic vapors to POM, i.e. particle association.

3. Investigation of the rate of photochemical decomposition of POM and of the nature of the major products.

As explained previously, investigation of POM formation processes was not pursued so attainment of objective #1 above was not attempted. On the other hand, it is readily apparent from the summary of results presented in this section that objectives #2 and #3 were not only attained but significantly exceeded. Indeed, it is considered that several of the findings of these studies have opened up important new areas of knowledge relating to the behavior of POM.
REFERENCES


