DETERMINATION AND BEHAVIOUR OF POLYNUCLEAR AROMATIC HYDROCARBONS DURING PRIMARY SEDIMENTATION

A thesis submitted to the University of London
in partial fulfilment of the requirements
for the degree of Doctor of Philosophy
in the Faculty of Engineering

by

Nicholas D. Bedding
B.Sc., A.R.C.S., C.Chem., M.R.S.C., M.I.W.E.M.,
M.I.W.Soc., M.R.I.P.H.H., F.R.G.S.

September 1989

Public Health and Water Resource Engineering
Department of Civil Engineering
Imperial College of Science, Technology and Medicine
London SW7 2BU
England

ABSTRACT

The municipal waste water treatment works is a major point source of polynuclear aromatic hydrocarbons (PAH) to lowland rivers. The determination and behaviour of these environmental carcinogens during primary sedimentation is important as the process represents the first stage in the quality regulation of surface waters abstracted for potable supply in areas where indirect water reuse is practised.

An analytical procedure was developed and validated for the determination of 14 PAH in raw sewage, primary effluent and primary sludge. Accuracy, in terms of determinand efficiency of recovery, was a mean of 84%; precision, in terms of total analytical error, ranged from ±10.3% to ±21.3% (95% confidence limits); and sensitivity, as expressed by detection limit, ranged from 0.01 to 0.05 $\mu g\ l^{-1}$.

The removal behaviour of PAH during primary sedimentation was evaluated by means of a pilot plant operated at a range of hydraulic (6.10-61.0 $m^3\ m^{-2}\ d^{-1}$) and suspended solids (SS) (300-1000 $mg\ l^{-1}$) loadings. Mean removals increased with molecular weight (MW) from 21.3% (MW 128) to 63.0% (MW 228), and subsequently decreased to around 52.1% (MW 278) due to preferential association of high molecular weight PAH with small particles (<53 μm) of poorer settleability. PAH removal correlated with SS removal with low molecular weight hydrocarbon removal dependent on SS loading and high molecular weight on hydraulic loading. Regression functions were formulated relating PAH removal to tank performance, enabling prediction of effluent and sludge quality and permitting calculation of discharge limits to sewers.

Reforms of the European Community surface and drinking water directives are proposed for more effective control of PAH in river basins, and recommendations are made on the pending PAH daughter directive under the dangerous substances directive. A monitoring programme for surface waters is presented. Changes in settling column practice for tank design are advised for improved determination of particle settling velocity distributions, and applications to reservoir sedimentation demonstrated.

To My Parents

The river Rhine, it is well known,
Doth wash your city of Cologne;
But tell me, Nymphs, what power divine
Shall henceforth wash the river Rhine?

Samuel Taylor Coleridge
(1772-1834)

ACKNOWLEDGEMENTS

I wish to record my appreciation to the Science and Engineering Research Council for the provision of a studentship.

I am especially indebted to Dr. J.N. Lester for his guidance, invaluable criticism and laudable patience. I am grateful to Prof. R. Perry for the opportunity to undertake the research and for his continued trust. Sincere thanks are due to Dr. A.E. McIntyre for technical expertise and advice, instruction in mass spectrometry and for encouragement. I gratefully acknowledge the support and critical opinion given by friends and colleagues in the Public Health and Water Resource Engineering Section.

My appreciation is extended to Thames Water Authority and particularly to Mr. E.G. Eves and Mr. D.M. Sindall at Hogsmill Valley Water Pollution Control Works for permission to site there and operate the primary sedimentation pilot plant; to Mr. C. Pitches and his workshop staff in the Department, especially Mr. P.F. Clifford and Mr. P. Hart, for commissioning of the pilot plant; and Mr. S.S. Gupta of the Section Laboratory for transportation of samples from the site to the laboratory and for all chemical oxygen demand determinations.

I am most indebted to the Department and College librarians; to Dr. T. Davison of the Department of Mathematics for statistical advice; to Mr. E. Schaeffer and Dr. A. Donev for assistance in the translation of German and Soviet papers respectively; to Dr. R.D. Wing for use of the Departmental word processing facilities; and to Mr. R. Packer of Reprographic Services for preparation of plates.

I am very grateful to Mr. T. Greenway of the School of Molecular Sciences, University of Sussex for helpful discussions on mass spectrometry; to Mr. N.R. Sumption of Thames Water Authority for information on Authority operational practice; and to Mr. G. Thompson of Binnie & Partners and Mr. H.M. McQueen for information on reservoir sedimentation engineering.

And finally, a big thank you to my parents and my brother James for their constant support and encouragement.

CONTENTS

Chapter		Page
ABSTRACT		2
ACKNOWLEDGEMENTS		5
CONTENTS		6
LIST OF TABLES		12
LIST OF FIGURES		18
LIST OF PLATES		19
NOTATION		20
1	INTRODUCTION	24
1.1	Water Quality Control in River Basin Management	24
1.2	Physicochemical Characteristics of PAH	27
1.3	Sources and Occurrence of PAH in Surface and Potable Waters	29
1.4	Significance to Human Health of PAH in Surface and Potable Waters	35
1.4.1	Toxicity Studies	35
1.4.2	Epidemiological Studies	38
1.5	Quality Standards and Legislation	40
1.5.1	Raw and Potable Waters	40
1.5.2	Waste Waters	42
1.5.3	Quality Criteria Selection	44
1.6	PAH Transportation Mechanisms in Raw Waters	45
1.6.1	Sorption	46
1.6.2	Surfactant Micellation	50
1.6.3	Hydrotropy	51
1.7	PAH Transformation Mechanisms in Raw Waters	52
1.7.1	Volatilisation	52
1.7.2	Photodegradation	53
1.7.3	Biodegradation	55

1.8	Behaviour and Removal of PAH During Waste Water Treatment Processes	57
1.8.1	Waste Water Treatment Unit Processes	57
1.8.2	Settlement and Primary Sedimentation	60
1.8.3	PAH Behaviour and Removal	65
1.9	Behaviour and Removal of PAH During Water Treatment Processes	72
1.9.1	Water Treatment Unit Processes	72
1.9.2	PAH Behaviour and Removal	72
1.10	Behaviour of PAH in Surface and Subsurface Environments	76
1.10.1	Urban Surfaces	76
1.10.2	Rural Surfaces	76
1.10.3	Subsurfaces	80
1.11	Analytical Methods for PAH	81
1.11.1	Extraction	81
1.11.2	Cleanup	83
1.11.3	Separation and Determination	84
1.11.4	Waste Water Methods and Analytical Requirements	86
2	OBJECTIVES	89
3	MATERIALS AND METHODS	92
3.1	Analytical Techniques	92
3.1.1	Development of a Procedure for PAH	92
3.1.1.1	Glassware	92
3.1.1.2	Solvents	92
3.1.1.3	Stock and Standard Solutions	92
3.1.1.4	Sample Collection	93
3.1.1.5	Sample Preservation	94
3.1.1.6	Statistical Analyses	94
3.1.1.7	Sample Extraction	94
3.1.1.8	Sample Cleanup Selection	95
3.1.1.8.1	Experimental Design	95
3.1.1.8.2	Preparative Thin Layer Chromatography	96
3.1.1.8.3	Liquid-Liquid Partition	97
3.1.1.8.4	Aluminium Oxide Preparative Column Chromatography	98
3.1.1.8.4.1	Selection of Adsorbent Mass	98
3.1.1.8.4.2	Selection of Adsorbent Deactivation	99

3.1.1.8.5	Silica Gel Preparative Column Chromatography	100
3.1.1.8.5.1	Selection of Adsorbent Mass	100
3.1.1.8.5.2	Selection of Adsorbent Deactivation	101
3.1.1.8.5.3	Column Calibration at 15°C	102
3.1.1.9	Validation of Column Chromatographic Procedure	102
3.1.1.10	Sample Determination	104
3.1.1.10.1	Capillary Column GC	104
3.1.1.10.1.1	Instrument and Calibration Procedure	104
3.1.1.10.1.2	Instrument Precision, Calibration Curve Data and Detection Limits	105
3.1.1.10.2	Capillary Column GC-MS	105
3.1.1.10.2.1	Instrument and Calibration Procedure	105
3.1.1.10.2.2	Instrument Precision, Calibration Curve Data and Detection Limits	108
3.1.1.10.2.3	Accuracy and Precision of Calibration Procedure	108
3.1.1.11	Evaluation of Systematic Error of GC-MS Column Chromatographic Procedure	108
3.1.1.11.1	Demonstration and Quantification of Bias	108
3.1.1.11.2	Dependence of Bias on Sample	109
3.1.1.11.3	Dependence of Bias on Determinand Concentration	109
3.1.1.12	Validation of Efficiency of Extraction Procedure	110
3.1.1.13	Sampling and Storage Parameter Investigation	110
3.1.1.13.1	Sample Integrity Over Time	110
3.1.1.13.2	Influence of Matrix on Sample Integrity	111
3.1.2	Routine Analyses	112
3.1.2.1	Total Solids	112
3.1.2.2	Suspended Solids	112
3.1.2.3	Chemical Oxygen Demand	112
3.2	Laboratory Studies: Physicochemical Behaviour of PAH in Raw and Settled Sewage	114
3.2.1	Assessment of Settleability of PAH	114
3.2.2	PAH Particle Size Distribution Analysis	114
3.2.3	Stability of PAH During Sedimentation	115

3.3	Pilot Plant Study: Removal Behaviour of PAH During Primary Sedimentation	116
3.3.1	Plant Description	116
3.3.1.1	General Design	116
3.3.1.2	Sewage Intake System	119
3.3.1.3	Hydraulic Loading System	119
3.3.1.4	Suspended Solids Loading System	119
3.3.1.5	Mixing Chamber System	120
3.3.1.6	Sedimentation Tank System	120
3.3.1.7	Flow Measurement System	121
3.3.1.8	Sludge Discharge System	121
3.3.1.9	Sampling System	121
3.3.2	Experimental Design	122
3.3.2.1	Process Parameter Selection	122
3.3.2.2	Sampling	123
3.3.3	Experimental Execution	124
3.3.3.1	Start-Up	124
3.3.3.2	Equilibration Period	125
3.3.3.2.1	Adjustment of Hydraulic Loading	125
3.3.3.2.2	Adjustment of Suspended Solids Loading	125
3.3.3.3	Sampling Period	126
3.3.3.4	Termination	127
4	RESULTS	128
4.1	Development of an Analytical Procedure for PAH	128
4.1.1	Capillary Column GC Determination	128
4.1.1.1	Resolution	128
4.1.1.2	Instrument Precision, Calibration Curve Data and Detection Limits	128
4.1.2	Sample Extraction	129
4.1.3	Sample Cleanup Selection	130
4.1.3.1	Preparative Thin Layer Chromatography	131
4.1.3.2	Liquid-Liquid Partition	132
4.1.3.3	Aluminium Oxide Preparative Column Chromatography	133
4.1.3.3.1	Selection of Adsorbent Mass	134
4.1.3.3.2	Selection of Adsorbent Deactivation	135
4.1.3.4	Silica Gel Preparative Column Chromatography	136
4.1.3.4.1	Selection of Adsorbent Mass	136
4.1.3.4.2	Selection of Adsorbent Deactivation	136

4.1.3.4.3	Column Calibration at 15°C	137
4.1.4	Validation of Column Chromatographic Procedure by GC	139
4.1.5	Capillary Column GC-MS Determination	146
4.1.5.1	Resolution	146
4.1.5.2	Instrument Precision, Calibration Curve Data and Detection Limits	146
4.1.5.3	Accuracy and Precision of Calibration Procedure	147
4.1.6	Validation of Column Chromatographic Procedure by GC-MS	147
4.1.7	Evaluation of Systematic Error of GC-MS Column Chromatographic Procedure	153
4.1.7.1	Evidence for a Matrix Effect Mediated by Determinand Sorption	153
4.1.7.2	Quantification of Bias	154
4.1.7.3	Dependence of Bias on Sample	156
4.1.7.4	Dependence of Bias on Determinand Concentration	158
4.1.7.5	Correction for Bias	160
4.1.8	Validation of Efficiency of Extraction Procedure	161
4.1.9	Overall Assessment of GC-MS Column Chromatographic Procedure	164
4.1.9.1	Comparison With GC Determination	164
4.1.9.2	Characterisation of Procedure Performance Characteristics	166
4.1.10	Sampling and Storage	169
4.1.10.1	Sample Integrity Over Time	169
4.1.10.2	Influence of Matrix on Sample Integrity	172
4.2	Physicochemical Behaviour of PAH in Raw and Settled Sewage	175
4.2.1	Assessment of Settleability of PAH	175
4.2.2	PAH Particle Size Distribution Analysis	176
4.2.2.1	Test of Determinand Sorption to Sieve Material	176
4.2.2.2	Distribution Analysis of Raw Sewage	177
4.2.2.2.1	PAH Particle Size Distribution on a Sample Volume Basis	179
4.2.2.2.2	PAH Particle Size Distribution on a Particle Mass Basis	183
4.2.3	Stability of PAH During Sedimentation	184

4.3	Removal Behaviour of PAH During Primary Sedimentation	187
4.3.1	Evaluation of Primary Sedimentation Pilot Plant Performance	188
4.3.1.1	Removal of Co-Determinands	188
4.3.1.1.1	Range of Removals Observed	188
4.3.1.1.2	Influence of Hydraulic Loading and SS Loading on Removals	191
4.3.1.2	Assessment of Removal of SS	193
4.3.1.2.1	Influence of Hydraulic Loading on Removal	193
4.3.1.2.2	Influence of SS Loading on Removal	194
4.3.2	Removal of PAH	195
4.3.2.1	Range of Removals Observed	195
4.3.2.2	Influence of Hydraulic Loading on Removals	199
4.3.2.3	Influence of SS Loading on Removals	200
4.3.2.4	Influence of Co-Determinand Removals on PAH Removals	202
4.3.2.4.1	Influence of SS Removal	202
4.3.2.4.2	Influence of NVSS Removal	204
4.3.2.4.3	Influence of VSS Removal	205
4.3.2.4.4	Influence of Total COD Removal	206
4.3.2.4.5	Influence of Soluble COD Removal	207
4.3.2.4.6	Relative Influence of Co-Determinand Removals	208
4.3.3	Formulation of Regression Functions Relating PAH Removal to Plant Performance	209
5	DISCUSSION	212
6	CONCLUSIONS	260
BIBLIOGRAPHY		274
APPENDIX 1		307
APPENDIX 2		308
APPENDIX 3		315
APPENDIX 4		317
APPENDIX 5		318
APPENDIX 6		335

LIST OF TABLES

		Page
1.	Major Parent PAH	26
2.	Physicochemical Characteristics of PAH	28
3.	Major Routes of PAH Into Surface Waters	30
4.	Contribution of Industrial Effluent and Urban Runoff to PAH Concentration (ng l^{-1}) in Raw Sewage	31
5.	Occurrence and Concentration (ng l^{-1}) of PAH in Various Waters	33
6.	Toxicity of PAH	35
7.	UK Epidemiological Studies on Health Risks Associated With Organic Substances in Water Supplies	39
8.	Removal of PAH During Waste Water Treatment After Reichert *et al*. (1971)	66
9.	Removal (%) of PAH During Waste Water Treatment After Petrasek *et al*. (1983)	68
10.	Removal (%) of PAH During Waste Water Treatment Processes After Hannah *et al*. (1986)	69
11.	Concentration (mg kg^{-1} Dried Sample) of PAH in Sewage Sludges from Three Surveys	71
12.	Concentration of PAH in a UK Water Treatment Works After Harrison *et al*. (1976a) and Removal in Three US Works After Basu & Saxena (1978b)	73
13.	Extraction and Preconcentration Methods for PAH	82
14.	Cleanup Methods for PAH	83
15.	Separation and Determination Methods for PAH	84
16.	Minimum Requirements for Analytical Method Validation	87
17.	Analytical Methods for PAH in Municipal Waste Waters	88
18.	GC-FID Instrument Settings	104
19.	MS-SIM Instrument Settings	107
20.	Flow Conditions and Corresponding Retention Times Adopted for the Primary Sedimentation Pilot Plant	122
21.	Experimentation Programme for the Primary Sedimentation Pilot Plant	123
22.	Sampling Programme for the Primary Sedimentation Pilot Plant	124
23.	GC Instrument Precision, Calibration Curve Data, Detection Limits and Sensitivity for PAH Determination by Flame Ionisation Detection	130
24.	Efficiency of Recovery of Determinand from TLC Plate	131

25. Efficiency of Recovery of Determinand from DMF Liquid-Liquid Partition 133
26. Efficiency of Recovery of Determinand from Aluminium Oxide Column 135
27. Efficiency of Recovery of Determinand from Silica Gel Column 138
28. GC Analysis of Sludge Sample and Evaluation of Efficiency of Recovery of Determinand 142
29. GC Analysis of Sewage Sample and Evaluation of Efficiency of Recovery of Determinand 143
30. Summary of Results for Efficiency of Recovery (%) of Determinand from Sludge and Sewage Sample Determined by GC 145
31. GC-MS Instrument Precision, Calibration Curve Data, Detection Limits and Sensitivity for PAH Determination by Selected Ion Monitoring 146
32. GC-MS Analysis of Sludge Sample and Evaluation of Efficiency of Recovery of Determinand 149
33. GC-MS Analysis of Sewage Sample and Evaluation of Efficiency of Recovery of Determinand 150
34. Summary of Results for Efficiency of Recovery (%) of Determinand from Sludge and Sewage Sample Determined by GC-MS 152
35. Demonstration and Estimation of Bias in GC-MS Determination of Treated Sample of Sludge 155
36. Demonstration and Estimation of Bias in GC-MS Determination of Treated Sample of Sewage 156
37. Evaluation of Dependency of GC-MS Bias on Sample 157
38. Evaluation of Dependency of GC-MS Bias on Determinand Concentration 159
39. Corrected Results for Efficiency of Recovery (%) of Determinand from Sludge and Sewage Sample Determined by GC-MS 160
40. Assessment of Efficiency of Extraction Procedure for Indigenous Determinand in a Sample of Sewage 162
41. Comparison Between GC and GC-MS Determination (µg) of Sludge Sample and Associated Spiked Subsamples 164
42. Comparison Between GC and GC-MS Determination (µg) of Sewage Sample and Associated Spiked Subsamples 165
43. Random, Systematic and Total Errors, and Detection and Quantification Limits for Analytical Procedure 168

44. Evaluation of Sample Integrity Through Analysis of a Sample of Raw Sewage Over an Extended Time Period 170
45. Effect of Absence of Preservation on Analysis of a Sample of Raw Sewage After 28 Days 172
46. Effect of Absence of Preservation on Analysis of a Sample of Distilled Deionised Water, Containing Determinand, After 28 Days 173
47. Assessment of the Effect of Sedimentation and Centrifugation on PAH in a Sample of Raw Sewage 175
48. Test of Determinand Sorption to Sieve Material Used in Particle Size Distribution Analysis 176
49. PAH and Particle Size Distribution Analysis of a Sample of Raw Sewage 177
50. PAH Particle Size Distribution in Sample of Raw Sewage Expressed as Microgram PAH per Litre Sample 179
51. Linear Regression Analysis of Filtrate PAH Mass on Filtrate SS Mass Obtained in Particle Size Distribution Analysis 181
52. PAH Particle Size Distribution in Sample of Raw Sewage Expressed as Microgram PAH per Gram, Dry Weight, SS 183
53. Assessment of the Influence of Volatilisation and Photodegradation on Removal of PAH in a Sample of Settled Sewage Over 48 h 184
54. Assessment of the Influence of Volatilisation and Photodegradation on Removal of PAH in a Sample of Distilled Water Over 48 h 185
55. Removal Efficiency and Mass Balance of SS, NVSS, VSS, Total and Soluble COD Obtained at Each Hydraulic and SS Loading of the Primary Sedimentation Pilot Plant 190
56. Influence of Hydraulic and SS Loading on Removal Efficiency (%) of SS, NVSS, VSS, Total and Soluble COD 191
57. Influence of Hydraulic and SS Loading on Removal Efficiency (%) of PAH 196
58. Mass Balance of PAH Obtained During the Primary Sedimentation Pilot Plant Experimentation Programme 198
59. Correlation of Removal Efficiency of PAH on Hydraulic Loading 200

60. Correlation of Removal Efficiency of PAH on SS Loading 201
61. Correlation of Removal Efficiency of PAH on Removal Efficiency of SS 203
62. Correlation of Removal Efficiency of PAH on Removal Efficiency of NVSS 204
63. Correlation of Removal Efficiency of PAH on Removal Efficiency of VSS 205
64. Correlation of Removal Efficiency of PAH on Removal Efficiency of Total COD 206
65. Correlation of Removal Efficiency of PAH on Removal Efficiency of Soluble COD 207
66. Correlation of Removal Efficiency of PAH on Removal Efficiency of SS, NVSS, VSS, Total and Soluble COD Over All Hydraulic and SS Loadings 208
67. Linear Regression Function for Removal Efficiency of PAH on Removal Efficiency of SS Achieved During Primary Sedimentation 209
68. Removal Efficiency (%) of SS for Pilot Plant Predicted by Five Performance Relationships for Primary Sedimentation Tanks 222
69. Accuracy and Precision of the Daily GC-MS Calibration Procedure for PAH Determination by Selected Ion Monitoring 307
70. Procedure Performance Characteristics 313
71. Mean Influent, Mean Effluent and Sludge Concentration of SS, NVSS, VSS, Total and Soluble COD Obtained At Each Hydraulic and SS Loading of the Primary Sedimentation Pilot Plant 315
72. Primary Sedimentation Data for Hogsmill Valley Water Pollution Control Works Over Period of Pilot Plant Experimentation Programme 317
73. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 0.5 DWF and a Mean SS Loading of 437 mg l^{-1} (SS_0) 319
74. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 0.5 DWF and a Mean SS Loading of 565 mg l^{-1} (SS_1) 320

75. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 0.5 DWF and a Mean SS Loading of 781 mg l^{-1} (SS_2) 321
76. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 0.5 DWF and a Mean SS Loading of 981 mg l^{-1} (SS_3) 322
77. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 1.0 DWF and a Mean SS Loading of 322 mg l^{-1} (SS_0) 323
78. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 1.0 DWF and a Mean SS Loading of 479 mg l^{-1} (SS_1) 324
79. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 1.0 DWF and a Mean SS Loading of 677 mg l^{-1} (SS_2) 325
80. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 1.0 DWF and a Mean SS Loading of 858 mg l^{-1} (SS_3) 326
81. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 3.0 DWF and a Mean SS Loading of 408 mg l^{-1} (SS_0) 327
82. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 3.0 DWF and a Mean SS Loading of 792 mg l^{-1} (SS_1) 328
83. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 3.0 DWF and a Mean SS Loading of 822 mg l^{-1} (SS_2) 329
84. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 3.0 DWF and a Mean SS Loading of 944 mg l^{-1} (SS_3) 330

85. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 5.0 DWF and a Mean SS Loading of 442 mg l^{-1} (SS_0) 331
86. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 5.0 DWF and a Mean SS Loading of 464 mg l^{-1} (SS_1) 332
87. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 5.0 DWF and a Mean SS Loading of 651 mg l^{-1} (SS_2) 333
88. Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 5.0 DWF and a Mean SS Loading of 767 mg l^{-1} (SS_3) 334
89. Linear Regression Function, Arcsin Transformed, for Removal Efficiency of PAH on Removal Efficiency of SS Achieved During Primary Sedimentation 335

LIST OF FIGURES

		Page
1.	Laboratory Settling Column Showing SS Isopercentage Removal Curve Data Obtained Therefrom, After Metcalf & Eddy (1979)	62
2.	Schematic Flow Diagram of the Principal Features of the Primary Sedimentation Pilot Plant	118
3.	Pilot Plant Sedimentation Tank Elevation	120
4.	GC-FID Chromatogram of a Mixed Standard Solution of PAH (10.0 $\mu g\ ml^{-1}$, Attenuation 1 x 32; Instrumental Conditions Given in Section 3.1.1.10.1.1)	129
5.	GC-FID Chromatogram of a Treated Sample of Raw Sewage (Attenuation 1 x 32; Instrumental Conditions Given in Section 3.1.1.10.1.1)	139
6.	GC-FID Chromatogram of the Treated Sample of Raw Sewage (Figure 5) Under Variable Attenuation	140
7.	Dependence of GC-MS Analytical Response Constant on Determinand Standard Addition Concentration	159
8.	GC-MS SIM Mass Chromatograms of a Treated Sample of Raw Sewage (Instrumental Conditions Given in Section 3.1.1.10.2.1)	166
9.	Integrity of a Sample of Raw Sewage Over an Extended Time Period	171
10.	PAH Particle Size Distribution of a Sample of Raw Sewage (Sample Volume Basis)	180
11.	Influence of Pilot Plant Hydraulic Loading on Mean Removal of SS	193
12.	Influence of Pilot Plant SS Loading on Mean Removal of SS	194
13.	Overall Mean Removals of PAH Achieved During the Pilot Plant Experimentation Programme	198
14.	Dependence of PAH Removal on SS Removal Achieved During Primary Sedimentation	210
15.	Relationship Between PAH Waste Water/Sludge Phase Concentration Factor (CF) and Octanol/Water Partition Coefficient (K_{OW}) for Pilot Plant Data	228
16.	Relationship Between PAH Dissolved/Particulate Phase Partition Coefficient (K_p) and Octanol/Water Partition Coefficient (K_{OW}) for Raw Sewage Sample	231
17.	Influence of Pilot Plant SS Loading on Ratio of Mean Removal of AE (R_{AE}) to Mean Removal of SS (R_{SS})	234
18.	Reservoir Sediment Trap Efficiency Curve After Brune (1953)	247

