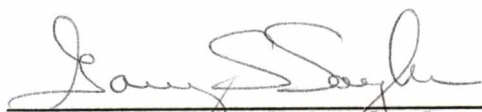


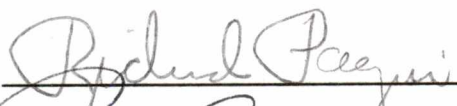
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I am submitting herewith a dissertation written by Manney Carrington Reid entitled "Characterization of Organic Contaminants Present in Coal Slurry Wastewaters." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Ecology.

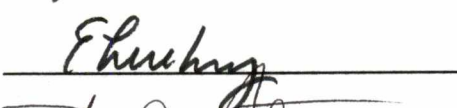


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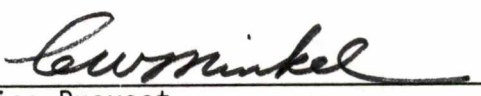








Accepted for the Council:



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CHARACTERIZATION OF ORGANIC CONTAMINANTS PRESENT
IN COAL SLURRY WASTEWATERS

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Manney Carrington Reid

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ABSTRACT

The qualitative and quantitative occurrence and fate of dissolved organic carbon (DOC) leaching into coal slurry transport waters was examined in laboratory generated coal slurries and wastewaters from the Black Mesa coal slurry pipeline. Laboratory slurries were formulated with both western coals (Wyodak, Montana Rosebud and Black Mesa) and eastern coals (Illinois #6 and Pittsburgh #8). The influence of selected physical/chemical parameters on the leaching of DOC material into slurry transport waters was examined. Slurry pH alteration, transport medium, slurry heating and coal storage age were all found to significantly affect slurry wastewater DOC loads.

Qualitative analysis of selected wastewaters demonstrated that the majority of organic compounds present in laboratory formulated coal slurry wastewaters were lower molecular weight species, < 1,000 MW. Fulvic acids represented 31 to 64% of the wastewater DOC loads for laboratory and pipeline generated slurry wastewaters. Oxidation and subsequent derivatization of slurry wastewater organic compounds produced five distinct compound classes, the most predominant being benzenecarboxylic acid and aliphatic dibasic acid esters.

Chlorination of coal slurry wastewaters produced substantial quantities of trihalomethane (THM). Primary THM precursors present in slurry wastewaters were coal derived fulvic acids. An analysis

of chlorinated and non-chlorinated coal slurry wastewaters for the presence of mutagenic agents as determined by the Ames assay demonstrated an absence of mutagenic activity in these samples.

TABLE OF CONTENTS

SECTION	PAGE
I. INTRODUCTION.	1
II. LITERATURE REVIEW	4
Comparative Effluent Analysis of Coal Utilization Technologies.	4
Analysis of Coal Conversion Effluents	4
Coal Slurry Preparation and Wastewater Generation	9
Inorganic Analysis of Slurry Wastewaters.	10
Organic Carbon Load of Coal Slurry Wastewaters.	17
Qualitative Characterization of Coal Slurry Wastewater Organics	20
Toxic and Mutagenic Effects	23
III. OBJECTIVES.	27
IV. MATERIALS AND METHODS	28
Reagents and Chemicals.	28
Coal Sample Procurement and Coal Preparation.	29
Coal Slurry Preparation and Processing.	32
Organic Carbon Analysis of Slurry Transport Wastewaters	32
Physical-Chemical Parameters Affecting DOC Levels	33
Transport Media	34
Transport Time.	34
Temperature	34
Characterization of Wastewater DOC.	35
Molecular Size Distribution	35
Adsorption Chromatography	37
Qualitative Analysis of DOC	38
Extraction Techniques	39
Coal Slurry/PAH Interactions.	40
Oxidative Decomposition	42
Derivatization of Wastewater Organics	42
Silylation.	43
Methylation	44
Chlorination of Wastewater Organics	46
Mutagenic Evaluation of Coal Slurry Organics.	48
V. RESULTS	52
Physical/Chemical Parameters Affecting Wastewater DOC Levels.	52
Coal Type	52

SECTION	PAGE
Transport Time.	54
Coal Slurry pH Adjustment	56
Transport Water Effects	56
Coal Slurry Dewatering Temperature.	58
Coal Storage Age.	60
Characterization of DOC Present in Coal Slurry Wastewaters	63
Qualitative Characterization of DOC	68
Derivatization Experiments.	71
Chlorination of Coal Slurry Wastewaters	87
Mutagenicity Assessment of Coal Slurry Wastewaters. .	91
VI. DISCUSSION.	98
Characterization of Wastewater DOC.	103
Chlorination of Coal Slurry Wastewaters	112
Mutagenic Assessment of Slurry Wastewaters.	116
VII. SUMMARY	118
VIII. CONCLUSIONS	122
REFERENCES CITED	126
APPENDIX	138
VITA	150

LIST OF TABLES

TABLE	PAGE
1. Effluent Characteristics of Coal Conversion Processes. .	6
2. A Comparison of Selected Water Quality Data Generated from Coal Slurry and Simulated Coal Slurry Wastewaters .	12
3. Range of Metals Present in Coal Slurry Mixtures.	14
4. Summary of Coal Types Used During Coal Slurry Investigations	30
5. Total Carbon Content of Simulated Slurry Wastewater Generated from Four Different Coal Types	53
6. Effect of pH Alteration on Dissolved Organic Carbon Levels in Montana Rosebud and Pittsburgh #8 Coal Slurry wastewater.	57
7. The Effect of Slurry Dewatering Temperature on Residual Wastewater DOC Levels.	61
8. Effect of Coal Storage on Slurry Wastewater DOC Levels .	62
9. Distribution of Fulvic Acid and Non-fulvic Acid Among Western Coals.	69
10. Distribution and Fate of Selected Polyaromatic Hydrocarbons in Coal Slurry Wastewaters.	72
11. Degradation Products Present in Slurry Wastewater Samples.	83
12. Relative Abundance of Compound Classes Present in Oxidized and Methylated Wyodak Fulvic Acid Samples . . .	86
13. THM Production Generated in Three Western Sub-bituminous Coal Slurry Wastewaters.	88
14. Production of THM in Fractionated and Non-fractionated Black Mesa Pipeline Wastewaters.	92
15. Mutagenicity Evaluation of Coal Slurry Concentrates Using the Ames Assay	94

TABLE	PAGE
16. Mutagenic Response of Strain TA-98 to Unconcentrated Black Mesa Pipeline and MRB Laboratory Generated Wastewaters.	96
17. Mutagenic Response of Strain TA-98 to Concentrated (25:1) Black Mesa Pipeline and MRB Laboratory Generated Wastewaters.	96
18. Mutagenic Response of Strain TA-98 to Concentrated and Chlorinated Coal Slurry Wastewaters.	97
19. Variability of Dissolved Organic Carbon Values Present in Western Coal Slurry Wastewaters	99
20. THM Production of Selected Humic/Fulvic Sources.	114

LIST OF FIGURES

FIGURE	PAGE
1. The Effect of Simulated Transport Time on Coal Slurry Wastewater DOC.	55
2. The Effect of Transport Water on Residual Wastewater DOC Levels.	59
3. Sephadex 6-25 Gel Profiles of Laboratory Simulated Wyodak and MRB Wastewaters and Black Mesa Pipeline Wastewaters	65
4. Ultrafiltration Molecular Weight Distribution of the Organic Constituents in Selected Coal Slurry Wastewaters.	66
5. Reconstructed Total Ion Chromatogram of Wyodak Fulvic Acid Degradation Products	75
6. Reconstructed Total Ion Chromatogram of an Additional Wyodak Fulvic Acid Sample	76
7. Reconstructed Total Ion Chromatogram of Wyodak Non-fulvic Acid Degradation Products	77
8. Reconstructed Total Ion Chromatogram of Black Mesa Fulvic Acid Degradation Products.	78
9. Reconstructed Total Ion Chromatogram of Black Mesa Non-fulvic Acid Degradation Products.	79
10. Reconstructed Total Ion Chromatogram of XAD Eluent Control	80
11. Reconstructed Total Ion Chromatogram of XAD Resin Base Eluent Control.	81
12. Compound Classes Represented in Wyodak Fulvic Acid Degradation Products.	85
13. The Production of Chloroform in Fractionated Wyodak Coal Slurry Wastewaters.	90
14. Glutaric Acid Dimethyl Ester.	139
15. Pimelic Acid Dimethyl Ester	139

FIGURE	PAGE
16. Benzoic Acid Methyl Ester	140
17. Adipic Acid Dimethyl Ester.	140
18. Malonic Acid Dimethyl Ester	141
19. Succinnic Acid Dimethyl Ester	141
20. p-Methoxybenzoic Acid Methyl Ester.	142
21. Suberic Acid Dimethyl Ester	142
22. 1,4-Benzenedicarboxylic Acid Dimethyl Ester	143
23. Methylbenzenedicarboxylic Acid Dimethyl Ester (Isomer). .	143
24. Tricarballic Acid Trimethyl Ester	144
25. 1,2-Benzenedicarboxylic Acid Dimethyl Ester	144
26. Dimethylfurancarboxylic Acid Dimethyl Ester	145
27. Phthalate Ester (Contaminant)	145
28. Methoxybenzenedicarboxylic Acid Dimethyl Ester (Isomer) .	146
29. 1,2,4-Benzenetricarboxylic Acid Trimethyl Ester	146
30. Benzenetetracarboxylic Acid Tetramethyl Ester (Isomer). .	147
31. Oxalic Acid Dimethyl Ester.	147
32. Furantricarboxylic Acid Trimethyl Ester	148
33. Methoxybenzenedicarboxylic acid dimethyl ester (Isomer) .	148
34. 1,2,3-Benzenetricarboxylic Acid Trimethyl Ester	149
35. Methoxybenzenetricarboxylic Acid Trimethyl Ester (Isomer).	149

I. INTRODUCTION

The use of coal as a source of energy in the U.S. has varied tremendously over the past century. During the early 1900's, 93% of the nation's total energy output was coal based (66). At present coal supplies approximately 22% of the nation's energy needs (28). In the short term, over-production of oil supplies on a global basis will likely dampen utilization of the nation's ample coal reserves. However, there can be little doubt that long term energy use trends will dictate significantly increased coal utilization in order to provide for the nation's expanding energy base. Proven U.S. reserves of coal now stand at 280 billion tons with the vast majority of easily recoverable near surface deposits being located in the western United States. Increased utilization of coal will likely entail the construction of greater numbers of conventional combustion facilities and coal transport systems, as well as the development of alternative coal utilization technologies such as coal liquefaction and gasification.

Coupled with the inception of coal conversion technology is a likely increase in the numbers of conventional combustion facilities in order to more effectively utilize the nation's abundant coal reserves. Increased utilization of coal for combustion purposes will require additional transportation modes for translocating coal reserves especially from western states to more populated and industrialized centers. Coal slurry pipelines have recently

received increasing attention as a potentially efficient and cost effective means of transporting coal over large distances (8,86,116). At present, the only operative pipeline is the Black Mesa pipeline which transports coal from northeastern Arizona to southern Nevada. The Black Mesa pipeline is 440 km in length and has been transporting approximately 5 million tons of coal per year since 1970. In addition, a minimum of eight additional coal slurry pipelines spanning approximately 7,500 km have been proposed in the United States or are in the preplanning stages (107).

Relatively little information is available concerning wastewater quality and discharge impact from coal slurry facilities. The potential environmental risks associated with coal slurry transport have received at best only modest attention. Like coal conversion technologies, coal slurry pipelines will require massive quantities of raw water. It is anticipated that in the transport of 175 million tons of coal per annum via slurry pipelines that approximately 120 million gallons of water per day will be required (107). Analysis of wastewater streams from both coal gasification and liquefaction facilities demonstrates the presence of both toxic and carcinogenic compounds in the form of phenols and PAH. It is unknown whether compounds similar to those already documented in coal conversion wastewaters will be present in variable degrees in coal slurry wastestreams. To date studies on coal slurry wastewaters have focused primarily on the leaching of inorganic constituents such as sulfates, total dissolved solids and heavy metals

into transport waters (7,38,80,93). Only limited information exists as to the quantities and classes of organic compounds that may leach during slurry transport conditions. From an ecological and environmental health perspective it is imperative that characterization on both an analytical and toxicological basis be made of these wastewaters in order to adequately assess the potential hazards associated with wastewater discharge into the environment. In light of the paucity of data existing in this area, this investigation was undertaken with the major goal of identifying and quantifying the organic constituents of coal slurry wastewater and to determine if their presence and concentration was of environmental and ecological concern.

II. LITERATURE REVIEW

I. Comparative Effluent Analysis of Coal Utilization Technologies

Environmental contaminants associated with wastewater derived from coal transport and utilization technologies share common origins: coal type, seam and overburden contaminants, and process water. Consequently, important information on wastewater characteristics of other coal utilization technologies, such as coal conversion, can provide predictive capability relative to coal slurry wastewater quality.

Analysis of Coal Conversion Effluents

During the past decade extensive research has been conducted in the area of coal conversion technology (13,20,36,52,68). Numerous process designs for the conversion of coal into liquid boiler fuels, cleaner combustible solids, and both low and medium BTU gases have been realized in the form of pilot plant facilities. The use of water is an essential raw material for these conversion processes, most importantly serving as a source of hydrogen in order to upgrade substrate carbon/hydrogen ratios (59). In addition, large amounts of water will be required for cooling, cleaning, gas scrubbing as well as for ash and slag quenching purposes (59, 102). Wastewater discharge estimates of 700 million tons/yr have been cited should these coal conversion technologies come on line by the year 2000 (59).

Characterization of wastewaters from a variety of both gasification and liquefaction pilot plant facilities demonstrate that large quantities of organic compounds may be present in these process streams (106,110,122). Reported Total Organic Carbon (TOC) levels range from 380 to 7,000 mg l⁻¹. The majority of the TOC (60-80%) is comprised of phenol and phenol derivatives (56,110). In addition compound classes such as polyaromatic hydrocarbons (PAH), both aliphatic and aromatic acids and nitrogen and sulfur heterocyclics have been documented in coal conversion wastewaters (56,110,122). Research emphasis has focused primarily upon characterization of pollutants and treatment technologies while little information exists concerning the toxic and/or potential long term effects, e.g., carcinogenic, mutagenic or teratogenic, due to discharge of either untreated or treated wastestreams. An adequate assessment of the potential environmental hazards associated with coal conversion technology upon aquatic systems and ultimately human health cannot be properly made until a more substantial data base is generated.

The organic composition of wastewaters generated from various gasification and liquefaction pilot plant facilities has been examined by several investigators (56,67,110). Process effluents are generated as a result of the use of water for gas, ash and slag quenching, stoichiometric requirements and cooling purposes. A summary of coal conversion wastewater characterization data is presented in Table 1. Organic contamination of process wastewaters

Table 1. Effluent characteristics of coal conversion processes.

Process	Type ^a	Ref.	COD ^b	BOD ₅ ^c	TOC ^d	Phenols	Solv. Extractables
Hygas ^e	g	67	3,100-5,100	-	-	560-900	-
Hygas ^f	g	67	7,000-14,000	-	-	1,300-2,000	40-90
SRC	L	25	-	-	6,330-30,000	4,770-11,880	-
Synthane	g	67	15,000-43,000	-	-	1,700,6,600	460-1,000
METC	g	67	16,900-57,000	-	-	300-2,950	-
H Coal	L	67	26,500-88,000	53,000	-	6,800	600
Exxon Donor Solv.	L	56	25,000-265,000	-	4,225-14,700	5,000-6,500	-
Lurgi	g	122	12,500	-	4,190	1,250	-
Texaco	g	122	-	-	-	760	-
British Gas Lurgi	g	122	21,000-30,000	-	-	3,500-6,500	-
Babcock & Wilson	g	122	1,200	600	300	1,000	-
Koppers-Toeck	g	122	420	-	40	-	-

^ag = gasification. L = liquefaction.

^bChemical oxygen demand, values reported in mg l⁻¹.

^cBiochemical oxygen demand, values reported in mg l⁻¹.

^dTotal organic carbon, values reported in mg l⁻¹.

^eCyclone and quench effluents.

^fQuench effluents.

is highly variable with respect to conversion process conditions. Technologies that utilize fluidized or entrained bed reactors with operating temperatures in excess of 1,050° C produce effluents with little organic contamination (67, 122). In addition, wastewater effluent quality within a given conversion process will also be dependent upon coal type. Kaczmarek and Robertaccio (56) examined wastewaters generated from three coals used in an Exxon Donor Solvent liquefaction pilot plant facility. Effluent TOC levels from Illinois, Wyoming and Texas coals ranged from 4,285 to 10,700 to 14,700 mg l⁻¹.

Luthy (67) examined wastewaters generated from both Hygas and British Gas Slagging Lurgi pilot plant facilities. Phenolic concentrations in the Hygas effluents ranged from 560-2,000 mg l⁻¹, while phenolic concentrations generated via the Lurgi process varied from 3,500-6,500 mg l⁻¹. Both quench condensates were found to have higher levels of phenol than found in coking plant effluents. Studies conducted on effluents generated from the Exxon Donor Solvent liquefaction pilot plant found phenol concentrations in the range of 500-5,600 mg l⁻¹. Chemical Oxygen Demand (COD) levels for these wastewaters varied from 75,000-265,000 mg l⁻¹ while organic acid concentrations ranged from 1,000-10,000 mg l⁻¹. In addition compound classes such as aldehydes, ketones, nitrogen and sulfur heterocyclics were reported to be present in wastewater streams. Specific compound identifications were not presented however. Data generated from three Solvent Refined Coal pilot plant

operations demonstrate that phenol may constitute 10-70% of the TOC found in process wastewaters for these facilities (25). Phenol was found to be the major constituent while significant quantities of meta-, ortho- and para-cresol and resorcinol were also documented. GC-MS analysis of the wastewaters also revealed the presence of naphthalene, substituted naphthalenes, phenanthrene and anthracene.

Information concerning the identification of organic species present in coal conversion wastewater effluents is scarce. Wastewaters generated from the Lurgi gasification plant in Sasolburg, South Africa were found to contain various aliphatic acids, phenol, alkyl-substituted phenols and aromatic amines (106). Aniline, pyridine, and alkyl-substituted pyridines were qualitatively identified in the effluents with concentration ranges of 1-177 mg l⁻¹. Stamoudis and Luthy (110) have investigated quench wastewaters generated from both Hygas and Slagging Fixed Bed (SFB) gasification pilot plant facilities. Effluent samples were fractionated into acid, base and neutral fractions, extracted with methylene chloride and analyzed using GC-MS techniques. Phenols and cresols were found to predominate in the acid subfractions for both conversion processes. Compounds partitioning with the base fraction were primarily nitrogen heterocyclics. Pyridine, picoline, aniline, quinoline and aminopyrrole were present at the parts per billion (ppb) level. Organic constituents present in the Hygas neutral fraction were found to span a wide range of

compound classes. Alkylated benzenes, cycloalkanes, cycloalkenes, biphenyls and indenenes were documented at the parts per billion level. Predominant organic species present in SFB effluents were toluene, benzonitrile, naphthalene, cycloalkanes and cycloalkenes.

Organic contaminants associated with coal conversion technologies will likely be dependent upon both conversion process conditions and coal source. Compounds previously documented in these effluents may also be present in wastewaters associated with coal slurry technologies. It is anticipated that environmental contaminants generated by these operations will also vary with process conditions and coal type.

Coal Slurry Preparation and Wastewater Generation

The coal slurry transport process can be divided into three basic components: preparation, slurry formulation and transport and coal-water separation (18). Slurry preparation consists of grinding both wet and dry coal samples such that 98.5% of the ground coal passes through a Tyler Mesh #14 Sieve (1.19 mm) while no more than 20% of the coal particles pass through a #325 Mesh Sieve (44 μ m). The ground coal is then mixed with transport water to form a slurry of approximately 50% dry coal by weight and delivered to the head of the pipeline for transport. Alternatively, it can be stored in tanks with mechanical agitation prior to transport. Coal-water separation represents the only wastewater source of the transport process itself. At the Black Mesa pipeline

separation is achieved via centrifugation. The separated water or centrate is then transported to a clariflocculator tank where flocculating agents are used to remove colloidal materials and coal fines. Transport wastewater use and potential reuse applications may include 1) in house use as power plant cooling water (presently used at the Mohave Power Station at the terminus of the Black Mesa pipeline) followed by environmental release or evaporation, 2) a return loop and reuse as transport water and 3) potential industrial and agricultural reuse applications. Reuse alternatives will be largely dependent upon the chemical water quality characteristics of raw transport water.

Inorganic Analysis of Slurry Wastewaters

Investigations conducted on both slurry and simulated slurry wastewaters have focused for the most part on the leaching of inorganic constituents (7,38,80,84,93,95,103). The identification and quantification of these materials are important for several reasons. First, discharge regulations for inorganic wastewater parameters have historically been more defined for inorganic versus organic constituents. Compliance with state and federal discharge regulations will necessitate the monitoring of dissolved solids, pH and metal concentrations in slurry wastewaters. Secondly, wastewater contaminants such as acids and heavy metals may, in sufficient concentration, be toxic to aquatic biota and therefore should be assessed (2,23,32,90). Finally, inorganic variables such as pH,

total dissolved solids and dissolved metal concentrations will in part regulate the extent to which organic materials leach into slurry transport waters through defining the ionic strength of the transport water and the possibilities for soluble metal-organic complex formation.

Table 2 summarizes the extant data concerning the leaching of inorganic constituents into both simulated and actual slurry transport waters. With the exception of the Illinois and Kentucky samples, the remaining samples are all ranked as either western subbituminous or bituminous coals. The data reflect a wide degree of variability with respect to the leaching of these materials. Part of the variation may be explained by the fact that slurry formulation varied with individual research endeavors, e.g., transport water and coal/water contact time. It is probable, however, that the largest source of variability lies in the inherent heterogeneity of coal itself, which may vary tremendously on a seam to seam basis (39,40).

Acidity/alkalinity values for the most part range near neutrality. The high pH level reported for the Black Mesa slurries reflect the fact that coal blending to control slurry pH occurs at the Black Mesa pipeline. Lowered pH values of coal slurry waters are generally indicative of the oxidation state of the coal itself. Iskra and Laskowski (53) have demonstrated that slurry acidity increases with the degree of coal oxidation.

Table 2. A comparison of selected water quality data generated from coal slurry and simulated coal slurry wastewaters.

Coal Type	Ref.	pH	Inorganic Parameters				
			Specific Conductance	TDS ^b	Alkalinity	Sulfates	Chloride
Jacobs Ranch	95	-	810-2,370	967-2,350	1-38	368-1,300	62-141
Black Mesa ^a	7	9.1	2,191	1,392	829	132	81
Black Mesa	103	8.4	1,493	1,090	491	74,185	41.5
Wasatch	7	6.9	-	1,470	50	550	180
Montana Rosebud	93	6.2-6.6	1,190-1,940	-	32-558	700-960	4.5
Kerr Mcghee	96	6.0-8.0	-	903-1,520	192-223	404-796	-
Kansas	80	7.6	-	3,420-3,610	15,45	2,250	1,500
Illinois	80	7.2	-	3,546-3,610	10-18	1,400	90
Kentucky	19	6.2	2,395	1,207-2,395	12.4	795-1,005	48-154

All values reported as mg l⁻¹ except pH. Conductivity reported as μ mhos/cm.

^aSamples taken from Black Mesa Pipeline.

^bTDS = Total Dissolved Solids.

Investigations concerning the dissolution of metals in slurry transport waters have been conducted by several research groups (7,38,93,96). A compilation of data relating slurry metal concentration and coal type is presented in Table 3. The data indicate that a wide range of variability exists with respect to coal type and the solubilization of metal species. In general, studies on trace element leaching have reported levels that are low and would not be expected to exceed most state or federal effluent guidelines.

The solubilization of trace elements as a function of percent coal in simulated slurries was the subject of a study by Godwin and Manahan (38). Coal water ratios were varied from 0.01-50% coal mixtures and the leaching behavior of selected metals was examined. Three types of behavior were noted. Type 1 behavior, exemplified by sodium, demonstrated a linear increase in concentration in response to increasing coal concentrations in the simulated slurry mixtures. Thus solubility limits do not appear to be exceeded for this type of metal. Calcium typified the second type of behavior, which displayed a linear increase until a coal concentration of 10% was reached at which point the calcium concentration became constant. This type of behavior would indicate that solubility limits for calcium species were likely reached. Type 3 behavior was typified by copper. Copper concentrations peaked at 2% coal water levels. This coal concentration corresponded to the maximum humic acid concentration in the slurry water. Godwin and Manahan hypothesized that this correspondence was due to the formation

Table 3. Range of metals present in coal slurry mixtures.

Coal Type	Ref.	Water Source	Soluble Metal Concentrations (mg l ⁻¹)									
			Al	Ag	As	Ba	Ca	Cd	Co	Cr	Cu	Fe
Montana Rosebud	93	tap			.014-.028					.001-.0015	.02-.03	
Montana Rosebud	93	saline			.017-.027					.06-.60	.07-.13	
Powder River	38	distilled	1.63				553				.047	.40
N. Dakota lign.	38	distilled	8.62				531				.057	2.35
Kerr-Mcgee/B.T.	96	lake					70-570				.003-.009	
Black Mesa	7	river		.005	< .001		22.8	.014			.011	.053
Wasatch	7	saline						< .002		< .01	< .02	
Wasatch	7	sewage eff.					90	< .008				< .02
Jacobs Ranch	95	reservoir		.002	< .002	932		.005	.028	.0085	.0086	
Kansas	86	distilled					1520					
Kansas	86	lake					1660					

Table 3. (Continued)

Coal Type	Ref.	Water Source	Soluble Metal Concentrations (mg l ⁻¹)									
			Hg	K	Li	Mn	Mg	Na	Ni	Pb	Se	Zn
Montana Rosebud	93	tap	.001-.008				25-66	55-79	.005	.02-.05		.03-.06
Montana Rosebud	93	saline	.002-.007			2.68		8,390-7,300	.01	.015-.037		
Powder River	38	distilled		8.08	.070	2.5-4.4	300	181.2				.156
N. Dakota lign.	38	distilled	.002-.007	8.08	.340	8.70	856.2	315.8				.207
Kerr McGee/B.T.	96	lake		10-25		.002	45-330	100-390	.001			.001-.0016
Black Mesa	7	river	.001						.015			.004
Wasatch	7	distilled	< .025			.020			< .22	< .22		< .010
Wasatch	7	saline	< .9				52	320		< .06		< .004
Wasatch	7	sewage eff.	< .9				62	212		< .06		< .004
Jacobs Ranch	95	reservoir	< .0002			.054			.31	.057	< .02	.052
Kansas	80	reservoir		11.1		3.5		48	.7	.10		
Kansas	80	lake		11.5				50		.12		
Kansas	80	sewage eff.		13.4		4.3			.8			
Illinois	80	lake		26.4				405				
Illinois	80	sewage eff.		29				375	.4			

Source: Reference 77.

of soluble metal-humate complexes. Elements behaving in a similar fashion to sodium were lithium and potassium. Type two behavior was attributed to the elements manganese, magnesium, cadmium and zinc. The elements behaving in a type 3 fashion were iron, copper and aluminum.

The leaching behavior of selected metals as a function of coal water contact time has been examined (80,93). Moore (80) investigated the dissolution of metals in a Kansas coal slurry over 16 days of simulated transport. Lead, manganese and nickel concentrations were all found to decrease with time while sodium concentrations remained relatively constant over the 16 day test period. Peavy has investigated the leaching of metals over time from Montana Rosebud coals under laboratory conditions (93). Concentrations of copper, mercury, and lead were found to decrease with increasing coal water contact time. Arsenic and chromium levels remained relatively constant through 12 days of simulated transport. Apparent increases through time occurred for manganese, sodium and zinc. Cooper et al. (19) have examined the leaching behavior of selected metals from simulated slurries formulated with eastern Kentucky coal. After 10 days of simulated transport, manganese, iron and lead concentrations in the slurry wastewaters were observed to increase substantially. Levels of both nickel and zinc peaked after several hours of simulated transport with a steady decline in solubilized levels occurring after this time.

Organic Carbon Load of Coal Slurry Wastewaters

Studies investigating the quantitative leaching of organic constituents into simulated coal slurry wastewaters have used a variety of methods for carbon determination. Five day Biochemical Oxygen Demand (BOD) (80,95,96), Chemical Oxygen Demand (COD) (7, 103), Total Organic Carbon (TOC) (54,84) and Dissolved Organic Carbon (DOC) (93) have all been employed as analytical tools for the characterization of organic carbon in slurry wastewaters. Direct comparisons between reports using different methods are, at best, tenuous given the fact that the analytical methodologies used vary with respect to the type of carbon that is amenable to analysis.

