

ORGANIC COMPOUNDS IN EFFLUENTS RELATED TO COAL COMBUSTION

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ABSTRACT

Organic compounds in the various effluents from the efficient combustion of coal at power plants do not appear to be an environmental problem. This conclusion is based on interpretation of results obtained during a five-year study of samples of stack gas, sluice water, and fly, stack and grate ash from the combustion of coal alone and mixtures of coal and refuse derived fuel (RDF). Dioxins and furans were not present in these samples at the detection limit of 10 ppT. Alkanes, chlorinated benzenes, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), aliphatic acids and other miscellaneous compounds were found but the amounts were below those found in ambient urban air. These low levels of organic compounds are obtained only under steady state conditions of high combustion temperature, excess oxygen, small fuel particles and sufficient residence time. An added benefit of coal combustion was the removal, presumably by adsorption, of aromatic contaminants from the water used to sluice the fly and grate ash.

INTRODUCTION

The release of organic pollutants into the environment from the burning of coal has been of periodic concern ever since the industrial revolution in England. This concern has resurfaced recently due to the shift to coal as the major fuel for generating electricity in the U.S.A.

Because of this environmental concern, an extended study of the Ames power plant for generating electricity was begun in 1977. This study included all types of pollutants such as NO_x , SO_x , total suspended particles, fly ash, grate ash, and trace elements as well as the organic compounds from the combustion of coal alone and mixtures of coal and refuse derived fuel (RDF). The results in this report are confined to the organic compounds found in all of the solid, liquid and gaseous effluents related to the combustion processes.

At the start of this study in 1977, the analytical methodology was inadequate for the characterization of organic compounds in the various effluents. Thus, priority was given to: 1) identifying the analytical difficulties; 2) devising methods to resolve the most critical problems; and 3) using evolving methodologies to determine those components judged to pose a threat to the environment.

As an aid in establishing the analytical problems, published data were compiled and reviewed for coal combustion and waste incineration (1). Important conclusions drawn from this review were: 1) only a limited number of organic components had been identified in the effluents; 2) the identified components reflected analytical capabilities and interests rather than a true distribution; 3) reliable quantitative data were not available; and 4) the data base was insufficient for predicting the probable environmental effects associated with the combustion of coal.

A critical examination of the analytical procedures used prior to 1977 showed these to be inadequate for the determination of organic compounds in combustion effluents; of special concern were the short-comings in sample collection methods. These short-comings are delineated in a review published recently (2). Because of these sampling uncertainties, the continuous development and validation of new procedures and sampling systems was an essential element of this study.

Coincident with the development of sampling procedures were the constant iterative improvements in extraction, separation, identification and quantitation of organic compounds. Special emphasis was placed on selected compound classes such as the polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs),

chlorinated benzenes, and chlorinated dibenzo-p-dioxins (dioxins). The best available procedures were used to determine these components because they have known acute or chronic effects and previous studies suggested that they might be present in effluents from the combustion of coal alone and combination coal/RDF.

EXPERIMENTAL SECTION

SAMPLING PROCEDURES

Stack Vapor.-Vapor phase organic components present in the stack effluent were sampled by three different procedures. An EPA Method 5 train was equipped with an organic module and used during the early stages. This sampler allowed the stack gas to pass over the accumulated particles during the entire sampling period and thus gave rise to the possibilities of adsorption, sublimation and chemical transformations of organic components. When the equipment became available, the Method 5 train was supplanted by a Source Assessment Sampling System (SASS). This system allowed larger volumes of gas to be sampled and reduced the contact between accumulated particles and the stack gas. The complexity of the SASS made this system undesirable for use when the only goal was to obtain a sample of vapor phase components. A third sampling system was the Ames Vapor Sampling System (AVSS) described by Junk and Richard (3). This sampling system largely eliminated contact between vapor phase components and particles. The AVSS provided a simple and effective accumulation of organic components from very mild atmospheres such as ambient air and very severe atmospheres such as stack gas.

Stack Ash.-Samples of stack ash were obtained using the EPA Method 5 and the SASS. On occasion, large amounts of stack ash were collected conveniently by placing a custom-designed tray into the stack for 24 hours. This tray collected the particles that settled from the disturbed gas stream.

Fly Ash.-Fly ash samples were collected directly from the hoppers of the cyclone and electrostatic precipitator used for particle control.