LIST OF PLATES

		Page
1.	View of the GC-MS System	106
2.	View of the Primary Sedimentation Pilot Plant	117

NOTATION

PAH = Polynuclear Aromatic Hydrocarbons

A = anthracene
$A\text{-}d_{10}$ = deuterated anthracene
AE = acenaphthene
AY = acenaphthylene
BaA = benz[a]anthracene
BaP = benzo[a]pyrene
BbF = benzo[b]fluoranthene
BeP = benzo[e]pyrene
BF = benzofluoranthenes
BghiP = benzo[ghi]perylene
BjF = benzo[j]fluoranthene
BkF = benzo[k]fluoranthene
CH = chrysene
DBahA = dibenz[a,h]anthracene
F = fluorene
FL = fluoranthene
IP = indeno[1,2,3-cd]pyrene
N = naphthalene
P = pyrene
PA = phenanthrene

Prefixes

p = pico (10^{-12} x)
n = nano (10^{-9} x)
μ = micro (10^{-6} x)
m = milli (10^{-3} x)
c = centi (10^{-2} x)
k = kilo (10^{3} x)
M = mega (10^{6} x)

Greek/Mathematical Symbols

r = correlation coefficient
σ = standard deviation
Σ = sum

Abbreviations, Symbols & Units

a = annum
A = ampere
A = analytical response
ABS = acrylonitrile-butadiene-styrene
amu = atomic mass unit
ASTM = American Society for Testing and Materials
atm = atmosphere
BOD = biological oxygen demand
b.p. = boiling point
C = concentration
^{o}C = degree Celsius
CF = concentration factor
CMC = critical micellar concentration
COD_{sol} = soluble (filterable) chemical oxygen demand
COD_{tot} = total chemical oxygen demand
COPA II = Control of Pollution Act Part II
corr. = corrected
d = day
DMF = dimethylformamide
DMSO = dimethylsulphoxide
DOC = dissolved organic carbon
DOM = dissolved organic matter
DWF = dry weather flow
E = effluent
EC = European Community
EI = electron impact
EPA = Environmental Protection Agency
EQO = environmental quality objective
EQS = environmental quality standard
ES = emission standard
eV = electronvolt
f_{OC} = mass fractional organic carbon content
FID = flame ionisation detection
g = gram
$\underline{g}$ = gravitational acceleration
GC = gas chromatography
GC-MS = gas chromatography-mass spectrometry
h = hour
H = Henry's Law Constant
ha = hectare
HPLC = high performance liquid chromatography

Hz = hertz
I = influent
i.d. = internal diameter
IUPAC = International Union of Pure and Applied Chemistry
K_{OC} = K_P normalised to f_{OC}
K_{OW} = n-octanol/water partition coefficient
K_P = dissolved/particulate phase partition coefficient
l = litre
LD_{50} = median lethal dose
m = metre
M = molar
MAC = maximum acceptable concentration
MB = mass balance
MDL = method detection limit
min = minute
mol = mole
MS = mass spectrometry
MW = molecular weight
m/z = mass to charge ratio
N = normal (concentration)
ND = non-detectable
NQ = non-quantifiable
NVSS = non-volatile suspended solids
NWC = National Water Council
pH = hydrogen ion concentration, negative logarithm of
p.p.b. = parts per billion
p.p.m. = parts per million
PTFE = polytetrafluoroethylene
QRA = quantitative risk assessment
R = removal
$\underline{R}_F$ = relative band speed to front
rev = revolution
RQO = river quality objective
RS = repetitive scanning
RSD = relative standard deviation
RWA = Regional Water Authority
s = second
S = sludge
SIM = selected ion monitoring
SS = suspended solids
t = tonne
THM = trihalomethane
TLC = thin layer chromatography

Torr = torr
TS = total solids
UES = uniform emission standard
UK = United Kingdom
US(A) = United States (of America)
USSR = Union of Soviet Socialist Republics
UV = ultraviolet
V = volt
VSS = volatile suspended solids
V/V = volume by volume
W = watt
WHO = World Health Organization
W/V = weight by volume
W/W = weight by weight

1. INTRODUCTION

1.1 Water Quality Control in River Basin Management

The Greek physician Hippocrates (ca. 460-357 B.C.) in his book 'De Aere Aquis Locis' (About Air, Water and Places) related the occurrence of certain diseases to the presence of stagnant waters (Susser, 1973). Although catastrophic epidemics of diseases such as Asiatic cholera and typhoid which struck London in the nineteenth century have now been eliminated by major improvements in the bacteriological quality of the River Thames and supplies drawn therefrom, present-day concern is directed more toward the effect on health of the chemical composition of water (Young, 1985).

It has become increasingly necessary for many developed countries to draw supplies from surface water sources, particularly lowland rivers, in order to meet domestic and industrial requirements for water at acceptable costs. Many of these rivers, which number some of the world's greatest such as the Thames, Rhine, Seine and Ohio, are required by modern society to cope with a multiplicity of other uses, ranging from irrigation and land drainage, and conveyance of sewage and other wastes to the sea, to transport, fisheries and recreation.

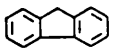
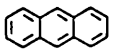
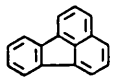
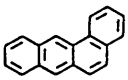
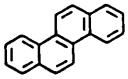
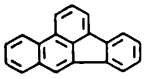
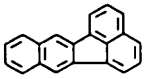
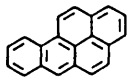
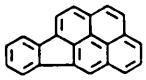
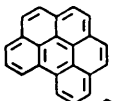
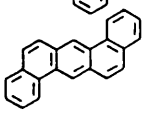
Lowland rivers may typically contain treated sewage and industrial effluent, and urban and rural runoff. The production of potable water from such rivers requires careful management of water quality. Approximately one third of water supplies in the UK are derived from lowland rivers containing sewage effluent and more than seven million consumers receive water from sources containing a mean of at least 10% sewage effluent (Ridgway, 1985). In the River Thames the mean proportion of river flow due to sewage effluent increases along its course to reach a maximum of 14% near the lowest abstraction point, which, during dry weather, can reach a maximum of 141% (Water Resources Board, 1973). The overall mean proportion in the Thames Basin is reported to be 12% (Jamieson & Nicolson, 1984).

Concern over organic micropollutants in river basin management, already reflected in quality standards and legislation, is likely to increase in future with the growth of industrialization and urbanisation. Some 70000 chemicals are available on the commercial market worldwide, with an estimated additional 1000 entering the market each year, bringing a concomitant increase in production tonnage: a doubling approximately every eight years in the case of US organic chemicals (Lewis, 1985). A proportion of these chemicals will inevitably find their way into surface waters. In the Thames Basin the projection for water demand is a 25% increase for the period 1986/7-2006/7, thereby placing a further demand on surface water abstraction which currently represents 58% of the total supply (Jamieson & Nicolson, 1984). The increased demand will bring a corresponding increase in discharges to the same source.

Polynuclear (polycyclic) aromatic hydrocarbons (PAH) are of particular concern in water quality control as they represent a major and ubiquitous class of environmental carcinogens possessing a marked recalcitrance. They constitute a homologous series of two or more condensed rings (benzene nuclei) (Table 1). They are neutral (i.e. non-polar) and hence are hydrophobic, possessing low aqueous solubilities and a pronounced tendency to sorb to particulates and solid surfaces. The PAH in Table 1 are the parent (unsubstituted) PAH which the US Environmental Protection Agency (EPA) has judged necessary to regulate, as 'priority pollutants', in discharges to the aquatic environment (Keith & Telliard, 1979). Six of the list, FL, BbF, BkF, BaP, IP and BghiP, constitute the former World Health Organization (WHO) PAH recommended for monitoring in drinking water (World Health Organization, 1970, 1971), of which the potent carcinogen, BaP, has been the subject of most interest.

In addition to the parent PAH, substituted PAH containing functional moieties such as alkyl ($-CH_3$), hydroxy (-OH), nitro ($-NO_2$) and carboxy ($-CO_2H$) groups, and heterocyclic PAH where atoms of nitrogen, oxygen or sulphur replace one or more ring carbon atoms, are generally found to co-exist. They commonly derive from the incomplete combustion at

TABLE 1
Major Parent PAH

PAH[a]	Abbrev.	Molec. weight	Molec. formula	Molec. struc.	No. rings
Naphthalene	N	128	$C_{10}H_8$		2
Acenaphthylene	AY	152	$C_{12}H_8$		3
Acenaphthene	AE	154	$C_{12}H_{10}$		3
Fluorene	F	166	$C_{13}H_{10}$		3
Phenanthrene	PA	178	$C_{14}H_{10}$		3
Anthracene	A	178	$C_{14}H_{10}$		3
Fluoranthene	FL	202	$C_{16}H_{10}$		4
Pyrene	P	202	$C_{16}H_{10}$		4
Benz[a]anthracene	BaA	228	$C_{18}H_{12}$		4
Chrysene	CH	228	$C_{18}H_{12}$		4
Benzo[b]fluoranthene	BbF	252	$C_{20}H_{12}$		5
Benzo[k]fluoranthene	BkF	252	$C_{20}H_{12}$		5
Benzo[a]pyrene	BaP	252	$C_{20}H_{12}$		5
Indeno[1,2,3-cd]pyrene	IP	276	$C_{22}H_{12}$		6
Benzo[ghi]perylene	BghiP	276	$C_{22}H_{12}$		6
Dibenz[a,h]anthracene	DBahA	278	$C_{22}H_{14}$		5

[a] IUPAC systematic name, except for benzo[b]fluoranthene (benz[e]acephenanthrylene).

temperatures exceeding 700°C of organic matter (hydrocarbon based materials), and have been found in a wide variety of environmental matrices ranging from water, air and soil to plants, food and fossil fuels (Neff, 1979).

In localities where urban runoff and industrial effluent are routed via combined sewerage to the municipal waste water treatment works, the treated effluent may serve as the major point source of PAH in a lowland river. The primary concern of PAH in the context of river basin management is with the possible effect on human health and hence of the impact of PAH on drinking water quality. The potential health effect of PAH is carcinogenesis; cancer is the leading cause of death between the ages of 35 and 64 in the UK (Office of Population Censuses and Survey, 1985). Therefore with regard to PAH, the sewage treatment works can be considered as the first stage in the regulation of potable water quality in river basins employing indirect water reuse. The possible multiplicity of upstream effluent discharges leading to build-up of recalcitrant substances and contamination of potable supplies may be controlled in practice by integral operation of the three 'elements' consisting of sewage treatment, river self-purification and water treatment, in a manner consistent with optimal river basin management.

1.2 Physicochemical Characteristics of PAH

The physicochemical characteristics of water pollutants determine to a large degree their behaviour in the aquatic environment and their susceptibility to control by environmental engineering systems. The most important parameters relating to PAH are given in Table 2. The data are not complete. The parameters are interrelated, and each varies in a more or less regular fashion with molecular weight (MW). The aqueous solubilities of the priority pollutant PAH range over a very wide five orders of magnitude, in general decreasing quasi-logarithmically with increasing molecular weight. The suite of PAH may therefore be expected to display a wide range of behaviour characteristics in the aquatic environment.

TABLE 2
Physicochemical Characteristics of PAH

PAH	Boiling point[a] (°C)	Vapour pressure[b] (Torr)	Aqueous solubility[c] (μg l^{-1})	log K_{OW}[d]	H[e] (atm m^3 mol^{-1})
N	218	0.23	31700	3.36	3.6×10^{-4}
AY	265		16100	3.94	
AE	279		3930	4.03	1.9×10^{-4}
F	293		1980	4.47	2.1×10^{-4}
PA	340	6.80×10^{-4}	1290	4.57	1.3×10^{-4}
A	340	1.95×10^{-4}	73	4.54	1.4×10^{-3}
FL	375	5.10×10^{-6}	260	5.22	1.0×10^{-5}
P	393	6.85×10^{-7}	135	5.18	1.3×10^{-6}
BaA	435	1.10×10^{-7}	14	5.91	1.2×10^{-7}
CH	448		2.0	5.91	1.5×10^{-6}
BbF			1.5	6.04	
BkF	480	9.59×10^{-11}	0.8	6.04	
BaP	310	5.49×10^{-9}	3.8	6.50	7.5×10^{-6}
IP		1.01×10^{-10}	0.19		1.1×10^{-5}
BghiP		1.01×10^{-10}	0.26	7.10	2.1×10^{-5}
DBahA			2.49	7.19	

[a] Weast (1987).
[b] N, Mackay & Wolkoff (1973); PA, A, Jordan (1954); FL, IP, McVeety & Hites (1988); P, BaA, BkF, BaP, Pupp *et al.* (1974); BghiP, Radding *et al.* (1976). All data at 25°C.
[c] Mackay & Shiu (1977), except: AY, Walters & Luthy (1984a); BbF, BkF, IP, Wise *et al.* (1981); DBahA, Means *et al.* (1980a). All data at 25°C.
[d] log n-octanol/water partition coefficient. N, PA, A, P, Karickhoff *et al.* (1979); AY, AE, F, FL, BaA, CH, BaP, BghiP, DBahA, Walters & Luthy (1984a); BbF, BkF, Environmental Protection Agency (1979). All data at 25°C.
[e] Henry's Law Constant. N, AE, F, PA, A, McCarty (1980); FL, P, BaA, CH, Petrasek *et al.* (1983); BaP, IP, BghiP, McVeety & Hites (1988). All data at 25°C.

PAH aqueous solubilities are sensitive to temperature (Whitehouse, 1984; May *et al.*, 1978). Solubility of PA increases from 2.01 to 6.16 μmol l^{-1} and A from 53.9 to 248 nmol l^{-1} between 4.6 and 25.3°C, BaA from 21.3 to 37.4 nmol l^{-1} between 3.7 and 25.0°C, and BaP from 2.64 to 6.09 nmol l^{-1} between 8.0 and 25.0°C (Whitehouse, 1984). Dependence on salinity is appreciably less with PAH aqueous solubilities generally decreasing with increasing salinity (the 'salting out' effect) (Whitehouse, 1984; Eganhouse & Calder, 1976; Rossi & Thomas, 1981).

1.3 Sources and Occurrence of PAH in Surface and Potable Waters

A knowledge of sources of PAH in the environment is essential for effective management of water quality in river basins. Natural sources of PAH include grass and forest fires, geological sedimentary diagenesis, and biosynthesis by micro-organisms and plants, but the latter two continue to be controversial (Neff, 1979). Of generally agreed superior significance are the anthropogenic sources consisting chiefly of PAH formation during the combustion of organic matter (Harrison et al., 1975).

Major sources were estimated by Suess (1976) in terms of vapour phase emissions of BaP to the atmosphere (t a^{-1}). Data for the US were as follows. Heat and power generation: coal 34% (nearly all residential), oil and gas <1%, wood 3%; industrial processes: coke production 15%, catalytic cracking <1%; refuse and open burning: enclosed incineration 3%, open burning (refuse fires, grass and forest fires, etc) 43%; vehicles 2%. Equivalent inventories for liquid and solid phase waste emissions do not appear to exist. Other sources include crude and refined petrochemicals which are relatively enriched in three-ring PAH, and a very limited industrial manufacturing of N, A and P (Dierckxsens et al., 1987).

Of more direct concern are the routes of PAH into surface waters (Table 3). Atmospheric PAH, subject to meteorological conditions and physicochemical degradation, may return to the earth's surface via bulk (wet and dry) and vapour phase deposition. Data on concentrations of PAH, particularly BaP, in industrial effluents and as summarised by Neff (1979), are confined to major commercial enterprises. There is a lack of data on the contribution of medium to small scale industrial concerns and for PAH other than BaP. EPA (Environmental Protection Agency, 1982) measured mg l^{-1} concentrations of individual PAH in a wood preserving plant effluent. PAH in domestic effluents are generally considered to arise from cooking, washing, human excreta and sewer inflow/infiltration (Andelman & Suess, 1970), and constitute a relatively low background level. Urban runoff can contain high concentrations of PAH

TABLE 3
Major Routes of PAH Into Surface Waters

Route	Concentration/flux (BaP)	Ref.
Point		
Industrial effluents		
-coke oven	1400-25000 ng l^{-1}	A
-petrochemical	50-5000 ng l^{-1}	B
Domestic effluents	7.8-73.3 ng l^{-1}	C
	9-70 ng l^{-1}	D
	16-35 ng l^{-1}	E
Non-Point		
Urban runoff/deposn.	234000-255000 ng m^{-2} a^{-1}	F
	1000-10000 ng l^{-1}	G
Aerial deposition		
-wet/dry	14700, 27000 ng m^{-2} a^{-1} (wet+dry)	H
	5100-9500 ng m^{-2} a^{-1} (wet+dry)	
	4.2-12.9 ng l^{-1} (wet)	I
	6400 ng m^{-2} a^{-1}/7.8 ng l^{-1} (wet)	
	13900 ng m^{-2} a^{-1}/11.9 ng l^{-1} (wet)	J
-vapour phase	Unquantified	
Fossil fuel spills	Unquantified	K

A Walters & Luthy (1984b); one plant, USA.
B Samoilovich & Redkin (1968); one plant, USSR.
C Lewis (1975); five works with industrial contribution, UK.
D Borneff & Kunte (1967); two secondary treatment works with industrial contribution, W. Germany.
E van Luin & Starkenburg (1985); six secondary treatment works with industrial contribution, Holland.
F Harrison & Johnston (1985); motorway, UK.
G Cole *et al*. (1984); two cities, USA.
H Schrimpff (1984); two regions, W. Germany.
I Thomas (1981); four sites (alpine to heavy-industrial), W. Germany.
J Quaghebeur *et al*. (1983); two sites, Belgium.
K Neff (1979).

(Cole *et al*., 1984) arising from high deposition fluxes from vehicle exhaust (Harrison & Johnston, 1985). The contribution of vehicle condensate (sump oil) and tyre and road (bitumen, asphalt) abrasion to concentrations in runoff are subject to controversy but are generally agreed to be of secondary importance. Concentrations of PAH in rainfall can approach those in domestic effluents (Table 3). However, dry (i.e. particulate) deposition continues to deposit a steady quantity of PAH. Gschwend & Hites (1981) have calculated that, assuming an individual PAH atmospheric concentration of 1 ng m^{-3}, dry depositional flux in northeastern US should range between 3000 and

150000 ng m^{-2} a^{-1} as against a lower wet depositional flux of 800-3000 ng m^{-2} a^{-1}. McVeety & Hites (1988) in a careful study in the Great Lakes region determined that dry deposition of PAH dominated the wet mechanism by an average ratio of 9:1. Quaghebeur et al. (1983) found PAH concentrations in Belgian rain to be highly dependent on season. Maximum fluxes and concentrations in the winter period were two orders of magnitude greater than those in the summer. The authors ascribed the high winter concentrations to household heating.

It is evident from Table 3 that where industrial effluents and urban runoff are routed via combined sewerage systems for treatment, the receiving waste water treatment works becomes a major point source of PAH entering surface waters. The behaviour of PAH in this point source is therefore critical in determining PAH impact on the quality of subsequent potable supplies. Industrial effluent can increase PAH concentrations in domestic effluents, and furthermore, periods of rain can, via runoff, increase concentrations by two to three orders of magnitude over dry weather values (Table 4). Accumulation of pollutants in treatment sludges may affect disposal operations.

TABLE 4
Contribution of Industrial Effluent and Urban Runoff to PAH Concentration (ng l^{-1}) in Raw Sewage[a]

PAH	Domestic sewage	Sewage High % industry		Domestic sewage Dry weather	Heavy rain
FL	793	3420	2660	352	16350
P	398	3120	2560	254	16050
BaA	224	1360	343	25	10360
BbF	584	870	525	39	9910
BkF	54	460	336	22	4180
BaP	47	100	368	1	1840
IP	61	930	476	17	4980
BghiP	78	480	120	4	3840

[a] Borneff & Kunte (1965); municipal waste waters, W. Germany.

The dominant route (Table 3) for a particular surface water environment will be geographically dependent. Numerous workers have sought to identify major routes through determination of the relative abundancies and distributions of unsubstituted and substituted (particularly alkyl homolog) sedimentary PAH and comparison with known source profiles. Giger & Schaffner (1978) attributed 'street dust' as the major source of PAH in sediments, Readman et al. (1984a) road runoff as the primary route to the Tamar Estuary, UK, Hoffman et al. (1985) highway runoff as the primary route to the Pawtuxet River, Rhode Island, US, and Borneff & Kunte (1965) road runoff to surface waters. Hoffman et al. (1984) reported that urban runoff accounted for 16% of the total input of low molecular weight PAH (N, alkylated N and F) but 71% of high molecular weight PAH (PA, FL, P, BaA, CH, BaP and BeP) entering Narragansett Bay, US. The remaining 84% of the low molecular weight PAH derived from treated sewage effluents, whereas for the high molecular weight compounds 18% was attributed to sewage effluents and 10% to atmospheric fallout.

The potential control of surface water routes of PAH are more readily facilitated for point rather than non-point sources. An examination of the behaviour and amenability to control of PAH in non-point sources is of importance in river basin management (Section 1.10).

The occurrence of the six WHO PAH in various waters is given in Table 5. The generally very low concentrations observed in ground water are thought to be derived from the infiltration of rain water through PAH-containing soils (Suess, 1976; Hellmann, 1982; Borneff & Kunte, 1969). Concentrations in soils, upland streams and reservoirs remote from sources of PAH are judged to arise from long-range aerial transport (Bjørseth & Olufsen, 1983).

Lowland rivers exhibit variable but relatively high concentrations. Values for the six WHO PAH in eight UK rivers abstracted for potable supply individually ranged from approximately 1-150 ng l^{-1} (Crane et al., 1981). No clear relationship was apparent between PAH concentrations and the time of year. In an extensive survey of W. German rivers BaP concentration was found to range between 0.8 and

TABLE 5
Occurrence and Concentration (ng l^{-1}) of PAH in Various Waters

PAH	Ground water[a]	Upland stream[b]	Reservoir[c]	Lowland river[d]	Lowland river[e]	Tap water[f]
FL	<0.1-2.7	3-7	5.9-11.4	21.3-192	379-761	ND- 8.9
BbF		<1		12.2- 67.0	76-362	ND- 1.2[g]
BkF		<1	0.4- 3.3	4.2- 21.6	130-173	ND- 0.7
BaP	<0.1-0.5	<1-3	0.7- 5.4	1.1- 6.5	4- 43	0.2-1.6
IP	<0.1-0.4	<1	<1.0- 4.9	12.5- 32.0	116-217	ND- 2.2
BghiP	<0.1-0.3	<1-2	1.5- 6.6	8.0- 25.9	42-105	ND- 4.0

[a] Quaghebeur & De Wulf (1978); six catchments in each of six geological formations (over two years), Belgium.
[b] Crane et al. (1981); two upland moorland streams, UK.
[c] Lewis (1975); four reservoirs, UK.
[d] Borneff & Kunte (1964); River Main at Seligenstadt, W. Germany.
[e] Borneff & Kunte (1965); River Aach at Stockach, W. Germany.
[f] Basu & Saxena (1978b); ten supplies, USA; ND = non-detectable.
[g] BjF.

40.4 ng l^{-1}, other PAH usually varying within one order of magnitude (Grimmer et al., 1981). In a careful investigation along the W. German stretch of the River Rhine, the sum of the six WHO PAH exhibited a four-fold increase from the Swiss to the Dutch border (Hellmann, 1980, 1987). Very high concentrations can be measured depending on geographical location (degree of urbanisation, industrialization, etc.) and hydrological conditions. Rivers have been shown to contain concentrations in excess of 1000 ng l^{-1} (BaP) below discharges of petrochemical works (Samoilovich & Redkin, 1968). During periods of high river flow, PAH concentrations have been observed to rise nearly one order of magnitude due to resuspension of sediments (Fielding & Packham, 1977).

PAH in tap water are generally reported to occur at low concentrations, rarely exceeding more than a few ng l^{-1} individually (Basu & Saxena, 1978b; Benoit et al., 1979; Crane et al., 1981). The presence of all priority pollutant PAH has been reported in Canadian tap waters with 'total' PAH levels correlated with population density

within a water basin (Benoit et al., 1979).

An additional route of PAH into drinking waters is via leaching from coal tar and bitumen (petroleum asphalt) coated distribution pipes and storage tanks. A laboratory investigation of bitumen pipe determined that less than the equivalent of 10 ng l^{-1} for the sum of the six WHO PAH was leached and was deemed insignificant (Miller et al., 1982), but a study of coal tar pipe showed appreciable leaching of the same PAH depending on the nature of the water (Crane et al., 1981). Very high levels (up to 905 ng l^{-1} for BaP and 47000 ng l^{-1} for FL) were found up to week 2 of the experiment with surface water and up to week 9 with ground water. Thereafter levels approached blank (i.e. background) concentrations except for FL which only stabilised around week 20 both for the surface (320 ng l^{-1}) and ground water (180 ng l^{-1}). Coal tar linings have been shown to contain concentrations of individual (carcinogenic) PAH of typically 0.1-1% by weight, but substantially less so for bitumen linings (Alben, 1980; Crane et al., 1981), and concern has been expressed over the potential shedding of fine coal tar particulates with aging of linings (Bull, 1985; Crane et al., 1981). For these reasons both the UK Water Research Centre (Crane et al., 1981) and WHO (World Health Organization, 1984) recommended the discontinued use of coal tar based linings for distribution pipes, and none have been laid in the UK since 1977.