Five day BOD values of 7-11 mg l⁻¹ have been reported for coal slurry wastewaters at the ETSI pilot plant facility (95). Jacobs Ranch coals were used during the course of the investigation. Jordan and Plummer (96) examined BOD₅ levels generated from bench scale slurry wastewaters using Kerr-McGee coals. BOD values ranged from 70-165 mg l⁻¹. Moore (80) reported BOD₅ levels of 60 mg l⁻¹ for simulated slurries using Kansas coals. Illinois coals examined under identical test conditions were found to generate wastewaters with BOD₅ levels in the 10-20 mg l⁻¹ range. Anderson et al. (7) used COD as a means of assaying the organic constituents of Wasatch coal slurries. COD levels of 3 mg l⁻¹ were reported for this coal type. In contrast, Godwin and Manahan (38) reported a COD level of 2,000 mg l⁻¹ for wastewaters generated from North Dakota lignite

slurries. Moore (80) investigated the COD of wastewaters generated from Kansas and Illinois coal slurries. Average COD values of 92 and 23 mg l⁻¹ were reported for these respective coal types. DOC analysis was used by Peavy (93) in order to assess the leaching of organic compounds from Montana Rosebud coals. Reported DOC levels for this coal type ranged from 12-28 mg l⁻¹. Non-volatile TOC was used by Johnson (54) to assay carbon levels in wastewaters generated from bench scale Wyodak coal slurries. Carbon levels ranged from 40-387 mg l⁻¹. Simulated slurries using Wyodak, Black Mesa and Illinois #6 coals were examined for TOC levels by Newton et al. (84). Average TOC values for the three wastewaters were 17.9, 19.8 and 10.5 mg l⁻¹, respectively.

Due to the heterogeneity of coal, the dissolution of organic compounds into slurry wastewaters will be highly dependent upon both coal type and rank. However, physical-chemical parameters such as coal storage age, transport medium and slurry pH will also determine overall carbon loads in slurry wastewaters. Coal is a highly reactive organic polymer which reacts readily with oxygen under ambient conditions (5,21). The subsequent oxidation of coal, a process commonly referred to as weathering, results in a net increase in the oxygen content of coal and an increase in the hydrophilic character of surface molecules (5). Investigations concerning the effects of coal storage age on the leaching of organic materials into slurry wastewaters have been conducted by Plummer and Jordan (95). Results from this study demonstrated that

significant increases in slurry wastewater TOC could be expected with increasing coal storage periods prior to slurry formulation. In addition, coal storage temperature was found to significantly impact wastewater effluent DOC.

Transport medium used in slurry formulation and its influence upon DOC loads in resulting wastewaters has been the subject of several investigations (7,80,93). Peavy (93) examined saline water as a transport medium for Montana Rosebud coals. DOC levels in the saline slurry were found to be reduced by one half relative to distilled water slurries. Peavy hypothesized that the lowered organic concentrations were due to a salting out effect. Anderson et al. (7) examined the COD generated from Wasatch coal slurries formulated with primary sewage effluents. An initial COD of 83 mg l⁻¹ was reported for the sewage effluent while the wastewater generated for the coal sewage effluent slurry was found to have a negligible COD. Moore also examined the effects of sewage effluent on coal slurry wastewater quality (80). Using a municipal wastewater effluent and Wyodak coal, Moore demonstrated that COD levels in the wastewaters decreased rapidly over time.

The pH of coal slurry mixtures has been examined as a potentially significant parameter affecting slurry wastewater carbon loads. Peavy (93) using Montana Rosebud coal, buffered coal slurries over a pH range from 6-10. Results generated from the experiment demonstrated that DOC levels increase significantly with increasing pH.

Qualitative Characterization of Coal Slurry Wastewater Organics

Several investigations have pursued a qualitative assessment of the organic compounds leached into coal slurry wastewaters (7,54,80,84,93,95). Analytical techniques used for characterization purposes have ranged from gel permeation chromatography to identification at the compound level using GC-MS analysis.

Johnson (54) examined the behavior of organic constituents leached from Wyodak coal slurry wastewaters on a Sephadex G-25 column. Elution profiles indicated that the majority of compounds exhibited behavior typical of smaller molecular size compounds. Johnson hypothesized an average molecular weight of 100 for the organic compounds present in Wyodak wastewaters.

Chromatographic analysis of the organic constituents in Montana Rosebud slurry wastewaters has been performed by Peavy (93). Slurry wastewater organics were analyzed using a C-18 reverse phase column coupled to an HPLC system. The results of this investigation demonstrated broad and non-discrete chromatographic patterns for the organic materials. Peavy hypothesized that the compounds were primarily humic and/or fulvic acids in nature. Work by Johnson (54) using similar column conditions to those of Peavy found Wyodak slurry wastewaters to contain materials yielding chromatograms over a broad range of ultraviolet detector wavelengths.

Anderson et al. (7) extracted coal slurry wastewaters generated from Wasatch coals with methylene chloride. The extract was dried, reextracted in hexane and benzene, fractionated using

column chromatography then subjected to analysis by gas chromatography (GC) and GC coupled with mass spectrometry (GC-MS). Three milligrams of organic material were extracted from the wastewater. Of this amount approximately 12% on a mass carbon basis was amenable to GC analysis. Roughly 25% of the peaks generated via GC-MS were tentatively identified, 12 of them as alkyl-substituted naphthalenes. The most prominent peak was attributed to dimethylnaphthalene. Total organic carbon levels of the initial slurry leachate were not presented; thus the total fraction of organic materials amenable to solvent extraction and GC/MS identification could not be determined.

Newton et al. (84) examined Wyodak, Black Mesa and Illinois #6 coal slurry wastewaters for the presence of phenolic compounds. Prior to identification, wastewater organics were methylated with dimethyl sulfate rendering the phenols more easily subject to solvent extraction and analysis by GC-MS. The concentration of phenol and substituted phenols ranged from 1-27 ppb in the simulated wastewaters. Wastewater effluents from the Black Mesa pipeline were also analyzed for the presence of phenolic compounds. A range of 1-54 ppb of phenol and substituted phenols were reported for this wastewater. Total organic carbon levels for the three simulated coal slurry wastewaters averaged 14 mg l^{-1} . Thus on average, phenols constituted approximately 0.01% of the total amount of organic carbon present in the slurry wastewaters. The remaining organic material was hypothesized to be humic and/or fulvic acid

in nature. In addition to phenol analysis of selected wastewaters, Newton et al. examined the behavior of nitrogenous bases, aryl thiophenes and other neutral organic compounds in slurry systems. Selected compounds were added to the transport water prior to slurry formulation at initial concentrations of 100 ppb. Coal samples were then added and allowed to remain in slurry form for 3 days at which time, solvent extraction of the aqueous phase with hexane was performed in order to assess compound partitioning. The nitrogenous compounds pyrrole, pyridine, aniline, quinoline and diphenylamine were employed in the investigation. After coal water separation, analysis of the wastewater demonstrated that greater than 99.8% of the test compounds were removed from the aqueous phase, most likely sorbed onto the coal surface. The same experiment was conducted using 10 perdeuterated neutral organic compounds which included phenanthrene-d10 and benz[a]anthracene-d12. Results from this experiment revealed that again, greater than 99% of the test compounds were removed from the wastewater phase. The authors concluded that these types of compounds, while present in the coal matrix, would not likely solubilize into the aqueous phase during slurry transport.

Analysis of simulated coal slurry wastewaters for the presence of priority pollutants has been performed by several research groups (80,95). Plummer and Jordan (95) examined the wastewaters generated from the ETSI pilot plant for priority pollutants. Several samples were analyzed for all 129 current EPA regulated priority

pollutants. Although a small number of metals, all in low concentration were documented, none of the organic priority pollutants was detected. The same authors also examined bench scale coal slurry wastewaters for the presence of priority pollutants (96). Priority pollutants were found to be absent from these simulated slurries generated with Kerr-McGee coals. Analysis of priority pollutants in Kansas and Illinois coal slurry wastewaters was performed by Moore (80). Characterization by GC-MS revealed the absence of priority pollutants in these simulated wastewaters.

Toxic and Mutagenic Effects

While knowledge of the chemical composition of a wastewater is important for regulatory purposes, it generally provides little overall information concerning the potentially adverse biological effects, either acute or long term, that may arise through environmental discharge. In addition certain pollutants produce adverse effects below their present analytic limits of detection (15). Short term bioassays can serve as effective tools in assessing the potential biological hazards associated with discharge of a compound or complex effluent mixture (15,29). The use of bioassays coupled with chemical characterization provides for a more encompassing evaluation of a given waste material or wastestream.

The Ames assay has been widely recognized and employed for the detection of mutagenic agents in environmental samples (3,17,98, 108). Employing the Salmonella mutagenesis test system developed

by Ames, Epler (30) determined that nitrogen heterocyclics are a major source of mutagens present in coal derived liquids and shale oils. In a similar study of coal derived liquids from a Solvent Refined Coal facility, Wilson et al. (119,120) demonstrated that primary aromatic amines (PAA) contributed significantly to the mutagenic activity of these materials. Mutagenic responses were shown to be directly proportional to PAA concentrations in SRC liquids. Hydroxy polycyclic aromatic compounds generated from the pyrolysis of coal generated a positive response using the Ames assay (49). Photochemical reaction products of these materials generated in the presence of nitrogen monoxide were found to increase the mutagenic response by a factor of 10. In addition the Ames assay has been successfully used to determine the presence of mutagens in effluents from chlorinated wastewater treatment facilities (24,27,81), industrial wastewaters such as pulp mill effluents (74,83) and river waters receiving industrial discharges (41,108, 114).

While the Ames assay has been widely accepted as an effective tool for mutagenic assessment of pollutants, its ability to predict the overall degree of biological hazard associated with a waste or wastewater is limited. No individual bioassay will be sensitive to all chemicals or for that matter all potential effects generated by a given pollutant. Toxicity, reproductive impairment and teratogenicity are also potentially adverse biological effects resulting from the presence of harmful chemicals in the environment. Thus

bioassays that assess these potential responses should also be included, if possible, in evaluation of complex wastes or waste streams.

Information regarding the characterization of coal slurry wastewater effluents via bioassays is scarce. Hoeffner and Manahan (50) examined the effects of coal humic acid on cultures of the green algae Chlorella vulgaris. The humic acids used in the study were generated by the partial oxidation of a Wyoming subbituminous coal with hydrogen peroxide followed by dissolution into a 12M NaOH solution. Humic acids are thought to represent a sizeable fraction of the organic constituents present in coal slurry wastewaters and may likely be present in discharged effluents from coal slurry dewatering facilities (84,93). The results of the study demonstrated that humic acids in low concentrations stimulated algal growth. Humic acid concentrations of 210 mg l⁻¹ produced a lag phase of 4 days in Chlorella cultures followed by normal growth patterns. Phytotoxicity due to varying humic acid levels was not observed in any of the experiments.

Coal slurries are only mildly toxic to coliform bacteria. Margler and Rogozen (69) examined the survival of coliform bacteria exposed to simulated coal slurry conditions formulated with primary sewage effluent. Only minor reductions in the numbers of total coliforms were observed in the slurry filtrates. Fecal Streptococci numbers were not significantly impacted by exposure to coal slurry

conditions. However, greater than 99.8% loss of infectivity was observed for E. coli C. phage. Mechanisms responsible for the observed loss of infectivity were not determined.

III. OBJECTIVES

A lack of fundamental knowledge relating both to the nature and extent of organic pollutants present in coal slurry wastewaters is apparent given the paucity of data pertaining to this subject area. Wastewaters derived from coal slurry transport processes containing high levels of undefined organic contaminants may pose an unacceptable environmental burden if discharged into the environment. Therefore the objectives of this study were formulated to assess the environmental significance of organic pollutants present in these wastewaters. The specific objectives of this investigation were four-fold, encompassing;

1. An evaluation of the physical/chemical parameters that regulate the leaching of organic materials during the coal slurry transport process.
2. A qualitative determination of the organic constituents comprising DOC loads in slurry pipeline wastewaters.
3. A determination of the trihalomethane production potential of slurry wastewaters upon chlorination.
4. An assessment of the mutagenic activity of both unchlorinated and chlorinated coal slurry wastewaters.

IV. MATERIALS AND METHODS

I. Reagents and Chemicals

The following solvents, methylene chloride, cyclohexane and methanol, employed during the extraction and derivatization experiments were all Fisher HPLC grade (Fisher Scientific, Norcross, GA) solvents and used without additional purification methods. Dimethyl sulfoxide spectranalyzed solvent was also obtained from Fisher as was potassium permanganate certified ACS grade, used during the oxidation studies.

Sylon HTP, employed for derivatization purposes, was supplied by Supelco (Supelco, Inc., Bellefonte, PA). The reagent is a mixture of hexamethyl-disilazane and trimethylchlorosilane dissolved in pyridine. Methyl iodide employed in initial methylation experiments was obtained from Aldrich (Aldrich Chemical Co., Milwaukee, WI). Both tetrahydrofuran (THF) and ethyl ether, employed as solvents for these experiments, were obtained from Fisher. The THF was histological grade, the ether certified ACS grade; both were used as received.

The diazomethane precursor, N-methyl-N-nitroso-p-toluenesulfonamide, with the tradename Diazald was obtained through Aldrich.

The ^{14}C compounds used in the course of the PAH sorption studies were supplied by Amersham (Amersham Corp., Arlington

Heights, IL). The scintillation fluid used for determination of ^{14}C activity was Ready Solv-HP-B and was supplied by Beckman (Beckman Inst., Fullerton, CA).

Positive mutagen standards, 2-aminofluorene and methyl-N-nitro-N-nitrosoguanidine (MNNG), used in the Ames Assay were obtained from Aldrich. The S-9 rat liver microsomal mix was commercially prepared by Litton Bionetics (Litton Bionetics Corp., Charleston, SC).

II. Coal Sample Procurement and Coal Preparation

A variety of coal types was used in the generation of laboratory based coal slurry wastewaters. Because coal slurry pipelines have been proposed for all geographic locations in the U.S., coals from both the western and eastern parts of the country were employed. The wastewater quality of slurry mixtures generated from both eastern and western coal would be expected to vary due to differences in trace element distribution, leachable organic moieties and inherent variability within a given coal type. A summary of coal type, regional origin, rank and pre-history of each coal used during the investigation is presented in Table 4. Illinois #6 (Ill #6), Pittsburgh #8 (Pitt #8), Wyodak and Montana Rosebud (MRB) coals were obtained from Oak Ridge National Laboratory, Oak Ridge, TN (Courtesy of Dr. Ed Davis). These coal samples were mined in 1978 and subsequently stored in sealed 55 gallon drum containers at the Oak Ridge facility. Ill #6 and Pitt #8 were felt to be

Table 4. Summary of coal types used during coal slurry investigations.

Coal Sample	Region	Rank	Pre-History
Wyodak ^a	western	subbituminous	Sample mined in 1978 Powder River Basin; north-eastern Wyoming, strip-mined; unwashed.
Wyodak ^b	western	subbituminous	As above; mined in 1983.
Montana Rosebud ^a	western	subbituminous	Sample mined in 1978 Powder River Basin; south-eastern Montana, strip-mined; unwashed.
Montana Rosebud ^b	western	subbituminous	As above; mined in 1982.
Black Mesa	western	subbituminous	Coal stock pile pulverized samples at pipeline head; samples shipped in 1981. Collected also in 1982.
Illinois #6	eastern	bituminous	Sample mined in southern Illinois, 1978, unwashed, relatively oxidized.
Pittsburgh #8	eastern	anthracite	Sample mined in mideastern Pennsylvania, 1978, unwashed, relatively oxidized.

a,bRepresents two different samples of the same coal type.

representative of most eastern coals. Total sulfur concentrations were 4.4 and 2.8%, respectively, for each coal type. Both Wyodak and MRB coals were felt to be representative of coal types in the heavily mined Powder River Basin Region of southeastern Montana and northeastern Wyoming. Additional freshly mined Wyodak samples were obtained from the Kerr-McGee Coal Company, courtesy of Mr. Bill Utzog. Additional MRB samples were provided by Peabody Coal Co., St. Louis, MO (courtesy of Dr. John Arnold). Black Mesa raw coal, which is the feed coal for the Black Mesa pipeline, was obtained from the Black Mesa Pipeline Co., Flagstaff, AZ (courtesy of Mr. Jim Shelley). Black Mesa pipeline centrate sample wastewaters (wastewaters generated after removal of the coal via centrifugation) were obtained from Southern California Edison, Mohave Generating Station, Laughlin, NV (courtesy of Mr. Ken Smith). These samples were either transported on ice (3 day travel time) or shipped air freight (2 day travel time). These samples were stored at 5°C prior to analysis. Additional 50 gallon drum samples of Black Mesa slurry centrate were obtained from the Mohave Power Generating Station, courtesy of Mr. Greg Hosing.

Upon arrival, coal samples were sufficiently ground using a variety of mills to pass through a number 600 U.S. Standard sieve (Tyler mesh #40). This size reduction resulted in coal particle diameters of less than 0.390 mm. For larger pieces of coal, initial size reduction was accomplished by passing the sample through a Hammermill Crusher (Holmes Brothers, Inc., Danville, IL). These

samples were further reduced in size by using either a Pulverizer Mill (Holmes Brothers, Inc., Danville, IL) or a Thomas-Wiley Laboratory Mill (Thomas Scientific, Philadelphia, PA).

III. Coal Slurry Preparation and Processing

Simulated coal slurries were prepared as a 50:50 mixture (Weight/Weight) of surface dry coal with the desired transport medium. Slurries were prepared in various volumes up to 12 liters in glass vessels equipped with Teflon lined screw caps. When appreciable head space existed, the atmosphere was replaced with nitrogen gas. The mixed slurries were then either mechanically shaken or magnetically stirred for various periods of time. At selected time intervals, samples were withdrawn or slurries were sacrificed to monitor appropriate transport water chemical parameters. Upon removal, slurries were subjected to centrifugation at 10,000 rpm for 10 minutes in a Sorvall RC-2B centrifuge (Ivan Sorvall, Inc., Norwalk, CN) in order to separate the coal particles from the water. The centrate was then subjected to filtration through Gelman Type A-E glass fiber filters (Gelman, Inc., Ann Arbor, MI) and 0.4 μm Nucleopore polycarbonate membranes (Nucleopore Corp., Pleasanton, CA) to remove coal fines. The residual transport water was then stored at 5°C when necessary prior to further analysis.

IV. Organic Carbon Analysis of Slurry Transport Wastewaters

Dissolved organic carbon (DOC) analyses of slurry wastewaters were conducted using either an Oceanography International

064B carbon analysis system (Oceanography International, College Station, TX) or a Beckman Model 915 Total Organic Carbon Analyzer (Beckman Instruments, Fullerton, CA). Both instruments were used in the direct injection mode. Using oxygen as the carrier gas, samples are swept into a combustion tube and heated to an operating temperature of 950°C. Organic carbon is oxidized to CO₂ which is then measured by a non-dispersive infrared analyzer. Prior to analysis the wastewaters were acidified to pH 2 and purged with nitrogen gas to remove inorganic carbon species. Potassium biphthalate was used as the carbon source for generating standard curves used in calculating DOC concentration of the original slurry. Standard curves were obtained prior to each day's analysis. Duplicate injections of both samples and standards were made using a Hamilton CR700-200 syringe (Hamilton Company, Reno, NV).

V. Physical-Chemical Parameters Affecting DOC Levels

The initial focus of this study was directed towards an assessment of the significant physical-chemical parameters affecting the leaching of organic materials into simulated transport wastewaters. Factors such as coal type and coal storage age, transport time, transport media, and slurry pH were examined as potentially significant factors influencing the degree of organic contamination in residual transport waters. Because these factors will vary with individual pipeline units, it may be anticipated that wastewaters of highly variable quality will be generated with each pipeline.

Transport Media

Initial coal slurries were formulated with laboratory generated doubly distilled water. Additional transport media included secondary treated sewage effluent and lake water. The treated sewage effluent was obtained from a local treatment facility in Knoxville, TN. Lake water samples were obtained from Melton Hill Reservoir, a Tennessee Valley Authority impoundment of the Clinch River located at Oak Ridge, TN. DOC measurements of transport media were made prior to each slurry formulation.

Transport Time

The slurry pipelines presently proposed are of variable length (107), the shortest being 183 miles in length and the longest approaching 1,500 miles in length, with estimated transit times of 2 and 15 days, respectively (80, 93). Thus coal water contact times will be site specific. For this investigation coal water contact times varied over a period of 2 weeks. Initial DOC readings were taken after 1 hour of contact time with termination of all time course experiments after 12 days of simulated transport.

Temperature

Present operating conditions at the Mohave Power Plant, the dewatering facility of the Black Mesa pipeline, call for the heating of coal slurries prior to coal removal via centrifugation. This step facilitates the coal separation process (109). Slurries are passed through a heat exchanger and heated to a temperature

of 60°C. Selected laboratory simulated slurries were subjected to heat treatments at 60°C for 30 minutes directly preceding the centrifugation dewatering step. This coal water separation method was felt to be representative of the dewatering conditions employed at Mohave except that filtration rather than flocculation was used to remove coal fines.

VI. Characterization of Wastewater DOC

Molecular Size Distribution

The molecular size distribution of organic constituents in selected slurry wastewaters was determined via gel permeation chromatography (GPC). This method effects separation of solute molecules on the basis of their respective hydrodynamic volumes, i.e., effective molecular size (121). Sephadex G-75 and G-25 medium gels (Pharmacia Fine Chemical, Inc., Piscataway, NJ) with fractionation ranges of 5,000-75,000 MW and 1,000-5,000 MW, respectively, were used in the investigation. A Pharmacia 100 x 1.6 mm water jacketed column was packed with the appropriate gel and tested for packing irregularities by visual observation of eluting Blue Dextran 2000 bands. For void volume determination, Blue Dextran 2000 was used. The inclusion volume was determined by passing a solution of sucrose through the column with subsequent monitoring of eluent DOC levels. Wastewater samples applied to the column were concentrated in order to increase relative carbon loading on the column prior to separation. A Buchi vacuum rotoevaporator

(Brinkmann Insts., Inc., Westburg, NY) was used to effect a sample concentration of 10:1. A borax buffer, pH 8.6, was employed as the column eluent. Flow rates for the various runs were on the order of 1-2 ml min⁻¹. Post-column eluent was collected in 4 ml fractions using an Eldex Mini II fraction collector. The eluted fractions were subjected to DOC, UV absorbance and fluorescence analysis.

Sample UV absorbance (254 nm) measurements were performed on a Perkin-Elmer Model 200 spectrophotometer (Perkin-Elmer Corp., Norwalk, CT). Fluorescence was measured with a Turner Model III fluorometer (Sequoia-Turner Corp., Mountain View, CA). A 7-54 excitation filter with a λ max of 340 nm was used. Maximum transmission at λ max was 0.79 T_0 and the band width was 140 nm.

Ultrafiltration (UF) was employed as an additional means of assessing the molecular size distribution of organic constituents present in concentrated slurry wastewaters. This technique effects solute separation by filtration through membranes of known molecular weight (MW) permeability. Like GPC, effective molecular weight values will be primarily dependent upon molecular configuration, ionic strength of the solution and possible sorption interactions with the membrane itself. To minimize sorption error, Amicon YM ultrafiltration membranes (Amicon Ltd.) were chosen for this investigation. These filters are hydrophilic membranes exhibiting a low non-specific binding capacity which favors increased solute recovery. Membranes were conditioned according to the manufacturer's

guidelines. An Amicon 52 stirred cell with a N_2 operating pressure of 40 psi was used as the filtration apparatus. Concentrated samples were added to the stirred cell assemblies which utilized either YM5 (5,000 MW cutoff) or YM2 (1,000 MW cutoff) filtration membranes. Using these two filters, the organics in the slurry water were divided into three fractions: 1) greater than 5,000 MW, 2) less than 5,000 MW but greater than 1,000 MW and 3) less than 1,000 MW. Recovery of DOC in the various fractions was monitored by DOC analysis as previously described. The volume of sample retained and passing through the membrane was used in calculating a recovery and fractionation budget for the procedure.

Adsorption Chromatography

Adsorption chromatography has been increasingly used in recent years as an effective analytical means of removing organic solutes from water systems (57,58,60,112). Because wastewaters generated from certain western coals had properties similar to solutions containing elevated levels of humic/fulvic constituents, i.e., highly colored, elevated DOC levels and strong UV absorbance, studies were undertaken to determine what extent of the DOC present in slurry wastewaters could be procedurally classified as humic/fulvic acids. Amberlite XAD-8 resins (Rohn & Haas, Philadelphia, PA) were employed throughout the course of this investigation. XAD-8 is a macroreticular resin with a polyacrylic-ester polymer backbone which has been shown to be successful in quantitatively

isolating humic materials from water samples (1,22,73,113). Resin cleanup procedures prior to column packing were those of Thurman and Malcolm (113). Acidified slurry wastewaters (pH 2) were passed through a 100 x 1.6 mm glass column containing XAD-8 resin at flow rates of 8-10 ml min⁻¹. A 0.1N NaOH solution was then passed in an ascending mode through the column to remove the sorbed humic/fulvic component. The initial column volume was discarded while an additional 2-3 column volumes containing the eluted humic/fulvic fraction were collected and saved. DOC analysis was used to monitor the elution of humic and fulvic acids from the resin column. The eluted humic/fulvic acid solution was acidified to a pH of 1 with concentrated HCl and centrifuged. The precipitate was classified as humic acid and the organic fraction remaining in solution was operationally classified as fulvic acid. Three operationally classified fractions were obtained with this procedure, 1) a humic acid fraction, 2) a fulvic acid fraction and 3) a nonfulvic acid fraction.

VII. Qualitative Analysis of DOC

A variety of techniques were employed in order to characterize the organic components present in slurry wastewaters. These included solvent extraction, preparative high pressure liquid chromatography (HPLC) followed by mass spectrometry and oxidation/derivatization coupled with gas chromatography-mass spectrometry (GC-MS) of fractionated organic slurry samples.

Extraction Techniques

Initial attempts to isolate the organic components in slurry wastewaters involved conventional solvent extraction techniques. Simulated slurry wastewaters were fractionated into acid, base and neutral components with subsequent extraction by methylene chloride. Concentrated slurry wastewaters (10:1) were acidified to a pH of 2 and extracted three times with equal volumes of methylene chloride. The aqueous phase containing the basic organic constituents was then made basic with 25% NaOH and extracted three times with equal volumes of methylene chloride. The initial organic phase containing the neutrals and acids was then extracted with 1) a 5% NaOH solution which removed the acidic components in their respective salt forms followed by 2) methylene chloride to remove the neutral fraction. The aqueous phase containing the acidic components was acidified to pH2 and extracted three times with methylene chloride. The separated acid, base, neutral fractions were then concentrated via evaporation under N₂ gas.

In addition, the procedure developed by Natusch and Tomkins (82) for the isolation of polycyclic organic compounds was employed in this investigation. Slurry wastewater samples concentrated 10:1 via rotary evaporation were extracted three times with equal volumes of cyclohexane. The combined organic phase was then partitioned three times with equivolume amounts of dimethyl sulfoxide (DMSO). The DMSO was then diluted with two volumes of water. This solution was then back extracted three times with cyclohexane.

Concentration of the back extracted cyclohexane fraction was accomplished via evaporation under N_2 . Concentrated samples from both methods were analyzed using Gas Liquid Chromatography (GLC). GLC analysis was performed with a Perkin-Elmer (Perkin Elmer Inst., Norwalk, CT) 3920 gas chromatograph equipped with a flame ionization detector. A glass column (6 ft x 1/4 in OD x 2mm ID) packed with Chrom Q 80/100 coated with 3% OV-101 was employed. Nitrogen was employed as the carrier gas with a flow rate of 40 ml min⁻¹. Additional operating conditions were as follows; injector temperature 275°C, detector temperature 300°C, column temperature 100-175°C programmed at 8°C min⁻¹.

VIII. Coal Slurry/PAH Interactions

Studies were undertaken in order to assess the behavior of polyaromatic hydrocarbon compounds, known to be present in coal (46), during simulated coal slurry conditions.

¹⁴C-naphthalene, ¹⁴C-phenanthrene, and ¹⁴C-benzo(a)pyrene were employed as model PAH compounds in this investigation. The compounds were added in acetone (25 µl) to separate 50 ml flasks of distilled water giving final concentrations of 1.3 mg l⁻¹ ¹⁴C-naphthalene, 22 µg l⁻¹ ¹⁴C-phenanthrene and 28 µg l⁻¹ ¹⁴C-benzo(a)pyrene. Fifty grams samples of Wyodak coal were added to the flasks. The slurries were then stirred for a period of 24 hours at which time the contents of the flasks were centrifuged

as previously described and filtered through glass fiber filters. Aqueous samples were then dispensed in Ready Solv-HPB scintillation fluor and counted for ^{14}C -activity. Standards, quench and filter controls were also analyzed during these experiments.