Grate Ash.-Grate ash samples from stoker-fired units were collected from hoppers located below the grates. Grate ash from the tangentially-fired units was removed from the boilers by sluicing so samples were obtained by filtering the sluice water collected at the outlet of the pipe used to transport the sluiced ash to a settling pond. Additional ash samples were collected from the settling pond as sediment samples.

EXTRACTION PROCEDURES

Adsorbents.-A macroreticular resin, XAD-2, was used as the adsorbent in the AVSS, the SASS and the EPA Method 5 sampling train. Organic compounds accumulated on the resin were recovered by elution with methylene chloride. Diethyl ether was used as an eluent, instead of methylene chloride, when subsequent determinations were performed by gas chromatography with electron capture detection. Other eluents and desorption techniques were tested and found to offer no significant advantages (3).

Water Condensates.-When stack gas was cooled during sampling, water vapor condensed. The organic components in these condensates were extracted with methylene chloride. Diethylether, pentane and isooctane were used as alternative extraction solvents when subsequent gas chromatographic determinations required the use of electron capture detectors.

Ashes (Particles).-Because there were no standard and accepted procedures among the many described in the literature for the extraction of organic components from particles, several techniques were critically evaluated. Soxhlet extraction with benzene,

benzene-methanol, benzene saturated with hydrogen chloride, toluene, toluene-methanol, and methylene chloride were evaluated. Sonic extractions using a probe or a bath with a variety of solvents and pretreatment procedures using aqueous acids and water were also tested. No technique resulted in significant improvement in the extraction of the cross-section of different organic components associated with the various particle effluents. Consequently, the traditional Soxhlet extraction using benzene-methanol was used most frequently.

CLASS SEPARATIONS

Chromatographic and solvent partitioning procedures were used to separate organic components recovered from particles into chemical classes to facilitate their ultimate determinations in less complex mixtures. The procedure included the separation of PAHs on Sephadex (4) and the separation of components on the basis of polarity using alumina (5), silica gel (6), Florisil (7), the polystyrene-divinylbenzene resin XAD-4 (8), and the traditional solvent partitioning into acid, base and neutral fractions. Preparatory scale, normal-phase, high-performance liquid chromatography with amine and cyano columns was used to separate mixtures on the basis of polarity and to partially separate PAHs (9).

The Soxhlet extraction of particles with benzene-methanol yielded PAHs plus many non-polar and polar organic compounds which interfered with the gas chromatographic separations. The interfering compounds were removed using standard solvent partitioning with DMSO (10), DMF (11), or nitromethane (12).

COMPOUND SEPARATIONS

Gas chromatography was used for the separation of individual organic components. Columns packed with Dexsil 300 (Supelco Inc., Bellefonte, PA) provided the separation of the high boiling point PAHs during the early stages of this study. Later, as the column technology advanced rapidly, capillary columns coated with SE-52 and SE-54 (J&W Scientific, Rio Rancho, CA) were used almost exclusively. These columns were found to be applicable to the efficient separation of a diverse assortment of organic components in complex mixtures.

IDENTIFICATION AND QUANTITATION

Combination gas chromatography/mass spectrometry (GC/MS) was used for the identification of the organic components extracted from the various combustion effluents. Quantitation of organic components was normally obtained using external standards and gas chromatography. The quantitation by gas chromatography was periodically checked on randomly chosen samples using appropriate techniques of combination GC/MS.

CONFIRMATIONS AND VALIDATIONS

For positive identifications by GC/MS, the full mass spectrum of a tentatively identified component was compared to the mass spectrum of an authentic sample. If the spectra were identical, within experimental error, and if the gas chromatographic retention times of standard and unknown components on a 30-meter SE-54 fused silica capillary column agreed within two seconds, the identification was considered positive. When the amount of material present was insufficient for detection using full scan GC/MS techniques, the more sensitive single and multiple ion monitoring techniques were employed. Confirmation in these cases consisted of coincidences of retention times of mass chromatograms of the unknown and of the authentic sample. For chlorinated materials, the molecular ions contained additional information about the chlorine isotope distribution. Confirmation in those cases included the correct isotope ratios for the number of chlorines in the molecule.