It is important to place tap water PAH in the context of other components (Bedding et al., 1982). In a survey of UK drinking waters derived from a wide variety of sources (Fielding et al., 1981), organic compounds occurring at concentrations in excess of 1000 ng l^{-1} were usually trihalomethanes (THM), trichloroethene, tetrachloroethene and some fatty acids, and furthermore, substantially greater numbers of compounds were identified in waters abstracted from rivers receiving municipal and industrial effluents than elsewhere (Packham et al., 1981).

1.4 Significance to Human Health of PAH in Surface and Potable Waters

1.4.1 Toxicity Studies

PAH number among the relatively few organic micropollutants for which there exists a reasonable body of information on toxicology. Indeed, PAH are associated with the earliest identified carcinogens. Data compiled from a recent WHO monograph (World Health Organization, 1983) are presented in Table 6.

TABLE 6
Toxicity of PAH[a]

PAH	Carcino-genicity	Muta-genicity	Terato-genicity	Toxicity[b] (mg kg^{-1})
F	IE	IE	ID	ID
PA	IE	LE	ID	700
A	No	No	ID	>430
FL	No	LE	ID	2000[c]
P	No	LE	ID	514
BaA	Yes	Yes	IE	Yes
CH	LE	LE	ID	>320
BbF	Yes	IE	ID	ID
BkF	Yes	IE	ID	ID
BaP	Yes	Yes	Yes	250
IP	Yes	IE	ID	ID
BghiP	IE	IE	ID	ID
DBahA	Yes	Yes	ID	ID

Key: Yes = sufficient evidence
LE = limited evidence
IE = inadequate evidence
No = no evidence
ID = no/inadequate data.

[a] Compiled from World Health Organization (1983); data for experimental animals. No data supplied for N, AY and AE.

[b] LD_{50} values for mouse (body weight).

[c] Rat.

The toxicity of a compound refers to its intrinsic capacity to cause injury, including the potential to induce carcinogenic, mutagenic and teratogenic effects; the hazard associated with a compound is the capacity of that substance to cause injury under the circumstances of exposure; quantitative risk assessment (QRA) refers to the

quantification of this hazard (Hunt & Fawell, 1987). Data on carcinogenicity (induction of malignant neoplasms), mutagenicity (induction of mutations in a cultured cell or organism) and teratogenicity (toxicity to a foetus) (World Health Organization, 1983) have very largely been obtained from experimental animals, but WHO warns that 'in the absence of adequate data on humans, it is reasonable, for practical purposes, to regard chemicals for which there is sufficient evidence of carcinogenicity in animals as if they presented a carcinogenic risk to humans.' These include BaA, BbF, BkF, BaP, IP and DBahA (Table 6). Occupation associated skin cancers in man, however, are considered to provide strong evidence of the positive role of PAH in certain kinds of human cancer (Santodonato et al., 1981).

Concentrations of organic micropollutants in drinking water are rarely high enough to exert acute (i.e. short-term) toxic effects, rather interest is primarily focussed on potential chronic (long-term) toxicity arising from long-term exposure to low concentrations, the principal toxic effect of concern being carcinogenicity.

In toxicity studies experiments are performed on individual compounds, mixtures and drinking water extracts, and QRA performed on the data obtained. Hosmer (1986) identified the major components of QRA in drinking water application as hazard identification, dose-response assessment, human exposure assessment, and risk characterisation. QRA enabling determination of acceptable levels of exposure to organic compounds in drinking water are essentially of two types. The first, for non-carcinogens, is based on application of 'safety factors' (10-1000) (Lewis, 1985) depending on the quality of the data and the nature and magnitude of the health risk, to 'no observable adverse effect' dose levels of chemical in animal studies. The approach assumes a threshold level of effect in the dose-response relationship, and gives rise to acceptable daily intakes (ADI) for humans, taking into account other sources of exposure (air, food).

The second approach, for carcinogens such as PAH, is based on the 'single cell mutation theory' of cancer initiation

which states that the initiating event in carcinogenesis is a mutation in a somatic cell, and where it is generally considered that there is no threshold level of effect. Mathematical models of the carcinogenic process based on dose-response curves from animal experiments, and entailing various assumptions, estimate the risk to human populations. Both WHO (World Health Organization, 1984) and EPA (Environmental Protection Agency, 1980) employed a conservative multi-stage linear extrapolation model with consideration of other sources of exposure. WHO considered that the uncertainties in the estimation of risk were considerable and stated that a variation of two orders of magnitude could exist (i.e. from 0.1 to 10x the number). The model derived a concentration (for BaP) for drinking water (Section 1.5) based on an acceptable risk defined as one additional cancer per 100000 population over a lifetime exposure (70 years, 2 l consumption per day by a 70 kg person) to the agent concerned.

It is important to appreciate that the costs of managing risks via quality standards in a water quality control programme are significantly affected by the method of risk assessment and the safety factors employed. Furthermore, major shortcomings in QRA remain (Santodonato et al., 1981; Kool et al., 1982). Calabrese & Gilbert (1986) identified five unresolved issues:

1. Quantification of exposure.
2. Rational extrapolation of data from animal to human populations.
3. Toxicological interactions viz. synergism, antagonism and addition.
4. Positive stimulation by sub-harmful concentrations (hormesis concept).
5. High risk/disadvantaged groups (e.g. infants, etc as described by Boulos (1978), and including future generations).

Mutagenicity assays are short-term tests normally employing cell systems (bacterial, microbial; plant and animal), of which the most widely used is the Ames Salmonella/mammalian microsome test. The assays' validity lie in the strong correlation between mutagenicity in the tests and carcinogenicity in animals of one or another species. The

tests are not quantitative: they indicate only the potential of an agent to be mutagenic or carcinogenic. They are generally rapid and inexpensive to execute and can be performed on single compounds, mixtures, and concentrated and unconcentrated water samples. The considerable influence of experimental procedure on the results has been discussed (Tye, 1986; Forster & Wilson, 1981; Kool et al., 1982).

1.4.2 Epidemiological Studies

Epidemiological investigations are generally of three types: aggregate population studies (the most common), and case-control and longitudinal studies where individuals are examined retrospectively and prospectively respectively. Investigations, particularly in the US, examining the relationship between use of river water as a source of drinking water and cancer morbidity and mortality have been summarised (Shy, 1985; Crump & Guess, 1982; Wilkins et al., 1979). Most of these have compared surface versus ground water and examined chlorination and chlorination by-products, principally THM, and especially chloroform which has been demonstrated to be carcinogenic (Bull, 1985). Investigations pertaining to the UK are listed in Table 7. In these, two possible hypotheses were considered concerning health risks associated with water supplies of differing qualities:

1. That cancer mortality is related to the degree of sewage effluent in a water source.
2. That cancer mortality is related to the product of natural organic compounds in, and chlorination treatment of, a water source.

The first hypothesis would implicate lowland rivers and the second predominantly upland catchments, as 'chloroform to total THM ratio is highest in upland catchments' (Carpenter & Beresford, 1986).

Major difficulties are associated with epidemiological surveys, particularly the presence of confounding variables and the choice of index of pollution. However, Beresford (1983) stated that in spite of interpretational problems common in aggregate studies, the UK and US studies provide 'some consistent epidemiologic evidence of a small health

TABLE 7
UK Epidemiological Studies on Health Risks
Associated With Organic Substances in Water Supplies[a]

Location	Health outcome	Water variable	Cancer implicated[b]	Ref.
London, 29 boroughs	Mortality, 1968-74	% Reuse[c], 1971	None	A
London, 14 boroughs	Incidence, 1968-74	% Reuse, 1971	Stomach (F) All urinary (F) Bladder (F) Esophagus (M)	B
UK, 141 urban areas	Mortality, 1969-73	% Reuse, 1951	Stomach (M) Intestine (M)[d]	C
UK, 238 urban areas	Mortality, 1969-73	% Upland, 1971	Stomach (F) Intestine (F)	D

A Beresford (1981).
B Beresford (1983).
C Beresford et al. (1984).
D Carpenter & Beresford (1986).
[a] Aggregate population studies with weighted analysis and adjustment for socioeconomic characteristics.
[b] Sites implicated; M = male, F = female.
[c] Measure of reuse = (% dry weather domestic sewage effluent flow)/(mean river flow).
[d] Negative association.

risk associated with the reuse of drinking water.' An assessment of the contribution of PAH cannot be made at present.

Human exposure to PAH via ingestion of drinking water must be placed in context. Exposure via air and especially food is generally considered to be far higher. The relative contribution of drinking water to PAH exposure has been estimated to be 0.1-0.3% of the total (World Health Organization, 1984). An examination of the PAH content of the UK diet has been presented by Dennis et al. (1983). However, it should be noted that the form of ingestion of PAH may modify their toxic effect.

1.5 Quality Standards and Legislation

Control strategies for management of water quality are essentially of two types:

1. Concentration limits for individual pollutants or pollutant groups.
2. Additional unit treatment processes.

The application of concentration limits as a control strategy is potentially straightforward but is constrained by the availability of appropriate analytical procedures. Additional unit processes, referred to in general as best practical means (BPM), best available technology (BAT) economically achievable and best practical technology (BPT) currently available, describe appropriate treatment techniques such as granular activated carbon. Control strategies consisting of numeric quality standards are the most widely favoured (Bedding et al., 1983b).

1.5.1 Raw and Potable Waters

The European Community (EC) directive relating to the quality of water intended for human consumption (Council of the European Communities, 1980) stipulates a maximum acceptable concentration (MAC) of 200 ng l^{-1} for the sum of FL, BbF, BkF, BaP, IP and BghiP. This is identical to the former WHO European and International limit (World Health Organization, 1970, 1971). The more recent WHO Guidelines (World Health Organization, 1984) give a limit for BaP only of 10 ng l^{-1}. Fulfilment of the UK legal obligation that drinking water should merely be 'wholesome' is, in the case of Thames Water Authority's operations (Jamieson & Nicolson, 1984), based on adherence to the EC drinking water directive, the WHO Guidelines and 'Report 71' (Department of the Environment, 1982).

The US National Interim Primary Drinking Water Regulations specify maximum contaminant levels for six pesticides and four THM (Cotruvo et al., 1986). These are now under revision under the 1974 Safe Drinking Water Act, and the Revised Primary Drinking Water Regulations, although they embody a large increase in the number of organic contaminants in the form of synthetic (and volatile) organic compounds, including disinfection by-products, do

not include PAH.

The EC Environment Action Programme forsees a number of directives relating water quality to particular use-based objectives (e.g. drinking, bathing). The directive concerning the quality required of surface water intended for the abstraction of drinking water (Council of the European Communities, 1975) classifies surface waters into three categories based on the level of treatment employed. MAC for PAH corresponding to categories A1 (simple physical treatment and disinfection) and A2 (normal physical treatment, chemical treatment and disinfection) are identical to that contained in the drinking water directive, but for category A3 representing the highest degree of treatment for (presumably) surface waters of poor quality ('intensive physical and chemical treatment, extended treatment and disinfection') the criterion is 1000 ng l^{-1} for the sum of the six PAH.

Present and future UK policy is to control river quality through use-based quality standards. The 1973 Water Act gave administrative expression to the concept of integrated river basin management of the hydrological cycle by setting up the ten Regional Water Authorities (RWA). Water quality management is achieved by stating the objective for a water body in terms of the use to which it is to be put (an 'environmental quality objective' or EQO), and for each use defining a standard(s) judged to maintain the use-based objective (an 'environmental quality standard' or EQS). The EQO/EQS approach assumes that it is legitimate to make proper use of the assimilative or self-purification capacity of the receiving water. RWA have set short- and long-term EQO and EQS for rivers according to a National Water Council (NWC) classification (National Water Council, 1978) consisting of five EQO (or re-named RQO - river quality objectives), and four EQS (biological oxygen demand, dissolved oxygen, ammonia and toxicity to fish) appropriate to each EQO. The classification harmonises with the EC surface water directive (A1, A2, A3 classification).

1.5.2 Waste Waters

The EQS form the basis for deriving 'consent conditions' (local emission standards) for individual effluent discharges into waters of a set EQO. Discharges are covered by the 1974 Control of Pollution Act Part II (COPA II), only presently being implemented. The powers of COPA II repeal and update those of the Rivers (Prevention of Pollution) Act 1951 and 1961, the Clean Rivers (Estuaries and Tidal Water) Act 1960, and the Water Resources Act 1963 (Matthews, 1987).

The EC directive on 'pollution caused by certain dangerous substances discharged into the aquatic environment' (Council of the European Communities, 1976) divides substances between a black (List I) and a grey list (List II). The criteria for inclusion in the black list are toxicity, persistence and propensity to bioaccumulate. The enactment is an enabling directive only and specific substances are to be covered by daughter directives, of which a few have already appeared. Of a provisional black list of 129 are included A (No. 3), N (No. 96) and 'PAH in particular BaP and BbF' (No. 99) (Commission of the European Communities, 1982). Hence, although it is the intention that PAH are to be subject to legislation in a future directive, it is not clear which PAH are to be included.

Black list substances are to be controlled either by EQS or by uniform emission standards (UES), the latter preferred on the continent. Furthermore, the enabling directive states that, where necessary, UES are to be laid down for discharges of substances into sewers. But even with application of EQS, the criteria may well form the basis for the calculation of future consent conditions. UK trade effluent control, as practised by Thames Water Authority for example, although imposing effluent limitations on various organic substances and solvents, does not at present contain restrictions on PAH (Sumption, 1987). A set of EQS for PAH, however, are already effectively specified for three grades of water for potable supply in the surface water directive.

The UK Government has recently proposed a 'Provisional Red List' of 26 pollutants selected on the criteria of toxicity, persistence, bioaccumulability and rate of production (Department of the Environment, 1988a). One PAH (A) is included in a 'Priority Candidate List' of 23 pollutants. The Government proposes to set EQS for the red list substances and to apply technology-based emission standards (ES) on the concept of 'best available technology not entailing excessive costs' (BATNEEC) to processes responsible for significant point source discharges. For diffuse sources of red list pollutants it is proposed to utilise more monitoring. The newly formed Her Majesty's Inspectorate of Pollution (HMIP) (Ponsford, 1987) seeks to adopt an integrated cross-media approach to pollution control. Regulation of emissions to land, water and air under the 'best practicable environmental option' (BPEO) philosophy aims to ensure consistency of standards over all environmental compartments.

In the US, EPA is seeking to control 129 'priority pollutants', including the 16 PAH (Table 1), in effluent discharges under the 1972 Federal Water Pollution Control Act and the 1977 Clean Water Act (Keith & Telliard, 1979; Glaser et al., 1981). UES are being set for particular sectors of industry but it is acknowledged that more stringent 'site-specific' limits may need to be applied. The latest EPA 'Water Quality Criteria' (Environmental Protection Agency, 1980) are limited to three PAH. Limits are given to support freshwater life (plant and animal) which involved toxicological evaluations (acute and chronic) similar to those for humans (Section 1.4.1): N 620 and AE 520 $\mu g\ l^{-1}$ (chronic toxicity), and FL 3980 $\mu g\ l^{-1}$ (acute). The criteria represent guidelines only for State regulatory authorities.

The UK does not possess mandatory regulations covering contaminants in sewage sludge. There exist, rather, guidelines for best practice in the use of sludge, with recommended limits for certain elements and micro-organisms, but not for organic substances (Department of the Environment, 1981). A draft EC directive on sludge disposal to land is based on the same principles as the UK guidelines but its mandatory nature and more stringent

criteria have raised concern (Matthews, 1983). A proposed directive on the dumping of waste at sea may entail restrictions on disposal of sludge by this means as practised by Thames Water Authority (Side, 1986).

1.5.3 Quality Criteria Selection

The criteria normally employed for selection of an organic substance for control in a particular water by a quality standard are:

1. Concentration and frequency of occurrence of compound.
2. Toxicity.
3. Susceptibility to removal by treatment processes.
4. Availability of an analytical procedure.

A fifth criterion, rate of compound manufacture or use, is occasionally applied. The criteria normally employed for selecting a numerical value as the quality standard depends on the water type. For drinking water, toxicity of the substance to humans is the criterion. For a surface water, the derivation of an EQS for a particular EQO involves application of the toxicity criterion to the appropriate 'target organism' or entity (e.g. fish) protected by the EQO. However, for waste waters, the derivation of an emission standard (ES) or effluent discharge consent condition from the EQS theoretically involves quantification of behaviour and removal of compound during municipal waste water treatment (where discharge to surface water is indirect via sewer), quantification of the diluting capacity of the receiving water and of the physical, chemical and biological behaviour of the substance in the water accounting for any self-purification, a consideration of existing inputs and of (industrial) pretreatment steps that are technically and economically feasible to take. Although mathematical models (steady state and dynamic) are available for use in this respect, there is generally at present considerable imprecision in the setting of consent limits.

Organic substances discharged to sewers can exert four potential impacts:

1. On sewer and waste water treatment plant fabric and personnel.
2. On plant performance (oxidation and sludge digestion).
3. On receiving water, via the effluent.
4. On sludge disposal operations.

Concentrations of PAH in raw sewage are generally such as to impact on categories 3 or 4 only.

An approach for the determination of consent conditions (Water Research Centre, 1976) involves an assessment of probable removal of substance during waste water treatment, effect of dilution during discharge to sewer and receiving water, and consideration of limiting criteria for sludge disposed to arable land. Anthony & Breimhurst (1981) presented a method to determine maximum plant influent concentrations of priority pollutants from various limiting criteria (sludge digestion, sludge disposal and receiving water). In a more elaborate treatment Rossman (1982) described a model for determining levels of industrial pretreatment and municipal sewage treatment for a given pollutant to meet all relevant environmental criteria and standards at minimal cost. Clearly, for the derivation of standards and the control of PAH, high quality data are required of behaviour and removal in waste water treatment processes.

1.6 PAH Transportation Mechanisms in Raw Waters

An examination of PAH transportation and transformation mechanisms (Section 1.7) in raw waters is important not only for assessing the potential self-purification capacity of the river as a natural unit process for these substances, but also in defining the basic mechanisms which may account for PAH behaviour and removal in water and waste water treatment unit processes (Bedding *et al.*, 1983a). A transportation mechanism is defined herein as a physical agent modifying pollutant aqueous solubility and hence normal hydrodynamic (solute) behaviour.

1.6.1 Sorption

The association of PAH with particulate matter is of fundamental importance in determining PAH transport in the aquatic environment and the rates and routes of transformation processes. The term 'sorption' will hereafter refer to this association, the term including both adsorption and absorption. Precise mechanisms of organic pollutant association are not appreciated, although it is generally understood that physical sorption via hydrophobic bonding (van der Waals forces) pertains to neutral (i.e. non-polar) compounds, and chemical (covalent) and electrostatic (ionic) bonding applies to more polar/charged molecules (Voice & Weber, 1983).

Sorption behaviour is characterised by means of a sorption isotherm, a plot of solid phase concentration of sorbing compound (solute) versus aqueous phase concentration at equilibrium. Karickhoff *et al.* (1979) determined isotherms for a number of PAH on three natural sediments and found linearity over a range of equilibrium aqueous phase concentrations up to approximately 50% of the compound's aqueous solubility. Sorption data were well represented by the linear form of the Freundlich relation:

$$C_S = K_P C_W \qquad (1)$$

where C_S = equilibrium solid phase concentration of solute ($\mu g\ g^{-1}$)

C_W = equilibrium aqueous phase concentration of solute ($\mu g\ l^{-1}$)

K_P = partition coefficient (a constant)

K_P was therefore the ratio of concentrations in the two phases and could be likened to a 'binding affinity': the larger K_P, the higher the concentration sorbed.

Furthermore, Karickhoff and co-workers reported a significant positive correlation between K_P and the mass fractional organic carbon content (f_{OC}) of the sorbents of various particle size fractions. And when K_P was normalised to f_{OC}, the resultant constant, K_{OC}, exhibited a high positive correlation to the octanol/water partition

coefficient (K_{OW}, Table 2) of the solute. The relationship was represented by:

$$\log K_{OC} = 1.00 \log K_{OW} - 0.21 \quad (2)$$

An inverse correlation was found between K_{OC} and solute aqueous solubility, but was inferior.

Means et al. (1980a) obtained similar results for sorption of PAH on 14 soil and sediment samples of a wide range of physicochemical properties. Sorption of heterocyclic and substituted PAH (Means et al., 1980b, 1982) and other hydrophobic compounds have yielded general relationships of the form:

$$\log K_{OC} = A \log K_{OW} + B \quad (3)$$

where A and B are constants. Thus K_{OC} values are characteristic of the sorption process for particular solute/sorbent combinations, with sorbent organic carbon content appearing to be the major factor in determining sorbent capacity. As PAH K_{OW} increase with increase in molecular weight (Table 2) PAH K_{OC} for a given sorbent increase with molecular weight, as shown by values ($K_{OC} \times 10^3$) presented by Karickhoff et al. (1979) for N 1.3, A 26 and P 84, and Means et al. (1980a) for P 44-85 and DBahA 565-3059.

The 'solids effect' reported in laboratory sorption studies for a variety of solutes whereby K_P typically decreased with increasing sorbent (solids) concentration (as reviewed by O'Connor & Connolly (1980)) has recently been rationalised. The effect, which if genuine would have had major environmental implications, was suggested by Voice et al. (1983) and Voice & Weber (1985) to be an (experimental) procedural phenomenon caused by a failure to take cognizance of microparticulate or macromolecular/dissolved organic matter accounting for sorption of a portion of the solute. Experimental confirmation was subsequently provided by Gschwend & Wu (1985).

PAH sorption to humic acids constitutes another transportation mechanism. Initial studies related to analytical implications (Gjessing & Berglind, 1981; Carlberg & Martinsen, 1982). More recent investigations by Landrum et al. (1984) and McCarthy & Jimenez (1985) on sorption to Aldrich humic acid showed partition coefficients to equate approximately to PAH K_{OW}. Values of K_{OC} (x 10^3) presented by McCarthy & Jimenez (1985) for N (ca. 1) and A (ca. 10) approximated those obtained for sorption on soils/sediments by Karickhoff et al. (1979). Gauthier et al. (1987) presented partition coefficients for the binding of P to 14 humic and fulvic acids. K_{OC}, which varied by as much as a factor of ten, was found to correlate with degree of aromaticity of humic material. Landrum and co-workers also compared results with sorption to natural dissolved organic carbon (DOC) and found considerable variation among partition coefficients for samples of similar DOC concentration, suggesting geographic and even seasonal variation of DOC as causes. Johnsen et al. (1986) presented evidence of seasonal variation in extent of PAH sorption to humic acids.

Whitehouse (1985) examined the effect of freshwater and saline 'dissolved organic matter' (DOM) on six PAH. Greatest sorption occured with PAH of low aqueous solubility and with DOM of terrestrial origin. Ultrafiltration experiments suggested that matter of relatively high molecular weight (MW >500) was responsible for sorption. PA and A were unaffected by DOM, in agreement with Boehm & Quinn (1973).

Wijayaratne & Means (1984) investigated the sorptive behaviour of natural estuarine colloids (MW <5000). Sorptive capacity, as shown by K_{OC} (x 10^3), for N (4) and A (510), was determined to be considerably greater than that of humic acid (McCarthy & Jimenez, 1985) and that of soils/sediments (Karickhoff et al., 1979).

Hydrophobic solute sorption kinetics and reversibility have until recently received scant attention. Sorption models assume a condition of dynamic equilibrium and complete reversibility, but evidence of often encountered inefficient and time consuming analytical extraction

procedures for solutes have caused the assumption to be queried (Voice & Weber, 1983; Karickhoff and Morris, 1985). The few reports on sorption kinetics exhibit contrasting results. Sorption of hydrophobic compounds on soils, sediments and suspended solids has been shown to be achieved within 24 h (Karickhoff et al., 1979; Means et al., 1980a), within 4 h (Voice et al., 1983) and within 1 h (Weber et al., 1983). Complete reversibility, however, has been shown by Karickhoff et al. (1979) and Gschwend & Wu (1985). Clearly, it is of importance to determine sorption kinetics in time frames of considerably less than 24 h, and to determine reversibility, in order to assess pollutant behaviour in the rapid and dynamic conditions of water and waste water treatment.

In a major study, Karickhoff (1980) observed 'kinetic factoring' for PA, A and P sorption on natural sediment suspensions. Aqueous phase concentrations were found to decrease apparently rapidly (5-15 min) and then to approach equilibrium at a much reduced rate. Karickhoff proposed that two kinetically distinct components are associated with sorption of solutes: a rapid (labile) and a slow (non-labile). The latter component was postulated to reflect diffusive transfer of the solute to less accessible sites within the sorbent matrix (i.e. an intraparticle process). Desorption kinetics were found to be identical. A model predicted that approximately 50% of solute sorbs rapidly, with days to weeks required for completion of non-labile sorption. Limited experimental data revealed a reciprocal variation in non-labile sorption rate with K_p for a given solute on different sorbents and for different solutes on the same sorbent. In a subsequent paper (Karickhoff & Morris, 1985) work was developed on labile sorption rate and its dependence on solids concentration and K_p. Studies of K_p itself have suggested that the dependence of the coefficient on temperature and ionic strength is largely unpredictable (Karickhoff, 1984).

Sorption equilibrium theory has important environmental implications. The observed linear Freundlich partition coefficients imply that a constant proportion of solute in a given solute/sorbent combination and sorbent concentration is sorbed. A change in solute aqueous phase

or sorbent concentration in the water column will effect either sorption or desorption to restore equilibrium at the value given by the partition coefficient. Reichert et al. (1971) reported that 60% of PAH in surface waters are sorbed to particulates and Lewis (1975) observed 84-98% for the River Trent, UK. Along the length of the River Rhine, Hellmann (1980, 1987) reported that the sum of the aqueous phase concentrations of the six WHO PAH varied little, rarely exceeding 50 ng l^{-1}, but that the sorbed species accounted for the gradual increase in total PAH concentration downstream from approximately 100 to 400 ng l^{-1}. The importance of suspended solids was again shown in the River Mosel where the observed dependence of PAH concentration on river flow was attributed to the PAH solid phase concentration (Hellmann, 1981).