An alternative method to liquid-liquid extraction was attempted in an effort to quantitatively remove the organic compounds from the aqueous wastewater matrix. This procedure was performed on XAD fractionated slurry wastewaters. Selected nonfulvic acid fractions were lyophilized using a Virtis 10-010-BA freeze dry unit (Virtis, Inc., Gardner, NY). The residues were then subjected to continuous extraction using a micro-soxhlet extractor with methanol as the solvent. The methanol was then concentrated under N_2 gas and chromatographed on a DuPont 803 Preparative HPLC (DuPont Inst., Wilmington, DE) equipped with a Zorbax ODS reverse phase preparative column. The solvent was 100% methanol with a flow rate of 6 ml min^{-1} . Sample injection size was $75 \mu\text{l}$ and the detector wavelength was set at 254 nm. Successive sample injections and peak collections were performed. The combined samples containing the fractionated peaks were then blown to dryness and the solid residues weighed and analyzed via Mass Spectrometry (MS). A Hewlett Packard 5980A double focusing mass spectrometer was employed for analysis. Samples were introduced via direct probe with an ionization energy of 70 eV. Mass scans were performed from 0-500 mass units.

IX. Oxidative Decomposition

The partial oxidation of selected coal slurry fulvic acid and non-fulvic acid organic fractions was performed according to the procedure of Liao et al. (63). A potassium permanganate carbon ratio of 1:1 was maintained for all samples oxidized. The reaction conditions employed were as follows; all samples were made basic (pH 10) with NaOH. A sample was then placed in a round bottom flask equipped with a magnetic stirrer and heated in an oil bath maintained at 65°C. Appropriate quantities of permanganate (depending upon relative amounts of carbon present in each sample) were then added over the first hour of heating. The reaction was allowed to continue for an additional 2 hours at which time the sample was removed from the bath. Tests were performed for excess permanganate at this time. The solution at ambient temperature (25°C) was then brought to pH 12 with NaOH and filtered through Gelman Type A-E glass fiber filters. After filtration the pH was reduced to 5 with solutions of concentrated and 1N HCl. The filtered and pH adjusted samples were then concentrated by lyophilization with a Virtis freeze dry unit:

X. Derivatization of Wastewater Organics

Derivatization of organic compounds is commonly used as a means of enhancing GC quantitation (97,121). In addition the volatility of higher molecular weight compounds may be enhanced through derivatization. In order to improve GC analysis of the

organic components present in XAD fractionated slurry wastewaters, derivatization of these materials was accomplished. Three different procedures were employed during the course of this investigation.

Silylation

Lyophilized samples of both Wyodak and Black Mesa pipeline wastewaters fulvic acid and nonfulvic fractions were initially derivatized with Sylon HTP. Ten milligrams of lyophilized samples were mixed with 1 ml Sylon HTP. The reaction mixtures were then sealed in glass ampoules. Two reaction conditions were employed. The first involved heating the samples at 65°C for 1 hour in a water bath and the second set of conditions called for heating the samples at 100°C in an autoclave under ambient pressure for a period of 2 hours. After heating the samples were centrifuged to separate the suspended and solubilized components. The supernatant was pipetted from the ampoule and subjected to gas chromatographic analysis.

A Perkin-Elmer model 3920 gas chromatograph equipped with an FID detector was used throughout the course of this investigation. A glass column (9 x 1/4 in O.D. x 2 mm I.D.) packed with OV-17 liquid phase and a 30M OV-101 glass capillary column were both employed. Flow rates for the capillary column were 1-2 ml min⁻¹ while a rate of 40 ml min⁻¹ of nitrogen was used for the packed column. The following temperature parameters were employed; detector 300°C, injector 275°C, column 75-275°C at 4°C min⁻¹.

Methylation

Initial methylation of XAD fractionated Wyodak and Black Mesa Pipeline slurry wastewaters was performed using a modification of the procedure developed by Liotta (65). This method which employs methyl iodide as the methylating agent has been successful in derivatizing pyridine soluble surface coal constituents. The procedure calls for the use of a quaternary ammonium hydroxide as the base. The modification of the method involved using sodium hydroxide in lieu of the ammonium hydroxide. Concentrated fulvic and nonfulvic acids were basified to pH 12 with concentrated NaOH and mixed with equal volumes of tetrahydrofuran (THF) which served as the bridging solvent between substrates and the methylating reagent. To this mixture 3 ml methyl iodide were added. The reaction mixture was initially purged with N₂, then capped and stirred magnetically under ambient temperature conditions for a period of 24 hours. Distillation of the organic fraction was employed to remove the THF and any unreacted methyl iodide. The remaining aqueous sample containing a small quantity of precipitate was extracted three times with ethyl ether, followed by lyophilization of the aqueous fraction. The lyophilized samples were then extracted three times with methanol. Sample fractionation produced three component parts, 1) a THF volatile fraction, 2) an ether soluble fraction and 3) a MeOH soluble component. The fractionated samples were then analyzed via GC. GC conditions were similar to those described in the previous section.

In addition, diazomethane was employed as a methylating agent for the fractionated slurry samples. The procedure followed was that of Black (12). Diazald was selected as the diazomethane precursor. Fulvic acid and nonfulvic acid oxidized derivatized samples generated from Wyodak and Black Mesa pipeline wastewaters were methylated using this procedure. Reagent controls were performed duplicating sample handling (XAD column separation, rotary evaporation, lyophilization) procedures to account for the possibility of contamination and artifact formation.

The generation of diazomethane was accomplished by initially dissolving Diazald in ethyl ether. From a separatory funnel, this solution was slowly dripped into a reaction flask containing a mixture of ethanol, potassium hydroxide and water. The reaction flask, submerged in an oil bath, was previously heated to and maintained at a temperature of 65°C. The ethereal-diazomethane distillate generated in the reaction flask was condensed by means of an acetone-dry ice condenser which was connected to a receiving flask containing the lyophilized samples suspended in methylene chloride. Upon cessation of the yellow distillate, noted by a disappearance of yellow color from the reaction flask, the receiving flask was removed, stoppered and with the addition of a bar magnet placed on a magnetic stirrer for an additional period of 2 hours. At the end of this time, the reaction was quenched by the addition of 10 ml of a 1N HCl solution. The biphasic mixture was then separated by means of a separatory funnel. The organic fraction

was dried overnight with magnesium sulphate, then filtered through glass wool. Samples were then concentrated under N₂ gas to a final volume of 1 ml.

GC-MS analyses of the methylated samples were performed on a VG-Micromass 7070F double focusing mass spectrometer which was interfaced to a Hewlett Packard 5710A gas chromatograph. Compound separation was accomplished through the use of a 15M DB-17 (Alltech Ass., Deerfield, IL) capillary column temperature programmed from 70-280°C at 8°C min⁻¹. A split ratio of 1:9 was used for sample introduction onto the column. An ionizing energy of 70 ev was maintained for all samples. Data generated during the course of GC-MS analyses were obtained from a VG-Micromass 2035F/B data system.

XI. Chlorination of Wastewater Organics

Studies were undertaken to determine whether organics leached into simulated slurry wastewaters and Black Mesa pipeline generated wastewaters would serve as precursors in the formation of tri-halomethanes (THM). In addition, XAD fractionated slurry samples were also examined for THM formation potential (THMFP).

Initial chlorination studies involved simulated coal slurry mixtures. Three day simulated coal slurries were filtered and diluted with doubly distilled H₂O to a final DOC level of ≤ 10 mg. Solution pH was allowed to vary during these experiments. All fractionated slurry samples were buffered at pH 7.0 using a phosphate

buffer. Chlorine to carbon ratios of 2:1 were maintained throughout the course of the investigation. Slurry wastewaters were chlorinated by the addition of appropriate amounts of sodium hypochlorite depending upon the DOC of the wastewater and mixed in a magnetically stirred, Teflon capped vessel. After 2 minutes of reaction time, sub-fraction aliquots of the chlorinated slurries were dispensed into headspace free glass bottles and sealed with Teflon lined crimp caps. Samples were then incubated at 20°C in the dark. THM measurements were performed after 24, 48 and 96 hours of incubation. Sample quenching at the appropriate time interval was performed by injection of 1 ml of a 2N sodium thiosulfate solution into the sealed bottle. Free residual chlorine measurements using the diethyl-p-phenylene diamine (DPD) method (44,91) were performed after initial chlorination was completed. Sodium hypochlorite for chlorination of the wastewaters was obtained by diluting commercial bleach solution to the desired strength. The chlorine solution was standardized prior to each assay using the Iodometric Method as outlined by Standard Methods (44).

In addition to the simulated slurry samples XAD fractionated Wyodak and Black Mesa pipeline centrate wastewaters were also chlorinated according to the procedure just described. Further fractionation of these samples was accomplished by using YM2 ultra-filtration membranes (1000 MW cutoff). Selected fulvic acid fractions were separated into two classes; those compounds with molecular weights greater than 1,000 and those with molecular weights of

1,000 or less. Isolation and quantification of THM's was accomplished through the use of the purge and trap developed by Bellar and Lichtenberg (10).

XII. Mutagenic Evaluation of Coal Slurry Organics

The mutagenic potential of selected coal slurry wastewater concentrates was initially examined using the Salmonella typhimurium histidine auxotrophic reversion assay developed by Ames et al.

(3). The method's simplicity, short duration, and relative inexpense have enhanced its use as the most frequently utilized technique for assessing the biological activity of both compounds and complex mixtures of environmental concern. This bacterial test system employs several strains of histidine mutant Salmonella typhimurium. The inability to produce histidine and thus reproduce unless in the presence of this amino acid results from either a single base mutation in several strains or deletion of bases in other strains. Compounds capable of interacting with the bacterial chromosome and producing either base-pair or frameshift reverse mutations give rise to histidine independent cells. Thus the numbers of mutational events are assessed by the number of cells that grow due to the acquired ability to produce histidine. In order to increase the sensitivity of the assay, several additional mutations have been incorporated within the tester strains. The excision repair system has been deleted as well as the lipopolysaccharide membrane of the bacteria. The loss of the lipopolysaccharide

envelope surrounding the bacteria facilitates the movement of potential mutagens into the cells. The excision repair mutation increases the probability that once a mutational event has occurred that it will be expressed as a revertant colony. In addition, in order to more closely mimic mammalian systems, microsomal enzymes are routinely introduced with the test compounds. These enzymes may under certain conditions activate potentially mutagenic compounds into forms that may more readily interact with cellular DNA. Strains TA 97, 98 and 100 were kindly provided by Dr. Bruce Ames. Wastewaters were concentrated 10:1 via rotary evaporation and filter sterilized through Nalgene Type S sterilization filter units (Fisher Scientific, Norcross, GA). The wastewater concentrates were tested in a range of 50-250 μ l. Prior to the testing of samples, the tester strains were checked for histidine auxotrophy, uvr B and LPS/rfa mutations and the presence of the R factor plasmid. Positive controls, using 2-aminofluorene for strains TA-97 and TA-98 and methyl-N-nitro-N-nitrosoguanidine (MNNG) for TA-100 were performed to insure that the tester strains were functionally responsive to known mutagenic agents. S-9 rat liver microsomal enzyme preparation was employed to test for potential mutagens requiring enzymatic activation. The sterile wastewater concentrates, derived from 3 day simulated slurries, were mixed with an overnight Salmonella typhimurium culture and minimal amounts (115) of biotin (25 μ M) and histidine (25 μ M), then poured onto Vogel Bonner plates

and incubated at 37° C for 48 hours as described by Ames (3). After incubation, visible colonies were scored as histidine revertants. All analyses were performed in triplicate.

The modified fluctuation test as outlined by Levin et al. (62) was used as a supplemental mutagen screening procedure. Previous research (34, 42, 43) has shown the test to be sensitive to extremely low concentrations of mutagens. Samples tested using the fluctuation test included both unconcentrated and concentrated (25:1) filter sterilized coal slurry wastewaters. In addition, chlorinated concentrated wastewater samples were also analyzed using this method. Chlorination of selected wastewater concentrates (25:1) was performed in a manner described in the previous section.

Overnight Salmonella strains TA-97 and TA-98 were transferred to fresh growth media (43) and allowed to obtain log phase growth (1×10^8 cells ml). Twenty-five μ l of the log phase culture were then transferred into 100 ml assay media containing 1 μ M biotin and 0.25 μ M histidine. Sterilized test samples were added in the concentration range of 50-500 μ l for wastewater concentrates and 0.5-10 ml for unconcentrated samples. Five μ g ml⁻¹ bromocresol purple was added to the assay media as a pH indicator of growth. Forty-eight 2 ml aliquots of each sample were then pipetted into Costar Assay plates (Hybridoma, Atlanta, GA). Samples were then incubated for a period of 4 days at 37°C at which time growth of revertants was scored visually by noting a change in well color.

Positive responses were noted as tubes that changed from purple to yellow while negative (non-revertants) tubes remained purple in color.

V. RESULTS

I. Physical/Chemical Parameters Affecting Wastewater DOC Levels

The influence of coal type, simulated transport time, slurry pH adjustment, transport medium, slurry dewatering temperature and coal storage age were all examined as potentially significant parameters affecting the leaching of soluble organic constituents from coal slurry mixtures. Coal types examined during the course of these experiments were three western coals, Wyodak, Black Mesa, and Montana Rosebud (MRB), and two eastern coals, Illinois #6 (ILL #6) and Pittsburgh #8 (Pitt #8).

Coal Type

A comparison of four coal types used during the course of this investigation and their respective total carbon content remaining in centrifuged wastewaters is presented in Table 5. The data were generated from three separate slurry experiments and are presented as mean values plus or minus one standard deviation. Wastewater samples were not acidified and purged prior to carbon analysis; thus, the data represent Total Carbon (TC) concentrations present in the slurry wastewaters. As demonstrated in Table 5, western coal slurry wastewaters contain two to five times more total soluble carbon as compared to the eastern coal wastewater examined. Also noted in Table 5 are dramatic pH differences between both western

Table 5. Total carbon content of simulated slurry wastewater generated from four different coal types.

Coal Type	pH	Total Carbon mg l ⁻¹		
		Day 3	Day 7	Day 10
MRB	5.5	198 ± 75 ^a	182 ± 72	119 ± 57
Wyodak	5.4	102 ± 32	100 ± 18	95 ± 18
Illinois #6	1.8	44 ± 23	44 ± 16	41 ± 8
Pittsburgh #8	2.1	38 ± 11	29 ± 8	31 ± 15

^aData are presented as mean values plus or minus one standard deviation unit.

and eastern coal slurries. Western coal slurry pH ranged from 5.5-7.0 while eastern coal slurries were highly acidic with pH ranges from 1.8 to 2.1.

Transport Time

Data relating the effects of increasing transport time on residual dissolved organic carbon (DOC) levels present in simulated slurry wastewaters are presented in Figure 1. After 4 days of simulated transport all three western coals exhibited an increase in DOC wastewater concentrations. However, by day 8 residual DOC values were not found to be significantly different from time 0 values generated after 1 hour of simulated transport. Overall DOC concentrations for MRB and Wyodak slurry wastewaters as reported in Figure 1 are substantially higher than TC levels for these same coal types as described in Table 5. Variation in slurry formulation may have been responsible for the observed differences. Slurries were stirred magnetically during total carbon experiments while mechanical shaking was employed during the examination of transport time effects. Differences in coal age may also have contributed to the variable results. In contrast, DOC levels generated from coal slurries made with the eastern coal Ill #6 are seen to remain relatively constant with a mean value of 40 mg l^{-1} over 8 days of simulated transport. Collectively the data presented in Table 5 and Figure 1 demonstrate that eastern coal slurries exhibited DOC loads that were substantially lower than those generated for western

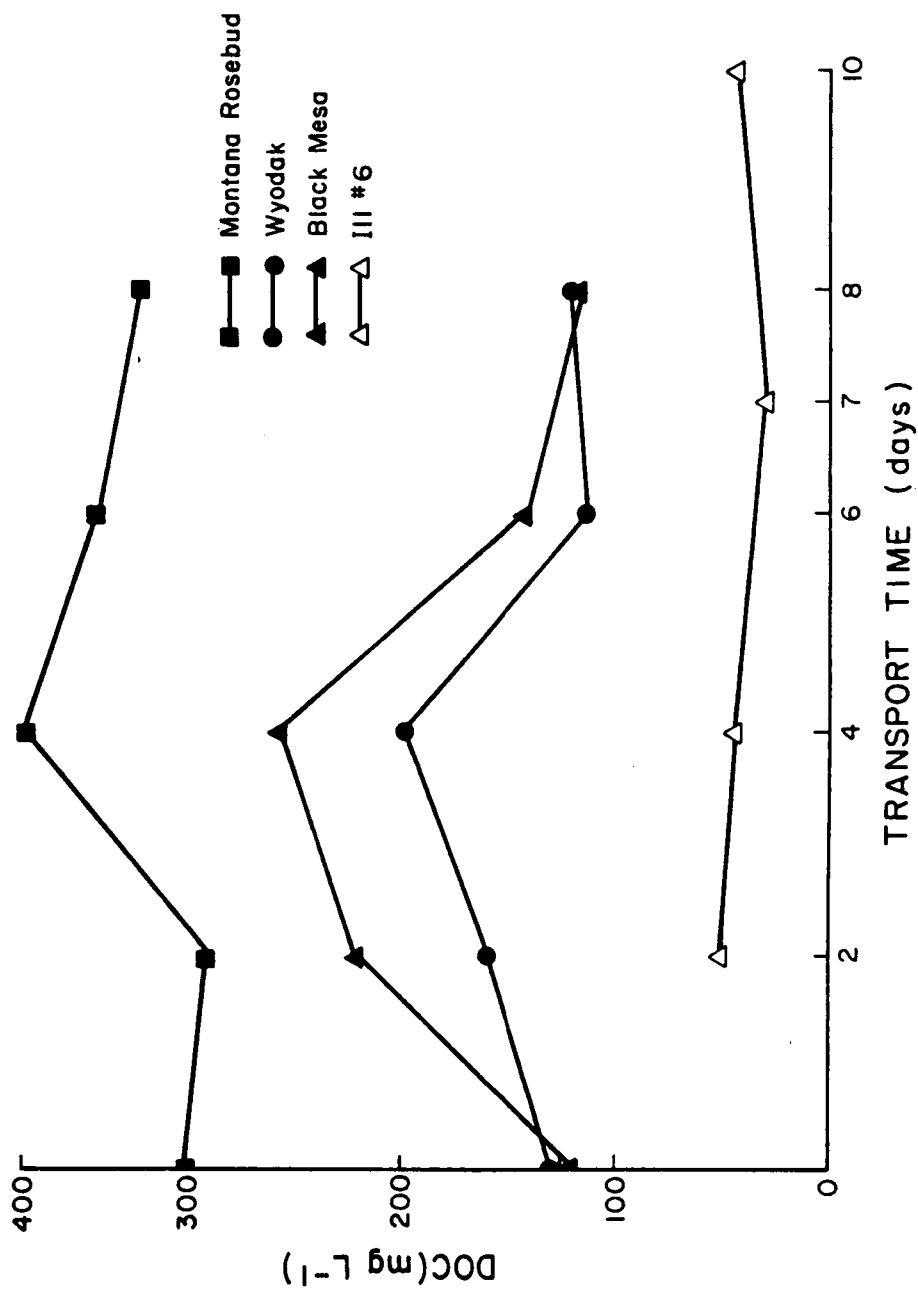


Figure 1. The effect of simulated transport time on coal slurry wastewater DOC.

coals. Slurry pH for the three western coals averaged 5.5 while the pH for the Ill #6 slurry was 2.0 during these experiments.

Coal Slurry pH Adjustment

Slurries generated at the Black Mesa pipeline are pH adjusted by means of coal blending in order to achieve a final pH of 7.2 prior to transport. The pH adjustment is necessary in order to avoid caking problems during water removal in the centrifugation process. It may be anticipated that coal slurries demonstrating acidic levels will be neutralized prior to transport. Because significant differences existed with respect to slurry pH and residual DOC levels for western and eastern coals, experiments were performed to examine the effect of increased pH on the leaching of DOC into residual slurry wastewaters. Data demonstrating the effect of pH on DOC levels generated from MRB and Pitt #8 simulated coal slurries are presented in Table 6. As indicated, pH adjustment of MRB slurries from 5.4 to 7.1 resulted in a net 10% increase in the leaching of soluble organic constituents. The alteration of Pitt #8 slurries from acidic to neutral conditions had no effect on slurry DOC loads. However, highly alkaline conditions (pH 12) caused a fivefold increase in wastewater DOC levels for this coal type.

Transport Water Effects

Comparative studies were undertaken to examine the influence of various transport media on DOC levels in coal slurry wastewaters.

Table 6. Effect of pH alteration on dissolved organic carbon levels in Montana Rosebud and Pittsburgh #8 coal slurry wastewater.

Coal Type	Initial pH	Final ^a pH	DOC mg C l ⁻¹
MRB	5.4 ^b	5.4	335
	7.1	6.9	370
Pittsburgh #8	2.0 ^b	2.0	29
	7.1	5.4	21-15
	12.1	9.9	125

^apH after 4 days of simulated transport.

^bpH of unadjusted slurries.

Lake water and sewage effluent were employed as transport media with doubly distilled water serving as a control. Wyodak, MRB and Black Mesa coals were formulated as slurries and subjected to simulated transport times of up to 10 days. The initial DOC value of the sewage effluent was 28 mg l^{-1} whereas both the distilled and lake water exhibited DOC levels of less than 1 mg l^{-1} . These results are presented in Figure 2. In all cases DOC concentrations in the residual transport water decreased over time for coal slurries formulated with clarified sewage effluent or lake water. The decrease in DOC levels was most pronounced for the Black Mesa slurries which demonstrated a 95% reduction in organic load in the sewage effluent sample and an overall 91% carbon removal rate for the lake water sample. Relative rates of carbon removal for Wyodak and MRB slurries were approximately equal for both sewage and lake water slurries. The sewage effluent slurries for both coal types exhibited a 37% reduction in carbon levels whereas the lake water slurries demonstrated an overall removal rate of 25% for the 10 day period.

Coal Slurry Dewatering Temperature

Coal slurries formulated with both Black Mesa and Wyodak coals were subjected to up to 8 days of simulated transport conditions and subsequently heated to 60°C for a period of 30 minutes prior to coal water separation via centrifugation. Slurries were kept in suspension through magnetic stirring and, at appropriate

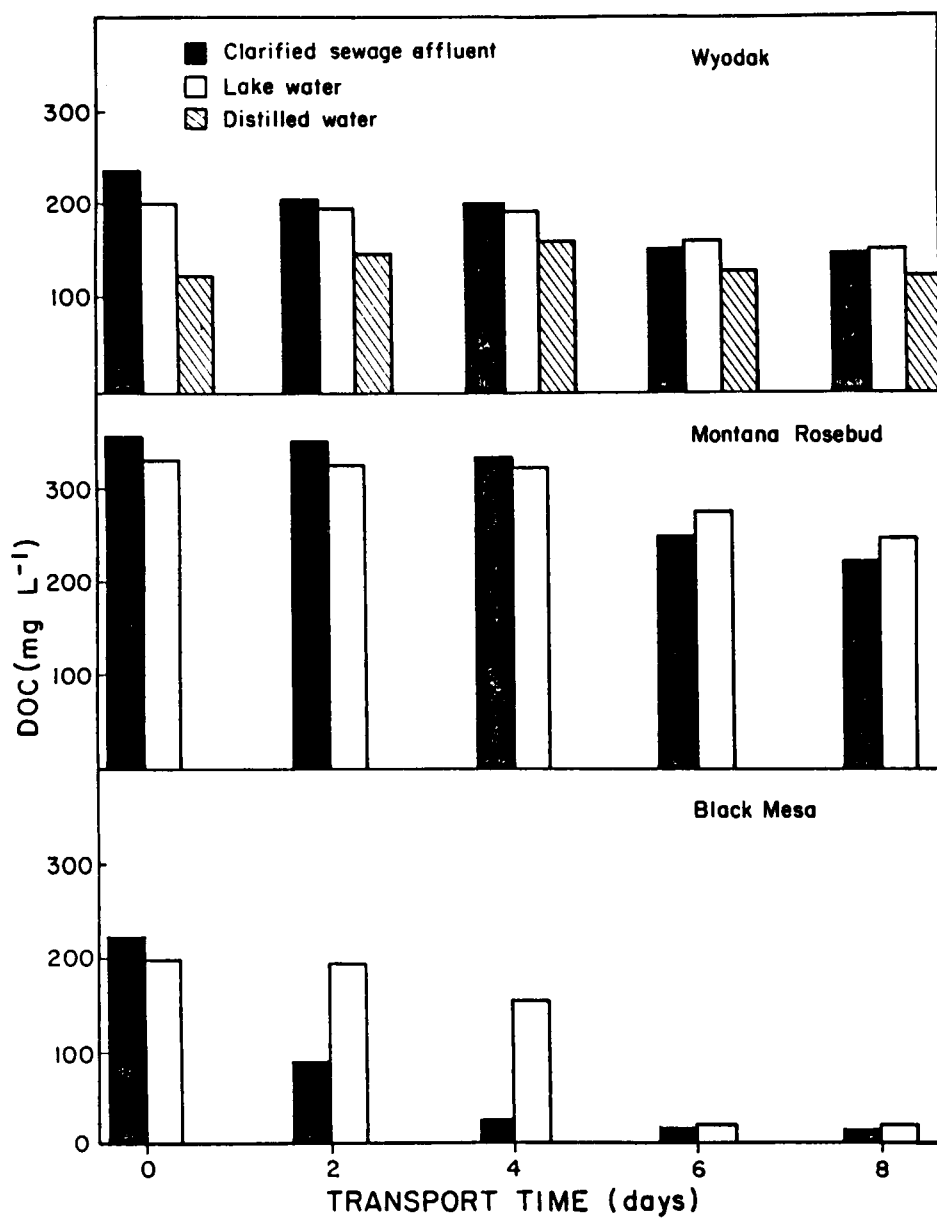


Figure 2. The effect of transport water on residual wastewater DOC levels.

time intervals, samples were withdrawn from the slurry for treatment and/or subsequent DOC analysis. The results of this study are presented in Table 7. Levels of DOC present in heat treated slurries increased relative to non-heat treated controls for both samples and over all points examined. A mean 2.5 fold increase in DOC levels over the 8 day period was observed for heat treated Black Mesa samples as compared to non-heated slurry controls. A mean 1.3 fold increase in DOC due to heating occurred for Wyodak coal slurries. However, the relative increase due to heating was observed to decrease with increasing simulated transport time. This result is not readily explained. These data do, however, demonstrate that slurry heating prior to coal separation will result in variable but elevated DOC loads in residual wastewaters.

Coal Storage Age

Data relating storage age of coal to resulting DOC levels generated from slurries formulated with laboratory aged coal are presented in Table 8. Ground coal samples were exposed to ambient laboratory conditions with temperatures in the range of 25-30°C over a 10 month period. All three coal samples used in these experiments were received from their place of shipment as freshly mined coal. Black Mesa I and Black Mesa II samples represent two separate shipments of coal received from the Black Mesa pipeline. As demonstrated in Table 8, a sevenfold increase in DOC levels was observed for aged Wyodak coals when compared to initial values.

Table 7. The effect of slurry dewatering temperature on residual wastewater DOC levels.

Coal Type	Simulated Transport Time (Days)				
	0	2	4	6	8
Black Mesa	24.1 ^a	25.8	34.0	52.3	41.6
Black Mesa (60°C)	70.8	65.2	86.7	59.6	55.8
Wyodak	141.6	168.4	85.4	85.7	77.5
Wyodak (60°C)	207.4	221.2	135.8	110.5	91.2

^aValues reported in mg l⁻¹.

Table 8. Effect of coal storage on slurry wastewater
DOC levels.

Storage Time (Months)	Wyodak	DOC mg l ⁻¹	
		Black Mesa I	Black Mesa II
1	20	25	15
2	71	65	33
3	81	--	--
6	110	--	--
10	144	130	--

An approximate five-fold increase in DOC concentrations was observed for Black Mesa I samples after 10 months of storage.

The results of these studies demonstrate that substantially higher DOC wastewater loads are present in western coal slurries when compared to Ill #6 and Pitt #8 eastern coal slurry mixtures. In addition the variability associated with western coal slurries was approximately three-fold higher as compared to eastern coal slurry samples. The studies relating physical/chemical variables to residual wastewater DOC loads indicate that transport water, slurry heating and coal storage age will be significant parameters regulating overall DOC levels in slurry wastewaters. Increasing coal storage age and slurry temperatures prior to coal water separation will lead to increasing DOC levels in residual wastewaters while the selection of the appropriate transport medium may contribute to overall reductions in residual wastewater DOC. Further experimentation was directed towards a qualitative characterization of organic constituents responsible for elevated DOC levels in these slurry wastewaters.