Validation of the methodology used for components that could not be detected in extracts of particle samples was obtained by extraction of surrogate samples. The

surrogate sample for PAHs was soot generated from an air-starved methane flame. The positive results obtained from this soot sample have been reported elsewhere (13). The surrogate sample for dioxins was an incinerator ash obtained from Dow Chemical Company. Results obtained from analysis of extracts of this ash sample were $\pm 50\%$ of the published values for the tetra-, hexa-, hepta- and octachloro- isomers (14). This agreement substantiated the validity of the analytical protocol used to screen the effluent samples for dioxin compounds.

RESULTS AND DISCUSSIONS

IDENTIFIED COMPONENTS

A combined listing of all the compounds identified in extracts of the vapor and particles in the stack, fly and grate ash effluents from the combustion of coal at the Ames power plant are listed in Table I. Similar compounds have been observed for extracts from a second coal-fired power plant located at Iowa State University. Therefore, this list may be partially representative of coal combustion in semi-modern boilers. Certainly, many more organic compounds than the listed 78 are present in these effluents but so far these have not been positively identified. Indeed, a 1980 review of organic compounds from coal combustion (1) taken from all the literature reports had only 106 compounds identified.

Table I. List of Organic Compounds Present in Effluents From Coal Combustion

ALKANES - Methane, Decane, Undecane, Hexadecane, Heptadecane, Octadecane, Nonadecane, Eicosane, Heneicosane, Docosane, Tricosane, Pentacosane, Hexacosane, Octacosane, Triacontane, Dotriacontane, Trimethylcyclohexane, Dimethylcyclohexane
AROMATICS - Toluene, Xylene, Propylbenzene, Butylbenzene, Biphenyl, Terphenyl, Naphthalene, 1-Methylnaphthalene, 2-Methylnaphthalene, Methylindene, Acenaphthene
PAHs - Benz(a)pyrene, Anthracene, Fluoranthene, Fluorene, Pyrene
ACIDS - 2-Ethylbutanoic, Nonanoic, Decanoic, Dodecanoic, Tridecanoic, Tetradecanoic, Pentadecanoic, 9-Hexadecenoic, Hexadecanoic, Heptadecanoic, Octadecanoic, Benzoic
PHENOLS - Phenol, o-Cresol, Ethylphenol, Butylphenol, 2,4-Dichlorophenol, 2,4,6-Trichlorophenol
CL COMPOUNDS - Tetrachloroethylene, Tetrachloroethane, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 1,2,4-Trichlorobenzene, 1,2,3-Trichlorobenzene, 1,2,3,4-Tetrachlorobenzene, 1,2,3,5-Tetrachlorobenzene, Pentachlorobenzene, Hexachlorobenzene, 2,3,2',5'-Tetrachlorobiphenyl ^a , 2,5,3',4'-Tetrachlorobiphenyl, 2,4,5,2',5'-Pentachlorobiphenyl, 2,4,5,2',4',5',5'-Hexachlorobiphenyl
O, N, P, S COMPOUNDS - Acetophenone, Methylacetophenone, Phthalic Anhydride, Methylbenzoate, Indanone, Dibenzofuran, Diethylphthalate, Dibutylphthalate, Diisobutylphthalate, Di(2-ethylhexyl)phthalate, Diphenylamine
^a The characteristic Arochlor 1254 profile was observed but only four isomers were positively confirmed.

QUANTITATION

It was not possible to obtain exact quantitative values for all the identified components associated with each of the effluents from coal combustion. The amounts varied because of the analytical problems mentioned in the experimental section and different firing conditions. However, semi-quantitative values have been obtained for many of the components and these values are proposed to be reasonable estimates of the amounts of organic compounds expected from the efficient combustion of coal in a modern power plant. A discussion of some important compound classes and the amounts in the various effluents is given below. In general, the amounts are much lower than would be predicted from a review of the limited quantitative data available in the literature.

Polycyclic Aromatic Hydrocarbons (PAHs).—The most highly studied class of compounds in combustion effluents is the PAHs. However, very little information about the amounts present in the vapor phase and on particles in the effluents from the efficient combustion of coal is available. The data in Table II partially fills this informational gap. The amounts in the vapor phase varied according to the firing conditions and the stack temperature that was ~ 240°C. Even if all these PAHs were to condense on the particles, the amounts are well below the multiple µg/g quantities present on ambient air particles.