Another implication of sorption theory is that the hydraulic dynamics of particles are of major importance in the dynamic behaviour of pollutants (O'Melia, 1980). Particle deposition will tend to result in high concentrations in lowland river sediments of up to mg kg^{-1} (dry weight) individual PAH (Borneff & Kunte, 1965), but bioturbation, hydraulic scouring and other sediment-water interactions can resuspend solute-laden particles to the water column.

1.6.2 Surfactant Micellation

PAH 'solubilisation' by incorporation into surfactant or detergent micelles is limited by the critical micellar concentration (CMC) which is usually between 10 and 50 mg l^{-1} of surfactant: concentrations between 0.1 and 1.0 mg l^{-1} have been shown to have no effect on PAH aqueous solubilities (Lewis, 1975; Böhm-Gössl & Krüger, 1965). At the CMC, large increases in PAH aqueous solubilities have been observed (Klevens, 1950), increases of 10^2-10^8 being reported by Krasnoschekova & Goubergrits (1983). However, surfactant concentrations in raw and waste waters are generally well below the CMC.

1.6.3 Hydrotropy

Hydrotropy refers to the increase in aqueous solubility of an organic solute by the presence of organic co-solutes. A wide variety of substances have been shown to effect increases in PAH solubility (BaP mainly): organic solvents (methanol, ethanol, dioxane, acetone) (Suess, 1972), n-butyric and d,l-lactic acid (Ekwall & Sjöblom, 1952), purines (Weil-Malherbe, 1946), nitrogen-containing organic compounds (Eisenbrand, 1971), and various co-solutes including PAH themselves (Eganhouse & Calder, 1976). The effect is generally small except for high concentrations of the mediating substance which are unlikely to be found in all but the most grossly polluted raw and waste waters. Ekwall & Sjöblom (1952) observed significant solubilisation of BaP only for concentrations of butyric acid >1.1 M and lactic acid >4.3 M, with subsequent linear dependencies of solubility on concentration of acid noted; solubility increases attained several orders of magnitude. Weil-Malherbe (1946) reported that there existed either an approximate linear or approximate quadratic relationship between the concentration of BaP and purine. Effect of purine on solubilisation was gradual, however, and a noticeable effect was observed with as little as 0.005% purine. The mechanism of hydrotropy is probably via solute-solute interaction and/or formation of solid solutions.

1.7 PAH Transformation Mechanisms in Raw Waters

PAH are subject to removal by four major mechanisms in aquatic systems: volatilisation, photodegradation, biodegradation and chemical degradation.

1.7.1 Volatilisation

The theoretical basis for describing the transfer of organic solutes across an air-water interface has been succinctly put by Liss & Slater (1974). The mass transfer coefficient, K_L, for a particular solute is given by:

$$K_L = \frac{H\ K_g\ K_l}{(H\ K_g) + K_l} \qquad (4)$$

where K_L = mass transfer coefficient (m d^{-1})
H = Henry's Law Constant (atm m^3 mol^{-1})
K_g = gas phase mass transfer coefficient (m d^{-1})
K_l = liquid phase mass transfer coefficient (m d^{-1})

K_l is a measure of the rate of transport of solute from water to interface, and K_g that of interface to air. Both K_l and K_g are influenced by mixing within the respective phases: K_l primarily by water turbulence and K_g by wind. The rate of volatilisation under a given set of conditions is described by a first order (exponential) decay with rate constant equal to K_L divided by liquid depth. Rate therefore increases with H (4) and hence, for PAH, increases in general with decreasing molecular weight (Table 2).

Southworth (1979) computed theoretical maximum volatilisation rates for four PAH under conditions of varying current and wind velocity for a stream 1.0 m deep at 25°C. Under conditions of high current (1 m s^{-1}) and high wind velocity (4 m s^{-1}), rates of volatilisation, particularly of low molecular weight PAH, were predicted to be substantial (half-lives (h) being N 3, A 20, BaA 150 and BaP 500). However, for relatively deep (>1 m), slow moving rivers (<1 m s^{-1}) with little or no wind, volatilisation rates, particularly of high molecular weight compounds,

were predicted to be insignificant.

Effect of organic pollutant sorption on volatilisation is not well understood, but Mackay et al. (1980) suggested that only the dissolved solute volatilises, with the sorbed solute desorbing to restore equilibrium, the role of sorption and sedimentation therefore counteracting solute upward diffusion and volatilisation. In a study of atmospheric deposition of PAH to water surfaces, McVeety & Hites (1988) reported that surface volatilisation accounted for 10-80% of the total output flux depending on the volatility (vapour pressure) of the PAH, with sedimentation accounting for the remainder. Approximately 80% of the input flux of the most volatile PAH studied (C_{14}; PA and A) was lost through volatilisation, and as the vapour pressure decreased with increase in molecular weight (Table 2), the importance of sedimentation increased, to reach a maximum for C_{22}.

It is generally considered that compounds possessing a Henry's Law Constant greater than 10^{-3}-10^{-4} atm m^3 mol^{-1} will be subject to volatilisation (Gowda & Lock, 1985) and where this is the case, the mechanism may be the major transformation process in the aquatic environment (Smith et al., 1980). Table 2 indicates that only PAH of molecular weight up to and including 178 are susceptible to volatilisation. Matter-Müller et al. (1981) examined unit process conditions of water and waste water treatment under which volatilisation may assume importance.

1.7.2 Photodegradation

Two principal classes of photolytic reaction have been observed for hydrophobic compounds in aqueous systems: direct photolysis and indirect or sensitized photolysis. In the former, the molecule (chromophore) undergoes chemical reaction as a direct consequence of absorbing photons, whereas in the latter, reaction is initiated through photon absorption by some chromophore (sensitizer) other than the substrate itself and capable, too, of altering its photolytic behaviour (rates and products) (Zafiriou et al., 1984; Zepp et al., 1984).

Known sensitized photolysis mechanisms of hydrophobic solutes consist of direct sensitizer-chromophore reaction via chromophore sorption (e.g. to suspended particles), or indirect reaction via energy transfer (through formation of singlet oxygen giving rise to photo-oxidation) or electron or hydrogen transfer (Zafiriou et al., 1984). Free radical reactions generally remain speculative. Zafiriou et al. (1984) and Zepp et al. (1984) reviewed evidence for sensitization by humic substances producing photo-oxidation reactions through formation of singlet oxygen.

Suspended particles can further influence photolytic behaviour of organic compounds by modifying the attenuation (absorbance) of the water body to the incident radiation as well as modifying its dispersion (scattering) (Miller & Zepp, 1979; Oliver et al., 1979). Furthermore, sorption to suspended solids can lead to sedimentation and removal of chromophore from the photic zone when vertical mixing is limited.

Photochemical studies of PAH in the liquid phase have mostly been conducted in non-aqueous solvents with high PAH concentrations. Only a few have utilised primarily aqueous systems (Andelman & Suess, 1971; Zepp & Schlotzhauer, 1979; Zadelis & Simmons, 1983; Smith et al., 1978; Mill et al., 1981). In a laboratory investigation Zepp & Schlotzhauer (1979) determined direct photolysis rates of PAH and showed that they could be described by a first order rate equation. Computed near-surface photolytic half-lives in clear water on a clear day ranged from 0.54 h for BaP to 71 h for N. Effect of sorption with sedimentation was also computed. Photosensitized oxidation by singlet oxygen was shown to be essentially negligible. Mill et al. (1981) observed quenching of BaA and BaP by humic acid. Photodegradation products appeared to be quinones.

Neff (1979) reviewed PAH-particulate photolytic reactions, which have been confined exclusively to laboratory examinations. 'Batochromic shifting' of sorbed ketones entailing shifts in the absorption spectra has been observed (Leermakers & Thomas, 1965). The precise identities, and thus the toxicity and persistence, of photodegradation products in general remain unknown.

1.7.3 Biodegradation

Micro-organisms capable of degrading PAH in numerous water and soil systems consisting of various pure and mixed cultures have been reviewed (Neff, 1979; Connell & Miller, 1980, 1981; Santodonato et al., 1981). Higher molecular weight PAH have been reported to undergo little or no degradation in pure cultures (Groenewegen & Stolp, 1976; McKenna & Health, 1976) or in natural mixed culture populations from estuarine rivers (Lee, 1977), freshwaters (Herbes, 1981; Herbes & Schwall, 1978) and settled domestic waste water (Tabak et al., 1981). However, very few studies have investigated PAH biodegradation kinetics in freshwater systems at low concentrations and in the presence of multiple substrates. A recent exception is that of Heitkamp & Cerniglia (1987) who, in two freshwater and one estuarine sediment/water aerobic microcosms, observed half-lives (weeks) for N of 2.4-4.4, PA 4-18, P 34->90, and BaP 200->300. The mineralization of PAH of more than four rings totalled only 0.2-6.5% after eight weeks.

Microbial mineralization of organic compounds to carbon dioxide and water for carbon and energy aquisition, required for biomass accretion, needs to be distinguished from cometabolism (i.e. co-oxidation or secondary utilisation) whereby partial metabolism occurs alongside utilisation of an alternative primary growth substrate. Cometabolism is believed to be operative in the degradation of pollutants at too low a concentration or of too refractory a nature to sustain a steady state biomass (Namkung et al., 1983). Alexander (1985) recently warned of the existence of threshold concentrations required for cometabolism.

In addition to potential biodegradation of organic micropollutants, effects of pollutants on micro-organisms and other biota is of importance in controlling and maintaining viable populations and river self-purification capacity. Aspects of PAH uptake, metabolism and depuration (clearance) including acclimatization and bioconcentration have been reviewed by Neff (1979), Connell & Miller (1980, 1981) and Santodonato et al. (1981). Low molecular weight PAH have been shown to be acutely toxic to aquatic animals

at concentrations of 200-10000 μg l^{-1} and deleterious sub-lethal responses in aquatic organisms are sometimes observed at concentrations in the range 5-100 μg l^{-1} (Neff, 1979). High molecular weight PAH tend to be chronically toxic, and thus hazardous under long-term exposure. PAH sub-lethal effects (e.g. on growth, reproduction, behaviour) pertaining to bacteria and aquatic plants and animals, and effect of external factors (e.g. suspended solids, co-contaminants) on PAH bioavailability and toxicity, have been assessed by Neff (1979).

A fourth PAH removal mechanism, chemical degradation, consists mainly of oxidation but is only of significance under extreme chemical conditions of disinfection during water treatment (Section 1.9).

The relative importance of the three transformation and the various transportation mechanisms for a given PAH will depend on the particular aquatic environment. Appropriate studies are comparatively few although models of PAH transportation and transformation utilising PAH physicochemical constants are utilised; two major ones being EXAMS (Baughman & Lassiter, 1978) and FOAM (Bartell et al., 1981). Bates et al. (1984, 1987) in investigations of a US urban estuary found PAH to be transported intact through the water column to the underlying sediments. Lee et al. (1978) presented results of studies of a controlled marine ecosystem enclosure which suggested that for low molecular weight PAH (N, PA, A) volatilisation and biodegradation would be the primary removal processes, whereas for the higher molecular weight compounds (FL, BaA, CH, BaP) primary mechanisms would be photodegradation and sedimentation.

Readman and co-workers in their studies of the Tamar Estuary, UK, determined two distinct groups of PAH: a low molecular weight cluster (N, PA, A) whose concentrations were independent of suspended solids, and a high molecular weight (FL, P, BaA, CH, BbF, BkF, BaP) whose concentrations were significantly correlated (Readman et al., 1982). Results indicated that volatilisation was an important mechanism for the former group with intact sediment burial the primary fate of the latter. Microbial degradation 'turnover times' for N ranged from 1 to 30 d and for BaP from 2000 to 9000 d.

1.8 Behaviour and Removal of PAH During Waste Water Treatment Processes

1.8.1 Waste Water Treatment Unit Processes

Influent raw sewage in conventional municipal waste water treatment initially undergoes preliminary treatment consisting of coarse solids removal by screening or straining and grit removal by settlement in grit chambers (Escritt, 1972; Institute of Water Pollution Control, 1973; Tebbutt, 1983; Barnes & Wilson, 1978; Metcalf & Eddy, 1979; Fair et al., 1966; Barnes et al., 1981). For plants treating combined sewage, that is foul sewage with surface water runoff, which are common in older developments, storm overflows situated after the grit removal chambers divert excess flows to stormwater sedimentation tanks. The tanks accept flows usually between three and six dry weather flows (DWF, defined as 'the average daily rate of flow as recorded on days when not more than one-tenth of an inch (2.5 mm) of rain has fallen in the 24 h' (Escritt, 1972)) thus serving to avoid hydraulic overloading of plant. Contents are pumped back to works. During prolonged storms, tank overflows are directed to the adjacent watercourse, the tanks then providing for the contents a typical retention time of 2 h at 6 DWF. Combined sewers normally possess storm overflows themselves to limit maximum flow to 6 DWF, but occasionally up to 12 DWF, excess flows being discharged to a nearby watercourse.

Primary treatment consists of settlement in sedimentation tanks which are of three types: horizontal flow (rectangular tanks), radial flow (circular tanks) and vertical flow (hopper-bottom tanks, for small works). Primary effluent contains typically 150 mg l^{-1} suspended solids (SS) and 200 mg l^{-1} biological oxygen demand (BOD) which might be acceptable for discharge to sea or to certain estuaries.

Secondary treatment is normally achieved by aerobic biological oxidation. In the activated sludge process, biomass is maintained in suspension by mechanical agitation or by air injected at the base of the aeration tank. Modifications to the conventional 'plug flow' process

include tapered aeration, step aeration and completely mixed systems. Activated sludge is clarified in secondary sedimentation tanks with a portion of the sludge ('returned activated sludge') diverted to the aeration tank, the remainder ('surplus activated sludge') either returned to the head of works for co-settlement with primary sludge or removed with primary sludge for treatment. Secondary treatment generally aims to produce an effluent of a quality suitable for discharge to inland waters, with the old 'Royal Commission' standard of 30 mg l^{-1} SS and 20 mg l^{-1} BOD normally being adopted. However, recommendations for relaxation or modification of this standard to suit the particular RQO have been made (Lester, 1979; Robinson, 1980; Bowden & Young, 1984), and the consent conditions of many sewage effluents have been modified under COPA II to accord with the receiving water quality. It is argued that the 30:20 standard as originally intended is an EQS, being subject to the proviso that the dilution in the receiving water is at least 8:1 with the BOD of the water being less than 2 mg l^{-1}.

Other types of activated sludge include high rate activated sludge, extended aeration, oxidation ditches, contact stabilisation, pure oxygen and deep shaft. Alternative secondary treatment processes include trickling (percolating) filters (low, high rate, and alternating double filtration) and, less commonly used, oxidation ponds (waste stabilisation ponds), aerated lagoons and rotating biological contactors.

Tertiary treatment (effluent polishing) may be necessary when more stringent or specific criteria are required for limiting effluent discharges. The main objective of tertiary treatment is removal of fine SS, and to achieve this filtration processes (microstraining, dual and mixed media filters, pebble bed clarifier) and biological processes (grass filtration/overland flow, land/rapid infiltration, tertiary ponds/lagoons) may be employed. Disinfection is sometimes effected, too, as a tertiary process.

Advanced waste water treatment (water reclamation) is employed for a number of purposes: removal of nitrogen, phosphorus, residual organic compounds and/or dissolved (inorganic) salts. Nitrification (conversion of ammonia to nitrate via nitrite) is usually required of effluents before discharge to rivers, and although this may be achieved in secondary processes with higher mean cell retention times and after completion of carbonaceous oxidation, production of nitrified effluents can be achieved by ammonia stripping (by addition of lime, at pH 11), breakpoint chlorination or by use of ion-exchange resins. Denitrification (nitrate to nitrogen and other gaseous forms) may also be required. Removal of phosphorus can be facilitated by chemical precipitation (with lime) or by biological means. Residual organic compounds, including synthetic organic contaminants, may be reduced by activated carbon or ion-exchange resins, and dissolved salts by the latter or by reverse osmosis or ultrafiltration.

The sludges produced during sewage treatment may undergo preliminary treatment in the form of thickening by, typically, gravity or by gas flotation or centrifugation, and may subsequently be stabilised by digestion. Anaerobic digestion is the most common process, but aerobic digestion and lagooning are occasionally utilised. This may be followed by conditioning, usually by chemical agents (iron salts, aluminium sulphate or lime, and aided on occasion by polyelectrolytes), but thickening, elutriation and heat treatment are alternatives. Subsequent dewatering may be accomplished by pressure filtration, vacuum filtration, belt pressing, centrifugation or lagooning, or in small works by drying beds. Treatment liquors from conditioning and dewatering are often returned to the head of works.

Approximately 45% of the cost of treating sewage in the UK is incurred by sludge treatment and disposal (Matthews, 1985). The treatment sludge undergoes depends to a certain extent on mode of disposal which, in the UK, is determined by the BPEO. Disposal routes (1980/1) include: application to agricultural land as a fertilizer and soil conditioner (44%), dumping at sea (31%), landfilling (21%) and incineration (4%) (Matthews, 1985). Land treatment (land farming) and composting are not practised in the UK.

1.8.2 Settlement and Primary Sedimentation

The main process objective of primary sedimentation is removal of settleable solids accomplished gravitationally on the basis of the difference in specific gravity between the particles and the fluid medium. An understanding of the principles governing sedimentation behaviour is essential for the effective design and operation of settlement tanks which constitute the first unit process. Four classes of settling behaviour are distinguished on the basis of the nature and concentration of particles (Anderson, 1981; Metcalf & Eddy, 1979; Barnes et al., 1981):

Class I: Discrete particle settling.
Settlement of particles with no interparticulate interaction, in a suspension of low particle concentration.

Class II: Flocculent particle settling.
Settlement of flocculating particles increasing in mass and hence settling velocity.

Class III: Hindered and zone settling.
Hindered settlement occurs when particle concentration in a suspension is so increased that the upward motion of fluid around a settling particle hinders (reduces) settling velocities of neighbouring particles. Zone settlement occurs with higher particle concentrations. Under these conditions interparticulate forces cause all particles to settle at the same rate, and the suspension settles as a blanket with a solid-liquid interface at the top.

Class IV: Compressive settling.
At very high solids concentrations, interparticle contact forms a cohesive structure, which compresses from the weight of sedimenting particles.

All four classes may be exhibited at various depths in a secondary sedimentation tank, but in a primary tank only Class I and II are observed, with Class III confined to the lower layer of the sludge thickening compartment. (Class IV usually occurs in special sludge thickening tanks.)

Class I behaviour is adequately described by Stoke's Law, which considers terminal settling velocities (rapidly reached) of particles of various sizes (diameters) and densities. The theory treats spherical, discrete particles only (i.e. those which do not change in size or density and do not interact) under conditions of uniform flow; other particle shapes can be considered, though. Class II behaviour arises from agglomeration of particles and colloidal matter through particle collision. Flocculent particles tend therefore to increase in mass and hence settling velocity, which increase with depth of suspension.

The ideal sedimentation tank concept developed by Hazen (1904) and Camp (1946) forms the basis for arriving at relationships utilised in the design of tanks. The tank model consists of four zones: an inlet zone, a sedimentation zone, an outlet zone and a sludge zone, and considers settlement of discrete particles under conditions of continuous flow. There are four major assumptions:

1. Quiescent conditions in the sedimentation zone.
2. Uniform flow across the sedimentation zone.
3. Uniform SS concentration in the inlet zone.
4. Particles entering the sludge zone are not subject to scouring.

From a consideration of Stoke's Law it is found that all particles with a limiting settling velocity equal to or greater than V_S will be removed according to:

$$V_S = \frac{Q}{A} \qquad (5)$$

where Q = rate of flow into tank ($m^3\ d^{-1}$)
A = surface area of tank (m^2)

Q/A, termed the surface loading rate (or surface overflow rate), thus controls removal of particles. Particles of settling velocity V in which $V<V_S$ are assumed to be fractionally removed in proportion to V/V_S. Thus for Class I particles, removal is independent of tank depth. The surface loading rate is the main design criterion for primary sedimentation tanks. For Class II particles, settlement requires adequate tank depth or retention time to be provided to allow flocculation to take place.

The performance of primary sedimentation tanks is normally assessed in terms of the removal efficiency of SS. Tank performance relationships have been proposed in terms of the ratio between tank diameter and height (Annesini et al., 1979) and other parameters, but the two major process parameters are considered to be surface loading rate and influent SS concentration (Smith, 1969; Escritt, 1972; Construction Industry Research and Information Association, 1975; Tebbutt & Christoulas, 1975). The higher the surface loading rate, the smaller the proportion of particles with limiting settling velocity V_S (5) and thus the lower the overall removal, or alternatively, the direct inverse proportionality between surface loading rate and theoretical hydraulic retention time for a tank of fixed depth and surface area, means that the higher the hydraulic loading the shorter the retention time and therefore the lower the removal of SS. The dependence of SS removal efficiency on influent SS concentration (SS loading) is a direct consequence of flocculation: the greater the number-concentration of flocculent particles, the greater the rate of particle collision and agglomeration, and thus the greater the rate of sedimentation. For purposes of tank design, empirical data on SS undergoing Class I and II settlement is provided by the use of quiescent settling column tests ('batch settlement columns') (Figure 1). Particle limiting settling velocities and effect of tank depth and retention time on sedimentation of representative

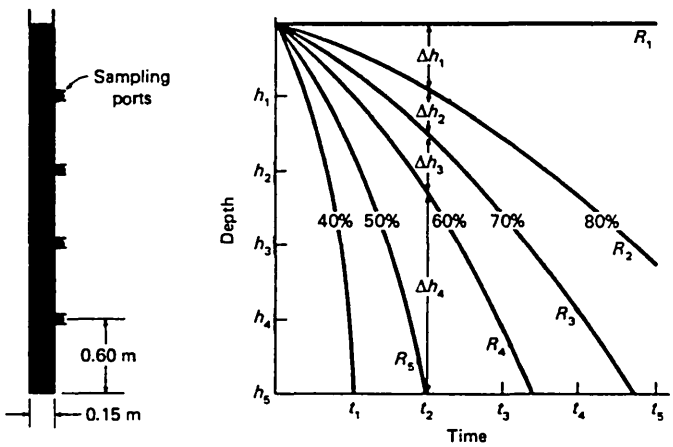


FIGURE 1
Laboratory Settling Column Showing SS Isopercentage Removal Curve Data Obtained Therefrom, After Metcalf & Eddy (1979)

samples of waste water to be treated are determined in columns of height equal to the maximum depth to be considered for the tank in question. As a first step towards this, SS isopercentage or isoconcentration removal curves are plotted from the SS determinations obtained at each sampling port at regular intervals. For a flocculent suspension the lines are curvilinear, and not linear as would be the case for a suspension of discrete particles. The more pronounced the curvature of the settling curves, the greater the flocculation. The main design criterion for primary tanks, the surface loading rate (5), involves an initial selection of the maximum rate of flow into the tank. In the UK, with a northern temperate climate, it is common practice to design for 3 DWF. To this must be added the maximum rate of return of any secondary sludge and works liquors. From this design flow is selected the surface loading rate, from which the required tank surface area may be calculated (5), and either tank depth or retention time chosen for any required SS removal efficiency, from the results of the settling column tests.

Apart from the difficulties associated with obtaining representative samples for the settling column tests, the data obtained must be modified to account for differences between the tests and conditions encountered in sedimentation tanks, consisting of continuous flow with diurnal variations in flow and SS. Tank hydraulic behaviour in practice is such as to cause wide departure from uniform and ideal plug flow distribution. Two major sources of departure are short-circuiting due to density currents arising from differences in density between the influent and tank contents, and mixing due to hydraulic turbulence at tank inlet and outlet (Tebbutt, 1983). The effects of these, together with the influence of wind on the surface, mean that sedimentation tanks do not achieve their theoretical and empirical (settling column) performance. Allowances must be made for these in the design, and the selected surface loading rates are divided and retention times multiplied by a suitable safety factor, typically 1.25-1.75 (Ramalho, 1983), 1.25-1.50 (Metcalf & Eddy, 1979), 1.5-2.0 (Valioulis & List, 1984a), 1.7-2.5 (Barnes et al., 1981).

Typical tank designs are as follows. The surface loading rate for all types of tank is usually around 30 with a maximum of 45 $m^3 m^{-2} d^{-1}$ (Institute of Water Pollution Control, 1973; Barnes et al., 1981). Nominal retention time (at maximum flow) is typically 2 h (Institute of Water Pollution Control, 1973), but can range from 1.5 to 3 h (Barnes et al., 1981). Tank depth is usually 1.5 to 4 m, with radial flow tanks commonly possessing a 7.5^{o} floor slope and a diameter of 5-50 m (Institute of Water Pollution Control, 1973; Barnes et al., 1981). (In addition to removal of settleable solids, tank design must also consider the gravity sludge thickening function, and this, normally secondary, objective may limit the design criteria (Tebbutt, 1983).)

Settled solids as sludge are directed towards the sludge thickening compartment normally by mechanical scraper blades moving along the tank floor. Primary sludge is withdrawn under hydrostatic pressure usually once per day, and is typically 3-7% solids dry weight (Institute of Water Pollution Control, 1973).