II. Characterization of DOC Present in Coal Slurry Wastewaters

Initial molecular weight characterization of Black Mesa pipeline and Wyodak concentrated (10:1) slurry wastewater organics using Sephadex G-75 gels resulted in minimal resolution of DOC constituents. Elution profiles for both wastewaters demonstrated

peaks, as monitored by DOC analysis, at the inclusion volume of the column. Sephadex G-25 gel with a nominal fractionation range between 5,000 and 1,000 apparent molecular size was then employed to achieve greater resolution of the slurry wastewater samples. Typical gel profiles on G-25 gels for Wyodak, MRB and Black Mesa samples are presented in Figure 3. Elution profiles for both Wyodak and MRB slurries demonstrate that the majority of fractionated organic constituents are lower molecular sized compounds. Greater than 90% of the fractionated DOC for both samples was observed to elute prior to the column inclusion volume which corresponds to an approximate molecular weight of 1,000. Elution patterns for Black Mesa pipeline DOC indicate a broader distribution of organic compounds is present in the pipeline wastewater sample. In addition, a sizeable fraction of the Black Mesa pipeline sample was observed to elute beyond the inclusion volume, indicating the occurrence of gel-solute interactions.

Ultrafiltration studies were conducted as an additional means of fractionating both laboratory prepared and Black Mesa pipeline wastewaters on the basis of apparent molecular size. Results from these experiments are presented in Figure 4. A mass balance of the organic materials present in the three size classes was performed by total organic carbon analysis. Recovery of the fractionated carbon ranged from 70% to 94%. These data indicate that, for both Wyodak and MRB laboratory prepared coal slurries, the majority of the organic contaminants in the resulting wastewater

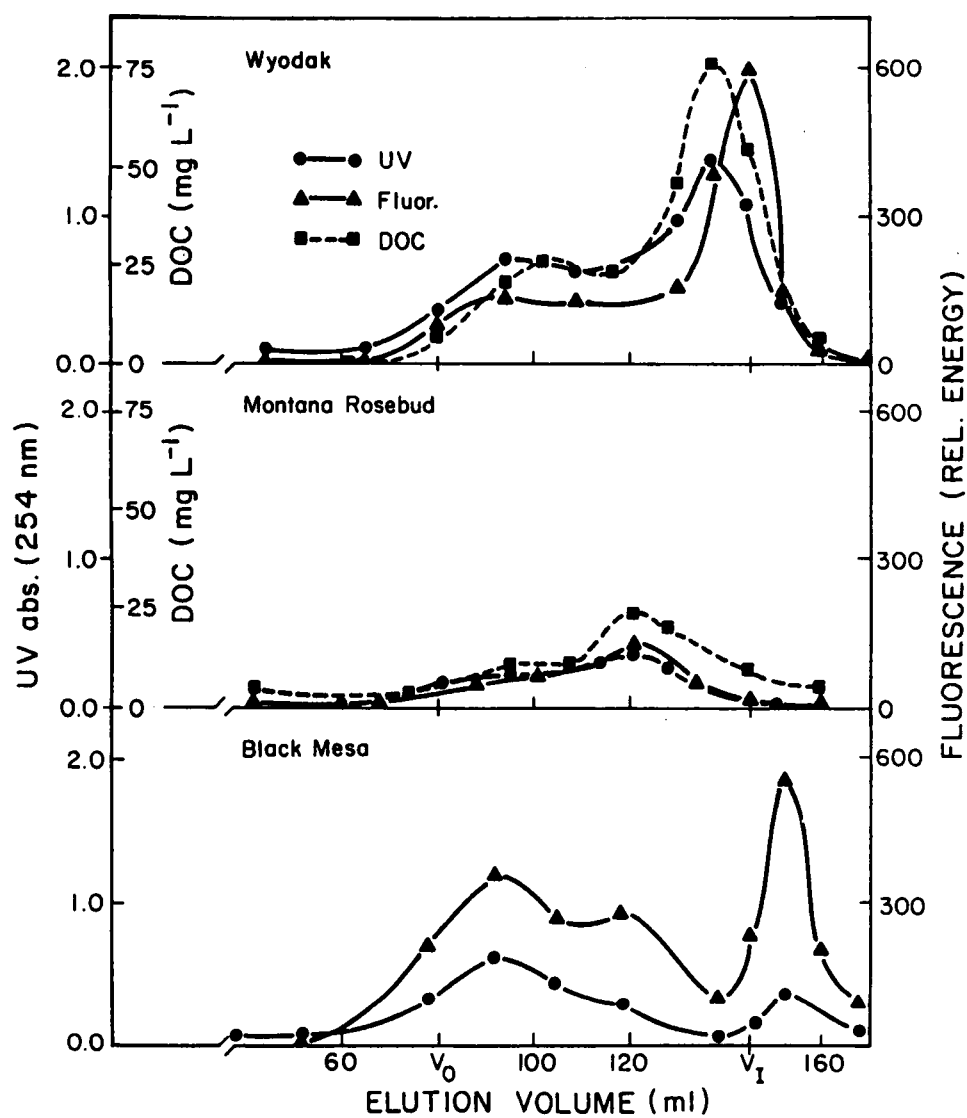


Figure 3. Sephadex 6-25 gel profiles of laboratory simulated Wyodak and MRB wastewaters and Black Mesa pipeline wastewaters.

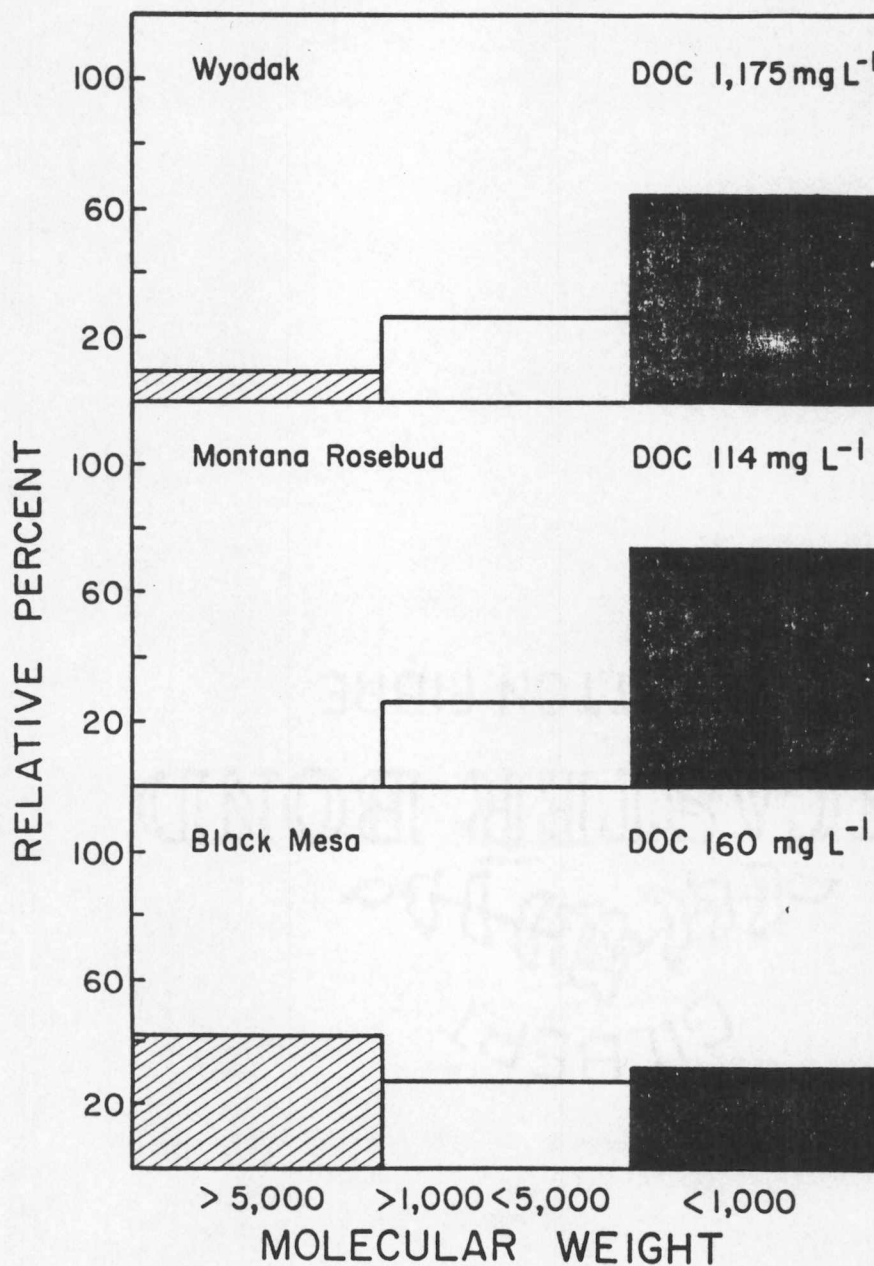


Figure 4. Ultrafiltration molecular weight distribution of the organic constituents in selected coal slurry wastewaters.

is comprised of compounds with molecular weights of 1,000 or less. For Wyodak samples, 62% of the DOC present in the slurry wastewater was comprised of compounds with molecular weights of 1,000 or less. MRB samples were characterized as having 74% of the total DOC present contained in the 1,000 or less category. Both Wyodak and MRB demonstrated approximately equivalent amounts of organic material which fractionate in the greater than 1,000 but less than 5,000 cutoff range. In this particular molecular weight category approximately 28% of the DOC present in Wyodak samples could be classified as intermediate in molecular weight, whereas for the MRB samples the value was approximately 26%. Organic constituents with molecular weights greater than 5,000 were not found in the MRB wastewater whereas this same size class accounted for 9% (on a mass carbon basis) of the total organic load in the Wyodak wastewater. Organic compounds present in the Black Mesa sample exhibited a more even distribution across the three size classes.

Additional fractionation studies were conducted in order to determine respective concentrations of humic and fulvic acid present in coal slurry wastewaters. Using XAD-8 resins as previously described, coal slurry wastewater samples were fractionated into three procedurally defined classes. Humic and fulvic acid classes are initially retained by the resin column with subsequent removal accomplished by base elution. Humic acids are then precipitated from solution at pH 1. The third class of organic compounds are not retained by the XAD resin and are

operationally defined as non-fulvic acids. Results from the fractionation of both laboratory prepared and Black Mesa coal slurry wastewaters are presented in Table 9. Data are presented as mean percent values with standard deviations where applicable. Humic acid content for all slurry wastewaters tested was found to be less than 1% and therefore was omitted as a subclass. As demonstrated in Table 9, fulvic acid content of slurry wastewaters is dependent upon coal type. For laboratory prepared coal slurry samples, Wyodak wastewaters were consistently found to contain fulvic acid concentrations approaching 50% while the majority of organic species present in MRB slurry wastewaters may be defined as non-fulvic in nature. Fractionation of Black Mesa pipeline wastewaters using XAD-8 resins revealed that the majority of organic compounds present in these samples may be classified as fulvic acid in origin.

III. Qualitative Characterization of DOC

Initial efforts designed to qualitatively determine coal slurry wastewater organic compounds focused on conventional solvent extraction techniques. GLC analyses of concentrated methylene chloride extracts derived from both Wyodak and MRB wastewaters demonstrated an absence of solvent extractable components as determined by this particular method. The liquid-liquid extraction technique developed by Natusch and Tomkins (82) for the isolation of polycyclic organic compounds was also employed to determine

Table 9. Distribution of fulvic acid and non-fulvic acid among western coals.

Coal Type	N	Fulvic Acid	Non-fulvic Acid
Wyodak	5	49.4 $\pm$ 5.0%	50.6 $\pm$ 5.7%
Black Mesa Pipeline	2	64.0 $\pm$ 1.4%	36.0 $\pm$ 1.4%
Montana Rosebud	1	31%	69%

N = Number of determinations.

if non-polar organic species were present in residual slurry wastewaters. This method as demonstrated by Natusch and Tomkins may be utilized to quantitatively remove non-polar constituents such as naphthalene, acenaphthylene and anthracene from aqueous systems with subsequent identification by GLC analysis. Attempts at removing organic species from Wyodak and MRB wastewaters amenable to analysis via the Natusch method proved unsuccessful. GLC analyses of concentrated cyclohexane extracts derived from Wyodak and MRB wastewaters revealed no additional peaks relative to those found in solvent controls. Following the unsuccessful attempts to isolate non-polar organic constituents present in coal slurry wastewaters by solvent extraction techniques, an alternative procedure for the isolation of solvent extractable materials was attempted. Initially a lyophilized non-fulvic acid sample derived from XAD fractionated Wyodak wastewaters was soxhlet extracted over a period of 24 hours. The methanol extract was then concentrated and chromatographed on a preparative HPLC unit. Using this procedure, six fractions representing resolvable peak components were collected. Approximately 20 injections were performed with successive collections of the fractionated peaks. Fractionated samples were then blown to dryness and analyzed using mass spectrometry. Electron impact spectra generated from these samples produced no clearly identifiable components or fragmentation patterns.

These studies suggested that non-polar organic species such as PAH compounds were not present at detectable levels in simulated

slurry wastewaters as determined by the previous analyses. However in order to more quantitatively assess this hypothesis, studies were undertaken to examine the fate of selected PAH additions to simulated coal slurry mixtures. Slurries made with Wyodak coal and double distilled water were dosed with ^{14}C -naphthalene, ^{14}C -benzo(a)pyrene or ^{14}C -phenanthrene. Labelled compounds in acetone were initially added to the water to give effective concentrations of 1.4 ppm, 27 ppb and 22.8 ppb for the three respective compounds. After 24 hours of simulated transport, slurries were centrifuged, filtered and aqueous samples counted for ^{14}C activity. The results of this experiment are presented in Table 10. The data demonstrate that greater than 99.8% of the labelled compounds added to the slurry mixtures are removed during the transport process. It is believed that sorption removal by coal surface sites is responsible for the disappearance of ^{14}C activity from solution.

The negative results generated from the previous experiments suggested that the organic components present in coal slurry wastewaters were not readily amenable to removal by solvent extraction techniques or sufficiently volatile to be quantified via GLC analysis. Efforts were then undertaken to enhance the volatility of slurry wastewater organic species through derivatization techniques, thus facilitating their removal from the wastewater matrix.

Derivatization Experiments

All derivatization experiments were conducted with XAD fractionated slurry wastewater samples. Initial studies employed

Table 10. Distribution and fate of selected polyaromatic hydrocarbons in coal slurry wastewaters.

PAH	(dpm)		% Removal
	Initial Slurry Count	Final Wastewater Count	
¹⁴ C-naphthalene	8.6×10^6	4.5×10^5	99.9%
¹⁴ C-benzo(a)pyrene	8.5×10^5	1.5×10^3	99.8%
¹⁴ C-phenanthrene	6.5×10^5	1.7×10^3	99.8%

the silylating reagent Sylon HTP and fulvic and non-fulvic acid samples derived from Wyodak coal slurry wastewaters. Results generated from the use of this derivatizing agent demonstrated an absence of volatile components as determined by GLC analysis. Attempts were then made to derivatize XAD fractionated wastewater organic species using methyl iodide as the active methylating agent. In these experiments basified fulvic and non-fulvic acid samples derived from Wyodak and Black Mesa pipeline coal slurry wastewaters were mixed with prescribed quantities of methyl iodide in THF. Using this derivatization method with subsequent GLC analyses, no volatile components were observed for any of the samples tested. The third derivatizing agent examined was diazomethane. Fulvic and non-fulvic acid samples from both Wyodak and Black Mesa pipeline wastewaters were subjected to derivatization using this method. Unlike previous derivatization experiments, oxidation of the organic constituents was performed using potassium permanganate prior to methylation. This method proved effective in producing substantial quantities of volatile methylated products. This result may most likely be attributed to the oxidation of the organic substrates and not necessarily the increased derivatizing efficiency of diazomethane relative to either Sylon HTP or methyl iodide. GLC tracings of Wyodak fulvic acid methylated degradation products revealed the presence of over 65 resolved peaks equally distributed among low, medium and high boiling components (temperature program 70-275°C at 8°C min⁻¹). Wyodak non-fulvic acid degradation products

generated a total of 14 resolved peaks when subjected to identical analysis. Black Mesa pipeline fulvic acid samples produced fewer than 10 peaks, all eluting with equal distribution across the temperature program, while the Black Mesa non-fulvic acid sample produced fewer than five component peaks, all of which eluted in the first 2 minutes of the program.

Further analysis of permanganate oxidized and diazomethane derivatized Wyodak and Black Mesa pipeline coal slurry wastewater organic compounds was accomplished using GC-MS techniques. Analyses were performed using equipment of the Department of Environmental Sciences and Engineering at the University of North Carolina, Chapel Hill. Interpretation of mass spectral data was based on spectral comparisons made with previously catalogued mass spectra generated from the analysis of aquatic humic and fulvic acid degradation products (64). Common fragment ion collections (75,105) were also found to be helpful in identifying compound classes. Compound standards were not run during these analyses. However 72% of the identified compounds were matched to spectra of standards run previously on the same instrument (64), thus increasing the level of confidence in spectral interpretation.

Reconstructed GC-MS total ion chromatograms of the analyzed samples are presented in Figures 5-11. Oxidized fulvic acid samples generated from Wyodak coals were found to generate the greatest number of degradation products as well as the broadest distribution of peaks. Figures 5 and 6 correspond to two separate Wyodak fulvic

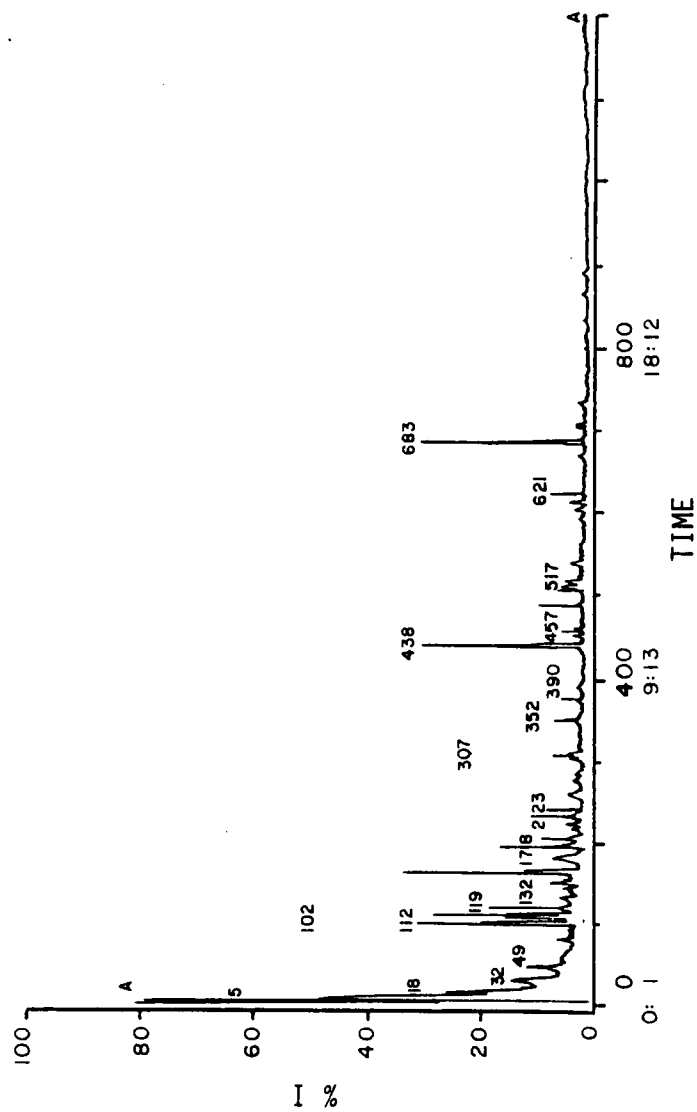


Figure 5. Reconstructed total ion chromatogram of Wyodak fulvic acid degradation products.

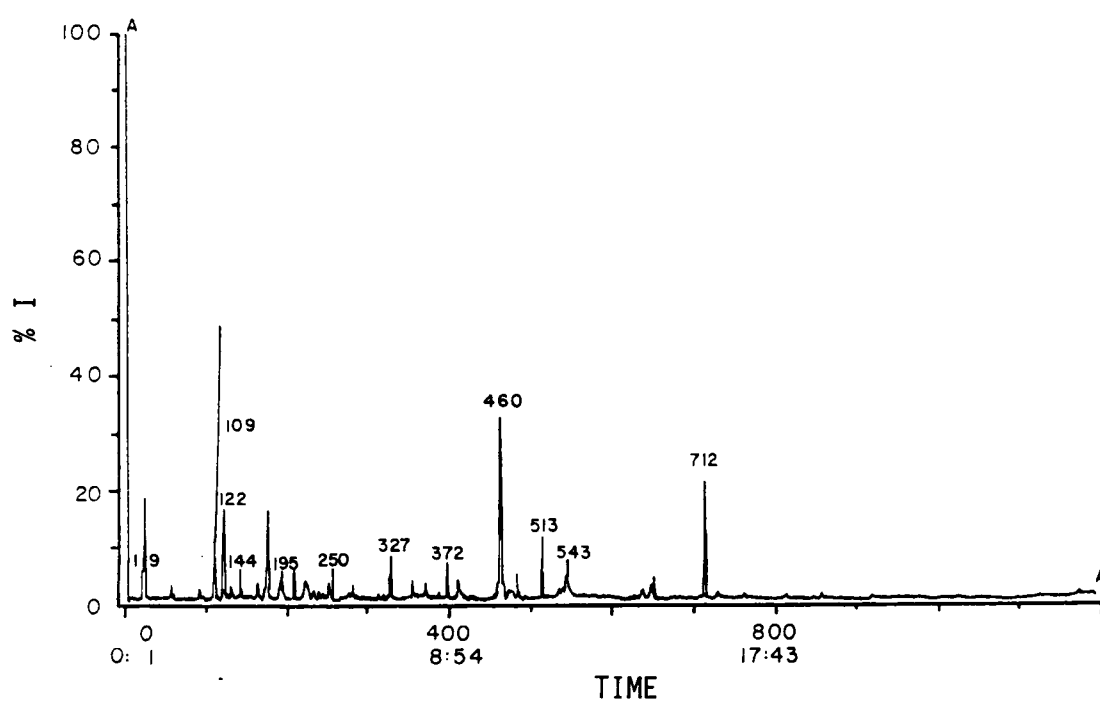


Figure 6. Reconstructed total ion chromatogram of an additional Wyodak fulvic acid sample.

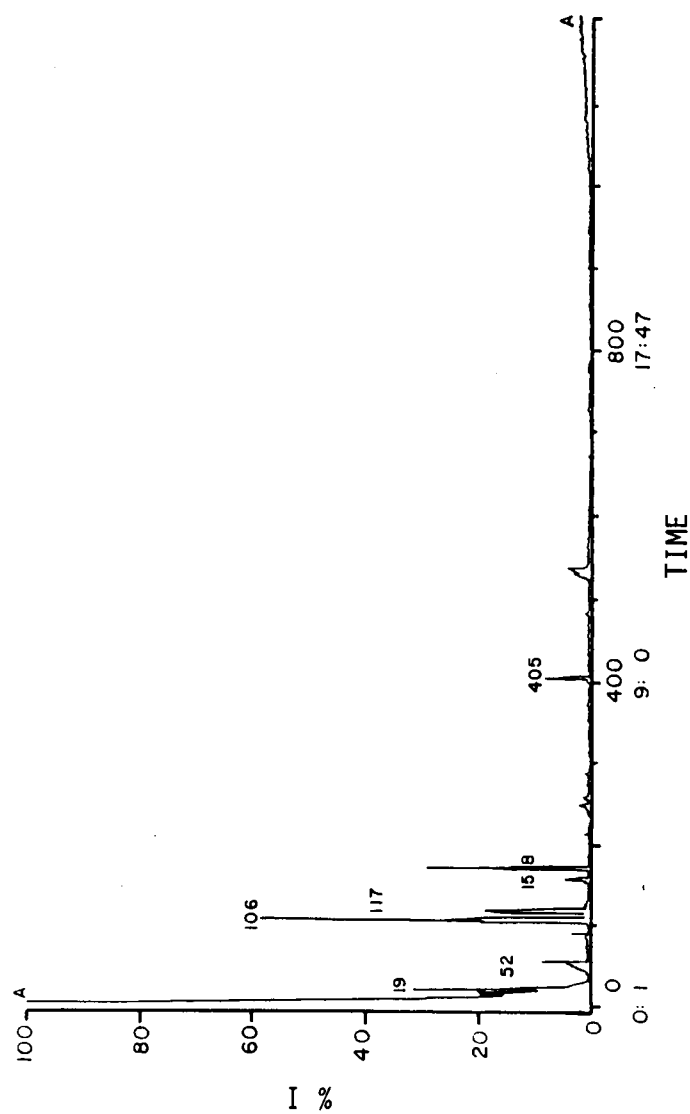


Figure 7. Reconstructed total ion chromatogram of Wyodak non-fulvic acid degradation products.

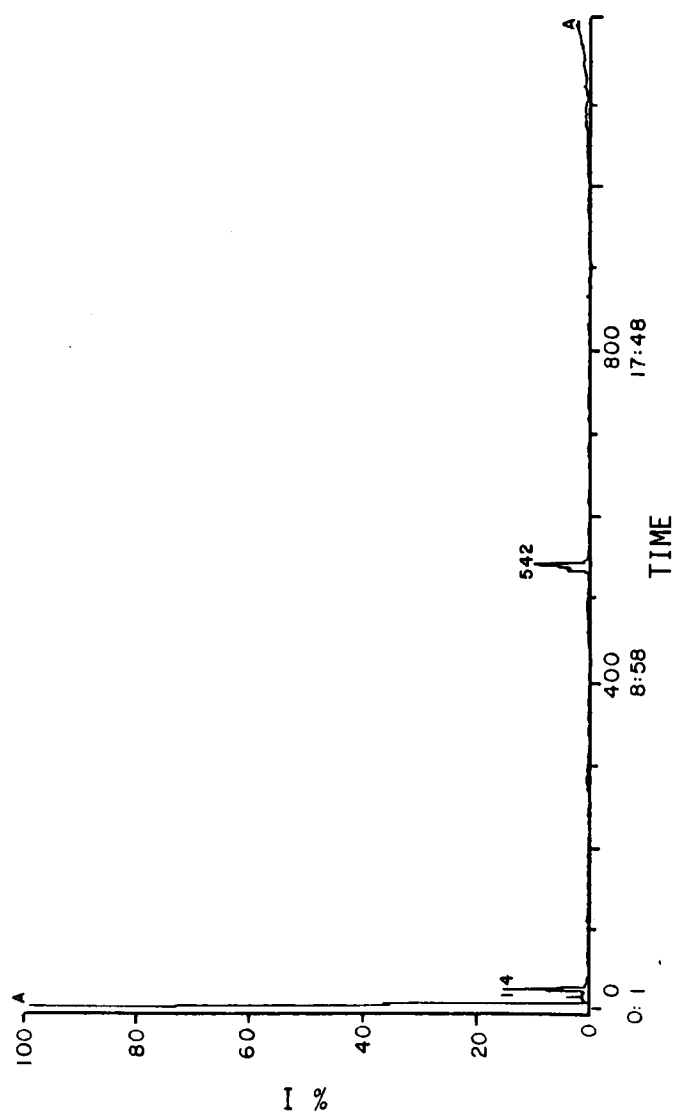


Figure 8. Reconstructed total ion chromatogram of Black Mesa fulvic acid degradation products.

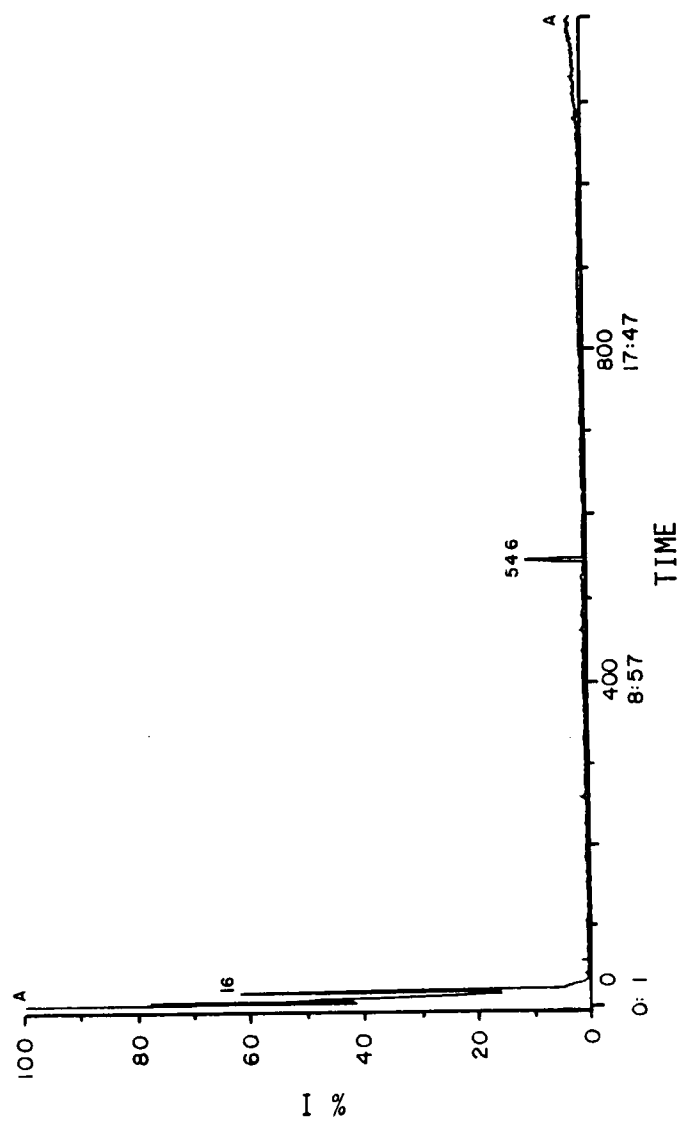


Figure 9. Reconstructed total ion chromatogram of Black Mesa non-fulvic acid degradation products.