Table II. Summary of PAHs in Effluents From Coal-Fired Power Plants

Compound	Concentration Range (ng/g)		Conc. Range Vapor Phase (ng/M ³) ^D
	Respirable Particles	Non-Respirable Particles	
Naphthalene	ND ^a -18	0.5-23	10-1800
Phenanthrene			26-640
Anthracene			0.4-100
Fluoranthene	0.2-0.3	0.05-1.5	0.5-240
Pyrene	0.2-7	0.08-1.1	0.2-2850
Chrysene	ND	ND-4	0.1-28
Benz(a)pyrene	ND	ND	0.1-120
Benz(a)anthracene	ND	ND-0.3	NM ^C
Benz(ghi)perylene	NM	NM	3-22

^a ND = Not detected at the limit of 0.05 ng/g.

^b Includes values reported by Midwest Research Institute (15, 16).

^c NM = Not measured.

Alkanes and Aromatics.—The distinction between aromatic and polycyclic was arbitrarily set at three conjugated six-member rings in Table I. With this definition the alkane and aromatic hydrocarbons with 30 entries dominate the list of identified components. These compounds are also present in the highest concentration in the different effluents. Ordinarily their concentrations were not measured because of a low interest in these kinds of compounds but in those instances where measurements were made, the amounts ranged from 10-1500 ng/M³ in the vapor phase and from 10-90 ng/g on the suspended particles in the stack effluents. These hydrocarbons were not quantitated for any of the fly and grate ash samples.

Aliphatic Acids and Phenols.—Eleven aliphatic acids and six phenols were determined as constituents of the vapor phase and associated with particle effluents. These acidic compounds and the amounts are listed in Table III. A range of values from 20 different sampling runs is shown for the C9, C12, C14, C16 and C18 acids and phenol to illustrate the fluctuations that can occur in the amounts of organic acids in the effluents. The extent of the variation attributed to changes in firing conditions and analytical difficulties in the determinations is unknown and needs further study.

Polychlorinated Biphenyls (PCBs).—The PCBs were observed in the stack effluents during the combustion of coal but these compounds were not produced in the combustion process by a de novo synthesis or from precursor compounds. The source of the PCBs was the air used to support the combustion. This indoor air contained 0.13 µg/M³ of PCBs; the concentration of PCBs in the stack gas was only 0.02 µg/M³ when coal containing no detectable level of PCBs was burned. For perspective, this emission level should be compared to the average ambient air level of about 0.006 µg/M³.

When the coal fuel was supplemented with RDF containing 8500 µg of PCBs/Kg of RDF, the amount of PCBs in the stack remained at the low level of 0.02 µg/M³.

Table III. Summary of Acidic Compounds in Effluents From Coal-Fired Power Plants

Acid	Concentration Range ^a	
	Vapor	Particles
2-Ethylbutanoic	200	NM ^b
Nonanoic	20-250	NM
Decanoic	10	20
Dodecanoic	80-800	90
Tridecanoic	NM	10
Tetradecanoic	100-300	8-600
Pentadecanoic	90	50
9-Hexadecenoic	50	NM
Hexadecanoic	40-300	40-270
Heptadecanoic	NM	20
Octadecanoic	80	40-150
Phenol	20-200	25-1000
o-Cresol	NM	NM
Butylphenol	NM	NM
2,4-Dichlorophenol	NM	0.1
2,4,6-Trichlorophenol	NM	0.05
Pentachlorophenol	NM	0.2

^a ng/M³ for vapors and ng/g for particles. Where a range is listed, these selected components were measured in 26 extracts.

^b NM = Not measured.

Calculations based on fuel inputs, stack gas flow, support gas input and PCBs in all the inputs and effluents showed that 99% of the PCBs in the input RDF were destroyed in the combustion process. The details of this investigation of the co-combustion of coal and RDF containing PCBs have been published elsewhere (17).

The explanation of the high destruction efficiency for the PCBs in the RDF is efficient combustion based on a combination of high temperature (~ 2000°F), excess oxygen at 22%, and adequate residence time and sufficient turbulence for the small coal and RDF particles in the combustion zone. This same combination of combustion conditions is the probable explanation for the undetectable levels of TCDD discussed below.