Rectangular tanks typically achieve an SS removal efficiency of 40-70% and circular tanks 50-75% (Institute of Water Pollution Control, 1973). SS concentration in primary effluent usually exceeds 100 mg l^{-1} and consists of non-settleable particles and colloids. Particles of diameter less than 100 μm, depending on density, are considered essentially non-settleable by Class I sedimentation (Tebbutt, 1983; Valioulis & List, 1984a). Influent SS concentration has been shown to be more important in controlling SS removal than surface loading rate by Tebbutt (1969), Anderson (1981) and March & Hamlin (1966) in studies of full-scale tanks, and by White & Allos (1976) in a study of a pilot-scale tank. The importance of flocculation during primary sedimentation is thus evident. Chemically assisted sedimentation is sometimes practised as a temporary expedient to relieve an hydraulically overloaded works or to precipitate phosphorus.

1.8.3 PAH Behaviour and Removal

Concentrations of PAH in municipal raw sewage are normally not sufficiently high to affect adversely plant performance (oxidation). Malaney *et al.* (1967) in a laboratory study of activated sludge reported toxic or inhibitory effects only at very high individual PAH concentrations of *ca.* 500 mg l^{-1}.

Organic micropollutants, including PAH, may be subject to removal in waste water treatment processes by four principle mechanisms (Lester, 1983, 1984):

1. Sorption onto settleable solids, with removal with primary and secondary sludges.
2. Volatilisation (stripping).
3. Biodegradation.
4. Chemical degradation.

The recalcitrance of PAH are such that conditions in waste water treatment are not conducive to removal by category 4. Similarly, removal by photodegradation is likely to be limited.

Borneff & Kunte (1967) examined PAH removal in three full-scale works. Single grab samples (one influent, one effluent; primary and secondary treatment) were collected, taking approximate account of retention times. Results were reported in terms of the sum of concentrations and hence mean removals of two groups of PAH: Σ5 'carcinogenic' compounds BaA, BbF, BjF, BaP, IP, and Σ10 consisting of Σ5 with FL, P, BkF, BghiP and perylene. Primary sedimentation removed 32-80% of Σ5 and 0-78% Σ10. With activated sludge treatment, overall removals were 88-99.7% of Σ5 and 81-99.7% of Σ10.

The study was subsequently extended (Reichert *et al.*, 1971) with what were judged to be more valid sampling methods (Table 8) on two full-scale plants, one employing primary sedimentation with parallel activated sludge and trickling filter streams, the other primary sedimentation with activated sludge only. Three sampling methods entailed: mixed samples composed of several single samples, single 24 h composite samples obtained by continuous 'wasting', and single samples taken at intervals. Mixed and single

TABLE 8
Removal of PAH During Waste Water Treatment
After Reichert et al. (1971)

PAH	Raw influent	Primary[a] effluent		Secondary[b] effluent			Overall rem. (%)
	Concn. (ng l^{-1})	Concn. (ng l^{-1})	Rem. (%)		Concn. (ng l^{-1})	Rem. (%)	
Plant A							
Method 1[c]							
Σ5[g]	919	630	31	TF	643	0	31
				AS	459	19	50
Σ10[h]	2400	2017	16	TF	1690	14	30
				AS	1397	26	42
Method 2[d]							
Σ5	2786	2348	15	TF/L	486	68	83
				TF/H	515	67	82
				AS	394	71	86
Σ10	6627	6132	8	TF/L	1357	72	80
				TF/H	1688	67	75
				AS	910	78	86
Method 3[e]							
Σ5	43093	4602	90	TF/L	387	9	99
				TF/H	768	8	98
				AS	487	9	99
Σ10	101481	11758	89	TF/L	973	10	99
				TF/H	2559	8.5	97.5
				AS	1623	9.4	98.4
Plant B							
Method 3[f]							
Σ5	20546	3938	81	AS	256	18	99
Σ10	42755	10884	75	AS	967	23	98

[a] Primary sedimentation.
[b] TF = trickling filter (L = lightly loaded, H = heavily loaded), AS = activated sludge.
[c] Mixed samples, taken at raw: 10h 15 (single); primary: 11h 20 - 11h 45; TF: 11h 55 - 12h 25; AS: 15h 45 (single).
[d] 24 h composite samples.
[e] Single samples, taken at raw/primary: 10h 20, 13h 10, 16h 00; TF: 11h 30; AS: 10h 30, 13h 20, 16h 05. Mean concentrations given.
[f] Single samples taken at raw/primary/AS: 08h 30, 12h 00, 15h 00. Mean concentrations given.
[g] Sum of five PAH: BaA, BbF, BjF, BaP, IP.
[h] Sum of ten PAH: As [g] with FL, P, BkF, BghiP, perylene.

sample times took account of retention times. The results suggested highly variable removal of PAH during primary sedimentation, with activated sludge appearing more effective than trickling filter treatment (the more heavily

loaded filter being less effective). No accompanying plant performance data were presented.

The same workers in a laboratory study found no biodegradation of BaP in activated sludge, in agreement with Malaney et al. (1967) who determined generally very high resistance to this treatment among PAH. Reichert et al. (1971) concluded that removal during secondary treatment was via sorption to solids. Moretti & Neufeld (1989) showed that the principle PAH partitioning mechanisms operating in an activated sludge process are solubility in the waste water phase and solubility in the biological sludge lipid phase. Rump (1981) observed, over a 32 d sampling period, BaP removal during full-scale activated sludge treatment which correlated with sludge volume index (SVI).

Mean overall removals for the six WHO PAH in six sewage treatment works (two activated sludge, two trickling filter and two oxidation pond) were reported by van Luin & Starkenburg (1985). The data were as follows: FL 95% (range 80->99%), BbF 90% (75-99%), BkF 90% (73-99%), BaP 88% (68-99%), IP 89% (69-99%) and BghiP 86% (72-99%).

The most comprehensive survey to date of pollutant removal in municipal sewage treatment (Environmental Protection Agency, 1982) involved 50 plants, but poor analytical methodology severely compromised the quantity and quality of data obtained for PAH. Removal data were obtained for only ten plants and for eight PAH. Activated sludge plants achieved removals of 33-100%, and trickling filter plants 41-100%. Removal values for primary sedimentation were available for N only and ranged from 34-59%.

Petrasek et al. (1983) in an activated sludge pilot plant spiked PAH at 50 $\mu g\ l^{-1}$ individually (in toluene, 25 $mg\ l^{-1}$) into the raw waste water influent. Eight sets of 24 h composite samples were collected. Even at the high spike levels employed, difficulties were experienced in analyte detection, limiting the quality of data obtained. Removals during primary sedimentation ranged from 22% for N to 107% for P (Table 9). The activated sludge process was more efficient effecting overall removals of 94-99%, and

TABLE 9
Removal (%) of PAH During Waste Water Treatment
After Petrasek et al. (1983)

PAH	Primary sedn.	Activated sludge				Overall
		Total	Sorption	Volat.+ biodeg.	Volat.[a]	
N	22.0	76.5	0.5	76.0	5-10	99.0
AE	41.0	56.0	4.0	52.0	5-10	97.0
F	51.0	47.0	3.0	44.0	5-10	98.0
PA	59.0	38.0	1.0	37.0	1- 5	97.0
A	67.0	30.0	5.0	25.0	25-50	97.0
FL	84.0	10.0	10.0	0	<1	94.0
P	107.0	0	0	0	<1	94.0
BaA	67.0	31.0	18.0	13.0	<1	98.0
CH	75.0	22.0	13.0	9.0	<1	97.0

[a] Estimate.

mass balance determinations demonstrated that during this process sorption was the primary removal mechanism for the higher molecular weight PAH, with biodegradation estimated to be the primary mechanism for the low molecular weight compounds (except for A, where volatilisation was judged to be more important). No data were reported on plant design or operation.

Hannah et al. (1986) reported removals in various pilot plant treatment processes (Table 10). Waste water was spiked at 100 μg l^{-1} individual PAH (in toluene, 70 mg l^{-1}). Removals were calculated from 11 sets of 24 h composite samples (each consisting of six grab samples). Lowest removals were observed for primary sedimentation which ranged from 13% for N to 22% for FL, with highest removals for activated sludge (with primary sedimentation) of 95-97%. Again, no data were supplied on plant design or operation.

PAH removal during tertiary treatment has been reported by Jenkins et al. (1985) who observed greater than 94% removal for N and PA during overland flow treatment. Bouwer et al. (1984) in a study of pollutant behaviour during rapid infiltration observed 50-99% removals for an aromatic

TABLE 10
Removal (%) of PAH During Waste Water Treatment Processes After Hannah et al. (1986)

	Clarification			Biological treatment			
PAH	A	B	C	D	E	F	G
N	13	20	23	28	97	64	87
PA	21	49	74	45	95	55	82
FL	22	61	87	53	95	64	77
P	18	61	88	54	95	63	75

A Primary sedimentation.
B Primary sedimentation plus filtration.
C Chemical clarification.
D Percolating filter (with primary sedimentation).
E Activated sludge (with primary sedimentation).
F Aerated lagoon.
G Facultative lagoon.

hydrocarbon class including the PAH N and PA. N and methyl-N in rapid infiltration of primary effluent have been investigated by Hutchins et al. (1984) and in waste water infiltration for ground water recharge by Bedient et al. (1983).

In advanced waste water treatment studies Reichert et al. (1971) examined removal of several PAH by ten brands of activated carbon for varying contact times and doses. The laboratory study showed generally high removals of greater than 99%. Other studies have been restricted to the lowest molecular weight PAH (especially N). Hrubec et al. (1983) investigated N and methyl-N removal by activated carbon and reverse osmosis, and Baird et al. (1979) the same compounds in four different pilot systems where no PAH were detectable in the effluents.

Reichert et al. (1971) observed coagulation and flocculation of BaP from synthetic sewage by various polymers and polyelectrolytes. Removals ranged from 48 to 96%.

The effect of PAH on sludge treatment has been subject to a limited study by Johnson & Young (1983). N 1-50 mg l^{-1} and P 1-10 mg l^{-1} exerted no significant toxicity or inhibition to bench-scale anaerobic digestion. Constable et al. (1986) investigated the effect of three bench-scale sludge treatment processes (heat treatment (to facilitate dewatering), anaerobic digestion, and anaerobic digestion plus polymer addition) on five PAH (AY, F, FL, P and BaP). Heat treatment achieved reductions in PAH ranging from 44% (FL) to 98% (AY), digestion alone generally had no effect but digestion plus polymer addition effected reductions ranging from nil (F) to 52% (BaP). In terms of solubilisation (mass in liquid phase relative to total mass in sludge), heat treatment significantly decreased dissolved levels of F but increased those of FL and P, digestion increased the soluble fraction of all compounds, but digestion with polymer addition decreased the soluble fraction of all. In terms of leachability (ratio of mass in leachate to mass initially present in sludge solids prior to leaching), less than 10% of each PAH was leached regardless of treatment process. The influence of heat treatment on the content of the six WHO PAH in sludges has been investigated in three sewage treatment works (Nicholls et al., 1979) and in a pilot plant (Nicholls et al., 1980). No significant remobilisation (resolubilisation) from the sludges into the treatment liquors was observed.

Typical concentrations of PAH in sludges are given in Table 11. Hagenmaier et al. (1986) reported that the sum of the six WHO PAH ranged nearly one order of magnitude for primary sludges from 33 sewage treatment works in W. Germany. Grimmer et al. (1980) in a survey of 25 works found sludge PAH profiles (relative concentrations) to be similar except for plants receiving separate sewage and for those largely serving industry. The results of McIntyre et al. (1981) showed that highest PAH concentrations were found in sludges from works receiving significant flows of industrial effluent. Wszolek & Wachs (1982) measured total concentrations of 0.1-1 mg kg^{-1} for PAH of six molecular weights in municipal sewage sludge ash residues from four cities. PAH in treated sludges are of potential concern in their disposal, particularly to agricultural land (Section 1.10).

TABLE 11
Concentration (mg kg^{-1} Dried Sample) of PAH in Sewage Sludges from Three Surveys

	A	B		C	
PAH	Range	Range	Mean	Range	Mean
F	0.34-11.43				
FL		0.61-51.60	6.16	0.54-7.67	2.18
P		0.90-47.20	5.74		
BaA		0.62-19.00	3.39		
CH		0.78-23.70	4.25		
BbF	0.06- 9.14	1.07-23.70[a]	4.37[a]	0.29-1.80	0.83
BkF	0.06- 4.57			0.15-1.00	0.42
BaP	0.12- 9.14	0.54-13.30	2.42	0.29-2.00	0.78
IP	0.06- 6.86	0.30- 7.40	1.44	0.24-2.08	0.76
BghiP	0.06- 9.14	0.40- 8.70	1.56	<0.1- 3.41	1.42

A McIntyre et al. (1981); 12 works (primary + digested), UK.
B Grimmer et al. (1980); 25 works (primary + digested), W. Germany.
C Witte et al. (1988); 31 works (primary + digested), W. Germany.
[a] Including BjF and BkF.

1.9 Behaviour and Removal of PAH During Water Treatment Processes

1.9.1 Water Treatment Unit Processes

Water treatment can employ a number of unit processes in various configurations depending on the quality of the raw water source. For abstraction from lowland rivers the relatively polluted nature of the source usually necessitates an extensive treatment sequence (Tebbutt, 1983; Barnes et al., 1981). Initial bankside storage for 10 to 14 d, or bank filtration as practised on the River Rhine, provide a degree of treatment. Otherwise, typical treatment includes screening, coagulation and flocculation (aluminium or ferric sulphate, or ferric chloride, with pH adjustment) followed by sedimentation (vertical, radial or horizontal flow, and latterly by dissolved air flotation). Subsequent filtration is achieved by slow sand and/or rapid gravity sand filtration, with final disinfection by chlorine (contact time 30 min or more (Barnes et al., 1981)), chloramines (1 h), ozone (5-10 min), or occasionally UV. Softening of stream by addition of lime is sometimes practised.

Specialised requirements needing additional unit processes include taste and odour removal by activated carbon (powdered and granular; added to flocculation tanks, or in bed form or as a sand replacement in filters) or by chlorine, chlorine dioxide or ozone; iron and manganese removal by aeration (with pH adjustment); fluoridation; corrosion control. Synthetic organic contaminants are amenable to removal by granular activated carbon, ion-exchange resins and aeration (for volatile compounds), and mineral/inorganic contaminants by reverse osmosis, ultrafiltration and ion-exchange resins.

1.9.2 PAH Behaviour and Removal

Studies on PAH behaviour and removal in pilot- and full-scale water treatment processes are limited, being generally confined to investigations utilising grab samples with no allowance for retention time (Borneff, 1969; Lewis, 1975; Basu & Saxena, 1978b; Harrison et al., 1976a; Crane

et al., 1981). The results of these investigations, though, suggested substantial reductions. One of the studies (Crane et al., 1981) of UK treatment plants, although suffering from problems of analyte detection, reported that all were capable of producing finished waters with PAH concentrations well below the EC 200 ng l^{-1} limit (for six PAH). Lewis (1975) and Crane et al. (1981) reported reductions of PAH during bankside storage; the former 31-47% and 51-78% at two locations for the sum of the six WHO PAH. Data reported by Harrison et al. (1976a) and Basu & Saxena (1978b) for works treating river water are given in Table 12.

TABLE 12
Concentration of PAH in a UK Water Treatment Works After Harrison et al. (1976a) and Removal in Three US Works After Basu & Saxena (1978b)

PAH	Concentration (ng l^{-1})				Removal (%)		
	River intake	After reserv.	After filtrn.[a]	After chlorn.[b]	Works A[e]	Works B[e]	Works C[e]
FL	150	140	81	45	100.0	92.2	89.9
P	100	75	45	18			
BaA/CH	90	72	33	12			
BjF	147[c]	132[c]	39[c]	21[c]	99.2	100.0	94.0
BkF					99.0	100.0	94.4
BaP		51[d]	30[d]	9[d]	99.0	99.3	91.1
IP	69	66	27	9	98.0	97.7	87.4
BghiP	72	63	33	9	98.0	91.7	76.6

[a] SS reduction during reservoir storage: 9 to 5 mg l^{-1}.
[b] Rapid gravity filtration, slow sand filtration.
[c] Including BbF and BkF.
[d] Including BeP.
[e] Lime softening, coagulation and filtration, activated carbon filtration, chlorination, fluoridation.

Laboratory, pilot- and full-scale studies on organic micropollutants in the context of water treatment have been dominated by the study of disinfection (chlorination) by-products, namely THM but more recently dihalo-acetonitriles and di- and trichloroacetic acid. THM have received special study as they are considered to be ubiquitous and to be the synthetic organic contaminants found in tap water at the highest concentrations. However,

THM and other specifically identified chlorination products have been judged to account for less than 2% of the mutagenic activity of chlorinated drinking water (Environmental Protection Agency, 1983). PAH have been suggested as the precursors of at least a portion of the mutagens produced (Alben, 1980).

Laboratory studies on PAH removal in water treatment processes have examined chlorination of PAH and effect of chlorine dose and contact time, PAH concentration, pH and temperature (Rav-Acha & Blits, 1985; Harrison et al., 1976a,b; Oyler et al., 1982, 1983). PAH chlorination rate has been shown to be proportional to dose of hypochlorous acid and to PAH concentration (Rav-Acha & Blits, 1985; Harrison et al., 1976b) with a complex dependence on pH (Harrison et al., 1976b). Typical reaction half-lives have been shown to range from 17 min for BaP to 900 min for FL (Rav-Acha & Blits, 1985). Oyler and co-workers (1982, 1983) showed a product dependence on pH, with oxygenated PAH (epoxides, phenols and quinones) tending to form at pH >6, and both oxygenated (quinone) and chlorinated PAH being formed at pH <6. Johnsen & Gribbestad (1988), however, failed to detect chlorinated PAH in the presence of humic substances.

Shiraishi et al. (1985) observed individual chlorinated PAH in Japanese tap water in the range 0.01-52.6 ng l^{-1} in coexistence with oxygenated and parent PAH, and Benoit et al. (1979) in Canadian tap waters reported a seasonal trend in oxygenated PAH concentrations. Nevertheless, the precise identities, concentrations and toxicities of PAH disinfection products liable to be produced under full-scale conditions of water treatment are largely unknown. Oyler et al. (1982) noted that 'nearly all of the compound types produced in the (laboratory) chlorination reactions of PAH have the potential for causing adverse biological response.' Hence, although removals of PAH during water treatment and 'reductions' during unit process chlorination are reported, the significance to human health of the unremoved portion and of the disinfection products is not clear.

Rav-Acha & Blits (1985) investigated laboratory reaction rates of PAH with chlorine dioxide and found them to be pH independent in the range pH 4.5-9.5. The rates compared to those of chlorination were highly variable. Half-lives ranged from nil (no reaction) for N and FL to 35 h for CH. Butkovič et al. (1983) reported extremely rapid ozonation reaction rates, essentially independent of pH. Reaction half-lives ranged from 0.18 s for P to 1.00 s for BaP.

The role of coagulation and flocculation followed by sedimentation and filtration in the removal of organic micropollutants has been poorly studied. DeLuca et al. (1983) reported 17.0-23.8% removal of N following coagulation and flocculation by aluminium sulphate, and Thébault et al. (1981) observed 62% removal of BaP both by aluminium sulphate and ferric chloride. For BaP (at $\mu g\ l^{-1}$ concentrations), Il'nitskii (1969) recorded removals of 56-69% for flocculation with sedimentation, and 89% for flocculation with filtration. Liao & Randtke (1986) reported negligible removal of N and PA following lime softening.

PAH are amenable to removal by granular activated carbon (GAC). Sorption isotherms for 11 PAH were shown to be best described by the Langmuir isotherm equation (Walters & Luthy, 1982) and partition coefficients (Walters & Luthy, 1984a) showed sorption to be two to three orders of magnitude greater than for soils/sediments (Section 1.6.1). High removals of PAH, frequently greater than 99%, have been observed in the laboratory (Reichert et al., 1971) and in the field (Borneff, 1969).

1.10 Behaviour of PAH in Surface and Subsurface Environments

The behaviour and amenability to control of PAH in diffusive (non-point) routes which constitute a significant PAH load to surface waters (Table 3) are of importance in river basin management. Characteristics of routes depend upon environment: surface (urban and rural) and subsurface.

1.10.1 Urban Surfaces

In an urban surface investigation, Hoffman et al. (1984) observed 14 PAH to be most concentrated in the first or second flushes following a storm, but no relationship between PAH mass load and rainfall for any of the PAH nor between total or individual PAH load and antecedent dry period was recorded. Mass loading factors were presented by land use: for BaP residential land factor was 0.194 g (cm rain)$^{-1}$ km^{-2}, commercial 0.164, industrial 3.71 and highway 5.18. Herrmann (1981) reported a strong first flush phenomenon and a high correlation between total PAH load and maximum flow, but no relationship between load and antecedent dry period. Barrick (1982) observed substantial correlation of mass loads of nine PAH on rainfall where, furthermore, concentrations and fluxes were well correlated to a 'street dust accumulation' index. The association of PAH with SS suggests that stormwater control systems employing settling basins and related structures may afford a measure of control through temporary retention of PAH-laden solids before resuspension. Ellis et al. (1985) noted removal efficiencies of 65-95% for six PAH in on-line sedimentation ponds in a north west London catchment.

1.10.2 Rural Surfaces

Although the contribution of rain-borne PAH to PAH in urban runoff has been reported as comparatively low (Herrmann, 1981), deposition fluxes and concentrations being two to three orders of magnitude less (Table 3), aerial deposition as a route in the more expansive rural environments that form a proportionately large surface area of river basin catchment represents a major source for river headwaters.

PAH on the soil surface are subject to runoff to surface waters and to percolation through soil profiles (horizons) to underlying ground waters, and can be exacerbated in circumstances where hazardous wastes containing PAH are landfilled or, more importantly, where PAH-containing sludges are applied to agricultural land. The latter can exert a more immediate health impact by interacting with crops and grazing animals. Sludge production is expected to increase by as much as 50% in West Europe as investment programmes in sewage treatment are concluded (Matthews, 1985).

Mechanisms and rates of PAH surface behaviour, runoff and percolation are poorly understood. Mass balances have been calculated by Schrimpff (1984) who, in an extensive two year study of 15 river basins in north east Bavaria, W. Germany, determined that approximately 1% of bulk (wet plus dry) aerial deposition of FL, BaP, IP and BghiP percolates to ground water, 2-4% escapes to streams and rivers via surface runoff, and 95-97% is detained and subject to transformation processes. Hellmann (1982) estimated that 10-50% of PAH in streams and rivers (termed 'soluble') can be accounted for by bankside ground water infiltration, and the remainder ('insoluble') accounted for by particulate PAH from soil runoff.

PAH concentrations in soil due to aerial deposition (and biological decay) have been measured in numerous instances. Borneff & Kunte (1963) measured concentrations of BbF + BjF of 25-110, BaP 1.5-4.0 and BghiP 10-70 $\mu g\ kg^{-1}$ in soils from W. German forests remote from industrial and urban centres. Bierl et al. (1984) measured concentrations of FL of 8-22 and BaP 3-13 $\mu g\ kg^{-1}$ in an agricultural area. Reductions in concentration approaching two orders of magnitude for the six WHO PAH were recorded (Walther et al., 1986) on descending from a 0-20 cm to a 80-100 cm soil horizon. Edwards (1983) in an extensive review of terrestrial PAH stated that typical endogenous concentrations (i.e. away from major sources) range from 1 to 10 $\mu g\ kg^{-1}$. These are 100-1000x less than typical concentrations in municipal sludge (Table 11).

Studies of PAH in sludge amended soils are comparatively few. Demirjian et al. (1987) studied behaviour of N, PA, FL, P, BaA and CH in soil horizons down to 61 cm for a soil receiving repeated sludge applications. At a low sludge application rate (56 t ha^{-1}) most PAH were substantially reduced (by volatilisation or biodegradation) with 0-40% remaining after 241 d. At a high application rate (448 t ha^{-1}) most PAH were stable 'probably because of persistent anaerobic conditions.' Only FL, BaA and CH were reduced to some degree. After 241 d, compounds in the 30.4-45.7 cm horizon at 10% or less of the concentration in the surface layer (0-15.2 cm) included CH (at 5%) and various alkylated N and PA, and were termed 'moderately leachable.' Compounds occurring at >10% were considered 'mobile' and included N (at 17%), PA (18%), FL (32%) and P (16%). BaA either degraded or adsorbed on the surface layer.

Diercxsens et al. (1987) in a two part study, reported that just after a single application of sludge (equivalent to 0.75 t ha^{-1}), low molecular weight PAH (MW 178-202) accumulated in the top 0-1 cm soil horizon, but three months later, concentrations fell to levels just before spreading. However, concentrations of high molecular weight PAH (MW 252-278) had increased due to atmospheric deposition. In a ten year experiment to study the long-term effects of sludge spreading (12 t ha^{-1} a^{-1}) on grassland (clover) plots on light and heavy soil, considerable increases in PAH concentrations were observed, the importance of which grew with PAH molecular weight. For the high molecular weight compound DBahA, increases were approximately 1200% for the light soil and 2000% for the heavy soil. For each PAH the heavy soil was found to accumulate more hydrocarbon than the light soil. Atmospheric input of PAH to soil was judged more important than sludge input, especially for high molecular weight PAH and for soils in or near urban areas. Jones et al. (1989) concluded of agricultural soils in south east England that the total PAH burden of the plough layer (0-23 cm) has increased approximately four- to five-fold since the 1890s due to atmospheric deposition alone, with some compounds (notably P, BbF and BaP) showing substantially greater increases. Of PAH percolation, they reported that

particle-bound translocation, in contrast to solution/ vapour phase transport, was the dominant mechanism of PAH migration through soil macropores.