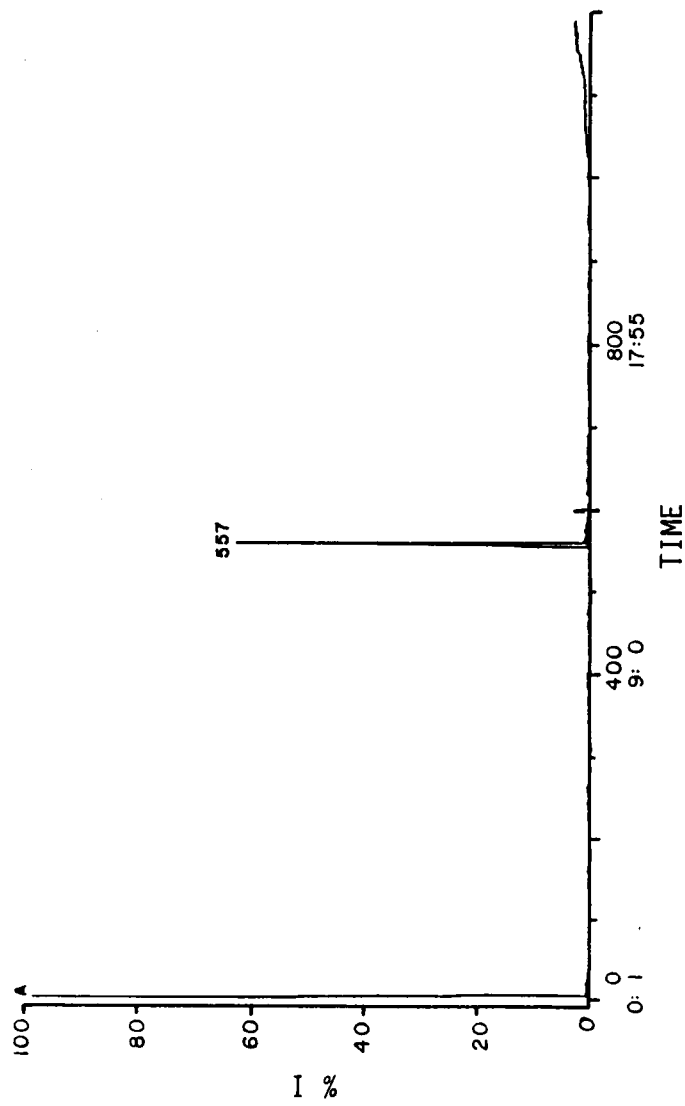


Figure 10. Reconstructed total ion chromatogram of XAD eluent control.

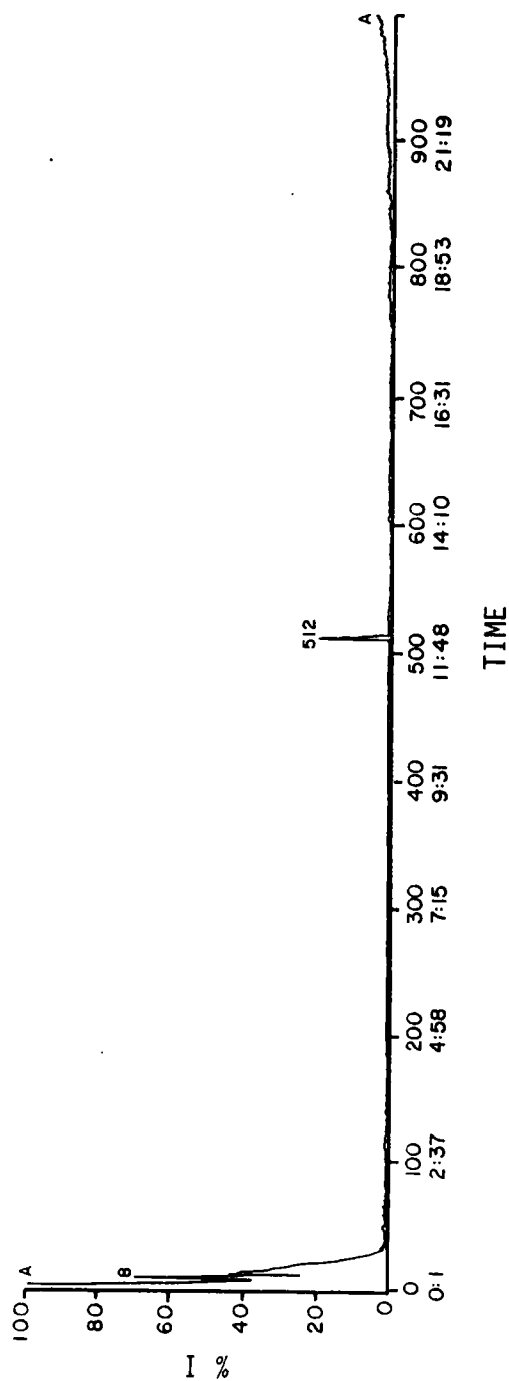


Figure 11. Reconstructed total ion chromatogram of XAD resin base eluent control.

acid samples subjected to oxidation and methylation. There is an excellent correspondence between the samples relative to both distribution and abundance of products. Degradation products generated from the non-fulvic acid Wyodak sample shown in Figure 7 are characterized by shorter retention times. As demonstrated in Figures 8 and 9, Black Mesa samples yielded chromatograms with few discernible peaks. The majority of the peaks present are due either to reagents or phthalate ester contamination (scan numbers 542 and 546). Phthalate ester contaminants were present in all samples, most notably in the reagent controls (Figure 10 scan number 557 and Figure 11 scan number 512).

Table 11 is a summary of the identified products generated from fractionated Wyodak and Black Mesa coal slurry wastewaters. Electron impact spectra of these compounds are presented in Appendix A. The compounds in Table 11 are listed in order of increasing elution time. As expected, there is a general correspondence with respect to elution profile and compound class. Aliphatic dibasic acid esters were observed to elute first. Compounds with intermediate retention times are the benzenecarboxylic and furan-carboxylic acid esters while the more heavily substituted benzene-carboxylic acid esters are characterized by the longest retention times. Degradation products generated from non-fulvic acids present in Wyodak coal slurry wastewaters were predominantly aliphatic in nature, while the only identifiable product present in Black Mesa samples was oxalic acid ester.

Table 11. Degradation products present in slurry wastewater samples.

Acid Esters	Scan #
<u>Wyodak Fulvic Acid--Figure 5</u>	
Oxalic acid dimethyl ester	32
Malonic acid dimethyl ester	49
Succinic acid dimethyl ester	102
Benzoic acid methyl ester	139
Glutaric acid dimethyl ester	164
Adipic acid dimethyl ester	178
Pimelic acid dimethyl ester	307
p-Methoxybenzoic acid methyl ester	352
Suberic acid dimethyl ester	375
Tricarballic acid trimethyl ester	390
1,2-Benzenedicarboxylic acid dimethyl ester	438
1,4-Benzenedicarboxylic acid dimethyl ester	450
Methylbenzenedicarboxylic acid dimethyl ester	489
Dimethyl furandicarboxylic dimethyl ester	507
Phthalate ester (contaminant)	517
Furantricarboxylic acid trimethyl ester	603
Methoxybenzenedicarboxylic acid dimethyl ester (isomer)	611
Methoxybenzenedicarboxylic acid dimethyl ester (isomer)	621
1,2,4-Benzenetricarboxylic acid trimethyl ester	683
1,2,3-Benzenetricarboxylic acid trimethyl ester	700
Methoxybenzenetricarboxylic acid trimethyl ester (isomer)	834
Benzenetetracarboxylic acid tetramethyl ester (isomer)	890
<u>Wyodak Non-fulvic Acid--Figure 7</u>	
Oxalic acid dimethyl ester	19
Malonic acid dimethyl ester	52
Succinic acid dimethyl ester	106
Glutaric acid dimethyl ester	171
Tricarballic acid trimethyl ester	405
Phthalate esters (contaminants)	525-530
1,2,3-Benzenetricarboxylic acid trimethyl ester	725
<u>Black Mesa Fulvic Acid--Figure 8</u>	
Oxalic acid dimethyl ester	23
Phthalate ester (contaminant)	542
<u>Black Mesa Non-fulvic Acid--Figure 9</u>	
Oxalic acid dimethyl ester	25
Phthalate ester (contaminant)	546

Degradation products generated from Wyodak wastewater organic species can be grouped into five compound classes. Depicted in Figure 12 are the following categories: A) benzenecarboxylic acid esters, B) methoxybenzenecarboxylic acid esters, C) furancarboxylic acid esters, D) aliphatic dibasic acid esters and E) aliphatic tribasic acid esters. The abundance of each of these classes relative to identified Wyodak fulvic acid degradation products is presented in Table 12. Collectively the benzenecarboxylic acid esters and substituted esters are predominant in terms of the numbers of products formed. Aliphatic dibasic acid esters were also observed to be major products. Minor degradation products identified were the furancarboxylic and aliphatic tribasic acid esters.

As demonstrated by the previously described characterization studies of both pipeline and laboratory generated coal slurry wastewaters, organic species leaching into coal slurry wastewaters are predominantly polar organic constituents with broad molecular weight ranges varying substantially with coal type. As determined by the various extraction procedures used during the course of this investigation, non-polar materials such as PAH were not present at detectable levels in the samples tested. Using an operationally defined fractionation procedure to quantitate humic/fulvic content of slurry wastewaters it was determined that 49% and 31% of the organic constituents present in Wyodak and MRB laboratory generated slurry wastewaters may be classified as fulvic acids while 64% of the organic constituents found in Black Mesa pipeline wastewaters

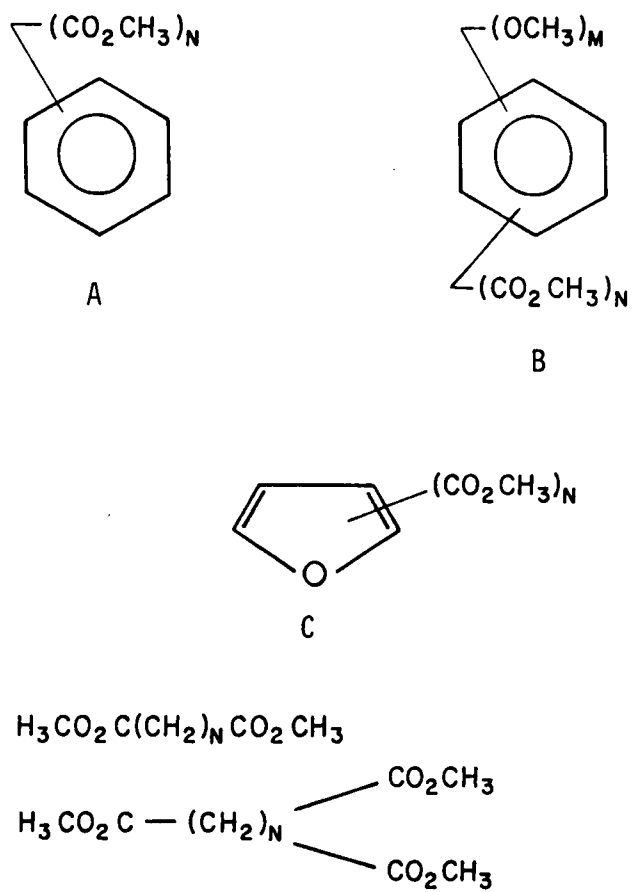


Figure 12. Compound classes represented in Wyodak fulvic acid degradation products.

Table 12. Relative abundance of compound classes present in oxidized and methylated Wyodak Fulvic Acid samples.

Compound Classes	Relative Percent
Benzenecarboxylic acid esters	30
Methoxybenzenecarboxylic acid esters	20
Furancarboxylic acid esters	10
Aliphatic dibasic acid esters	35
Aliphatic tribasic acid esters	5

were fulvic acid in nature. Humic acids were present in concentrations of less than 1% for all samples tested. Qualitative identification of oxidized and derivatized slurry organic species revealed the presence of five distinct compound classes, the most predominant being benzenecarboxylic and aliphatic dibasic acid esters.

Because fulvic acids represented a significant fraction of slurry wastewater DOC and because these compounds are known trihalomethane (THM) precursors in the presence of chlorine, additional studies were conducted in order to evaluate the potential for slurry wastewaters to serve as THM precursors upon chlorination.

IV. Chlorination of Coal Slurry Wastewaters

Chlorination studies were performed with the specific objective of determining whether organic constituents in coal slurry wastewaters may serve as precursors for the formation of THM when subjected to chlorination. Secondary objectives were to determine the qualitative fraction of the organic pool responsible for THM production. Initial studies focused on overall THM production generated from the chlorination of laboratory generated coal slurry wastewaters.

Trihalomethane formation potential (THMFP) of four chlorinated coal slurry wastewaters is presented in Table 13. Chloroform was the only THM detected in these samples; thus the results are presented as $\mu\text{mole CHCl}_3$ and normalized on a per milligram carbon

Table 13. THM production generated in three western sub-bituminous coal slurry wastewaters.

Sample	Undiluted DOC mg l ⁻¹	R _{xn} pH	THM in μ moles/mg C		
			24 Hrs.	48 Hrs.	96 Hrs.
Wyodak ^a					
Slurry 1	180	11.4	0.25	0.33	0.40 $\pm$.007
Slurry 2	130	7.5	0.20 $\pm$.002	-	0.29 $\pm$.009
Slurry 3	153	6.9	0.15 $\pm$.01	0.22 $\pm$.01	0.24 $\pm$.03
Montana Rosebud ^a					
Slurry 1	160	10.4	0.12 $\pm$.007	0.12 $\pm$.02	0.16 $\pm$.01
Slurry 2	144	7.2	0.13 $\pm$.03	0.13 $\pm$.004	0.14 $\pm$.01
Slurry 3	119	6.5	0.07 $\pm$.004	0.08 $\pm$.01	0.12 $\pm$.01
Black Mesa ^a					
Slurry 1	130	9.4	0.09 $\pm$.008	0.16 $\pm$.01	0.15 $\pm$.03
Slurry 2	15	6.9	0.25 $\pm$.009	0.35 $\pm$.03	0.45 $\pm$.06
Slurry 3	33	7.1	0.26 $\pm$.001	0.27 $\pm$.01	0.31 $\pm$.02
Black Mesa ^b					
Pipeline Centrate	48	7.0	-	-	0.59 $\pm$.04

^aAll laboratory prepared slurry systems prepared from the same coal batch except Black Mesa, where slurry 1 was prepared from a coal sample one year older than coal used from slurry 2 and slurry 3.

^bReal pipeline field sample taken after coal separation via centrifugation.

basis. The data represent THMFP for diluted slurry samples. Total THM production for individual slurries may be obtained by multiplying undiluted DOC values by diluted THM concentrations. Black Mesa pipeline centrate was observed to produce the largest concentration of THM after 96 hours of reaction time. On average for the laboratory prepared slurries, THMFP was seen to be greatest for Wyodak coal slurries followed by Black Mesa simulated slurries. Considerable variability is noted both within and among coal types relative to THMFP. Variation among Black Mesa slurries may be partly explained by the fact that two separate shipments of coal from the Black Mesa pipeline were used in the generation of the slurries. In addition, variability within coal types may likely have been influenced by the fact that pH was not controlled during these initial experiments.

Additional chlorination studies were conducted on fractionated fulvic and non-fulvic acid slurry samples. Isolated fractions were chlorinated to determine whether a relationship existed between THM production and fulvic acid content of slurry wastewater. Samples were pH adjusted to 7.0 prior to incubation for these experiments. The results of this study are presented in Figure 13. As demonstrated in this figure, fulvic acids isolated from Wyodak wastewaters are seen to be the predominant THM precursors after 96 hours of reaction time (0.33 vs. $0.12 \mu\text{mole CHCl}_3 \text{ mg}^{-1} \text{ C}$). This experiment was repeated using Black Mesa centrate samples with additional fractionation of the fulvic acid components. Using

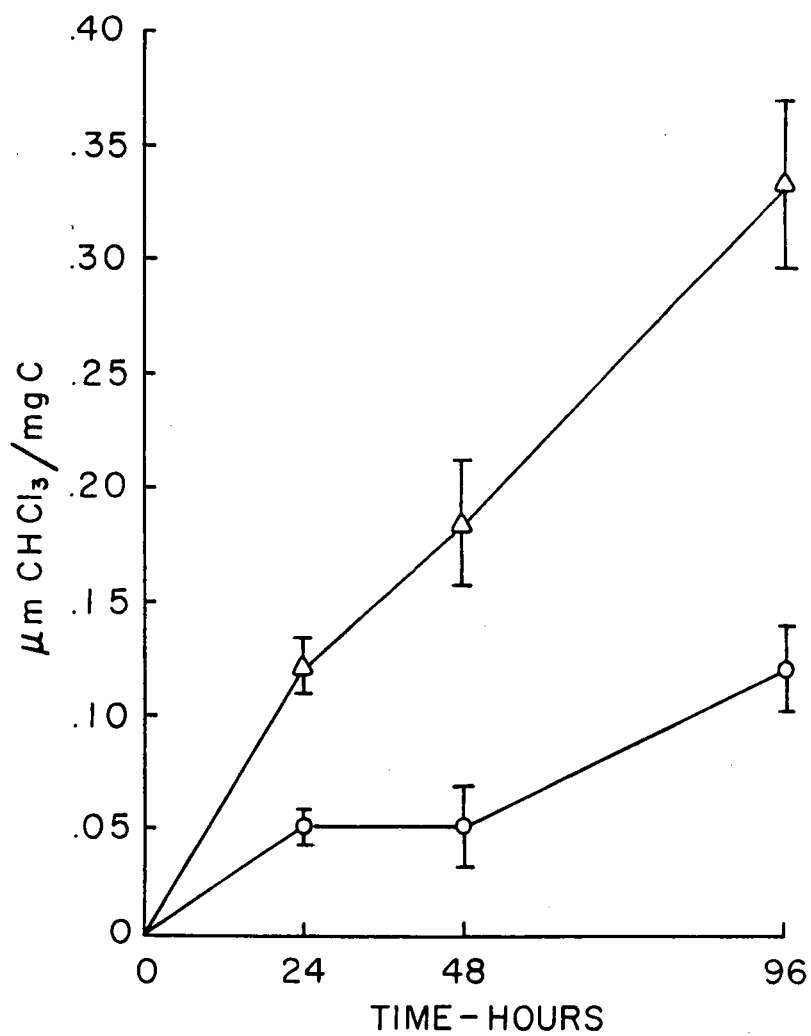


Figure 13. The production of chloroform in fractionated Wyodak coal slurry wastewaters. o = Wyodak non-fulvic fraction; Δ = Wyodak fulvic fraction.

ultrafiltration techniques, isolated fulvic acid samples were separated into less than and greater than 1,000 MW classes. Chlorination results from these samples are presented in Table 14. For the Black Mesa samples all THM production is represented by the fulvic acid component. Total THMFP for fractionated fulvic acid Black Mesa samples is seen to be twice that of Wyodak fulvic acids (0.79 vs. 0.33 $\mu\text{mole CHCl}_3 \text{ mg}^{-1} \text{ C}$, respectively). Analysis of THM production in Black Mesa pipeline chlorinated molecular weight fractionated-samples demonstrate that the less than 1,000 MW fulvic acids produce three times as much THM relative to the greater than 1,000 MW fulvic acid samples.

The results of these investigations demonstrate that chlorination of coal slurry wastewaters will result in the formation of THM. Total production of THM was variable with respect to coal type. Differences in THMFP likely reflect the broad spectrum of THM precursors present in coal matrices that may leach into waters during slurry transport. Fulvic acids leached during the slurry process were found to be the predominant THM precursors in chlorinated Wyodak slurry wastewaters and the exclusive THM precursors in chlorinated Black Mesa pipeline wastewaters.

V. Mutagenicity Assessment of Coal Slurry Wastewaters

In order to gain a more comprehensive understanding of the potential environmental hazards associated with coal slurry wastewater release, an assessment of their biological activity was made.

Table 14. Production of THM in fractionated and non-fractionated Black Mesa pipeline wastewaters.

Sample	Reaction Time	$\mu\text{Moles CHCl}_3/\text{mg Carbon}$	DOC	pH
BMPW Fulvic Acids	96	$0.79 \pm .08$	4.5	7.0
BMPW Non-Fulvic Acids	96	n.d.*	5.0	7.0
BMPW Fulvic Acids < 1,000 MW	96	$1.38 \pm .06$	4.0	7.0
BMPW Fulvic Acids > 1,000 MW	96	$0.62 \pm .06$	7.4	7.0

*n.d. = none detected.

Previous experiments during the course of this investigation demonstrated an absence of carcinogenic PAH compounds in slurry wastewaters; however, chlorination of selected wastewaters was found to produce measurable quantities of carcinogenic THM. These findings warranted additional studies of the potential biological effects associated with the release of both raw and chlorinated coal slurry wastewaters.

Initial testing was performed with the use of the standard plate Salmonella mutagenesis assay developed by Ames et al. (3). A positive response in the Ames assay is conditional upon a linear dose response relationship between the concentration of compound or compounds added and the number of revertant colonies formed. A minimum two-fold increase in induced revertant numbers relative to spontaneous revertant numbers (negative controls) is an additional criterion that must be demonstrated for a result to be judged positive via the assay. Prior to testing Wyodak, MRB and Black Mesa wastewaters were concentrated 10:1 via rotary evaporation. Data generated from this experiment are presented in Table 15. Mutagenic response generated in test plates was not significantly different than that noted for controls. This observation was true for tests performed both with and without S-9 enzyme addition. These results indicate that under the conditions employed, no mutagenic activity could be detected in concentrated 10:1 coal slurry wastewaters. DOC values for a typical Wyodak concentrate tested during the study were on the order of 1,400 mg l⁻¹. This represents a maximum dose

Table 15. Mutagenicity evaluation of coal slurry concentrates using the Ames Assay.

Coal Type	Dose Range (μl)	Salmonella typhimurium			His+ Revertants		
		S-9a	TA-97	TA-100	S-9a	TA-97	TA-100
Wyodak	0 (Control)	+	140	38	91	145	24
	50	+	170	28	107	156	32
	100	+	172	26	98	119	36
	200	+	169	20	103	147	29
	250	+	173	21	88	153	25
Montana Rosebud	0 (Control)	+	207	--- ^b	---	96	20
	50	+	203	---	99	98	18
	100	+	228	---	94	151	21
	200	+	192	---	98	145	31
	250	+	229	---	---	150	20
Black Mesa	0 (Control)	+	---	20	125	---	27
	50	+	---	31	121	---	17
	100	+	---	18	122	---	16
	200	+	---	---	116	---	---
	250	+	---	19	117	---	13

^aIndicates microsomal activation, Aroclor 1254 induced rat liver.

^bNot determined.

(250 μ l) of 0.35 mg of organic carbon per plate, the majority being non-volatile fulvic acids. For weak mutagen detection, greater concentrations of carbon present in slurry wastewaters may be necessary. Therefore further studies were conducted using Wyodak and Black Mesa wastewaters which were concentrated by a factor of 25 prior to Ames testing. Salmonella strains TA-97 and TA-98 were dosed with 0.250 μ l of these concentrated wastewaters both in the presence and absence of S-9 microsomal enzymes. Black Mesa and Wyodak wastewater concentrates produced a toxic response in both strains. In order to avoid toxic stresses on the tester strains due to increasing concentration factors, the fluctuation assay as described by Levin (62) was employed for further mutagenesis testing of both Black Mesa pipeline and MRB slurry wastewaters. The sample matrix included, unconcentrated, concentrated 25:1 and concentrated chlorinated wastewaters. The results of these experiments are presented in Tables 16-18. A lack of mutagenic response was noted for all samples at all dose levels employed. As demonstrated by the data, no substantial differences in revertant numbers were found among sample treatments relative to controls.

Table 16. Mutagenic response of strain TA-98 to unconcentrated Black Mesa pipeline and MRB laboratory generated wastewaters.

Dose μ l/Well	Positive Response			
	Black Mesa		MRB	
	TA-98	TA-98 + S-9	TA-98	TA-98 + S-9
0	18	29	13	23
10	0	3	15	23
20	2	5	9	27
100	11	19	32	25
200	29	32	16	30

Table 17. Mutagenic response of strain TA-98 to concentrated (25:1) Black Mesa pipeline and MRB laboratory generated wastewaters.

Dose μ l/Well	Positive Response			
	Black Mesa		MRB	
	TA-98	TA-98 + S-9	TA-98	TA-98 + S-9
0	18	29	13	23
1	0	0	19	26
5	0	2	15	17
8	0	9	12	20
10	9	15	9	20

Table 18. Mutagenic response of strain TA-98 to concentrated and chlorinated coal slurry wastewaters.

Wastewater Sample	Dose μ l/well	Positive Response	
		TA-98	TA-98 + S-9
MRB + HOCl	0	22	18
	1	28	16
	5	24	20
	8	19	17
	10	21	17
MRB HOCl control	0	16	18
	1	20	23
	5	13	24
	8	7	12
	10	12	12
Black Mesa HOCl	0	22	18
	1	21	10
	5	21	13
	8	16	15
	10	23	14
Black Mesa HOCl control	0	16	18
	1	13	22
	5	18	17
	8	7	13
	10	7	13

VI. DISCUSSION

The examination of various coal types used during the generation of bench scale coal slurry mixtures revealed that DOC levels for western coals on average were two to five times greater than those found for eastern coals. In addition the variability associated with DOC release from western coals was approximately three times greater as compared to DOC variability associated with the eastern coal slurries examined. Table 19 summarizes both the range and standard deviation associated with three western coals examined during the course of this investigation. The observed variability associated with western coal DOC levels may be inherent to the coals tested and thus make generalizations concerning an average DOC load for a given coal slurry process tenuous at best. Reports of DOC ranges within a given coal type are not present in the literature; however, previous studies have demonstrated wide variations among coal types with DOC values ranging from less than 25 mg^{-1} for Montana Rosebud coals (93), to 387 mg^{-1} for slurries generated from Wyodak coals (54).

Studies relating the length of transport time to residual DOC wastewater concentrations demonstrated that distilled water based slurries exhibited variations in DOC within a given run but levels were not seen to vary significantly between initial and final times. The increases in DOC levels (Figure 1, page 55) at day 4 may have been generated by increasing total coal surface

Table 19. Variability of dissolved organic carbon values present in western coal slurry wastewaters.

Coal Type	Number of Samples	Dissolved Organic Carbon (mg l ⁻¹)	
		Mean Value ± Standard Deviation	Range
Wyodak	30	153.2 ± 40.8	93 - 298
Montana Rosebud ^a	15	175.8 ± 110.9	25 - 324
Black Mesa ^a	16	99.2 ± 66.5	15 - 220

^aTwo separate shipments of Montana Rosebud and Black Mesa coal were used in the generation of these values.

area due to abrasion during simulated slurry transport. Observed DOC declines were likely due to readsorption phenomena. Peavy (93), examining the effects of simulated transport time on MRB slurry DOC concentrations, found little difference between initial and final DOC levels for this coal type after 12 days of simulated transport. Similarly, Moore (80) reported little variation in COD through time for Kansas and Illinois coals exposed to 8 days of simulated transport. These findings suggest that water extractable organic components present in coal are readily leached during the slurry process. Thus, increasing slurry transport time will not result in significantly increased residual wastewater DOC concentrations.