2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD).-At the detection limit of ten parts per trillion, no TCDD was found in the effluents from the combustion of coal in three different boilers at the Ames power plant (see summary table in reference 16 for description of boilers). This observation was confirmed at a second smaller coal-fired power plant located at Iowa State University. Even when the coal fuel was supplemented with RDF, which should contain the precursor compounds, no dioxins were observed in the vapor and particle samples taken from the effluents. Thus no de novo synthesis occurred during the combustion of coal alone and if dioxins were formed from precursor compounds in the co-combustion of coal and RDF, they were destroyed in the efficient combustion as explained above for the thermal destruction of the PCBs present in the RDF. The PCBs are destroyed at 1200°F (18) and a similar temperature is expected for the dioxins. This is well below the 2000°F operation of the boilers used for this study (19).

Chlorinated Benzenes.-Ten chlorinated benzenes were targeted for analysis in the stack effluents. The analytical results when coal alone was combusted are shown in Table IV. When the coal fuel was supplemented with RDF up to 20%, no consistent increase in the amounts of the chlorinated benzenes occurred although barely

detectable amounts of the tetra-, penta- and hexa- isomers were observed during some of eleven different combustions of coal with 20% RDF. Based on these results it appears as if the dichlorobenzenes, reported to be present in the RDF at the 8000 ug/Kg level (15, 16), were thermally destroyed with high efficiency in much the same manner as that documented above for the PCBs present in the RDF.

Table IV. Chlorinated Benzenes in Stack Effluent From Coal-Fired Power Plants

Chlorobenzene Isomer	Concentrations ng/M ³
1,2-Dichloro-	0.5
1,3-Dichloro-	ND ^a
1,4-Dichloro-	80
1,2,3-Trichloro-	3.9
1,2,4-Trichloro-	1.2
1,2,3,4-Tetrachloro-	ND
1,2,3,5-Tetrachloro-	ND
1,2,4,5-Tetrachloro-	ND
Pentachloro-	ND
Hexachloro-	ND

^a ND = Not detected at limit of 0.03 ng/M³; average of three runs.

The environmental effects from the emission of these chlorinated benzenes are estimated to be insignificant because of the low levels and the further dilution by factors of 10³ to 10⁵ in the atmosphere before any human or plant exposure.

Sluice Water.-There is a legitimate concern over the release of pollutants into the water environment following the utilization or disposal of the huge amounts of fly and grate ash produced during the combustion of coal. Our studies were restricted to the investigation of the possible release of organic pollutants only when fly and grate ash are sluiced to settling ponds and retained there as a disposal site. The water in the settling pond was checked periodically for organic compounds known to be present at low concentrations on the ash.

None of these known components were detected in the water at the conservative limit of one ppB. Indeed, this pond water did not contain any gas chromatographable organic compounds at the detection limit of 0.1 ppB even though the well water used for sluicing contained multiple ppB levels of aromatic compounds indicative of the coal tar that had contaminated the aquifer (19). Thus, the ash effluents from coal combustion appear to adsorb rather than release organic compounds into the water.

This adsorption feature was examined in an experiment where water containing 20 to 50 ppB of five aromatic hydrocarbons was mixed with fly ash for ten minutes at a water to ash weight ratio of 10 to 1. In this short contact time, the fly ash completely removed the organic components; this is vividly illustrated by the two gas chromatograms shown in Figure 1. The effective adsorption is probably due to the active forms of carbon, aluminum and silicon expected to be present in fly ash. For organic compounds then, fly ash provided desirable clean-up rather than undesirable contamination of water.

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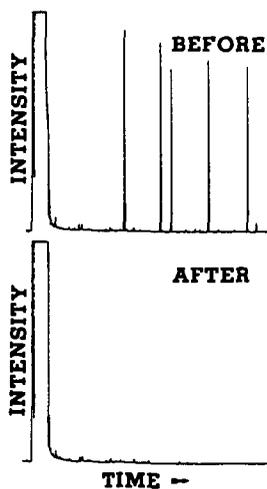


Figure 1.
Clean-up of water by coal combustion fly ash.
BEFORE - capillary column GC chromatogram with left to right major peaks being indan, 3-methylindene, naphthalene, 1-methylnaphthalene and acenaphthylene at 50 to 80 ppB in water before contact with fly ash.
AFTER - same chromatogram after water contacted with fly ash for ten minutes.