A 1280 d laboratory simulation of a 'landfarming' process explored the fate of PAH in an oil-rich sludge (Bossert et al., 1984). On completion of the experiment, 1.4, 47.4, 78.5 and 78.3% remained of three-, four-, five- and six-ring PAH respectively. Losses were attributed to a combination of biodegradation and abiotic removal mechanisms. (Losses from soil samples poisoned by 2% mercuric chloride were substantial, amounting to 48% of total PAH loss from biologically active soil.) Santodonato et al. (1981) and Harms & Sauerbeck (1983) reviewed the limited data on PAH biodegradation in soil. Southworth & Keller (1984) demonstrated that oil-rich sludge when disposed via landfilling may allow percolation of N and methyl-N.

The presence of appreciable concentrations of organic pollutants, including PAH, in sludge may cause adverse 'macroscopic' agronomic effects on sludge amended soil in terms of a deterioration in soil conditions or in crop yield and quality. Of greater significance is the potential microscopic effect consisting of a contamination of food supplies. This may be achieved by three basic mechanisms:

1. Uptake (absorption) of pollutant from the soil by plant roots with translocation to edible parts.
2. Pollutant sorption on plant surfaces during sludge application and from volatilisation from sludge.
3. Direct ingestion of contaminated soil or sludge by grazing animals.

PAH behaviour in soil-plant systems is poorly understood. Edwards (1983) and Harms & Sauerbeck (1983) reviewed evidence for plant uptake, translocation and metabolism of PAH. The latter concluded that cereal grains generally show a low uptake of organic contaminants from soil, with little or no translocation to edible parts. Both sources agreed that the principle source of contamination of vegetation by PAH is via aerial deposition (Table 3). A recent and major WHO report (Dean & Suess, 1985) judged PAH

in sludge to be of minimal risk to health provided good sludge management is practised (regular monitoring). However, Connor (1984) of the Harvard School of Public Health (US) in a major, but conservative, study deduced a positive risk.

1.10.3 Subsurfaces

Organic pollutant behaviour in subsurface environments is governed by a number of factors. Contaminant migration in the saturated (ground water) zone (after percolation from the unsaturated (vadose) zone) is subject to advection (bulk fluid movement) and dispersion (spreading, caused by molecular diffusion; and mechanical mixing, caused by zone heterogeneities) (Mackay et al., 1985). Furthermore, contaminant sorption on aquifer material serves to retard migration.

Data on PAH behaviour in the saturated zone is limited. Wilson et al. (1985) presented evidence for rapid biodegradation of low molecular weight PAH (N, AE, F) in ground water containing elevated concentrations of PAH from an abandoned wood creosoting plant. Turnover times were of the order of one week or less. No biodegradation was observed in pristine subsurface material from the same geological structure. Abdul & Gibson (1986) observed linear sorption isotherms for N, F, PA, A, FL and P in contact with two aquifer materials. It was subsequently shown for F (Abdul et al., 1986) that the partition coefficient increased linearly with f_{OC} of the aquifer material. Dzombak & Luthy (1984) considered retardation factors and estimated that PAH should undergo substantial retardation in ground waters within aquifer materials of moderate organic carbon content.

1.11 Analytical Methods for PAH

A prerequisite for the control of pollutants in surface waters is the existence of adequate and reliable analytical procedures. Analysis is required for the monitoring and assessment of pollutants in the water cycle, for monitoring the efficiency of water and waste water treatment processes with respect to removal of substances, and for ensuring compliance with quality standards.

It is important to appreciate analytical principles and technical constraints which affect the interpretation of data. PAH analysis has been reviewed by Bjørseth (1983), Futoma et al. (1981) and Lee et al. (1981). Examined below are the most widely used quantitative procedures for the determination of PAH in raw, potable and waste waters, with reference to municipal waste water methods whenever possible. Techniques are reviewed for extraction (and preconcentration), cleanup (isolation), and separation and determination. Semiquantitative PAH screening methods for source identification (Black et al., 1982) and for rapid, preliminary measurement (Riggin & Strup, 1984), and the sampling and monitoring aspects of analysis (temporal and spatial criteria) (Hunt & Wilson, 1986), are not specifically reviewed here.

1.11.1 Extraction

The purpose of an extractant (Table 13) is to remove PAH in as high a yield as possible from the sample with the minimum of coextractant or interfering material. The extraction step therefore also affords a degree of cleanup. Typical solvent extraction methods include use of cyclohexane, hexane, dichloromethane, acetone and benzene. Simple partitioning includes manual shaking and manual/automated stirring. The mixer-homogenizer device used almost exclusively is the Ultra-Turrax but more recently a laboratory disperser (McIntyre et al., 1981) has been used to good effect. Both devices release ultrasonic (ca. 20 kHz) as well as kinetic energy to the extracting medium, thereby eliciting efficient contact between solvent and sample. In their review, Lee et al. (1981) concluded that mixer-homogenizer and ultrasonication methods are generally

TABLE 13
Extraction and Preconcentration Methods for PAH

Method	Reference
Solvent Extraction	
Simple partitioning	Grzybowski et al. (1983)
Mixer-homogenizer	McIntyre et al. (1981)
Ultrasonication	Hagenmaier & Jäger (1979)
Soxhlet[a]	Aichberger & Reifenauer (1984)
Extraction Onto Solid Phases	
Macroreticular resins	
-Tenax GC	May et al. (1975)
-Amberlite XAD	Junk et al. (1974)
-polyurethane foams	Basu & Saxena (1978a)
-ion-exchange resins	Navratil et al. (1977)
Carbon	Laganà et al. (1980)
HPLC[b] pre-columns	May et al. (1975)

[a] Solid matrices only (e.g. dried sludges).
[b] High performance liquid chromatography.

superior to Soxhlet techniques with respect to extraction efficiency and repeatability. Techniques involving extraction onto solid phases can be problematic for particulate-containing aqueous matrices, but do offer the advantage of facile desorption of PAH by thermal or solvent stripping methods directly onto a gas or high performance liquid chromatographic column (Table 15).

Studies of PAH losses in samples have demonstrated determinand sorption to container glass walls from distilled water (Basu & Saxena, 1978a; Acheson et al., 1976), sorption to humic acids from surface water (Gjessing & Berglind, 1981; Carlberg & Martinsen, 1982; Johnsen et al., 1986), reductions in tap water (Johnsen et al., 1986), and decreasing extraction efficiencies with increasing incubation time of sediment suspensions (Karickhoff, 1980). There do not appear to be any reports on waste water sample integrity. The observations have led to diverse recommendations for sampling and storage: extraction within 24 h of collection (Department of the Environment, 1988b), immediate extraction in the collection vessel (Acheson et al., 1976), cooling to 4°C (Suess, 1982; Longbottom & Lichtenberg, 1982), filtration (through a 0.45 μm silver membrane filter) (Ogawa et al., 1981), preservation with

heavy metal salts (e.g. Ag_2SO_4) (Ogawa et al., 1981), chloroform (0.3% V/V) (Baralkiewicz et al., 1988) and formaldehyde solution (Shultz et al., 1976; for low molecular weight hydrocarbons). The losses reported in many cases can be ascribed to inefficient extraction. Basu & Saxena (1978a) reported that leaching of container with solvent achieved near complete recovery of glass-sorbed determinands, and Karickhoff (1980) showed that essentially complete extraction of PAH from sediment suspensions could be accomplished by ultrasonication or lengthy Soxhlet extraction.

1.11.2 Cleanup

One or more cleanup stages performed on the extract is usually required (Table 14). Dimethylformamide (DMF) and dimethylsulphoxide (DMSO) are regularly used in liquid-liquid partitioning and PAH are recovered by dilution of sample with distilled water and back extraction into an alkane solvent. Column chromatographic procedures employ typically the solvents cyclohexane, hexane and benzene. Eluent polarity is increased by the addition of suitable solvents. Gel permeation chromatography utilising Sephadex LH 20 with isopropanol as solvent is found in numerous

TABLE 14
Cleanup Methods for PAH

Method[a]	Reference
Liquid-Liquid Partitioning	
Dimethylformamide (DMF)	Grzybowski et al. (1983)
Dimethylsulphoxide (DMSO)	Searl et al. (1979)
Nitromethane	Hoffmann & Wynder (1960)
Acetone	Grimmer & Böhnke (1972)
Methanol	Hoffmann & Wynder (1960)
Column Chromatography	
Silica gel	Aichberger & Reifenauer (1984)
Aluminium oxide	Grimmer et al. (1978)
Florisil	Grzybowski et al. (1983)
Cellulose acetate	Griest et al. (1975)
Lipophilic gels	
-Sephadex LH 20	Grimmer et al. (1978)
-Bio-Beads	Snook (1976)

[a] One or more utilised in succession.

analytical schemes, but extremely slow flow rates (1-3 d) limit its application. Thin layer chromatography (TLC) finds use as a cleanup method but is more commonly employed in the final separation and determination stage. The number and nature of cleanup steps used in an analytical procedure frequently depends on the measuring instrument.

1.11.3 Separation and Determination

Resolution is a prime requirement for any instrumental measurement technique for the separation and determination (detection and quantification) of PAH (Table 15). The many isomeric forms of PAH produce great compositional complexity in environmental samples. TLC is a relatively rapid and inexpensive technique and very sensitive when combined with spectrofluorometric detection (detection

TABLE 15
Separation and Determination Methods for PAH

Method	Reference
Chromatographic[a]	
Thin layer chromatography (TLC)	
-visual	McIntyre et al. (1981)
-spectrofluorometry	Aichberger & Reifenauer (1984)
Gas chromatography (GC)	
-flame ionisation detection (FID)	Grimmer et al. (1978)
-electron capture (EC)	Bjørseth & Eklund (1979)
-photoionisation detection (PID)	Driscoll (1982)
-UV absorption/fluorescence	Searl et al. (1979)
-GC-MS	Lao et al. (1975)
High performance liquid chromatography (HPLC)	
-UV absorption/fluorescence	Grzybowski et al. (1983)
Mass Spectrometric (MS)[b]	
-electron impact ionisation (EI)	Giger & Blumer (1974)
-charge exchange-chemical ionisation (CI)	Lee & Hites (1977)
Spectroscopic[b]	
Luminescence	
-room temperature phosphorimetry	Scypinski & Cline Love (1984)
-synchronous luminescence spectroscopy	Vo-Dinh et al. (1978)
-Shpol'skii low temperature fluorescence	Kirkbright & DeLima (1974)
Nuclear magnetic resonance (NMR)	
-conventional single scan	Keefer et al. (1971)
-Fourier transform (FT) NMR	Bartle et al. (1977)
Infra-red (IR)	
-matrix isolation FTIR	Hembree et al. (1981)

[a] Chromatographic modes can be employed in a cleanup capacity ('multi-dimensional' techniques).
[b] Employed mainly for qualitative class/group characterisations. Spectroscopic methods sometimes employed as detection methods in GC and HPLC.

limits <5 ng). It is capable of good separations. Typical sorbents employed are silica gel, aluminium oxide, cellulose, cellulose acetate and polyamide, and they can be used singly and in combination, and with various solvent systems in one or two dimensions. The standard method for the determination of PAH in drinking water offered by WHO (Suess, 1982) is a two dimensional TLC spectrofluorometric procedure (after the extensive work of Borneff & Kunte (1969)), as is one of two presented by the UK Government (Department of the Environment, 1988b).

Gas chromatographic (GC) determination of PAH has been revolutionised by capillary columns which have now largely superseded packed columns. Capillary column GC (high resolution GC (HRGC)) offers very high resolution and its application to PAH analysis has been reviewed by Lee & Wright (1980). Glass and more recently fused-silica columns are used with a variety of stationary phases, SE-52 (methylsilicone gum with 5% phenyl groups) being the most popular. Columns are typically 10-25 m in length and 0.2-0.3 mm i.d. with film thickness of approximately 0.3 μm. Retention of PAH is related to the logarithm of determinand vapour pressure and hence to boiling point and molecular weight. A comparison of the various sample introduction techniques (split, splitless, cold trapping, on column) with respect to determinand discrimination and decomposition effects is given by Schomburg et al. (1977). Flame ionisation detection (FID) is the most widely used form of detection for PAH. It has the advantages of wide range of linear response, stability and sensitivity (detection limits of 0.1-0.5 ng), but its lack of specificity usually necessitates extensive cleanup of sample prior to use.

Mass spectrometric (MS) ionisation techniques for PAH produce generally an intense molecular ion (a singly charged intact molecule amid a limited number of secondary ions). Quantitative analysis is largely confined to capillary column GC-MS: more conventional direct insertion probe analysis is utilised mainly for qualitative investigations. The rapid elution times of capillary GC peaks (<10 s) demand rapid MS scanning with computerized data aquisition and reduction. The relatively simple

fragmentations (and thus mass spectra) of PAH permit effective use of single (or multiple) ion monitoring under a selected ion monitoring (SIM) mode of analysis, in place of conventional aquisition of complete mass spectra under a repetitive scanning (RS) mode. This allows for more sensitive (pg detection) and specific detection. GC-MS remains the most powerful technique for the analysis of complex mixtures.

Contemporary high performance liquid chromatography (HPLC) column technology does not approach the high resolution of capillary column GC but does offer improved column selectivity for isomeric PAH difficult to separate by GC. Both normal- and reverse-phase HPLC are used employing a variety of stationary phases with gradient elution of (various) mobile phases, but the most popular liquid chromatographic mode for PAH determination is reverse-phase on chemically bonded C_{18} stationary phases. UV absorption and fluorescence detectors, generally used in series, provide for PAH very high sensitivity (pg and sub-pg detection limits) and specificity (more so than for GC-MS where conventional mass spectra of many PAH isomers are identical).

1.11.4 Waste Water Methods and Analytical Requirements

Few analytical procedures are reported for the determination of PAH in municipal waste water and waste water sludge: most apply to relatively clean aqueous matrices. The waste water methods are nearly all poorly validated, in common with PAH analytical work in general which is characterised by an over-emphasis of 'high tech' procedures and a neglect of basic analytical fundamentals required for method assessment which is of crucial importance for the trace analysis (μg l^{-1}/p.p.b. or less) of extremely complex matrices. Determination of PAH is notoriously difficult and requires extreme care at all stages of the analytical protocol. Table 16 lists the minimum requirements for method validation judged to be necessary after the work and recommendations of Wilson (Hunt & Wilson, 1986). A quantitative statement of method performance characteristics in terms of analytical accuracy (expressed in terms of efficiency, that is the magnitude

TABLE 16
Minimum Requirements for Analytical Method Validation

Performance criterion	Measurement	Requirements
1. Accuracy	Efficiency	Each determinand Min. two determinand concns. Real sample
2. Precision	Estimate of error[a]	Each determinand Min. two determinand concns. Real sample
3. Sensitivity	Detection limit[b]	Each determinand

[a] Often includes accuracy, and sometimes called repeatability. (Reproducibility = variation due to different operators/ apparatus/laboratories/time.)
[b] Sensitivity is defined more exactly as 'rate of change of analytical response with concentration of determinand' (Hunt & Wilson, 1986).

and repeatability of determinand recovery at various concentrations), precision and sensitivity is essential before a decision can be made as to the suitability of a procedure, the confidence with which it can be used for a particular purpose, and the interpretation permitted of the results obtained, taking costs and time into consideration. Methods for determining PAH in municipal waste waters, with performance criteria satisfied, are listed in Table 17.

Analytical procedures with adequate validation are essential in the provision of high quality data necessary to provide a sound basis for decisions on effective control of pollutants. The role of the waste water treatment works as a major point source of PAH to surface waters for those treatment systems serving combined sewerage and industrial discharges (Table 3) is such that the works may be considered as an important initial process in the regulation of potable water quality in river basin water reuse schemes. The careful study of the effect of primary sedimentation on PAH by a comprehensively characterised analytical procedure is important for a number of reasons:

1. Primary sedimentation is the first stage in this process of regulation of receiving water quality and potable water quality.

TABLE 17
Analytical Methods for PAH in Municipal Waste Waters

Ref./ method	PAH	Sample type	Criteria satisfied[a]
McIntyre et al. (1981)			
TLC	WHO six	Sludge	- (Semiquant. method)
Aichberger & Reifenauer (1984)			
TLC	BaP	Sludge	3
Grimmer et al. (1978)			
GC	19	Sludge	2 (one concn.)
			3
Hagenmaier & Jäger (1979)			
HPLC	WHO six	Sludge	-
Mertens & Rittmann (1983)			
HPLC	WHO six	Sludge	2 (BaP only; one concn.)
			3 (BaP only)
Schössner et al. (1983)			
TLC	WHO six	'Waste water'	1 (tap water)
			2 (one concn.; standards)
Grzybowski et al. (1983)			
HPLC	16	Sewage eff.	1[b](one concn.; dist. water)
			2[b](one concn.)
Searl et al. (1979)			
GC	23	Sewage eff.	1[b]
			2[b]
Longbottom & Lichtenberg (1982)/ EPA Method			
GC/HPLC	16[c]	Sewage eff.	1[d]
			2[d]
			3[e]

[a] After Table 16.
[b] Mean for all PAH reported only.
[c] Priority pollutant PAH.
[d] Kinzer et al. (1984).
[e] Cole et al. (1981).

2. The accumulation of PAH in primary sludge may have implications for the disposal of such waste, particularly when applied to agricultural land.
3. PAH behaviour during primary treatment defines the load on the subsequent secondary treatment and sludge treatment processes.
4. Data on PAH removal during treatment is necessary in calculating potential consent conditions for industrial discharges of PAH to sewers.

2. OBJECTIVES

Reported studies of the behaviour of PAH during primary sedimentation (Section 1.8.3), although suggesting that the unit process may act as a significant point of removal, demonstrated major shortcomings. Borneff & Kunte (1967) and Reichert et al. (1971) reported only mean results for a number of PAH thus attaching a lack of importance to PAH physicochemical property and hence individual PAH behaviour. The Environmental Protection Agency (1982) reported results for N only. Petrasek et al. (1983) and Hannah et al. (1986) spiked plant influent with PAH to assist in the analysis and monitoring. Apart from the unrealistically high concentrations involved, the practice introduced potential variables in the guise of spike mixing efficiency, form of PAH in the matrix, and equilibration time (Section 1.6.1). The study conducted by Borneff & Kunte suffered from a poor sampling procedure consisting of the collection of single grab samples only, and although the procedure in the subsequent study of Reichert et al. represented an improvement, poor internal consistency was evident in the results. Borneff & Kunte, Reichert et al., Petrasek et al. and Hannah et al. failed to report accompanying plant performance data in the form of SS removals of importance in the interpretation of results. Furthermore, all five studies were conducted under conditions of varying hydraulic and SS loading, thus precluding conclusions of the influence of these two important process parameters on removal. The limited data from the studies do not suggest how typical the reported results are and thus the general applicability of the results.

Reports on PAH transformation processes in sewage matrices (Section 1.7 and 1.8.3) are confined to biodegradation which may be assumed to be of negligible importance as a removal mechanism during the comparatively rapid process of primary sedimentation. Volatilisation and more particularly photodegradation may be of significance during sedimentation, the latter by virtue of sensitization by suspended solids and dissolved matter. Although data exist on PAH sorption to suspended sediments (Section 1.6.1), data on proportion of PAH sorbed to sewage particulates are lacking, as are data on PAH particle size distributions

which would be of value in the interpretation of PAH settleability.

Analytical procedures for determination of PAH in municipal waste waters are on the whole poorly validated (Table 17). The procedure of McIntyre et al. (1981) was semiquantitative only, whilst that of Aichberger & Reifenauer (1984) was for the determination of BaP only, with detection limit presented as the sole performance characteristic. The method of Grimmer et al. (1978) lacked characterisation of accuracy but this was because it was a profile method. The procedure of Hagenmaier & Jäger (1979) was not accompanied by any performance characteristics. Mertens & Rittmann (1983) supplied performance data, accuracy excluded, for BaP only for their scheme. The method of Schössner et al. (1983) was characterised for accuracy and precision but the former was determined on a sample of drinking water and the latter on a mixed standard solution. Both Grzybowski et al. (1983) and Searl et al. (1979) provided performance data for procedure accuracy and precision but in both cases, and for both performance criteria, only mean values for all PAH were reported, accuracy in the former case being determined on a spiked sample of distilled water. EPA's method (Longbottom & Lichtenberg, 1982) for the determination of priority pollutant PAH was well characterised, fulfilling all the minimum requirements for method validation. However, this procedure, in common with all others, was only validated for one sample type: a procedure for the examination of PAH removal during primary sedimentation would need to be characterised with respect to raw sewage, primary effluent and raw primary sludge. Furthermore, the EPA procedure was chiefly validated with respect to an industrial waste water sample type containing relatively high concentrations of PAH. Borneff & Kunte (1967) and Reichert et al. (1971) in their studies of PAH removal during primary sedimentation utilised a modified TLC procedure after Kunte (1967) and Borneff & Kunte (1964), but reported no performance characteristics for the method. A knowledge of PAH sample integrity is required in order to assess the need for any preservation. Sampling and storage should be examined as an integral part of method validation. Current recommendations, which have not included municipal waste water to date, are diverse (Section 1.11.1).

In view of these considerations the work reported here has been undertaken with three specific objectives:

1. The development and evaluation of a capillary GC or capillary GC-MS technique for the determination of priority pollutant PAH in raw sewage, primary effluent and raw primary sludge, satisfying all the minimum requirements for method validation as laid down in Table 16 and displaying satisfactory numerical performance characteristics for accuracy, precision and sensitivity, followed by an evaluation of sample integrity with regard to PAH determination.
2. An assessment of the physicochemical behaviour of PAH in the sewage matrix, particularly:
   a). an appraisal of extent of PAH sorption to sewage particulates,
   b). an evaluation of PAH particle size distribution, and
   c). an appraisal of PAH susceptibility to volatilisation and photodegradation.
3. A study of factors influencing the behaviour and removal of PAH during the primary sedimentation process under controlled conditions by means of a pilot-scale treatment plant, particularly:
   a). an assessment of the extent and range of removals under a wide range of conditions of hydraulic and SS loading, and
   b). correlation of removals with plant performance in terms of SS and COD (chemical oxygen demand) removals,

   with monitoring of indigenous PAH by an adequate sampling procedure.

3. MATERIALS AND METHODS

3.1 Analytical Techniques

3.1.1 Development of a Procedure for PAH

3.1.1.1 Glassware

Borosilicate glassware was utilised throughout and was cleaned by soaking in a solution (5% V/V) of 'Decon 90' detergent (BDH Ltd., UK) for a minimum of 6 h. Subsequently, thorough rinsing with tap water with final rinsing (three times) with glass-distilled deionised water was performed, followed by oven-drying at 110°C. Polytetrafluoroethylene (PTFE) centrifuge bottles and chromatography column taps, polypropylene apparatus and volumetric glassware were similarly cleaned, but oven-dried at 60°C.

3.1.1.2 Solvents

Cyclohexane, n-hexane, acetone, dichloromethane and diethyl ether were of 'Distol' grade and light petroleum (b.p. 40-60°C) 'SLR' grade (Fisons Ltd., UK). Dimethyl-formamide was of spectroscopic grade (BDH Ltd., UK). n-Octane was of general purpose reagent grade (BDH Ltd., UK) and was purified by simple distillation in glass; the distillate was shown to be free from PAH and interferences.

3.1.1.3 Stock and Standard Solutions

Individual stock solutions of approximately 1 mg ml^{-1} were prepared in acetone from standard compounds N, AY, AE, F, BghiP and DBahA (Aldrich Ltd., UK), PA, A, CH and BaP (R.N. Emanual Ltd., UK), FL, P and BaA (British Carbonisation Research Association, UK) and BbF, BkF and IP (Phase Separations Ltd., UK). All standard compounds were of at least 95% purity by mass. From the stock solutions a series of ten calibration standards were prepared in octane, each one a mixed (i.e. composite) standard solution containing all PAH, at the following (individual component) concentrations: 0.0250, 0.0500, 0.100, 0.250, 0.500, 1.00, 2.50, 5.00, 10.0 and 20.0 μg ml^{-1}. A stock solution of

deuterated anthracene ($A\text{-}d_{10}$) (Aldrich Ltd., UK), of approximately 1 mg ml^{-1}, was prepared in octane for the provision of an internal standard for GC-MS determination, and for this purpose a second identical series of calibration standards was prepared, each containing $A\text{-}d_{10}$ dosed, from the stock solution, to the equivalent of 10.0 µg ml^{-1}. Stock and standard solutions were made up in 10 ml volumetric flasks, Teflon-sealed, stored at ambient temperature in the dark, and replaced after six months.

3.1.1.4 Sample Collection

Waste water samples were obtained from Hogsmill Valley Water Pollution Control Works (Thames Water Authority, UK), near Kingston-upon-Thames, Surrey. The design and construction of the plant (activated sludge) have been reported (Calvert et al., 1959), and subsequent operation and performance documented (Stanbridge, 1968). Design was based on a DWF of 33.0×10^3 m^3 d^{-1} (Stanbridge, 1968) but a recent DWF of 56.7×10^3 m^3 d^{-1} (ca. 700 l s^{-1}) has been reported (Eves, 1981). Primary sedimentation is carried out in four radial flow tanks, each of diameter 30.5 m and height (to top of sludge compartment) 4.9 m (Calvert et al., 1959), and of a design surface loading rate of 33.9 m^3 m^{-2} d^{-1} and hydraulic retention time of 2.69 h at 3 DWF (Stanbridge, 1968). The plant serves a combined sewerage system, with trade effluent constituting approximately 4% V/V of DWF, and deriving principally from metal plating and heat treatment works, a bakery, a dye works, a wine bottling enterprise and several research establishments (Stanbridge, 1968).