The pH of coal slurries will be expected to vary with the type of coal used in the slurry process, the result of relative oxidized pyrite content of the coal. Handling and storage of mined coal in an oxidizing environment prior to slurry formulation will facilitate the oxidation of pyritic materials present in the coal and in turn promote acidic conditions during slurry transport (33). In addition, the majority of leachable organic constituents in slurry systems are polar molecules containing ionizable moieties; thus pH will be an important variable in regulating DOC loads in slurry wastewaters. Increasing the pH of Pitt #8 slurries to highly alkaline conditions resulted in an approximate fivefold increase in slurry DOC loads. Similarly Peavy (93) found that increasing MRB slurries from pH 8 to pH 10 resulted in a net eightfold increase

in DOC levels for this wastewater. The pH of western coal simulated slurries examined throughout the course of this investigation ranged from 4.8-7.5 while Black Mesa pipeline centrate waters had an average pH of 8.0, which is partially controlled by coal blending. For the eastern coals Ill #6 and Pitt #8, the average slurry pH was 2.0. The low pH values recorded for the eastern coal samples are most probably due to pyrite oxidation which produces highly acidic conditions through the formation of sulfuric acid. Both coals were mined in 1978 and subsequently stored under aerobic conditions. Coal slurries generated with freshly mined Illinois coals have been reported to have an average pH of 7.2 (80).

It is anticipated that in western states where high quality water resources are scarce, low quality water, such as saline or wastewater effluent, may be used as transport media for coal slurry pipelines. Pronounced reductions in residual coal slurry wastewater DOC levels were demonstrated (Figure 2, page 59) using both sewage wastewater effluent and lake waters. Relative to the distilled water based coal slurry, all lake water and sewage effluent slurries exhibited an overall reduction in DOC levels over time. The most significant reduction occurred with the Black Mesa slurries where a greater than 90% removal was observed for Wyodak and MRB slurries. An average 30% removal was demonstrated by both sewage and lake water slurries for both coal types. Corroborating studies by Moore (80) demonstrated COD reductions of up to 40 mg l^{-1} day $^{-1}$ for Wyodak coal slurries formulated with municipal sewage

effluents. Similarly, Anderson et al. (7) examined coal slurries generated with Wasatch coals and sewage effluents and found initial slurry COD levels of 83 mg l^{-1} , while final slurry wastewater COD concentrations were negligible. Given the fact that significant reductions in DOC levels occurred in the presence of slurry waters containing high microbial biomass, it is probable that the observed diminution in carbon loads resulted directly from microbially mediated processes.

Studies examining the effects of elevated temperatures on slurry DOC levels demonstrated substantial increases in DOC concentrations due to heat treatment. The results suggest temperature dependent solubilities for some portion of the leachable organic constituents present in coal matrices. Operating experience at the Black Mesa pipeline has revealed that an approximate 30% increase in clariflocculating additives is needed to treat heated centrate wastewaters relative to non-heated slurry centrate waters (26). Thus while facilitating the coal-water separation process, it may be anticipated that slurry systems employing slurry heating will have to contend with elevated DOC levels in residual wastewaters.

An additional physical/chemical parameter found to impact wastewater DOC loads was coal storage age (Table 8, page 62). Slurry wastewater DOC concentrations increased steadily with increasing storage periods. Plummer and Jordan (95) observed a similar response with Jacobs Ranch coals stored over a 12 month

period in an aerobic environment. These results are interpreted as progressive spontaneous oxidation of the coal during storage resulting in a net increase of oxidized surface molecules capable of leaching into coal slurry transport waters.

I. Characterization of Wastewater DOC

The results obtained from the molecular weight characterization studies demonstrate that, for laboratory simulated slurries, DOC present in the slurry wastewaters is primarily comprised of compounds with molecular weights of 1,000 MW and less. In general there is a good correlation between the results generated by gel chromatography and the ultrafiltration studies. Both techniques demonstrate that simulated slurries differ from Black Mesa pipeline wastewaters in that higher molecular weight species predominate in the later while they constitute relatively little of the total organic load in the former samples. This difference may possibly be attributed to bacterially mediated processes. Black Mesa slurries contain a relatively stable microbial biomass prior to and during slurry transport. In contrast, laboratory generated slurries formulated with distilled water have very low bacterial densities. Previous studies examining the biological oxidation of coal slurry wastewater organic compounds have demonstrated that low molecular weight species removed are preferentially from slurry wastewaters while higher molecular weight species remain relatively unaffected (100,104). Thus it is probable that the reduced amounts

of low molecular weight species in the Black Mesa sample relative to the simulated slurries are a result of biologically mediated removal.

Experiments employed to assess humic/fulvic acid concentrations of coal slurry wastewaters demonstrated that fulvic acids represent a significant fraction of the organic load present in both laboratory and pipeline generated wastewaters. Fulvic acids are polyelectrolytic biopolymers with high charge densities and high surface areas (88). These chemical properties may make removal of these compounds by normal flocculation and/or adsorption methods difficult in waste treatment processes (88). In terms of pollution control the reactivity of these polymers towards metal complexation may present additional problems. Fulvic acids are known to concentrate selected alkaline earth and transition metals. Studies of sediment derived humic and fulvic acids have demonstrated sequestration of selected metals such as Cu, Fe, Pb, Ni, and Cr (85). In addition fulvic acids have also been found to preferentially bind to dialkyl phthalates (72), DDT (118), and tetrachlorobiphenyl molecules (45), thus increasing the mobility of these pollutants in aquatic systems. Hydrophobic compounds, if leached during the slurry transport process, may potentially partition with fulvic acids present in solution thus, in effect, solubilizing these species.

Solvent extraction studies of simulated coal slurry wastewaters as employed during the course of this investigation

demonstrated an absence of non-polar solvent extractable materials. In contrast to these findings, Anderson et al. (7) have reported the presence of alkyl substituted naphthalenes at the ppb level in benzene extracts of coal slurries formulated with freshly mined Wasatch coals and distilled water. This discrepancy may be related to differences in coal type or possibly choice of solvents used in the extraction process. Alternatively the possibility exists that non-polar materials, if leached into MRB and Wyodak wastewaters, could hydrophobically bind to fulvic acids and thus be rendered non-extractable by organic solvents. Previous research (51,92) has demonstrated that certain environmental pollutants, in particular aromatic amines, may covalently bond to humic materials. Both Wyodak and MRB wastewaters used during these studies exhibited DOC levels in excess of 100 mg^{-1} while Wasatch coal slurries generated wastewater TOC levels of less than 10 mg^{-1} . Labelled PAH addition studies however explained the absence of phenanthrene, benzo(a)pyrene and naphthalene in residual wastewaters. The addition of PAH compounds to slurry mixtures if bound to soluble fulvic acids would have been detected during ^{14}C determinations. Thus the hypothesis that non-polar constituents such as PAH might be solubilized through binding to fulvic acids was not supported by this evidence. Based on specific activities of the labelled compounds added, detection limits for these experiments were on the order of 1 ppb for naphthalene and 0.2 ppb for phenanthrene and benzo(a)pyrene. The results of this study would suggest that

if non-polar organic species such as PAH are present in coal slurry wastewaters their concentrations are at the sub parts per billion level.

Degradation studies of fractionated Wyodak and Black Mesa pipeline samples revealed qualitative differences in the organic composition of these wastewaters (Table 13). In addition, as demonstrated by these analyses, compositional differences were also noted between Wyodak fulvic and non-fulvic acid samples. Analysis of Wyodak fulvic acid degradation products revealed the presence of five distinct compound classes (Figure 12). Predominant among these were benzenecarboxylic and aliphatic dibasic acid esters. Parent polymers responsible for the observed distribution of products formed were likely combinations of aryl units linked by aliphatic bridges. Comparatively, non-fulvic acid Wyodak degradation products are comprised almost exclusively of aliphatic dibasic acids with only one aromatic compound, 1,2,3-benzenetricarboxylic acid ester, identified in this sample. This may in fact reflect a compositional change towards increasing aliphatic character in non-fulvic acids as compared to the highly aromatic fulvic acid fraction.

Analysis of Black Mesa fulvic acid degradation products demonstrated only one identifiable component, that being oxalic acid. Given the fact that roughly equivalent amounts of fulvic acids were subjected to permanganate oxidation (0.6 gm for Wyodak and 0.64 gm for Black Mesa) it can be inferred that a much greater percentage of the Black Mesa sample was terminally oxidized to

CO₂ as noted by an absence of any additional degradation products. Previous research concerning the oxidation of aquatic humic and fulvic substances with potassium permanganate has demonstrated that the use of harsh oxidants such as permanganate results in an enrichment of aromatic degradation products (101). It is believed that the stabilization of the aromatic nucleus through the pi electron system in effect serves to protect against oxidation by permanganate. The absence of a predominance of aromatic components in the Black Mesa fulvic acid sample suggests that parent materials were primarily aliphatic in nature. Alternatively, aromatic species containing substituents such as hydroxyl groups which may serve to facilitate the oxidations of the benzene ring could have been present.

In similar fashion to Black Mesa fulvic acid samples, Black Mesa non-fulvic acid samples generated only one identifiable product, oxalic acid. Mass concentrations of Wyodak and Black Mesa non-fulvic acids originally subjected to oxidation were 0.1 and 0.04 gm, respectively. Given the reduced amount of starting material in the Black Mesa sample, it is possible that additional degradation products were formed, but at levels below detection limits. However, given the fact that oxalic acid was the predominant product identified in oxidized Black Mesa non-fulvic acid samples, it may be inferred that parent materials comprising the Black Mesa sample were, like Black Mesa fulvic acids, largely aliphatic in character.

Analyses of degradation products derived from the oxidation and subsequent methylation of aquatic humic and fulvic materials by Liao (64) demonstrated that identified products were primarily benzenecarboxylic and aliphatic dibasic acid esters, a result similar to that observed for Wyodak coal derived fulvic acids. In contrast, analysis of aryl units from degraded aquatic humic materials indicated a high level of substitution, primarily tri-, tetra-, penta- and hexa- while lower substituted aromatic nuclei, most notably di- and tri-, were found to predominate in the Wyodak coal sample. In addition, phenylglyoxylic acid esters, not documented in coal derived fulvic degradation studies, were found by Liao (64) in aquatic humic and fulvic degraded samples. Liao suggested that the presence of these compounds could have been a result of the partial oxidation of PAH components present in the parent humic/fulvic matrix.

The present study documented that furancarboxylic acid esters were present as degradation products generated from Wyodak coals. The presence of furan derivatives in degradation studies of aquatic humic and fulvic materials has also been reported by Reuter et al. (101) and Liao (64). It is unknown whether these materials were part of the parent polymers or are in fact oxidative artifacts.

The primary caveat associated with degradative schemes designed to assess the ultimate content and structure of biopolymers lies in the fact that the choice of oxidant and subsequent oxidative conditions employed will largely determine product formation.

Thus, as in the case of documented furan components, it is not entirely clear or, for that matter, ascertainable whether these materials are in fact structurally related to the parent acids or are artifactual products. However, degradative studies are not solely without merit. The employment of oxidative techniques in a standardized manner for all samples examined in this investigation has documented qualitative compositional differences both within and among leachable organic compounds derived from two distinct coal slurry wastewaters. Wyodak fulvic acids are comprised of both aryl and aliphatic constituents while non-fulvic acids derived from Wyodak wastewaters may be considered primarily aliphatic in nature. In contrast, degradative analysis of fractionated Black Mesa pipeline organic materials indicated that parent compounds are predominantly aliphatic in character.

In general fulvic acids and biopolymers such as lignin are known to be subject to variable rates of oxidative degradation via both abiotic and biotic processes (35,71). While information relating to the chemical structure of ultimate degradation products is scarce, it is currently believed that both low molecular weight aliphatic and aromatic acids are ultimately produced and are then biodegraded (6). Studies of lignin degradation (31) have demonstrated the production of hydroxyphenyl and phenol species as well as other substituted benzene derivatives such as vanilic, ferulic and p-hydroxycinnamic acids via microbially mediated transformation of the parent material. The lack of documented aliphatic degradation

products may be related to the ease with which they are biodegraded (14), thus making their documentation in actively degrading microbial cultures a difficult endeavor. The chemically mediated degradation of leached polymeric constituents from coal slurry systems indicates that both aliphatic and aromatic units are present. It is attractive to assume that these products may, to some extent, be reflective of the types of compounds formed when naturally mediated oxidative processes are active in the presence of coal leached biopolymers. However, additional research is needed to assess this hypothesis.

The observed differences in compositional structure of leachable organic polymers derived from Wyodak and Black Mesa coals likely reflect variations in biogenetic origin of the respective coal types. Thus the qualitative nature of leachable slurry organic constituents ultimately results from the types of decaying plant materials originally transformed in the coalification process. Studies by Hedges et al. (47,48) concerning the nature and origin of sedimentary organic materials have demonstrated that lignins derived from varying sources, e.g., woody or non-woody gymnosperms and angiosperms produce unique chemical degradation products upon oxidation that may be used to characterize the initial composition of the original plant materials. Lignins derived from woody gymnosperms were found to be comprised almost exclusively of vanillyl monomeric structures while woody angiosperm lignins produce both syringyl and vanillyl structures upon oxidation. Non-woody gymnosperms and angiosperms were also found to produce unique lignin

degradation products that could serve as indicators of plant origin. Given the similarities between lignin and fulvic acid, it is attractive to assume that unique chemical signatures such as those found for lignin polymers also exist for coal derived fulvic acid polymers. Knowledge concerning the nature of coal bound biopolymers and the leaching potential of these substances would be of great predictive value with respect to the design of appropriate waste treatment control systems for coal slurry wastewaters. Given the limited number of coal samples examined during the chemical degradation experiments, it cannot be ascertained whether unique chemical signatures may be ascribed to coal slurry derived fulvic polymers. Further research employing a larger number of coal types would be required to assess this hypothesis.

A general picture of the qualitative nature of leachable coal slurry organic species emerged from this study. Compositionally, slurry wastewater DOC is represented by a broad spectrum of compounds with predominant molecular weights ranging from 1,000 and less. These compounds are polar, non-volatile species most likely generated from the oxidation of coal surface molecules. The presence of PAH was not documented in coal slurry wastewaters. Significant amounts of the DOC may be procedurally classified as polymeric fulvic acids. Chemical degradation of these materials demonstrated both aliphatic and aromatic structural components which varied both among and within coal types.

II. Chlorination of Coal Slurry Wastewaters

Studies investigating the chlorination of coal slurry wastewaters demonstrated that significant concentrations of volatile chloroform were generated when slurry wastewaters were incubated in the presence of HOCl . The chlorination of unfractionated wastewaters revealed that overall quantities of THM vary substantially both among and within coal types (Table 13). Variability of THM production within a given coal type during these studies may have been partially due to uncontrolled experimental conditions, in particular pH. Previous studies have demonstrated a positive correlation between increasing pH and elevated THM yields (78,94). Alternatively, the variability noted within a given coal type may be related to inherent non-homogeneity of coal derived THM precursors. It is anticipated that progressive oxidation of coal during mining, preparation and storage handling will result in increased DOC loads in slurry transport waters as well as likely changes in the qualitative nature of the leachable organic species. Thus, gradual transformations of THM precursors (primarily oxidative) could result in variable THM production, making generalization concerning THM formation versus coal type a difficult endeavor.

Data relating the chlorination of fractionated slurry wastewaters demonstrate that coal slurry fulvic acids were responsible for the majority of THM produced. This result was most striking for the Black Mesa pipeline samples where fulvic acids were the

exclusive precursors of THM. Overall production of THM generated from coal derived fulvic acids was found to be comparable to rates previously reported for other humic/fulvic acid systems as demonstrated by Table 20. While the data in Table 20 are not directly comparable due to variations in experimental conditions, it may be seen that the generation of THM from Wyodak and Black Mesa fulvic acid samples, in general, falls within the range of total THM production ($0.05\text{--}1.59\ \mu\text{mole CHCl}_3\ \text{mg}^{-1}\ \text{C}$) documented for other humic and fulvic acid systems.

Results from the molecular weight fractionation study suggest that lower molecular weight fulvic acids ($< 1,000$) on a mass basis produce greater concentrations of THM than do higher molecular weight fulvic acids ($1,000$). Oliver and Visser (88) examined THM production from chlorinated aquatic humic and fulvic acids previously fractionated via ultrafiltration. For lake and stream water derived fulvic acids, maximum chloroform production occurred in the $1,000\text{--}10,000$ MW fraction while the humic acid samples derived from the same location exhibited maximum chloroform yields in the $10,000\text{--}30,000$ MW range. The observed difference in THM production as a function of molecular weight between coal derived and aquatic fulvic acids may be source dependent. Alternatively differences in fulvic acid isolation could have contributed to the contradictory results. In the present study fulvic acids were fractionated using XAD resins followed by base elution, acid precipitation to remove the humic component and then ultrafiltration. In contrast, Oliver

Table 20. THM production of selected humic/fulvic sources.

Source	Ref.	$\mu\text{m CHCl}_3/\text{mg C}$	Cl ₂ Dose ^a	pH	Rxn Time ^b	Rxn Temp.
Wyodak Coal	-					
Fulvic acid	-	0.33	10	7	96	20
Black Mesa Coal	-					
Fulvic acid	-	0.59	10	7	96	20
Aquatic Fulvics	11	0.05	8	7	48	10
Humic acids	111	0.70	10	6.7	96	25
Aquatic Humic acids	94	0.11	8	8	48	15
Commercial						
Humic acid	11	0.39-0.50	5	7	96	20
River Water/Commercial						
Humics	78	0.25-0.33	10	7	96	20
Peat Humic acid	9	1.14-1.59	10	6.5	96	20
Commercial						
Humic acid	4	0.73	10-20	7	96	20

^aReported as mg l⁻¹.

^bRxn time in hours.

and Visser (88) separated humic and fulvic acids by ultrafiltration followed by acid precipitation. These procedural differences may have resulted in isolated fulvic fractions that were qualitatively unique, making comparison between the two samples difficult.

The present study addressed only one aspect of product formation relating to the chlorination of coal slurry wastewater organic compounds, that being the production of volatile THM species. Studies by Oliver (89) have demonstrated that aquatic fulvic acids when chlorinated produce equivalent amounts of volatile and non-volatile chlorinated compounds. Similarly, Glaze et al. (37) observed that the formation of non-volatile chlorinated species was twice that of volatile species formed when aquatic fulvic acids were chlorinated. Documented non-volatile chloro-organics generated from the reactions of aquatic humic acid and HOCl are chlorophenylethers, chlorobenzoates, chloronaphthalenes and chlorophenols (55,76). Given the similarities in coal derived fulvic acids to those of aquatic origin, it is probable that non-volatile chloro-organic species will be produced in similar yields when coal slurry wastewaters are chlorinated. The potential for formation of these compounds as well as the documented presence of the carcinogen chloroform in chlorinated coal slurry wastewaters will mandate careful evaluation of the potential biological hazards associated with the release of chlorinated coal slurry wastewaters.

III. Mutagenic Assessment of Slurry Wastewaters

As determined by the standard plate method of Ames employed during the course of this investigation, mutagenic activity was absent from all slurry wastewaters examined. A toxic response was noted in the testing of concentrated (25:1) Wyodak and MRB wastewaters. Attempts were not made to remove high inorganic salt levels prior to testing of these samples; thus the observed toxicity was most likely a result of excessive salt concentration in the media. Additional examination of concentrated Black Mesa pipeline and MRB wastewaters using the fluctuation test revealed no mutagenic activity in these samples. In addition the chlorination of concentrated Black Mesa and MRB wastewaters was not found to produce a mutagenic response. In contrast to these findings, the chlorination of drinking waters has been shown to result in the production of chlorinated non-volatile mutagens (16). Similarly, the chlorination of pulp mill effluents, containing lignin constituents, has been shown to result in the formation of non-volatile compounds that produce positive responses when assayed via the Ames method (61,99). Given the similarities in structural composition between lignin and fulvic acids (87), it may be anticipated that chlorination of fulvic acids may lead to the production of similar types of non-volatile mutagenic compounds. This hypothesis was not supported by virtue of the fact that negative results were generated with these samples in the mutagenesis assay. It must be noted

that procedural differences were present in the mutagenic assessment of coal slurry and pulp mill effluent wastewaters. Mutagenic compounds present in chlorinated pulp mill effluents were isolated on XAD resins followed by ether elution, evaporation to dryness and finally dissolution in DMSO. In the present study, concentrated samples were chlorinated for a period of 24 hours, quenched with sodium thiosulfate, filter sterilized and then analyzed for mutagenic activity. It is possible that matrix effects due to the nature of the concentrated coal slurry wastewaters could obscure the presence of positive mutagenic events. To address this question, additional research relating to isolated chlorinated by-products of chlorinated coal slurry wastewaters is needed.

VII. SUMMARY

The occurrence and fate of organic matter leaching into coal slurry transport water was examined for both pipeline and laboratory generated coal slurry wastewaters. Laboratory coal slurries were formulated with the western coals Montana Rosebud, Wyodak and Black Mesa and the eastern coals Illinois #6 and Pittsburgh #8. Using bench scale coal slurry generators, the effects of coal type, slurry heating, pH alteration, length of transport time, coal storage age and transport water were examined with respect to the regulation wastewater DOC.

The results from this phase of the investigation demonstrated significant levels of DOC in all laboratory formulated slurries. Western coals produced higher slurry DOC values (generally 100-200 mg⁻¹) than eastern coals which produced slurry DOC values consistently less than 50 mg⁻¹. These levels were significantly increased by alkaline pH transport conditions, increasing coal storage age, and slurry dewatering temperatures. In contrast, increasing simulated transport times for coal distilled water based slurries had no effect on final DOC concentrations.

Studies were then initiated to assess the qualitative nature of the organic constituents comprising wastewater DOC. Ultrafiltration analysis coupled with XAD resin column and gel chromatography were employed to assess the molecular weight characteristics and humic/fulvic content of these materials. Ultrafiltration

analysis of coal slurry wastewaters demonstrated that laboratory generated Wyodak and MRB wastewaters were comprised primarily of compounds with molecular weights of less than 1,000. In contrast Black Mesa pipeline wastewaters exhibited an approximately equal distribution of molecular weight fractionated species across the three categories employed, greater than 5,000 MW, greater than 1,000 MW but less than 5,000 MW and the third category less than 1,000 MW. G-25 elution profiles of these wastewaters demonstrated the presence of a predominance of lower molecular sized compounds for both Wyodak and MRB slurry wastewaters. Black Mesa G-25 gel profiles indicated a broader distribution of molecular sizes. An operationally defined approach to quantitate humic/fulvic content of slurry wastewaters was employed. The results of this study demonstrated an absence of humic acids in slurry wastewaters. Approximately 31 and 50% of the DOC present in MRB and Wyodak wastewaters, respectively, could be identified and classified as fulvic acid. For Black Mesa pipeline samples fulvic acid content was approximately 64%.

Attempts were initiated to assess the potential presence of non-polar PAH materials in slurry wastewaters. As determined by conventional solvent extraction techniques and the liquid-liquid extraction technique of Natusch and Tomkins, non-polar solvent extractable species were not present in Wyodak and MRB slurry wastewaters. To assess the behavior of PAH in the slurry system, ^{14}C labelled phenanthrene, naphthalene and benzo(a)pyrene

were added to slurry mixtures. Results from this study demonstrated that greater than 99.8% of these materials were removed from the aqueous phase.

Oxidative degradation studies followed by diazomethane derivatization was employed to assess the qualitative composition of coal slurry wastewater organic components. Degradation products generated from Wyodak fulvic acids revealed the presence of five distinct compound classes (Figure 12, page 90). Non-fulvic acids derived from Wyodak coal slurries generated fewer products, the majority being aliphatic acids (Table 11, page 83). Degradation of Black Mesa pipeline organic species resulted in the formation of only one identifiable compound, oxalic acid.

Additional studies were conducted to evaluate trihalomethane (THM) production generated through the chlorination of coal slurry wastewaters. Laboratory generated MRB and Wyodak and Black Mesa slurries all produced measurable THM upon chlorination (Table 13, page 88). Black Mesa pipeline wastewaters generated 0.59 $\mu\text{mole CHCl}_3 \text{ mg}^{-1}\text{C}$ after 96 hours of reaction time. Chlorination of fractionated Wyodak slurry samples demonstrated differences in THM formation potential on the basis of fulvic acid content. Wyodak fulvic acids produced twice the concentration of THM on a mass carbon basis when compared to non-fulvic Wyodak acids. Fulvic acids were the exclusive precursors of THM in Black Mesa pipeline samples.

Analyses were conducted relative to the mutagenic potential of laboratory prepared and Black Mesa generated coal slurry wastewaters. Using the Ames standard plate method and the fluctuation assay, the mutagenicity of unconcentrated, concentrated (both 10:1 and 25:1) and concentrated wastewaters subjected to chlorination was assayed. Results from these studies indicated a lack on mutagenic activity across all samples tested.

VIII. CONCLUSIONS

Analysis of both pipeline and laboratory generated coal slurry wastewaters generated during the course of this study has provided important information relating to the nature and extent of the dissolution of organic pollutants during coal slurry transport. The information present in this study may be useful in identifying factors affecting wastewater organic levels for individual slurry pipeline systems and where appropriate determining control technologies for treatment purposes. Examination of the slurry transport process has demonstrated that organic pollution potential of a given coal slurry process will be highly coal source dependent. Variables such as increasing coal storage age and slurry heating prior to coal water removal were found to effect elevated wastewater DOC concentrations. An additional physical/chemical parameter, the pH of a given slurry, will also control the loading of organic materials into slurry waters. It is expected that slurry pH will be maintained at levels approaching neutrality to prevent corrosion. However increasing levels of alkalinity will effect increasing DOC loads in transport waters. The use of transport fluids such as lake water and in particular sewage effluent were found to significantly reduce coal slurry wastewater DOC levels. This factor may be particularly useful for coal slurry systems employing coals that contain substantial quantities of leachable carbon.

An assessment of the qualitative nature of organic constituents comprising wastewater DOC demonstrated that leached compounds are broadly distributed in terms of molecular weight. The majority of laboratory prepared slurry samples contained compounds which exhibited molecular weights of 1,000 or less. An absence of lower molecular weight organic constituents in Black Mesa wastewaters was potentially attributed to microbially mediated removal. Significant quantities of slurry wastewater DOC (31-64%) may be procedurally classified as fulvic acid. Analysis of chemical degradation products generated from coal slurry wastewater samples revealed that qualitative differences exist with respect to organic structural composition and coal type. Compounds leached from Wyodak coals were comprised of both aliphatic and aromatic components, while Black Mesa pipeline organic materials were predominantly aliphatic in character. Knowledge concerning the nature of DOC species will be valuable in assessing the types and extent of wastewater reclamation needed for adequate treatment.

The potential use of coal slurry wastewaters as power plant cooling waters should be carefully evaluated in light of the THM formation potential data generated during this study. Coal slurry wastewaters when subjected to chlorination will produce measurable quantities of THM. In addition non-volatile chloro-organic species while not assessed in this study will likely result when coal slurry wastewaters are subject to presently practiced chlorination techniques. The extent to which these compounds may form and the

relative biological hazards associated with the release of these materials warrants further investigation.

An examination for potential mutagens present in coal slurry wastewaters and chlorinated wastewaters demonstrated an absence of such compounds as determined by Salmonella typhimurium mutant reversion assays. These studies demonstrate that the release of these wastewaters will not pose a mutagenic threat upon discharge. However, the potential for other biological effects associated with wastewater release cannot be properly assessed.

The following specific conclusions are based on the analysis of data generated from experiments conducted during this study.

1. A wide range of wastewater DOC values for individual coal slurry systems may be anticipated. Western coals on average exhibited two to five fold increases in DOC levels as compared to slurries generated from eastern coals.
2. Increasing coal storage age, slurry pH and dewatering temperature will result in elevated wastewater DOC loads.
3. The use of sewage effluents and/or lake waters as transport media in coal slurry processes resulted in substantial reductions in wastewater DOC levels.
4. Organic constituents present in coal slurry wastewaters are polar species with broad molecular weight distributions. The majority of these compounds exhibited molecular weights of 1,000 or less.

5. Fulvic acids were found to comprise 31-64% of total DOC present in the coal slurry wastewaters examined.
6. Chemical degradation of coal slurry wastewater organic materials demonstrated qualitative differences in structural composition both within and among coal types. Wyodak fulvic acids were comprised primarily of benzene-carboxylic and aliphatic dibasic acid esters while non-fulvic Wyodak acids were found to be predominantly comprised of aliphatic dibasic acid esters. The only degradation product generated from Black Mesa pipeline organic samples was oxalic acid. Parent materials for this coal type were predominantly aliphatic in character.
7. Chlorination of coal slurry wastewaters will result in the formation of THM. Fulvic acid components of coal slurry wastewaters were found to be the predominant THM precursors for Wyodak and Black Mesa coal slurry samples.
8. An absence of mutagenic activity was noted for unconcentrated, concentrated and concentrated chlorinated coal slurry wastewaters.