Samples of raw sewage were drawn from the inlet channel immediately preceding the distribution chamber of the four primary sedimentation tanks of the works. The sewage had previously been subjected to preliminary treatment in the form of grit removal and comminution, but contained returned flows in the form of surplus activated sludge (for co-settlement with primary sludge) and sludge treatment liquors. Samples of primary effluent were collected at the trough exit serving the peripheral weir of a tank, and raw primary sludge samples from the desludging chamber adjacent to a tank following daily desludging. Samples were stored

in vessels of appropriate size: 50 l tin-plated drums, and 2.5 and 1 l borosilicate glass bottles.

3.1.1.5 Sample Preservation

Samples were preserved immediately by the addition of formaldehyde solution (1% V/V) of analytical reagent quality (Fisons Ltd., UK), and stored at ambient temperature in the dark for a maximum of eight weeks. Formaldehyde has been used successfully as a biocide for preserving samples of raw sewage, primary effluent and primary sludge (Brunner *et al.*, 1988) and in preserving dissolved alkanes in natural waters (Shultz *et al.*, 1976). Unpreserved samples were extracted within 24 h of collection.

3.1.1.6 Statistical Analyses

Analytical results were generally reported to three significant figures with accuracy stated explicitly where appropriate, according to the recommendation of Hunt & Wilson (1986). Operations were ordinarily performed in quadruplicate where applicable. All mean values reported were arithmetic, with relative standard deviation (RSD) of the appropriate mean equal to one standard deviation (σ_{n-1}) divided by the population mean, and expressed as a percentage (otherwise known as coefficient of variation). All tests for significance (t test and t test assessing correlation coefficients for significance) were at the 95% level of confidence ($P = 0.05$). Linear regression analyses were unweighted. All distributions were assumed normal but percentage removal efficiency values, as closed data sets (i.e. bounded by values of 0 and 100%), were normalised by arcsin transformation for purposes of correlation analysis. All proportions and removals expressed as percentages were on a weight (pollutant) by volume (medium) basis (W/V) unless otherwise stated.

3.1.1.7 Sample Extraction

A 1.00 l sample of raw sewage or primary effluent was extracted with 150 ml of cyclohexane in a 1.5 l separating funnel by a laboratory disperser (Model X1920, Scientific

Instrument Co. Ltd., UK) for ca. 5 min at 50% full revolutions. McIntyre et al. (1981) (Section 1.11.1 and Table 13) showed the disperser to be a superior mixer-homogenizer device to the Ultra-Turrax, and superior to simple partitioning, for extraction of PAH from sewage samples. After separation of the phases, the aqueous layer was run off and retained, and the organic layer transferred to a 200 ml capacity PTFE centrifuge bottle. Centrifugation (Laboratory Centrifuge, Gallenkamp Ltd., UK) at 2000 rev min^{-1} (ca. 5000 g) for 20 min yielded a clear organic phase which was pipetted into a 250 ml round-bottomed flask. The remaining aqueous phase with solids was returned, with 3 x 1 ml washings (glass-distilled deionised water), to the separating funnel together with the original aqueous portion, and extracted as above with a further 100 ml of solvent. The extracts were combined and reduced to ca. 2 ml under reduced pressure at 28°C by means of a rotary evaporator (Rotavapor-R, Büchi A.G., Switzerland).

A sample of primary sludge was extracted in the same manner except that a sample volume of 50.0 ml was extracted directly in a centrifuge bottle, with centrifugation following immediately.

PAH loss during rotary evaporation was assessed as follows. A set of four ca. 3 ml portions of hexane in 5 ml round-bottomed flasks, each containing the equivalent of 10.0 µg each PAH from stock solutions, was evaporated just to dryness, and residues immediately re-dissolved in 1.00 ml volumes of octane for determination by GC. An identical set of standard mixtures was evaporated exactly 1 min past dryness before re-dissolution and determination of recoveries.

3.1.1.8 Sample Cleanup Selection

3.1.1.8.1 Experimental Design

Selection of one or more sample cleanup steps was assisted by the application of three techniques to each potential cleanup: treatment of a sample, treatment of a blank, and treatment of a standard mixture of PAH (equivalent to a

spiked blank), each technique performed in quadruplicate. This strategy permitted selection on a qualitative basis by allowing suitability of the cleanup step to be judged against the particular instrumental methods of determination adopted (GC and GC-MS), and on a firm quantitative basis by permitting efficiency and repeatability of recovery of each PAH to be determined. For purposes of rationalisation, samples were withdrawn in the form of subsamples (of 50.0 ml each) from a common large sample of primary sludge (25800 mg l^{-1} total solids (TS); preserved), and all determinations performed by GC, with GC-MS taking a later (Section 3.1.1.9) confirmatory role.

3.1.1.8.2 Preparative Thin Layer Chromatography

Solvent extracts of four sludge subsamples obtained by the method described previously (Section 3.1.1.7) were each transferred to a 5 ml round-bottomed flask with 3 x 1 ml washings (cyclohexane). After rotary evaporation just to dryness, residues were immediately re-dissolved in a minimum volume of dichloromethane (ca. 0.1 ml). Each was streaked onto a 200 mm x 200 mm TLC plate pre-coated with silica gel G, thickness 0.5 mm (Anachem Ltd., UK), having previously been activated at 110°C for 30 min. Transfer was completed with 3 x 0.1 ml washings (dichloromethane). Plates were developed with a mixed solvent system consisting of a mixture of diethyl ether and hexane (1+19 V/V) after McIntyre et al. (1981). Calibration of plate was previously accomplished by application, from stock solutions, to each of four plates the range of PAH as individual spots (ca. 0.1 µg each), with development as above. The PAH band position (R_F = 0.40-0.69) was visualized via fluorescence by irradiation of standard plates with 366 nm wavelength UV light (UV Lamp Box (16 W), Harovia Ltd., UK). (R_F values enclosed ranges observed for all four plates, and included the equivalent of an additional 2 mm as allowance for the non-fluorescing PAH AY and AE). The appropriate area on each sample plate was marked, and adsorbent scraped off with a stainless steel spatula into a sintered glass funnel and eluted with ca. 50 ml of cyclohexane into a 50 ml round-bottomed flask. Isolates were reduced to ca. 2 ml, transferred to a 5 ml

round-bottomed flask with 3 x 1 ml washings (cyclohexane), evaporated to dryness and each re-dissolved in 0.200 ml of octane for analysis.

Four blanks in the form of ca. 0.1 ml portions of dichloromethane underwent treatment exactly as above, and similarly for four standard mixtures in the form of ca. 0.1 ml dichloromethane portions containing 10.0 µg each PAH except isolates here were each re-dissolved in 1.00 ml of octane after evaporation to dryness in the 50 ml round-bottomed flasks.

Four sludge extracts were treated under a modified procedure whereby plates were developed with a mixed solvent system consisting of a mixture of diethyl ether and light petroleum (b.p. 40-60°C) (1+8 V/V) after the method of Thompson & Eglinton (1978) and after plate calibration as above (R_F = 0.63-0.80).

3.1.1.8.3 Liquid-Liquid Partition

Four sludge extracts underwent cleanup by liquid-liquid partitioning with dimethylformamide (DMF). The procedure followed was that of Bjørseth (1977) which was more detailed in description than that of Grimmer et al. (1978) or Grzybowski et al. (1983). Extracts obtained after centrifugation but before reduction (Section 3.1.1.7) were used i.e. the ca. 150 and 100 ml cyclohexane extracts obtained for each subsample. These were pipetted directly into a 300 ml separating funnel and shaken with 50 ml of a mixture of DMF and water (glass-distilled deionised; used throughout) (9+1 V/V) for 5 min. After separation of the phases, the lower DMF-water layer was transferred to a 200 ml separating funnel and the cyclohexane phase re-extracted with a further 25 ml of the DMF-water mixture. The two DMF-water phases were combined, and the PAH fraction back extracted into cyclohexane by shaking with 75 ml of water and 50 ml of cyclohexane for 5 min. The DMF-water layer was transferred to another 200 ml separating funnel and extracted with a further 25 ml of cyclohexane. The cyclohexane phases were combined in a 100 ml separating funnel, washed with 2 x 25 ml of water for 3 min each, and subsequently run into a 100 ml

round-bottomed flask and dried over sodium sulphate (anhydrous general purpose reagent, BDH Ltd., UK). The isolate was pipetted into another 100 ml round-bottomed flask, reduced to ca. 2 ml, transferred to a 5 ml round-bottomed flask with 3 x 1 ml washings (cyclohexane), and subsequently evaporated to dryness and re-dissolved in 0.200 ml of octane for analysis.

Four blanks in the form of 250 ml volumes of cyclohexane were treated as above. Similarly, four 250 ml portions containing 10.0 µg each PAH underwent treatment but isolates were each re-dissolved in 1.00 ml of octane after evaporation to dryness in the 100 ml round-bottomed flasks.

3.1.1.8.4 Aluminium Oxide Preparative Column Chromatography

3.1.1.8.4.1 Selection of Adsorbent Mass

Aluminium oxide (Merck 90 active, neutral, particle size 0.063-0.200 mm / 70-230 mesh ASTM, BDH Ltd., UK) was activated at approximately 400°C for ca. 6 h in a porcelain dish, and subsequently deactivated to 5.0% (±0.5%) (W/W glass-distilled deionised water), 24 h prior to dry-packing with tapping in 140 mm x 12 mm i.d. glass chromatographic columns. Calibration of columns containing 11.0, 8.0 and 5.0 g of adsorbent with respect to PAH fraction elution volume was accomplished by application of a standard mixture consisting of ca. 2 ml of cyclohexane containing 10.0 µg each PAH to each of four columns containing 11.0 g, four 8.0 g and four 5.0 g. Each application was accompanied by 3 x 1 ml washings (cyclohexane), followed by elution with cyclohexane (placed in a 100 ml reservoir). Eluate from each column was collected in 5.0 ml fractions in a 25 ml measuring cylinder, each fraction transferred to a 10 ml round-bottomed flask with 3 x 1 ml washings (cyclohexane). Fractions were evaporated to dryness and each re-dissolved in 1.00 ml of octane for analysis. An adsorbent mass of 5.0 g was provisionally selected.

A sludge extract was applied as above to each of four columns containing 5.0 g of adsorbent with the first 15.0 ml of eluate from each column collected as the PAH

fraction and transferred to a 25 ml round-bottomed flask with 3 x 1 ml washings (cyclohexane). Fractions were evaporated to dryness and each re-dissolved in 0.200 ml of octane for analysis. Three subsequent fractions of 10.0 ml each were collected from each column and treated in the same manner to test for continued elution of material.

Four blanks in the form of ca. 2 ml portions of cyclohexane were treated as for the sludge extracts, collecting the first 15.0 ml of eluate only, and similarly for four standard mixtures consisting of ca. 2 ml cyclohexane portions containing 10.0 µg each PAH, except that fractions were dissolved in 1.00 ml of octane.

3.1.1.8.4.2 Selection of Adsorbent Deactivation

Calibration of columns containing adsorbent (5.0 g), deactivated to 4.0% (±0.1%), 3.5% (±0.1%) and 3.0% (±0.1%) with respect to PAH fraction elution volume, was performed by application as above of a ca. 2 ml portion of cyclohexane containing 10.0 µg IP only to a single column of adsorbent at each deactivation. Progress of IP was followed visually via the compound's intense yellow colouration, aided by irradiation of column with UV light (UV Lamp (16 W), Harovia Ltd., UK). PAH fraction elution volume was estimated from total eluate volume collected in a 100 ml measuring cylinder after complete elution of IP, with allowance (5 ml) for DBahA; of the priority pollutant PAH, IP followed by DBahA are the last to elute from an aluminium oxide column (Lee et al., 1981).

A sludge extract was applied as above (Section 3.1.1.8.4.1) to a single column of adsorbent (5.0 g) at each deactivation, collecting the first 35.0 ml (4.0% deactivation), 50.0 ml (3.5%) and 70.0 ml (3.0%) of eluate. The PAH fractions were each transferred to a 100 ml round-bottomed flask with 3 x 1 ml washings (cyclohexane), reduced to ca. 2 ml, transferred again to a 5 ml round-bottomed flask with rinsings, and subsequently evaporated to dryness and re-dissolved in 0.200 ml of octane for analysis.

An adsorbent mass of 5.0 g at 5.0% (±0.5%) deactivation was adopted provisionally as suitable for cleanup, with the first ca. 30 ml of eluate collected (embodying a safety allowance) in a 50 ml measuring cylinder, and transferred to a 50 ml round-bottomed flask with 3 x 1 ml washings (cyclohexane).

3.1.1.8.5 Silica Gel Preparative Column Chromatography

3.1.1.8.5.1 Selection of Adsorbent Mass

Silica gel (Merck 40, particle size 0.063-0.200 mm / 70-230 mesh ASTM, BDH Ltd., UK) was prepared and packed in columns in a manner identical to that of aluminium oxide (Section 3.1.1.8.4.1). Calibration of column containing 11.0 g of adsorbent with respect to PAH fraction elution volume was performed by application of a standard mixture, consisting of a ca. 3 ml hexane portion containing 10.0 µg each PAH, to each of four columns with 3 x 2 ml washings (hexane). Eluent was hexane (placed in a 250 ml reservoir). Eluate from each column was collected in 20.0 ml fractions in a 25 ml measuring cylinder, each fraction transferred to a 25 ml round-bottomed flask with 3 x 1 ml washings (hexane), evaporated to dryness and re-dissolved in 1.00 ml of octane for analysis. To reduce PAH fraction elution volume, eluent polarity was subsequently increased. The calibration procedure above was repeated on four columns eluted with 5% and four with 2% (V/V) diethyl ether in hexane, with eluate collected in 5.0 ml fractions. Subsequently adsorbent mass was reduced to 5.0 g and calibration performed on four columns with hexane only as eluent; eluate was collected in 5.0 ml fractions up to a total eluate volume (per column) of 30.0 ml, with 10.0 ml fractions collected thereafter. An adsorbent mass of 5.0 g (with hexane as eluent) was provisionally selected.

Four sludge extracts cleaned up by aluminium oxide column chromatography (Section 3.1.1.8.4.2; 5.0 g of adsorbent at 5.0% deactivation) were each evaporated to dryness and re-dissolved in ca. 3 ml of hexane. Each was applied as above, with 3 x 2 ml washings (hexane), to a column containing 5.0 g of silica gel, and eluted with hexane.

The first 14.0 ml of eluate from each column was set aside and the subsequent 100.0 ml collected as the PAH fraction in a 100 ml measuring cylinder. This was transferred to a 100 ml round-bottomed flask with 3 x 1 ml washings (hexane), reduced to ca. 2 ml, transferred again to a 5 ml round-bottomed flask with rinsings, and subsequently evaporated to dryness and re-dissolved in 0.200 ml of octane for analysis. The first 14.0 ml of eluate, and four 10.0 ml fractions subsequent to the PAH fraction, collected from each column (as in the calibration procedure, with a 25 ml measuring cylinder and round-bottomed flasks), were each evaporated to dryness and re-dissolved in 0.200 ml of octane for analysis. These provided information on pre- and post-PAH fraction material.

3.1.1.8.5.2 Selection of Adsorbent Deactivation

Calibration of columns containing adsorbent (5.0 g) deactivated to 2.5% (±0.1%) and 1.0% (±0.1%) was performed by application of a standard mixture, as in the calibration procedure above (Section 3.1.1.8.5.1), to each of four columns at each deactivation. Eluate (hexane) was collected in 5.0 ml fractions up to a total eluate volume (per column) of 30.0 ml, with 10.0 ml fractions collected thereafter.

A sludge aluminium oxide isolate, evaporated to dryness and re-dissolved in ca. 3 ml of hexane, was applied as above (Section 3.1.1.8.5.1) to each of four columns containing adsorbent (5.0 g) at 2.5% deactivation, discarding the first 20.0 ml of eluate and collecting the subsequent 130.0 ml, and to four columns at 1.0% deactivation, discarding the first 25.0 ml, and collecting the subsequent 150.0 ml. PAH fractions were collected in a 250 ml measuring cylinder, and each transferred to a 250 ml round-bottomed flask with 3 x 1 ml washings (hexane), reduced to ca. 2 ml, and transferred to a 5 ml round-bottomed flask with rinsings, evaporated to dryness, and dissolved in 0.200 ml of octane for analysis. An adsorbent deactivation of 1.0% was provisionally adopted.

3.1.1.8.5.3 Column Calibration at 15°C

Between-batch repeatability of PAH fraction elution volume was improved by eluting at constant ambient temperature. Careful calibration of column (5.0 g of adsorbent at 1.0% (±0.1%) deactivation) as above (Section 3.1.1.8.5.2), was performed on four columns, at 15°C (±2°C).

Cleanup of a sludge aluminium oxide isolate, evaporated to dryness and re-dissolved in ca. 3 ml of hexane, on each of four columns (5.0 g at 1.0% deactivation) at 15°C, was performed as above (Section 3.1.1.8.5.2). The first 25.0 ml of eluate from each column was discarded, and the subsequent 160.0 ml collected. Five subsequent 10.0 ml fractions were collected from each column (as in Section 3.1.1.8.5.1) to test for continued elution of material.

Four blanks in the form of ca. 3 ml portions of hexane were treated as for the sludge isolates above, and similarly for four standard mixtures consisting of ca. 3 ml hexane portions containing 10.0 µg each PAH with final dissolution in 1.00 ml of octane.

An adsorbent mass of 5.0 g at 1.0% (±0.1%) deactivation, utilised at an ambient temperature of 15°C (±2°C), was adopted provisionally as suitable for cleanup, with the first 24 ml of eluate discarded and the subsequent 190 ml collected (the volumes embodying safety allowances).

3.1.1.9 Validation of Column Chromatographic Procedure

The overall efficiency and repeatability of recovery of PAH for the procedure (extraction, cleanup with 5.0 g of aluminium oxide deactivated to 5.0%, final cleanup with 5.0 g of silica gel deactivated to 1.0% and utilised at 15°C, and determination by GC (Section 3.1.1.10.1)), were assessed to quantify procedure accuracy and precision. Samples were spiked with known masses of PAH and the proportions remaining in the treated samples determined. The assessment was carried out on two samples (one of primary sludge and one of raw sewage) to determine the influence of sample type and particularly total solids (TS)

concentration on determinand recovery, and at three spike levels to assess the influence of determinand concentration on recovery. Four 50.0 ml subsamples of original sludge (25800 mg l^{-1} TS; preserved) were treated and determined for background (indigenous) concentrations of PAH, and subsequently four 50.0 ml subsamples were each spiked, from stock solutions, the equivalent of the mean background concentration of each PAH (1x), four subsamples spiked three times (3x) and a further four nine times (9x) the mean background concentration. Extractions were performed following a 4 h equilibration period to ensure that spiked determinand was in the same form in the matrix as the indigenous kind. The same protocol was followed on sets of four 1.00 l subsamples of a sample of raw sewage (983 mg l^{-1} TS), but included a preliminary examination of the effect of the preserving agent, formaldehyde, on the analytical procedure. Upon collection of the sample, four 1.00 l subsamples were withdrawn prior to immediate preservation of the remainder. The four subsamples together with four from the preserved batch were promptly extracted for determination of PAH, with the mean value for all eight subsamples taken as the mean background concentration of PAH for subsequent spikes.

Four blanks in the form of 1.00 l samples of glass-distilled deionised water underwent treatment by the procedure to ascertain procedure contribution to interferences. The distilled deionised water itself was determined directly for background contamination as follows. Four 1.00 l samples were extracted as for blanks, except after phase separation following extraction with the laboratory disperser (Section 3.1.1.7), the organic layer was transferred directly to a 250 ml round-bottomed flask, omitting centrifugation. The aqueous layer was returned and re-extracted and the organic phases combined and dried over sodium sulphate (anhydrous general purpose reagent, BDH Ltd., UK). The extract was transferred to another 250 ml round-bottomed flask, reduced to *ca.* 2 ml, transferred to a 5 ml round-bottomed flask with 3 x 1 ml washings (cyclohexane), and subsequently evaporated to dryness and re-dissolved in 0.200 ml of octane for determination.

The column chromatographic procedure was also validated by GC-MS by re-determination of all primary sludge and raw sewage treated subsamples and associated spikes, generated by the above protocol, by this instrumental method (Section 3.1.1.10.2). The four treated blanks were also re-determined by GC-MS. The column chromatographic procedure with GC-MS determination of treated samples constituted the final developed method (Appendix 2), and was employed for all subsequent analyses.

3.1.1.10 Sample Determination

3.1.1.10.1 Capillary Column GC

3.1.1.10.1.1 Instrument and Calibration Procedure

A Carlo Erba Fractovap 4200 gas chromatograph (Erba Science Ltd., UK) with a flame ionisation detector (FID) was equipped with a fused-silica capillary column 25 m x 0.20 mm i.d., wall-coated, film thickness 0.11 µm, with SE-34 liquid phase (Hewlett-Packard Ltd., UK). Instrument settings were as given in Table 18. Portions of 2.00 µl of treated samples and calibration standards were

TABLE 18
GC-FID Instrument Settings

Instrument parameter	Setting
Gas flow rates	
-Injection port: septum purge	5.0 ml min^{-1}
bottom split valve	50 ml min^{-1} (45 s after injection).
-Carrier gas (helium)[a]	0.600 ml min^{-1}
-FID[a]: hydrogen	30.0 ml min^{-1}
make-up (helium)	40.0 ml min^{-1}
air	400 ml min^{-1}
Injector temperature	280°C
Detector temperature	350°C
Temperature programme	100°C, 2 min; 10°C min^{-1} to 300°C, 9 min.

[a] Measured at room temperature (25°C).

injected using a 10 µl syringe (Hamilton 800 Series, Phase Separations Ltd., UK) into a 'Grob-type' split-splitless injector using the 'splitless hot-needle' injection technique (Grob & Grob, 1974; Grob & Grob, 1978). A Servoscribe 1s recorder (Gallenkamp Ltd., UK), 2 mV setting (calibrated), was used to record chromatograms. The GC oven temperature programme gave an analysis turn-round time of 39 min.

Determinand peak height was measured as analytical response. Weekly calibration employing six calibration standards of concentration 0.250, 1.00, 2.50, 5.00, 10.0 and 20.0 µg ml^{-1} (equivalent to 0.0500, 0.200, 0.500, 1.00, 2.00 and 4.00 µg l^{-1} respectively in samples of 1.00 l and final treated samples of 0.200 ml) were performed, with single determinations of calibration standards and treated samples. Linear regression analysis (unweighted) was used to construct a calibration curve through the six datum points for each PAH.

3.1.1.10.1.2 Instrument Precision, Calibration Curve Data and Detection Limits

Instrument precision with respect to analytical response and determinand retention time was estimated from eight consecutive injections of a 10.0 µg ml^{-1} calibration standard. Calibration curve linear ranges, and detection limits, were appraised by injection of the series of calibration standards 0.00500, 0.0100, 0.0200, 0.0500, 0.100, 0.200, 0.500, 1.00, 2.00 and 4.00 µg l^{-1} (equivalent 1.00 l sample concentrations, 4.00 µg l^{-1} marking the column loading capacity).

3.1.1.10.2 Capillary Column GC-MS

3.1.1.10.2.1 Instrument and Calibration Procedure

A JEOL JMS-D300 double-focussing mass spectrometer with a JMA-2000H data processing system (JEOL Ltd., Japan) was interfaced to an identical GC and capillary column (Section 3.1.1.10.1.1), the latter inserted directly into the ion source. A general view of the system is presented in Plate 1 and instrument settings displayed in Table 19.