REFERENCES CITED

REFERENCES CITED

1. Aiken, G. R., E. M. Thurman, R. L. Malcolm and H. F. Walton. 1979. Comparison of XAD macroporous resins for the concentration of fulvic acid from aqueous solution. *Anal. Chem.* 51:1799-1803.
2. Allen, H. E., R. H. Hall and T. D. Brisbin. 1980. Metal speciation: Effects on aquatic toxicity. *Environ. Sci. Technol.* 14:441-443.
3. Ames, B. N., J. McCann and E. Yamasaki. 1975. Methods for detecting carcinogens and mutagens with the *Salmonella*/mammalian microsome mutagenicity test. *Mutation Res.* 31:347-364.
4. Amy, G. L., P. A. Chadik, P. H. King and W. J. Cooper. 1984. Chlorine utilization during trihalomethane formation in the presence of ammonia and bromide. *Environ. Sci. Technol.* 18:781-786.
5. Andersen, N. E. and H. A. Hamza. 1982. The characterization of oxidized coal--A review. pp. 117-124. In: A. M. al Taweel (Ed.). *Coal: Phoenix of the 80's*. Proc. 64th CIC. Coal Symposium. Ottawa.
6. Anderson, D. W. 1979. Process of humus formation and transformation in soils of the Canadian great plains. *J. Soil Sci.* 30:77-84.
7. Anderson, O. L., M. B. Rogozen, L. W. Margler, P. Mankiewicz and M. H. Axelrod. 1978. Water pollution control for coal slurry pipelines. SAI-068-79-516.
8. Anonymous. 1976. How the coal slurry pipeline is working. *Environ. Sci. Technol.* 10:1086-1087.
9. Babcock, D. B. and P. C. Singer. 1977. Chlorination and coagulation of humic/fulvic acids. Presentation; 97th Ann. Amer. Water Works Conf. Anaheim, CA. May 8-13.
10. Bellar, T. A. and J. J. Lichtenberg. 1974. Determining volatile organics of microgram-per-liter levels by gas chromatography. *J. Amer. Water Works Assoc.* 66:739-744.
11. Bird, J. C. 1979. The effect of bromide on trihalomethane formation. M.S. Thesis. Univ. of Tennessee. Dept. of Civil Engr.

12. Black, T. H. 1983. The preparation and reactions of diazomethane Aldrichim. Acta. 16:3-10.
13. Braunstein, H. M., E. D. Copenhaver and H. A. Pfuderer (Eds.). 1976. Environmental, Health and Control Aspects of Coal Conversion: An Information Overview. Vols. I and II. Oak Ridge National Laboratory. ORNL/EIS-94.
14. Britton, L. M. 1984. Microbial degradation of aliphatic hydrocarbons. pp. 89-129. In Microbial Degradation of Organic Compounds. Gibson, D. T. (Ed.). Marcel Dekker, Inc. New York, NY.
15. Cairns, J. 1980. Biological monitoring: Part I--early warning systems. Water Res. 14:1179-1196.
16. Cheh, A. M., J. Skochdopole, P. Koski and L. Cole. 1980. Non-volatile mutagens in drinking water: Production by chlorination and destruction by sulfite. Science. 207:90-92.
17. Clark, C. R. and C. H. Hobbs. 1980. Mutagenicity of effluents from an experimental fluidized bed coal combustor. Environ. Mutagenesis. 2:101-109.
18. Cobb, D. B., C. D. Giles and F. O. Leavitt. 1978. Coal slurry storage and reclaim facility for Mohave generating station. Paper presentation. Pacific Coast Electrical Assoc. Engineering and Operating Conf. San Francisco, CA. March 16-17.
19. Cooper, S. D., J. D. Dietz, J. S. Taylor, M. J. Flint and M. R. Todd. 1983. Water quality characterization of an eastern coal slurry. Paper presentation. Second Conference of Municipal, Hazardous and Coal Wastes Management. Miami Beach, FL. Dec. 5-7.
20. Cowser, K. E. and C. R. Richmond (Eds.). 1980. Synthetic Fossil Fuel Technology. Ann Arbor Science. Ann Arbor, MI.
21. Cox, J. L. and C. R. Nelson. 1984. Coal weathering: causes, effects and implications. Amer. Chem. Soc. Div. of Fuel Chem. Annual Meeting. St. Louis, MO. 29:102-107.
22. Curtis, M. A., A. F. Witt, S. B. Schram and L. B. Rogers. 1981. Humic acid fractionation using a nearly linear pH gradient. Anal. Chem. 53:1195-1199.
23. Dailey, G. A. 1976. Microbial interactions. pp. 7-1/2-102. In Braunstein, H. M., E. D. Copenhaver and H. A. Pfuderer (Eds.). Environmental, Health and Control Aspects of Coal Conversion: An Information Overview. Vol. II. Oak Ridge National Laboratory. ORNL/EIS-95.

24. Denkaus, R., W.O.K. Grabon and O. W. Prozeky. 1980. Removal of mutagenic compounds in a wastewater reclamation system evaluated by means of the Ames Salmonella/microsome assay. *Prog. Water Tech.* 12:571-589.
25. Dileo, A. J. and D. M. Nicholas. 1980. Characterization of wastewater and monitoring its treatment. SRC I. Quarterly technical report. DOE/OR/03054-2.
26. Dina, M. L. 1976. Operating experiences at the 1580MW coal slurry fired Mohave generating station. Presentation. First International Conf. on Slurry Transportation. Battelle Memorial Inst. Columbus, OH.
27. Ellis, D. D., C. M. Jones, R. A. Larson and D. J. Schaeffer. 1982. Organic constituents of mutagenic secondary effluents from wastewater treatment plants. *Arch. Environ. Contam. Toxicol.* 11:373-382.
28. Energy Information Administration. 1984. Monthly Energy Review DOE/EIA 0035.
29. Epler, J. L., T. Ho, A. N. Hsie, F. W. Larimer, C. E. Nix and T. K. Rao. 1980. Short term mutagenicity testing. pp. 129-136. *In* Cowser, K. E. and C. R. Richmond (Eds.). *Synthetic Fossil Fuel Technology*. Ann Arbor Science. Ann Arbor, MI.
30. Epler, J., T. K. Rao, C. Ho and M. Guerin. 1979. Identification of mutagenic components of basic fractions from crude oils. *Environ. Mutagenesis* 1:172-189.
31. Flaig, W. 1964. Effects of micro-organisms on the transformation of lignin to humic substances. *Geochimica et Cosmochimica Acta.* 28:1523-1535.
32. Fowler, B. 1975. Heavy metals in the environment III. Overview. *Environ. Health Pros.* 12:125-126.
33. Friedman, S., and R. P. Warzinski. 1977. Chemical cleaning of coal. *J. Engineer. Power.* 99:361-365.
34. Gatehouse, D. 1978. Detection of mutagenic derivatives of cyclophosphamide and a variety of other mutagens in a "microtitre" fluctuation test without microsomal activation. *Mutation Res.* 53:289-296.
35. Ghoudry, G. G. 1981. Humic substances. Part II. Photophysical, photochemical and free radical characteristics. *Toxicol. and Env. Chem.* 4:261-295.

36. Giddings, J. M. and J. N. Washington. 1981. Coal liquefaction, products shale oil and petroleum: Acute toxicity to freshwater algae. *Environ. Sci. Technol.* 15:106-110.
37. Glaze, W. H., J. L. Burleson, J. E. Henderson, P. C. Jones, G. R. Peyton, R. Rawley, F. Y. Saleh and G. Smith. 1980. Analyses of chlorinated organic compounds formed during water chlorination. EPA final report. Grant #R-803007.
38. Godwin, J. and S. E. Manahan. 1979. Interchange of metals and organic matter between water and subbituminous coal or lignite under simulated coal slurry pipeline conditions. *Environ. Sci. Technol.* 13:1100-1104.
39. Gorbaty, M. L., J. W. Larsen and I. Wender (Eds.). 1982. *Coal Science*. Academic Press. New York, NY.
40. Gorbaty, M. L. and K. Ouchi (Eds.). 1981. *Coal Structure*. Adv. in Chemistry Series. American Chemical Society. Washington, D.C.
41. Grabon, W.O.K., R. Denkhaus and P. G. van Rossum. 1980. Detection of mutagens in wastewater, a polluted river and drinking water by means of the Ames Salmonella/microsome assay. *S. African J. of Science*. 76:118-123.
42. Green, M.H.L., B. A. Bridges, A. M. Rogers, G. Hurspool, W. J. Muriel, J. W. Bridges and J. R. Fry. 1977. Mutagen screening by a simplified bacterial fluctuation test: Use of microsomal preparation and whole liver cells for metabolic activation. *Mutation Res.* 48:287-294.
43. Green, M.H.L., W. J. Muriel and B. A. Bridges. 1976. Use of a simplified fluctuation test to detect low levels of mutagens. *Mutation Res.* 38:33-42.
44. Greenberg, A. E., J. J. Connors and D. Jenkins. 1981. *Standard Methods for the Examination of Water and Wastewater*. 15th edition. Am. Public Health Assoc. Washington, D.C.
45. Hassett, J. P. and M. A. Anderson. 1979. Association of hydrophobic organic compounds with dissolved organic matter in aquatic systems. *Environ. Sci. Technol.* 13:1526-1529.
46. Hayatsu, R., R. G. Scott, L. P. Moore and M. H. Studier. 1975. Aromatic units in coal. *Nature*. 257:378-380.
47. Hedges, J. I., H. J. Turin and J. R. Ertel. 1984. Sources and distributions of sedimentary organic matter in the Columbia River drainage basin, Washington and Oregon. *Limnol. Oceanogr.* 29:35-46.

48. Hedges, J. I. and D. C. Mann. 1979. The characterization of plant tissues by their lignin oxidation products. *Geochimica et Cosmochimica Acta*. 43:1803-1807.
49. Hirayama, T., M. Nohara, T. Ando, M. Tawaka, K. Fukui and S. Fujui. 1983. Mutagenicity of coal pyrolyzed products and their photochemical reaction products with nitrogen oxides in *Salmonella typhimurium* TA-98 and TA-100. *Mutation Res.* 122:273-278.
50. Hoeffner, S. L. and S. E. Manahan. 1980. Influence of coal humic acid on the growth of *Chlorella vulgaris* algae. *J. Environ. Sci. and Health*. 15:14-21.
51. Hsu, T. S. and R. Bartha. 1976. Hydrolyzable and non-hydrolyzable 3,4-dichloroaniline-humus complexes and their respective rates of biodegradation. *J. Agric. Food Chem.*, 24:119-122.
52. Hunt, V. D. 1983. *Synfuels Handbook*. Industrial Press, Inc. New York, NY.
53. Iskra, J. and J. Laskowski. 1967. New possibilities of investigating air oxidation of coal surfaces at low temperatures. *Fuel* 46:5-12.
54. Johnson, D. E. 1981. The effects of coal particle and the percentage of coal present in the slurry on the leaching of organic compounds from Wyodak coal. M.S. thesis. Dept. of Civil Engineering. Univ. Tennessee.
55. Jolley, R. C. 1973. Chlorination effects on organic constituents in domestic sanitary sewage treatment plants. Ph.D. Dissertation. Grad. Program in Ecology. Univ. of Tennessee.
56. Kaczmarek, S. A. and F. L. Robertcaccio. 1983. EDS coal liquefaction wastewaters: Zero discharge treatability studies. pp. 500-516. *In* *Proceedings. 38th Annual Purdue Industrial Waste Conference*. West Lafayette, Ind. May 10-12.
57. Kawabata, N. and T. Morigaki. 1980. Removal and recovery of organic pollutants from the aquatic environment 2. Removal and recovery of dodecylbenzenesulfonate from an aqueous solution by cross-linked poly (n-benzyl-4-vinylpyridinium halide). *Environ. Sci. Technol.* 14:1089-1093.
58. Kim, B. R., V. L. Snoeyink and F. M. Saunders. 1976. Adsorption of organic compounds by synthetic resins. *J. Water Poll. Contr. Fed.* 48:120-133.

59. Klein, J. A. 1980. National progress in control of wastewater from coal conversion processes. pp. 15-22. In Cowser, K. E. and C. R. Richmond (Eds.). Synthetic Fossil Fuel Technology. Ann Arbor Science. Ann Arbor, MI.
60. Kool, H. J., C. F. van Kreijl, H. J. van Kranen and E. deGreef. 1981. The use of XADresins for the detection of mutagenic activity in water. I. Studies with surface water. Chemosphere 10:85-98.
61. Kringstad, K. P., P. O. Ljungquist, F. de Sousa and L. M. Stromberg. 1981. Identification and mutagenic properties of some chlorinated aliphatic compounds in the spent liquor from kraft pulp chlorination. Environ. Sci. Technol. 15: 562-566.
62. Levin, D. E., E. L. Blunt and R. E. Levin. 1981. Modified fluctuation test for the direct detection of mutagens in foods with Salmonella typhimurium TA-98. Mutation Res. 85:309-321.
63. Liao, W., R. F. Christman, J. D. Johnson, D. S. Millington and J. R. Haas. 1982. Structural characterization of aquatic humic materials. Environ. Sci. Technol. 16:403-410.
64. Liao, W. 1981. Characterization of aquatic humic substances. Ph.D. dissertation. University of North Carolina. Dept. of Env. Sciences and Engr.
65. Liotta, R., K. Rose and E. Hippo. 1981. o-Alklylation chemistry of coal and its implications for the chemical and physical structure of coal. J. Org. Chem. 46:277-283.
66. Lorenze, de Otto. 1949. Combustion Engineering. Combustion Engineering Superheaters, Inc. Madison, WI.
67. Luthy, R. G. 1981. Treatment of coal coking and coal gasification wastewaters. J. Water Poll. Control Fed. 53:325-339.
68. Mangold, E. C., M. A. Muradaj, R. P. Ovellette, O. G. Farah and P. N. Cheremisinoff. 1982. Coal Liquefaction and Gasification Technologies. Ann Arbor Science. Ann Arbor, MI.
69. Margler, L. W. and M. B. Rogozen. 1980. Effect of coal slurry on wastewater bacteria and bacteriophage. J. Water Poll. Contr. Fed. 52:53-58.
70. Mathur, S. P. and E. A. Paul. 1967. Partial characterization of soil humic acids through biodegradation. Can. J. Microbiol. 13:581-586.

71. Mathur, S. P. 1967. Microbial utilization of soil humic acids. *Can. J. Microbiol.* 13:573-580.
72. Matsuda, K. and M. Schnitzer. 1971. Reactions between fulvic acid, a soil humic material and dialkyl phthalates. *Bull. Environ. Contam. Toxicol.* 6:200-203.
73. McCreary, J. J. and V. L. Snoeyink. 1980. Characterization and activated carbon adsorption of several humic substances. *Water Res.* 14:151-160.
74. Mckague, A. B., E.G.H. Lee and G. R. Douglas. 1981. Chloroacetones: Mutagenic constituents of bleached kraft chlorination effluents. *Mutation Res.* 91:301-306.
75. McLafferty, F. W. 1966. Interpretation of Mass Spectra: An Introduction. W. A. Benjamin, Inc. New York, NY.
76. Miller, J. W. and P. C. Uden. 1983. Characterization of non-volatile aqueous chlorination products of humic substances. *Environ. Sci. Technol.* 17:150-157.
77. Minear, R. A., G. J. Sayler, J. W. Davis and M. C. Reid. 1983. The State of Knowledge and Research Needs Assessment Coal Slurry Pipeline and Coal Cleaning Wastewater Characteristics. Draft Final Report to Electric Power Research Institute. Palo Alto, CA.
78. Minear, R. A. and C. M. Morrow. 1983. Raw water bromide: Levels and relationship to distribution of trihalomethanes in finished drinking water. Tennessee Water Resources Res. Center. Research Report #91.
79. Minear, R. A. and J. C. Bird. 1980. Trihalomethane: Impact of bromide ion concentration on the yield, species distribution, rate of formation and influence of other variables. In *Water Chlorination, Environmental Impact and Health Effects*. Vol. 3. R. Jolley (Ed.). Ann Arbor Science. Ann Arbor, MI.
80. Moore, J. W. 1981. Water quality considerations in the slurry pipelining of coal. Arkansas Water Resources Research Center. Univ. Arkansas. Publication #84.
81. Moore, R. L., L. L. Osborne and R. N. Davies. 1980. The mutagenic activity in a section of the Sheep River, Alberta, receiving a chlorinated sewage effluent. *Water Res.* 14: 917-920.

82. Natusch, D.F.J. and B. A. Tomkins. 1978. Isolation of polycyclic organic compounds by solvent extraction with dimethyl sulfoxide. *Anal. Chem.* 50:1429-1434.
83. Nestmann, E. R., E.G.H. Lee, J. L. Mueller and G. R. Douglas. 1979. Mutagenicity of resin acids identified in pulp and paper mill effluents using the Salmonella/mammalian-microsome assay. *Environ. Mutagenesis* 1:361-369.
84. Newton, A. S., P. J. Fox, H. Villareal, R. Raval and W. Walker. 1982. Organic compounds in coal slurry pipeline waters. Lawrence Berkeley Labs. LBA-15121.
85. Nriagu, J. O. and R. D. Coker. 1980. Trace metals in humic and fulvic acids from Lake Ontario sediments. *Environ. Sci. Technol.* 14:443-446.
86. Office of Technology Assessment. 1978. A technology assessment of coal slurry pipelines. Library of Congress Catalog Card #77-600023.
87. Ogner, G. and M. Schnitzer. 1970. Chemistry of fulvic acid, a soil humic fraction and its relation to lignin. *Can. J. of Chem.* 49:1053-1063.
88. Oliver, B. G. and S. A. Visser. 1980. Chloroform production from the chlorination of aquatic humic material: The effect of molecular weight, environment and season. *Water Res.* 14:1137-1141.
89. Oliver, B. G. 1978. Chlorinated non-volatile organics produced by the reaction of chlorine with humic materials. *Can. Res.* 11:21-22.
90. Pagenkopf, G. K. 1983. Gill surface interactions. Model for trace metal toxicity to fishes. Role of complexation, pH and water hardness. *Environ. Sci. Technol.* 17:342-347.
91. Palin, A. T. 1975. Current DPD methods for residual halogen compounds and ozone in water. *J. Amer. Water Works Assoc.* 67:32-34.
92. Parris, G. E. 1980. Covalent binding of aromatic amines to humates. I. Reactions with carbonyls and quinones. *Environ. Sci. Technol.* 14:1099-1106.
93. Peavy, H. S. and P. W. Jennings. 1981. Water pollution potential of coal slurry pipelines. EPA-600/7-81-082.

94. Peters, C. J., R. J. Young and R. Perry. 1980. Factors influencing the formation of haloforms in the chlorination of humic materials. *Environ. Sci. Technol.* 14:1391-1395.
95. Plummer, A. H. and B. Jordan. 1983. The ETSI coal evaluation plant wastewater characterization study. Proceedings of the Eighth International Technical Conference of Slurry Transportation. Slurry Transport Association. Washington, D.C.
96. Plummer, A. H. and B. Jordan. 1982. Coal slurry dewatering operations; wastewater treatability studies. Proceedings of the Seventh International Technical Conference on Slurry Transportation. Slurry Transport Association. Washington, D.C.
97. Poole, C. F. and A. Zlatkis. 1980. Derivatization techniques for the electron capture detector. *Anal. Chem.* 52:1002A-1016A.
98. Protic-Sabljić, M. and B. Kurelec. 1983. High mutagenic potency of several polycyclic aromatic hydrocarbons induced by liver postmitochondrial fractions from control and xenobiotic treated immature carp. *Mutation Res.* 118:177-189.
99. Rapson, W. H., M. A. Nazar and V. V. Bulsky. 1980. Mutagenicity produced by aqueous chlorination of organic compounds. *Bull. Environ. Contam. Toxicol.* 24:590-596.
100. Reid, M. C., J. W. Davis, G. S. Tayler and R. A. Minear. Characterization and biological treatability of organic contaminants in coal slurry transport water. *Water Res.* (in review). 1984.
101. Reuter, J. H., M. Ghosal, E.S.K. Chian and M. Giabbai. 1983. Oxidative degradation studies on aquatic humic substances. pp. 107-126. *In* R. F. Christman, E. T. Gjessing (Eds.). *Aquatic and Terrestrial Humic Materials*. Ann Arbor Science. Ann Arbor, MI.
102. Rubin, E. S. and F. S. McMichael. 1975. Impact of regulations on coal conversion plants. *Environ. Sci. Technol.* 9:112-117.
103. Sandhu, A. S. and R. L. Gandhi. 1981. Water quality simulation study of the Black Mesa coal slurry pipeline system. Fourth Annual Coal Technology Conference. Houston, TX.

104. Sayler, G. S., R. A. Minear, M. C. Reid and J. W. Davis. 1983. Enhanced reuse potential of coal slurry treatment water: Toxic organics assessment removal. Final Report. Office of Water Research and Technology. OWRT #C-00200R.
105. Silverstein, R. M., G. C. Bassler and T. C. Morrill. 1974. Spectrometric Identification of Organic Compounds. Third edition. John Wiley and Sons. New York, NY.
106. Singer, P. C., J. C. Lamb III, F. K. Pfaender and R. Goodman. 1979. Treatability and assessment of coal conversion wastewater. Phase I. EPA-600/7-79-248.
107. Slurry Transport Association. 1982. U.S. Coal Slurry Pipeline System. STA Newsletter. Washington, D.C.
108. Somani, S. M., R. G. Teece and D. J. Schaeffer. 1980. Identification of cocarcinogens and promoters in industrial discharges into and in the Illinois River. J. Toxicol. and Environ. Health. 6:315-331.
109. Southern California Edison. 1981. Mohave Generating Station. Units 1 and 2. Information Brochure. Southern California Edison. Los Angeles, CA.
110. Stamoudis, V. C. and R. G. Luthy. 1980. Biological removal of organic constituents in quench waters from high-Btu coal gasification pilot plants. Argonne National Laboratory. ANL/PAG-2.
111. Stevens, A. A., C. J. Slocum, D. R. Seeger and G. G. Robeck. 1976. Chlorination of organics in drinking water. J. Amer. Water Works Assoc. 68:615-620.
112. Suffet, I. H., L. Brenner, J. T. Coyle and P. R. Cairo. 1978. Evaluation of the capability of granular activated carbon and XAD-2 resin to remove trace organics from treated drinking water. Environ. Sci. Technol. 12:1315-1322.
113. Thurman, E. M. and R. L. Malcolm. 1981. Preparative isolation of aquatic humic substances. Environ. Sci. Technol. 15: 463-466.
114. Van Kreijl, C. F., H. J. Kool, M. DeVries, H. J. Van Krannen and E. DeGreef. 1980. Mutagenic activity in the rivers Rhine and Meuse in the Netherlands. Sci. of Tot. Environ. 15:137-147.

115. Vogel, H. J. and D. M. Bonner. 1956. Acetylornithase of E. Coli partial purification and some properties. J. Biol. Chem. 218:97-104.
116. Wasp, E. J. 1983. Slurry pipelines. Sci. Amer. 249:48-55.
117. Waters, M. D. 1980. A phased approach to the bioscreening of emissions and effluents from energy technologies. pp. 143-152. In Cowser, K. E. and C. R. Richmond (Eds.). Synthetic Fossil Fuel Technology. Ann Arbor Science. Ann Arbor, MI.
118. Wershaw, R. L., D. J. Burcar and M. C. Goldberg. 1969. Interaction of pesticides with natural organic material. Environ. Sci. Technol. 3:271-273.
119. Wilson, B. W., M. R. Petersen, R. A. Pelroy and J. T. Cresto. 1981. In-vitro assay for mutagenic activity and gas chromatographic-mass spectral analysis of coal liquefaction material and the products resulting from its hydrogenation. Fuel. 60:289-294.
120. Wilson, B. W., R. Pelroy and J. T. Creston. 1980. Identification of primary aromatic amines and mutagenically active subfractions from coal liquefaction materials. Mutation Res. 79:193-202.
121. Willard, H. H., L. L. Meritt, J. A. Dean and F. A. Settle. 1981. Instrumental Methods of Analysis. 6th Edition. D. Van Nostrand Company. New York, NY.
122. Wyatt, J. M., D. B. Cox and L. H. Woosley. 1980. Characterization, treatment and disposal of liquid and solid wastes from coal gasification facilities. Vol. I. Tennessee Valley Authority Division of Water Resources. Water Quality Branch.

APPENDIX

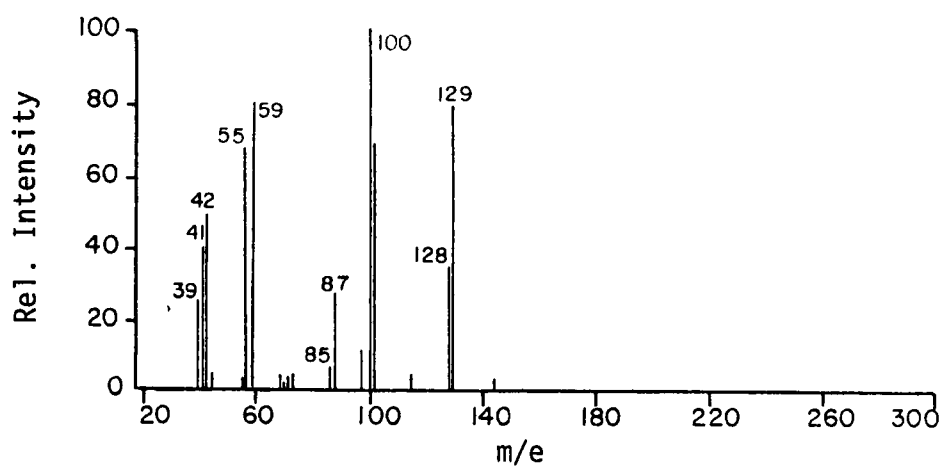


Figure 14. Glutaric acid dimethyl ester.

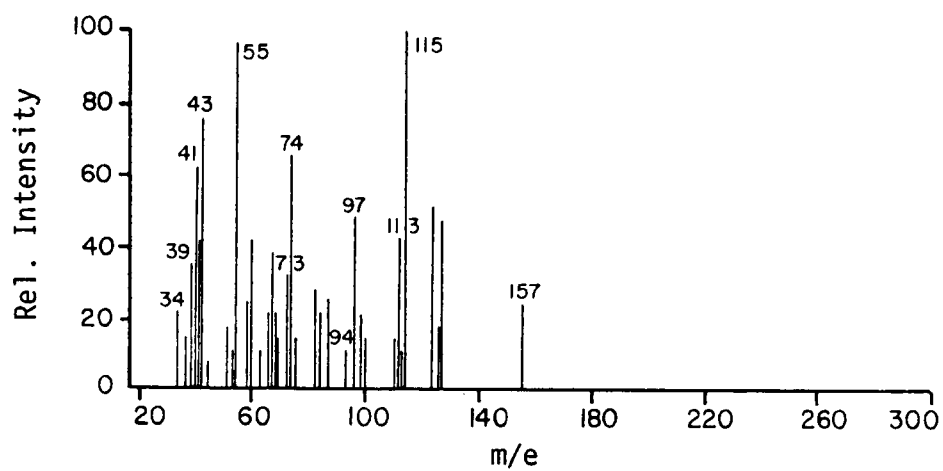


Figure 15. Pimelic acid dimethyl ester.

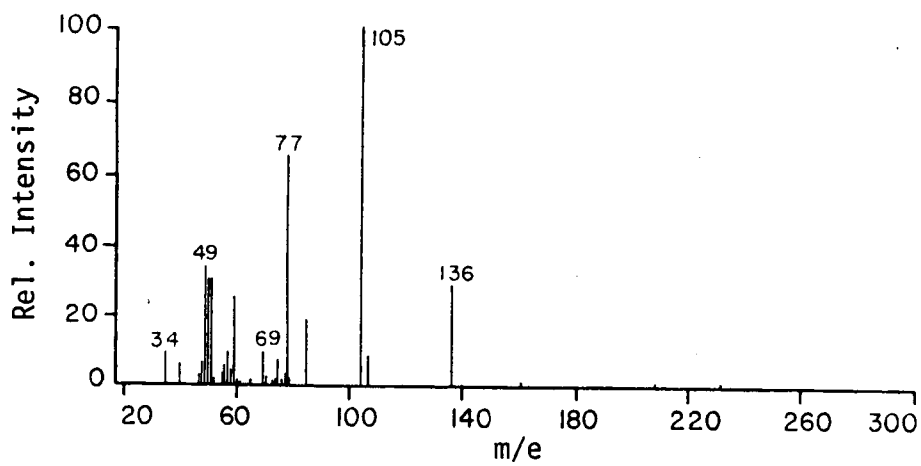


Figure 16. Benzoic acid methyl ester.

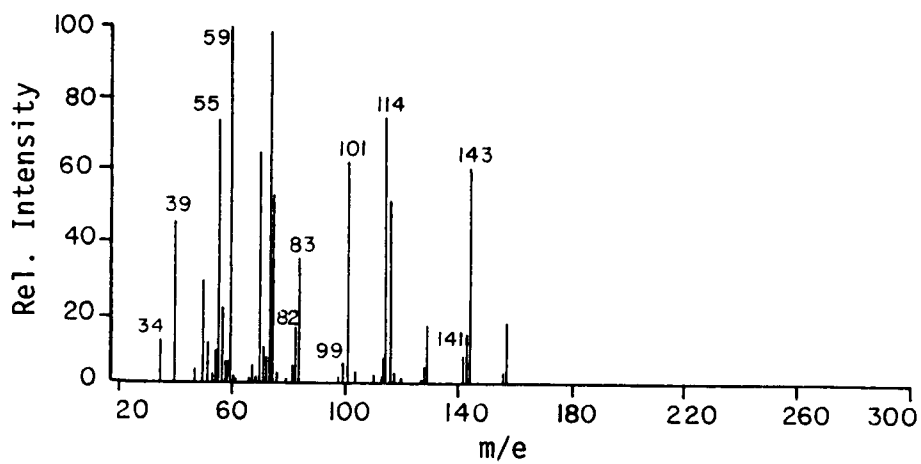


Figure 17. Adipic acid dimethyl ester.

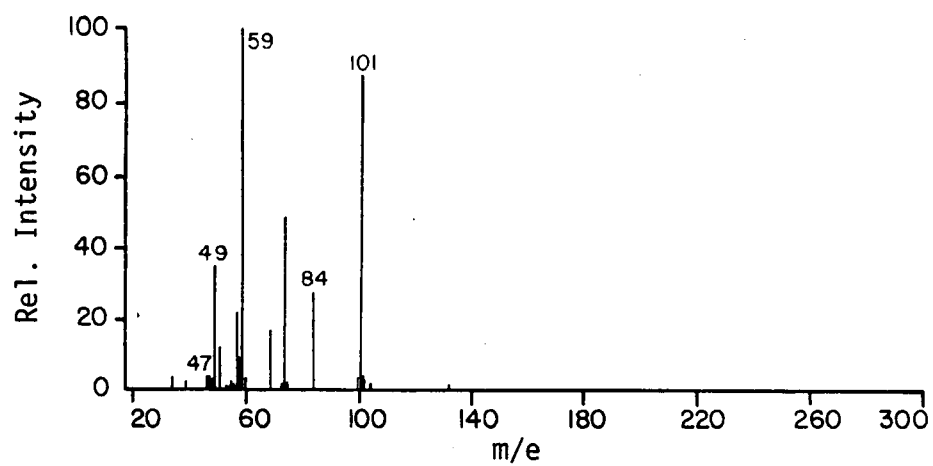


Figure 18. Malonic acid dimethyl ester.

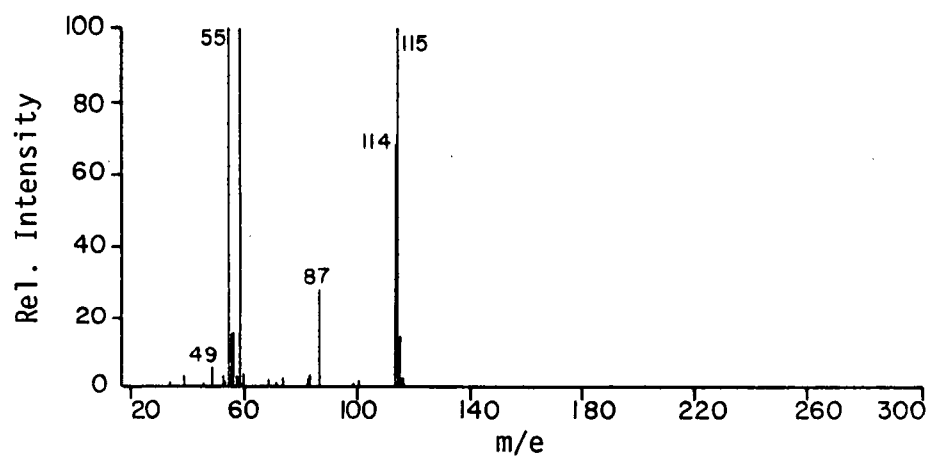


Figure 19. Succinic acid dimethyl ester.

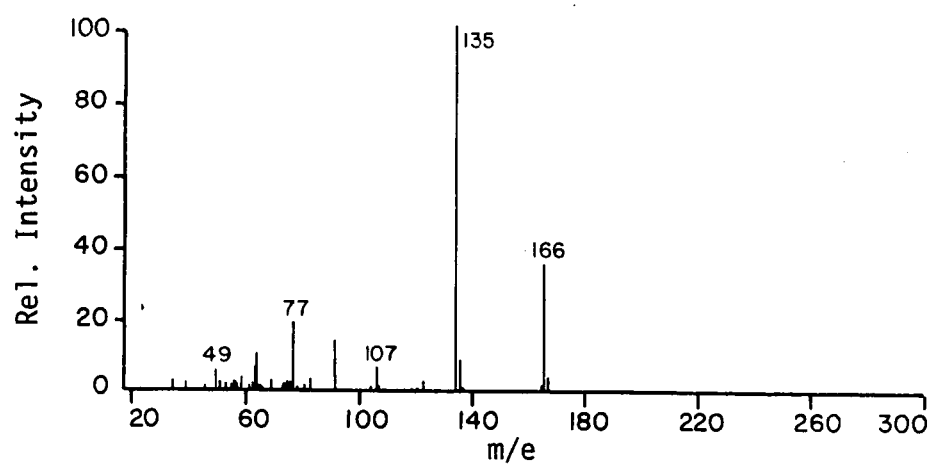


Figure 20. p-Methoxybenzoic acid methyl ester.

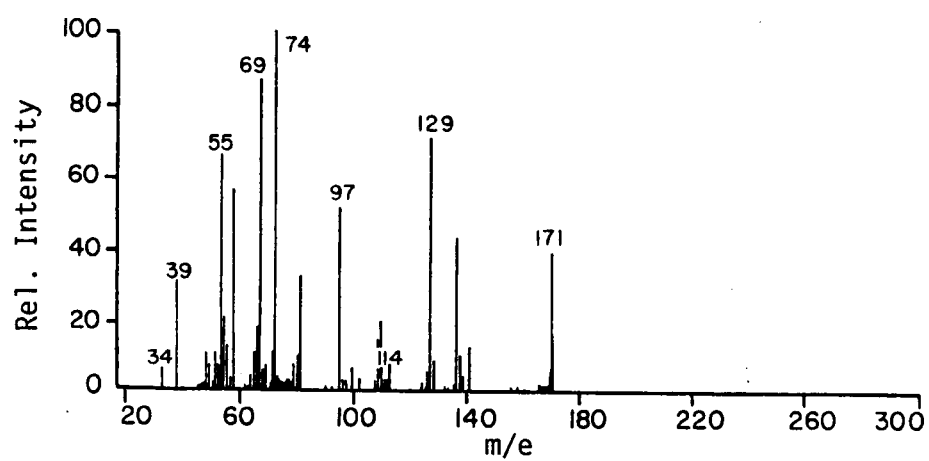


Figure 21. Suberic acid dimethyl ester.

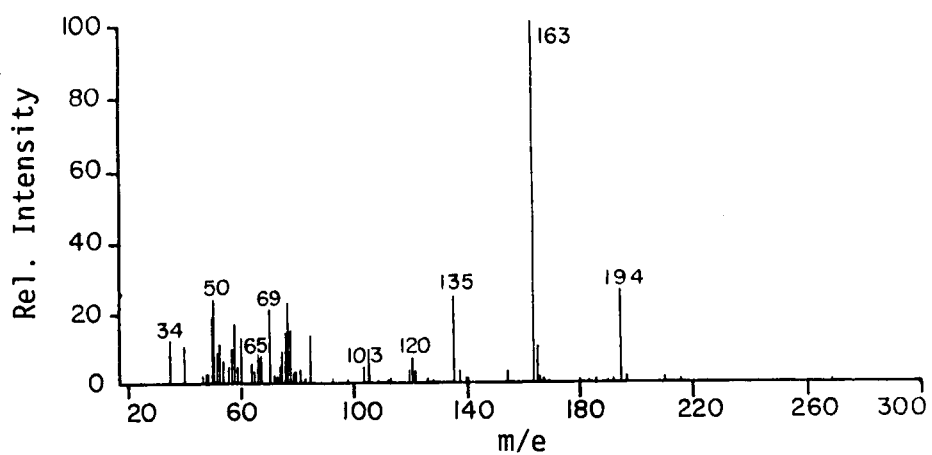


Figure 22. 1,4-Benzenedicarboxylic acid dimethyl ester.

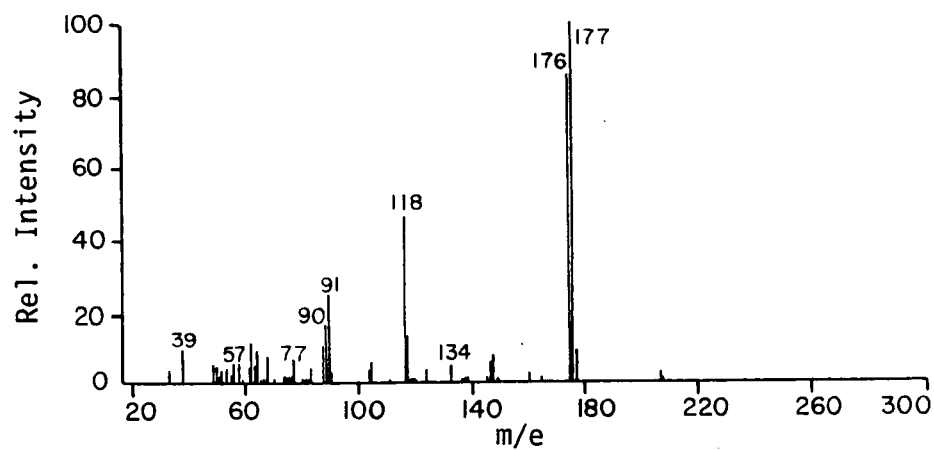


Figure 23. Methylbenzenedicarboxylic acid dimethyl ester (isomer).

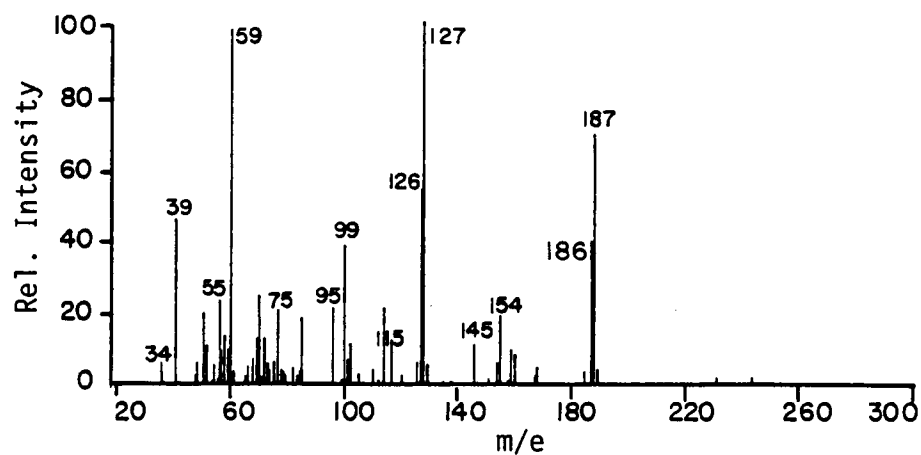


Figure 24. Tricarballic acid trimethyl ester.

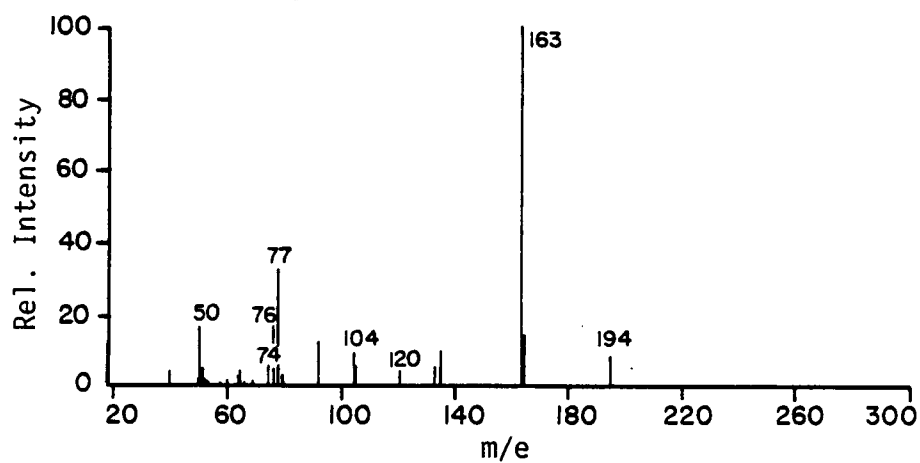


Figure 25. 1,2-Benzenedicarboxylic acid dimethyl ester.

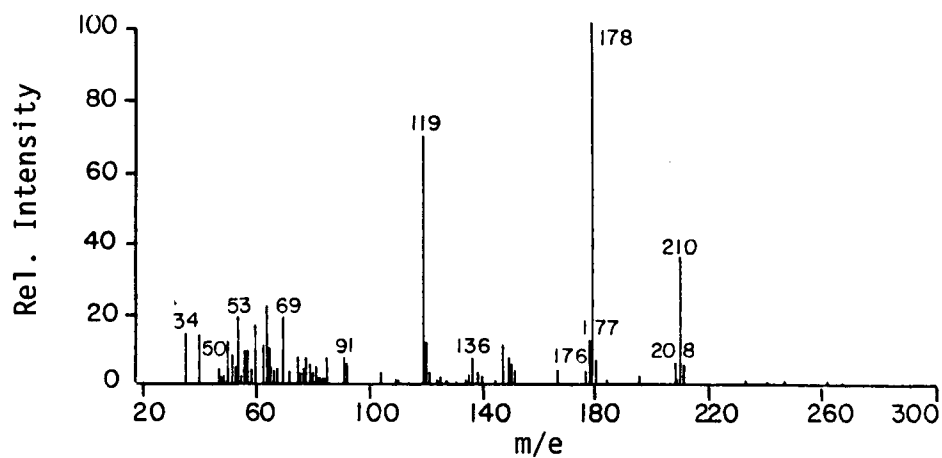


Figure 26. Dimethylfurancarboxylic acid dimethyl ester.

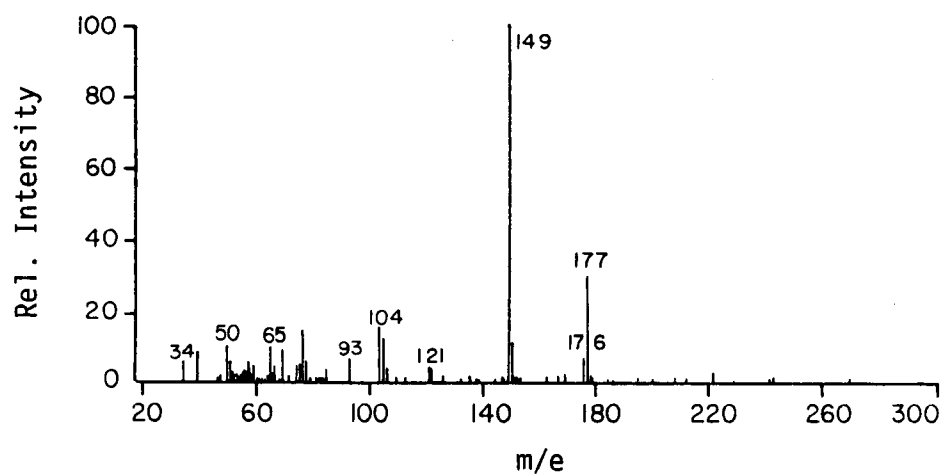


Figure 27. Phthalate ester (contaminant).

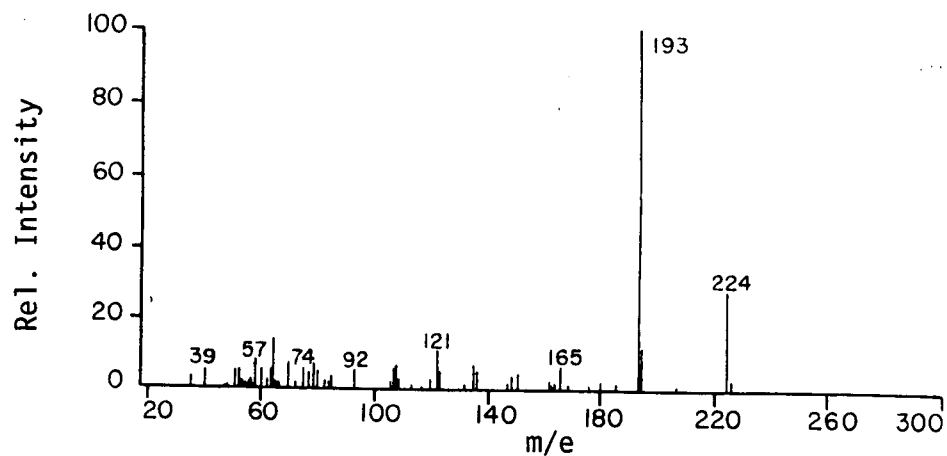


Figure 28. Methoxybenzenedicarboxylic acid dimethyl ester (isomer).

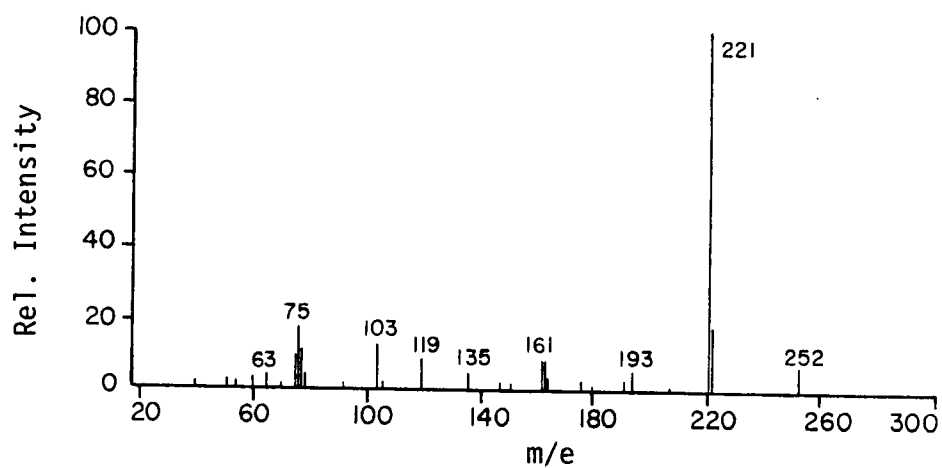


Figure 29. 1,2,4-Benzenetricarboxylic acid trimethyl ester.

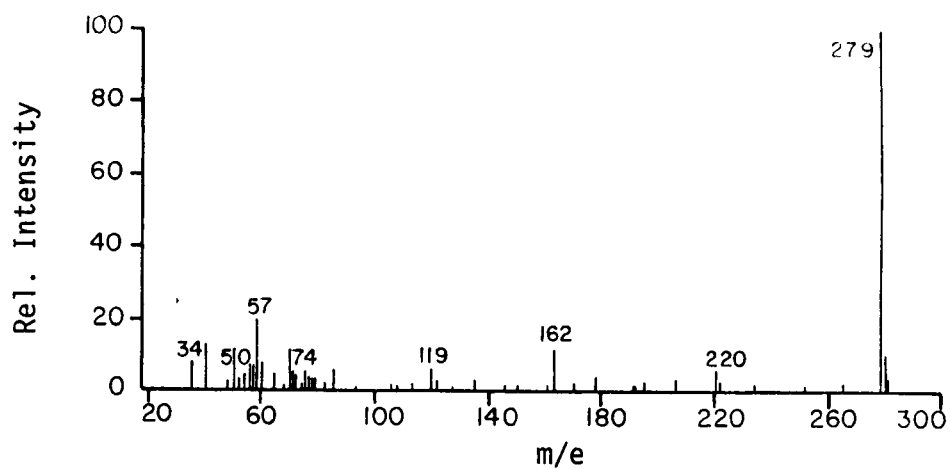


Figure 30. Benzenetetracarboxylic acid tetramethyl ester (isomer).

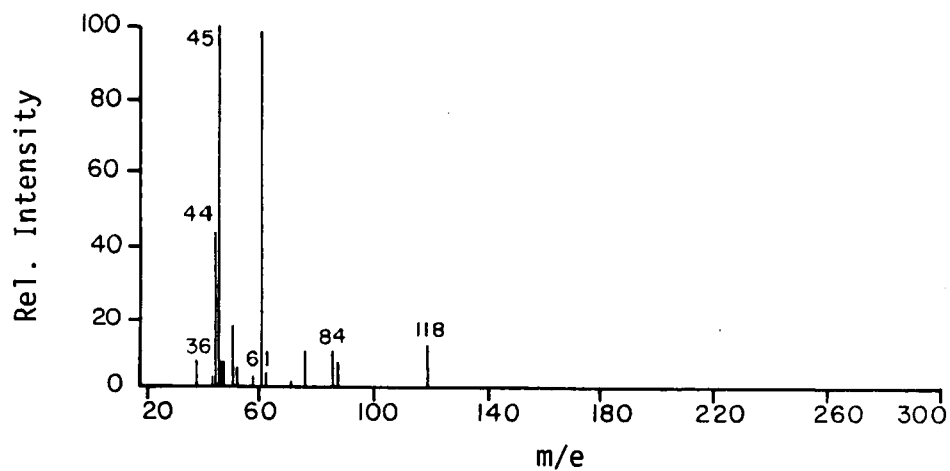


Figure 31. Oxalic acid dimethyl ester.

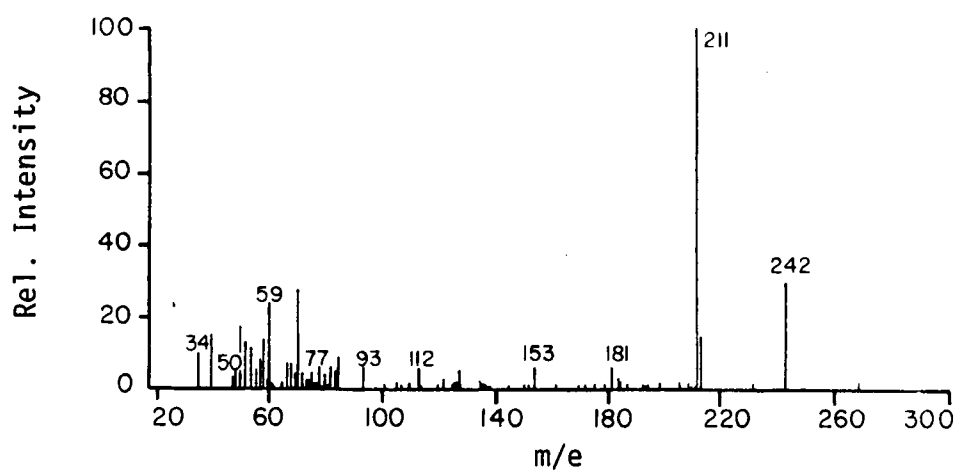


Figure 32. Furantricarboxylic acid trimethyl ester.

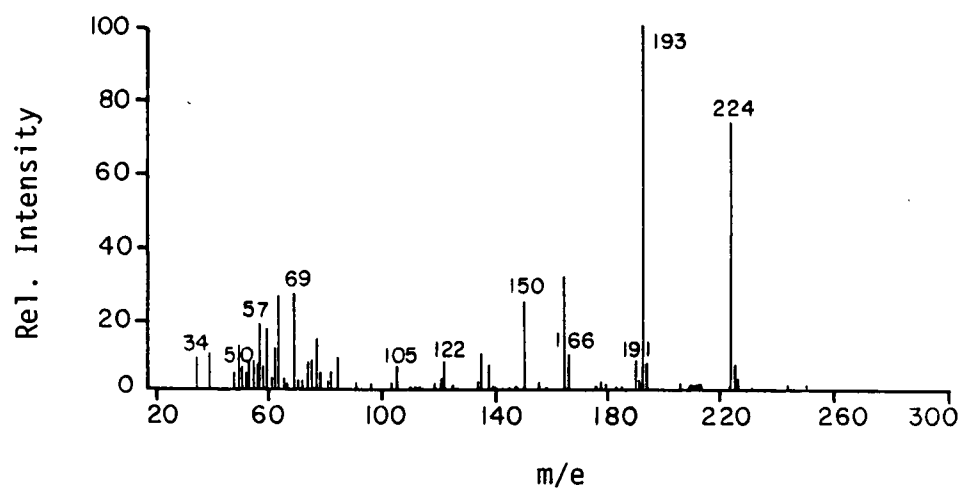


Figure 33. Methoxybenzenedicarboxylic acid dimethyl ester (isomer).

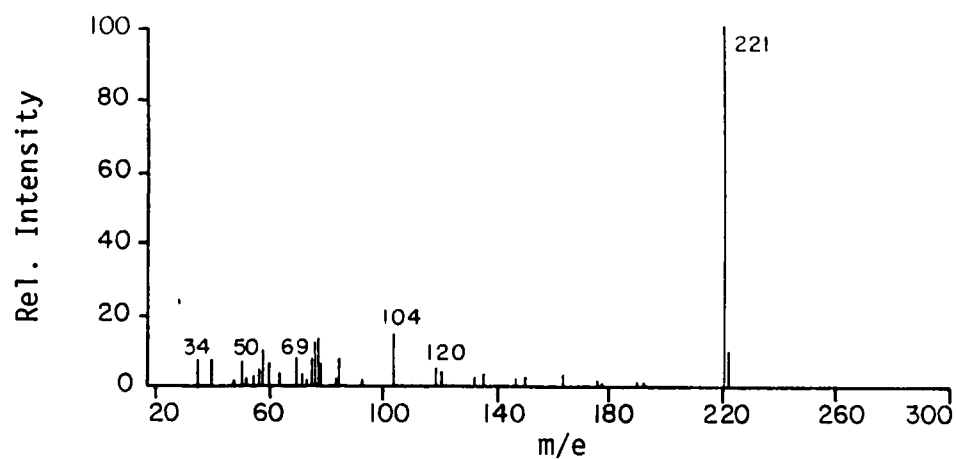


Figure 34. 1,2,3-Benzenetricarboxylic acid trimethyl ester.

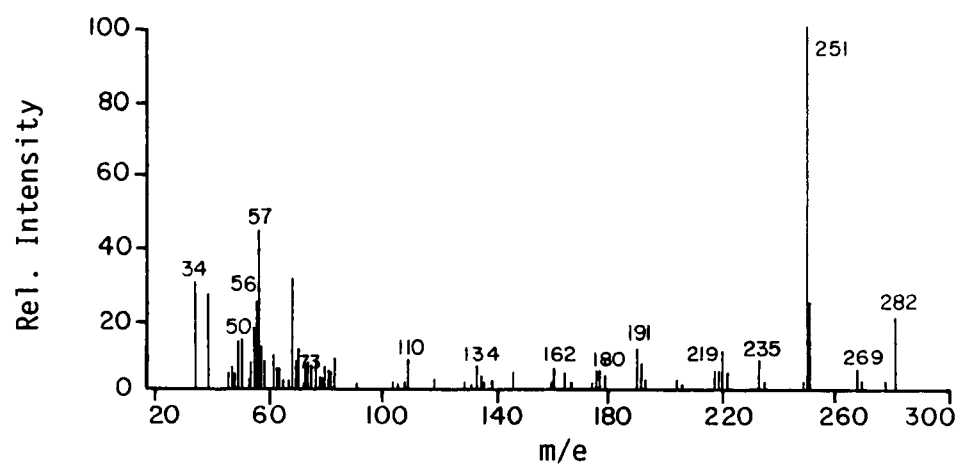


Figure 35. Methoxybenzenetricarboxylic acid trimethyl ester (isomer).

VITA

The author was born in Augusta, Georgia on October 26, 1953. Upon graduating from Oak Ridge High School, Oak Ridge, Tennessee, in 1971 he began his college studies at the University of South Carolina. In 1973 he attended the Universite de Paul Valery in Montpellier, France to study French art and history. He returned to the University of South Carolina in 1974 and matriculated in 1976 graduating Magna Cum Laude with a B.S. in biology. Upon graduation he accepted a position with the Environmental Sciences Division at the Oak Ridge National Laboratory. In 1978 the author took what could best be described as an early sabbatical to study the art of hammer dulcimer making. The following year he returned to the scientific arena to further his research studies and accepted a position as Research Associate with the Department of Microbiology at The University of Tennessee, Knoxville. In 1980 he entered the Ph.D. program in the Graduate Program in Ecology at The University of Tennessee, Knoxville. Following completion of the Ph.D. program in 1984, the author accepted a Postdoctoral Fellowship with IT Enviroscience in Knoxville, Tennessee.