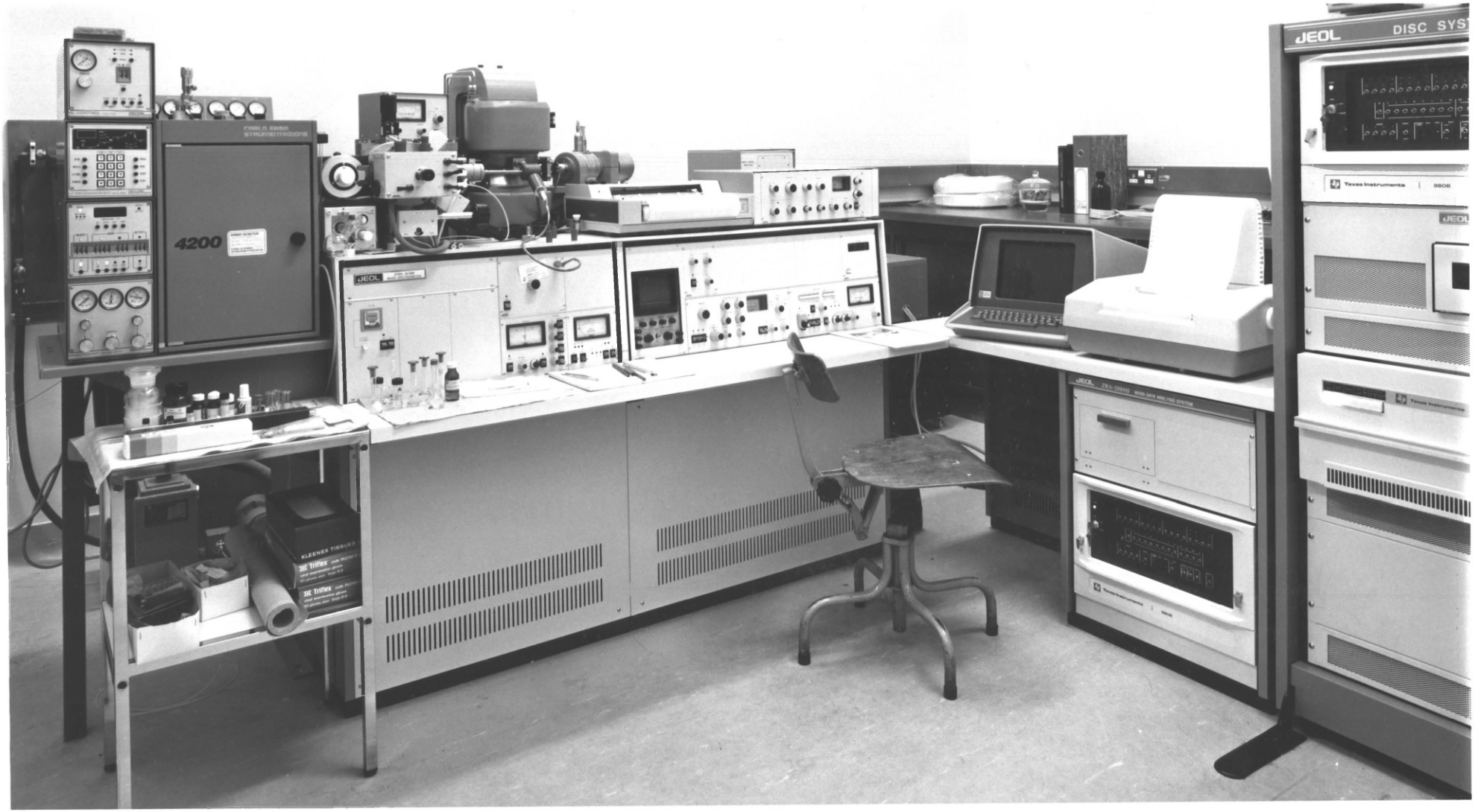


PLATE 1
View of the GC-MS System

TABLE 19
MS-SIM Instrument Settings

Instrument parameter	Setting
Ionising voltage	70 eV
Ionising current	300 μA
Ion source temperature	260°C
Scan range	40-500 μm
Mass sweep range	1.50 amu
Ion dwell time	0.1 s
Resolution	800
Electron multiplier	1.50 kV
GC-MS interface temperature	320°C

The selected ion monitoring (SIM) mode of operation of the MS under electron impact (EI) ionisation was employed, the molecular ion of each PAH (with m/z value equal to that of the molecular weight of the PAH) monitored as the characteristic ion. The full complement of ten channels was utilised to monitor the ten ions: m/z 152, 154, 166, 178, 188, 202, 228, 252, 276 and 278 (188 that of the internal standard, A-d_{10}). All other pertinent conditions, and injection techniques, were as for GC determination (Section 3.1.1.10.1.1) except that the final (maximum) oven temperature was held for 23 min, giving an analysis turn-round time of 53 min.

For the purpose of an internal standard for GC-MS determination, A-d_{10} was dosed, from stock solution, to the treated sample to the equivalent of 10.0 μg ml^{-1}. Integrated peak area of the characteristic ion of the determinand was measured, with 'analytical response constant' defined as the ratio of peak area of characteristic ion of determinand divided by peak area of characteristic ion of internal standard. Calibration employing three calibration standards of concentration 2.50, 10.0 and 20.0 μg ml^{-1} (equivalent to 0.500, 2.00 and 4.00 μg l^{-1} respectively in samples of 1.00 l and final treated samples of 0.200 ml; and containing internal standard), were performed daily, with single determinations of calibration standards and treated samples. The calibration curve through the three datum points for each PAH was constructed by linear regression analysis (unweighted).

3.1.1.10.2.2 Instrument Precision, Calibration Curve Data and Detection Limits

Instrument precision with respect to analytical response constant and determinand retention time, calibration curve linear ranges, and detection limits, were evaluated as in Section 3.1.1.10.1.2.

3.1.1.10.2.3 Accuracy and Precision of Calibration Procedure

The validity in terms of accuracy and precision of the daily calibration procedure employing three calibration standards was assessed by performing four replicate determinations of a 5.00 μg ml^{-1} calibration standard (equivalent to 1.00 μg l^{-1} in a 1.00 l sample), as test sample, on each of four consecutive days.

3.1.1.11 Evaluation of Systematic Error of GC-MS Column Chromatographic Procedure

3.1.1.11.1 Demonstration and Quantification of Bias

Initial evidence of a treated sample matrix effect giving rise to bias was obtained by injection of co-eluting PAH into the GC-MS. Mean analytical response constant for DBahA was recorded for four consecutive injections of octane (0.200 ml) containing 2.00 μg of the PAH (with internal standard). The operation was repeated after the addition of the equivalent of 2.00 μg of IP from a stock solution.

Bias was formally demonstrated and quantified by a method of standard additions performed on treated samples. The four replicate unspiked treated samples of primary sludge obtained previously (Section 3.1.1.9) were each diluted to 0.500 ml (octane) and the mean GC-MS analytical response constant (A_S) recorded for each PAH. Addition of the equivalent of 5.00 μg of each PAH from stock solutions to each treated sample was followed by re-recording of the mean analytical response constant (A_{SA}). Identical additions of PAH were made to four blanks in the form of four 0.500 ml aliquots of octane (containing internal

standard), and the mean analytical response constant (A_{BA}) determined. Recording of mean analytical response constants was performed within-batch, and for each PAH the factorial increase in mean analytical response constant of added PAH due to treated sample matrix calculated ($(A_{SA}-A_S)/A_{BA}$). Dilution due to additions was taken into account. The same operation was repeated on a subsequent occasion for the four replicate unspiked treated samples of raw sewage (unpreserved; Section 3.1.1.9).

3.1.1.11.2 Dependence of Bias on Sample

Dependence of bias on sample was tested on six treated samples: two of primary effluent (Sample 1, 314 mg l^{-1} suspended solids (SS); Sample 2, 261 mg l^{-1} SS), two of raw sewage (Sample 3, 853 mg l^{-1} SS; Sample 4, 909 mg l^{-1} SS) and two of primary sludge (Sample 5, 3060 mg l^{-1} SS; Sample 6, 5280 mg l^{-1} SS), for three PAH representative of the high molecular weight (MW) determinands suffering bias, BaA (MW 228), BaP (MW 252) and IP (MW 276). The internal standard was also tested to confirm formally the independence of analytical response for this compound on treated sample. The treated samples were each diluted to 0.400 ml (octane) and the GC-MS analytical response constant (A_S), relative to AY dosed at 10.0 µg ml^{-1} as temporary internal standard, recorded for the three PAH and A-d_{10}. A 3.00 µl aliquot of stock solution of determinand was added to each treated sample, transferring on each occasion 2.28 µg A-d_{10}, 3.48 µg BaA, 3.81 µg BaP and 3.18 µg IP. Analytical response constants (A_{SA}) were re-recorded, and analytical response constant due to added determinand calculated ($A_{SA}-A_S$) for each treated sample.

3.1.1.11.3 Dependence of Bias on Determinand Concentration

Dependence of bias on determinand concentration was ascertained by recording of GC-MS analytical response constant (A_S), relative to A-d_{10}, for the previous three representative PAH (BaA, BaP, IP; Section 3.1.1.11.2), in a treated sample (0.200 ml) of raw sewage (797 mg l^{-1} SS). A 0.40 µl aliquot of stock solution of determinand was added to the treated sample, transferring 0.464 µg BaA, 0.508 µg BaP and 0.424 µg IP, followed by re-recording of

analytical response constants (A_{SA}). An identical set of three 0.40 µl additions, with re-recording of analytical response constants, was carried out to a total of four sets, and analytical response constant due to total incremental addition calculated (A_{SA}-A_S) for each PAH.

3.1.1.12 Validation of Efficiency of Extraction Procedure

The efficiency of the extraction procedure on indigenous (unspiked) PAH was confirmed by performing four successive extractions on each of four 1.00 l subsamples of a sample of raw sewage (1160 mg l^{-1} TS; unpreserved) with sample treatment of each sequential extract. The first and second extracts of each subsample were obtained as normal (Section 3.1.1.7) but kept separate. The third and fourth extractions were performed as for the second extraction (with 100 ml of extractant). Each extract was reduced to ca. 2 ml, treated (by column chromatographic procedure) and determined by GC-MS.

3.1.1.13 Sampling and Storage Parameter Investigation

3.1.1.13.1 Sample Integrity Over Time

Sample integrity over an extended period of time was examined as an integral part of method validation. A large sample of raw sewage (1240 mg l^{-1} TS) was distributed between two 50 l tin-plated drums with the addition of the preserving agent (Section 3.1.1.5) to one, the containers being capped and stored at 15°C (±2°C). Four 1.00 l subsamples were taken from each container and determined promptly (by GC) for PAH, and subsequently after 7, 28 and 56 days. Upon completion of the experiment, sorption of PAH on the inner surfaces of the emptied vessel containing the unpreserved sample was tested by eluting the surfaces with 3 x 100 ml portions of the polar solvent acetone. A 50 ml portion of the combined washings was evaporated to dryness in a 50 ml round-bottomed flask, and the viscous residue transferred to a centrifuge bottle with 4 x 10 ml washings (cyclohexane). This was extracted and treated as for a sample of primary sludge (Section 3.1.1.7), and determined by GC.

3.1.1.13.2 Influence of Matrix on Sample Integrity

A sample of raw sewage (1020 mg l^{-1} TS) was divided into eight 1.00 l subsamples, four of which were preserved. Each subsample was stored in a stoppered 1.5 l separating funnel (as used for extraction; Section 3.1.1.7), and stored at 15°C (±2°C) in the dark. After 28 d, subsamples were extracted *in situ*, treated and determined for PAH. A parallel determination was performed with PAH spiked into glass-distilled deionised water at typical indigenous background concentrations. To each of eight separating funnels containing 1.00 l of water was spiked, from stock solutions, the equivalent of 1.00 µg of each PAH of molecular weight up to and including 228, and 0.250 µg of each PAH of molecular weight 252 and above. Four of these samples were preserved. All were stored under conditions identical to those for the subsamples of raw sewage. After 28 d, extraction (*in situ*), treatment and determination by GC was performed as for the direct determination of distilled deionised water samples given in Section 3.1.1.9.

3.1.2 Routine Analyses

3.1.2.1 Total Solids

Total solids (TS) concentration of samples was determined according to a standard procedure (Department of the Environment, 1984), with 100.0 ml of sample placed in a weighed nickel crucible which was subsequently evaporated to dryness on a steam bath. The crucible was re-weighed after oven-drying at 105°C for 2 h. Determination (single) of TS was performed immediately and before any sample preservation.

3.1.2.2 Suspended Solids

Total suspended solids (SS) concentration was determined gravimetrically according to the standard paper filtration method (Department of the Environment, 1984), utilising GF/C filter paper (Whatman Ltd., UK), which was oven-dried at 105°C for 1 h prior to weighing just before and after filtration of 50.0 ml of sample. Blank corrections were made for filter paper loss on washing. Primary sludge was diluted ten-fold (1+9 V/V glass-distilled deionised water) prior to filtration.

The dried filter was subsequently ignited in a furnace at 500°C for 30 min and re-weighed to determine the non-volatile suspended solids (NVSS) concentration; blank corrections were made for loss of filter paper on ignition. The volatile suspended solids (VSS) concentration was calculated by simple subtraction. Determination (single) of SS, NVSS and VSS was performed immediately and before any sample preservation.

3.1.2.3 Chemical Oxygen Demand

Total chemical oxygen demand (COD_{tot}) concentration was determined by a modification of a standard procedure (Department of the Environment, 1987; 1977 flask digestion titrimetric method). Samples for analysis were preserved by the addition of nitric acid (1% V/V). Portions of 1.00 ml of raw sewage, 2.00 ml of settled sewage or 1.00 ml of sludge (after ten-fold dilution) were withdrawn and

refluxed with 9.50 ml of an oxidising reagent mixture in a 250 ml reaction flask on an isomantle for 2 h. The mixture consisted of 9.00 ml of a combined solution of silver sulphate (7.89 g l^{-1}; BDH Ltd., UK) and potassium dichromate (1.61 g l^{-1}; BDH Ltd., UK) in sulphuric acid (79% V/V), and 0.50 ml of an aqueous solution of mercuric sulphate (200 g l^{-1}; Aldrich Ltd., UK) for suppression of chloride ion interference. After cooling and rinsing down the condenser with glass-distilled deionised water, the residual dichromate was titrated against a solution of ferrous ammonium sulphate (0.0625 N; BDH Ltd., UK), using two drops of ferrous phenanthroline indicator (Aldrich Ltd., UK).

Soluble (filterable) COD concentration (COD_{sol}) was determined on sample filtrate following SS determination (Section 3.1.2.2), with portions of 5.00 ml refluxed and titrated exactly as above. Determination (single) of COD_{tot} and COD_{sol} was performed immediately, and before any sample preservation with formaldehyde solution.

3.2 Laboratory Studies: Physicochemical Behaviour of PAH in Raw and Settled Sewage

3.2.1 Assessment of Settleability of PAH

Four 1.00 l subsamples of a sample of raw sewage (867 mg l^{-1} TS, 623 mg l^{-1} SS; unpreserved) were promptly determined for PAH. Another four were each placed in a 1.5 l tall-form beaker and allowed to settle for 2.3 h (tank retention time at 1 DWF for primary sedimentation pilot plant; Section 3.3). Each supernatant was siphoned off into a 1.5 l separating funnel for extraction (Section 3.1.1.7), and subsequently treated and determined. A further set of four 1.00 l subsamples was centrifuged in 200 ml capacity PTFE centrifuge bottles as in Section 3.1.1.7, with supernatants of each subsample pipetted into a separating funnel, as above, for extraction and subsequent determination. This permitted assessment of the PAH fraction not effectively amenable to settlement. SS, NVSS, VSS, COD_{tot} and COD_{sol} were determined for each raw subsample and subsample supernatant.

3.2.2 PAH Particle Size Distribution Analysis

Four 1.00 l subsamples of a sample of raw sewage (966 mg l^{-1} TS; unpreserved) were immediately determined for PAH. Subsequently, sets of four 1.00 l subsamples were filtered through nylon sieves (Henry Simon Ltd., UK) of 253, 150, 106 and 53 µm mesh directly into 1.5 l separating funnels, via a PTFE funnel, for filtrate extraction (Section 3.1.1.7) and subsequent treatment and determination. SS was determined for each raw subsample and subsample filtrate.

Sorption of PAH on sieve material was tested by filtration, through sieve of 53 µm mesh, of four 1.00 l volumes of glass-distilled deionised water each spiked, from stock solutions, the equivalent of 1.00 µg of each PAH of molecular weight up to and including 228, and 0.250 µg of each PAH of molecular weight 252 and above (as in Section 3.1.1.13.2). Each filtrate, collected as above, was extracted, treated and determined by GC as for the direct determination of distilled deionised water samples

given in Section 3.1.1.9.

3.2.3 Stability of PAH During Sedimentation

PAH susceptibility to removal via volatilisation and photodegradation during primary sedimentation was assessed on a sample of primary effluent as it was judged that the two mechanisms, if significant, would be operative in the topmost layer of the tank where the character of the contents would approach that of settled sewage. Furthermore, experiment duration of 48 h was considered to permit sufficient change to occur to allow accurate measurement of the effect and its extrapolation to shorter and more appropriate time intervals. Of a sample of primary effluent (361 mg l^{-1} TS, 110 mg l^{-1} SS; unpreserved), four 1.00 l subsamples were each placed in a 1.5 l separating funnel (as used for extraction; Section 3.1.1.7), stoppered and posited in the dark as control; four 1.00 l subsamples were each placed in a 1.5 l tall-form beaker (liquid surface area (cm^2) : height (cm) ca. 4:1) and stored in the dark and in the absence of draughts to test for volatilisation; and four subsamples in stoppered separating funnels, as for the control, were exposed to light (a mixture of natural and artificial) to test for photodegradation. After 48 h, subsamples were extracted *in situ* (phase separation for those in tall-form beakers achieved via a separating funnel), treated and determined.

A parallel and simultaneous determination was performed with PAH spiked into each of three sets of four 1.00 l volumes of glass-distilled deionised water, as in Section 3.1.1.13.2 and 3.2.2, and in vessels as above. Samples were stored alongside corresponding subsamples of primary effluent. Extraction *in situ*, treatment and determination by GC was performed as for the direct determination of distilled deionised water samples described in Section 3.1.1.9. Ambient temperature during the experiment ranged from 24 to 27°C.

3.3 Pilot Plant Study: Removal Behaviour of PAH During Primary Sedimentation

3.3.1 Plant Description

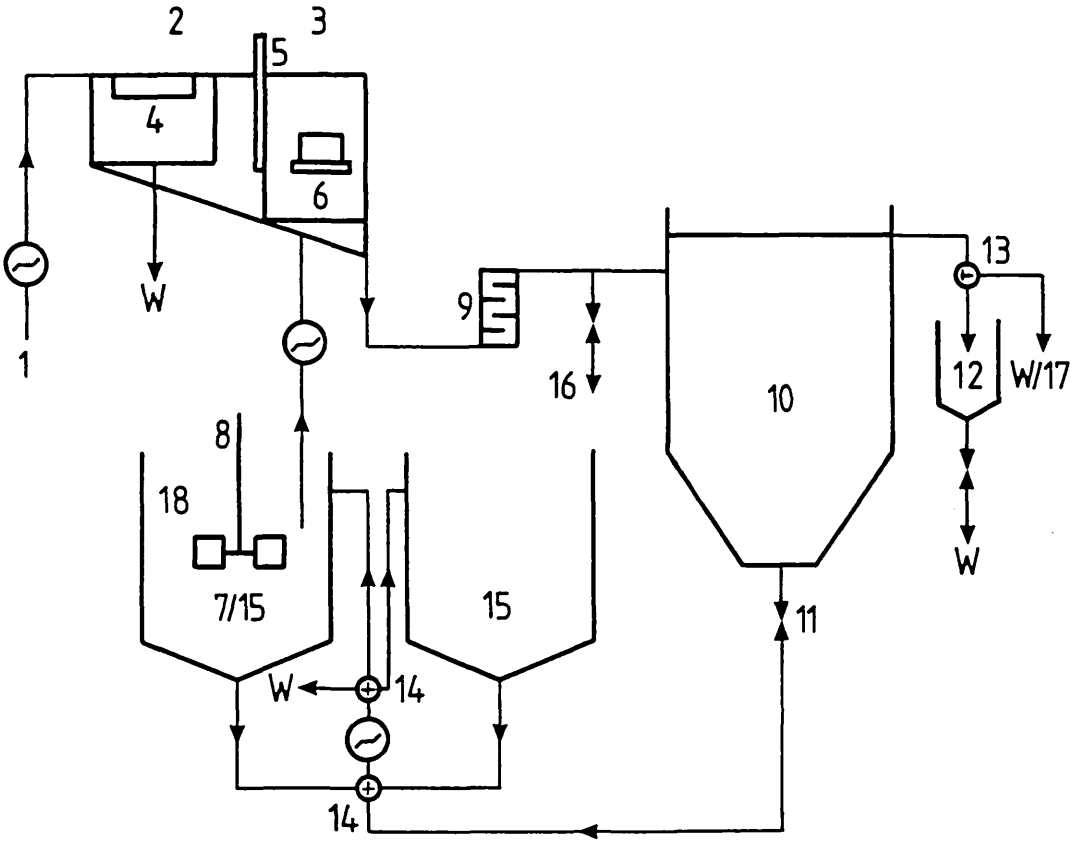
3.3.1.1 General Design

A primary sedimentation pilot plant was set up at Hogsmill Valley Water Pollution Control Works (Section 3.1.1.4) as a modified version of that reported previously (Rossin et al., 1982), and consisted of eight systems. An overall view of the plant is shown in Plate 2 and a schematic representation displayed in Figure 2. The sewage intake system drew raw sewage from the works for delivery to the hydraulic loading system. Suspended solids concentration was controlled by the suspended solids loading system at point of division of flow into two parallel streams, with subsequent homogenisation accomplished by twin mixing chamber systems and settlement by twin sedimentation tank systems. Flow rate was determined by the directing of tank effluent into a common flow measurement system. The sludge discharge system was operated at the termination of each experiment. Influent, effluent and sludge samples were provided by the sampling system.

The design and construction of the pilot plant was based on the twin radial flow sedimentation tanks, each of 1.46 m in height, 1.00 m i.d. and 60^{o} conical bottom, with flow rate of 0.333 l s^{-1} (28.8 m^3 d^{-1}) and theoretical hydraulic retention time of 0.76 h at a design surface loading rate of 36.6 m^3 m^{-2} d^{-1} (3 DWF). The plant superstructure was of steel, with all interconnecting pipework, including unions, elbows, valves and tee-joints, of 50 mm i.d. acrylonitrile-butadiene-styrene (ABS) material (Durapipe Ltd., UK). Exceptions were the raw sewage intake line which was constructed of 50 mm i.d. vulcathene tubing, the suspended solids loading system delivery lines which were of 10 mm i.d. silicone rubber tubing, the pipework associated with the sludge discharge system pump which was of 50 mm i.d. flexible polyvinyl chloride (PVC) tubing, and the main drainage line taking excess flows from the hydraulic loading system and waste flows from the sedimentation tank and flow measurement systems which was



PLATE 2
View of the Primary Sedimentation Pilot Plant



A Sewage Intake System
1 Works inlet channel

B Hydraulic Loading System
2 Constant head compartment
3 Distribution compartment
4 Fixed rectangular weir
5 Adjustable 30° V-notch weir
6 Adjustable rectangular weir

C Suspended Solids Loading System
7 Sludge slurry storage tank
8 Paddle stirrer

D Mixing Chamber System
9 Baffles

E Sedimentation Tank System
10 Primary sedimentation tank
11 Sludge discharge valve

F Flow Measurement System
12 Measuring tank
13 T-joint ball valve

G Sludge Discharge System
14 3-way valve
15 Sludge suspension storage tank

H Sampling System
16 Influent sampling point
17 Effluent sampling point
18 Sludge sampling point

Pump
W Waste

FIGURE 2
Schematic Flow Diagram of the Principal Features of the Primary Sedimentation Pilot Plant

of 100 mm i.d. ABS pipe (Durapipe Ltd., UK).

3.3.1.2 Sewage Intake System

The sewage intake system drew raw sewage from the inlet channel of the works immediately preceding the distribution chamber of the primary sedimentation tanks (Section 3.1.1.4). A submersible pump (Turo Type T1-32 UM2, Moffat and Bell Ltd., UK) delivered sewage at a constant rate whilst being supported, via a steel chain, inside a stainless steel drum attached to the channel wall. The drum was 0.90 m in height and 0.60 m in diameter and possessed circular holes 19 mm in diameter (38 mm between centres) in and around the base to act as screen.

3.3.1.3 Hydraulic Loading System

The hydraulic loading system was a perspex tank consisting of two separate compartments. Raw sewage was delivered to the first, which provided a constant head of waste water by diverting excess flow over two laterally positioned fixed rectangular weirs to waste. A 30^{o} V-notch weir, adjustable vertically, controlled flow of sewage into the second compartment. The particular angle of V-notch provided sensitive control of flow and was less susceptible to blockage. The second compartment split the flow into two streams by means of two adjustable rectangular weirs positioned laterally. All weirs in the system were protected by baffles to avoid turbulence at the liquid surface.

3.3.1.4 Suspended Solids Loading System

SS concentration of the raw sewage was amended, when required, by the continuous addition of a sludge slurry. This was made up from primary sludge diluted with an appropriate quantity of primary effluent, collected at appropriate points from the works (Section 3.1.1.4), in a ca. 0.7 m^3 stainless steel storage tank. Reconstitution of sewage in a similar manner has been reported successfully (White & Allos, 1976). Homogeneity of the sludge slurry was maintained by operation of a paddle stirrer at regular intervals. The sludge slurry was pumped by two flow

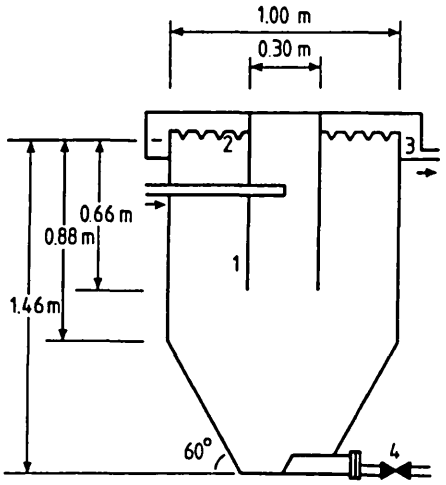
inducers (Model HRSV 214, Watson-Marlow Ltd., UK) from the storage tank into each stream in the second compartment of the hydraulic loading system.

3.3.1.5 Mixing Chamber System

Mixing chambers ensured complete mixing of raw sewage with additional SS prior to sedimentation. Each chamber, mounted vertically, consisted of a 155 mm i.d. ABS tube 0.40 m in length and contained four perspex baffles. Sewage entry was via the bottom of the chamber and exit via the top.

3.3.1.6 Sedimentation Tank System

Each sedimentation tank was constructed of glass fibre (K.T.S. Construction Co. Ltd., UK) of capacity 0.915 m^3 and dimensions as given in Figure 3. Sewage was admitted into the axis of the centrally positioned cylindrical stilling chamber. The effluent escaped through 21 45° V-notch weirs into a circular trough surrounding the top of the tank, and exited through a peripherally situated outlet pipe. A domed glass fibre lid covered the tank to prevent wind disturbance of the liquid surface.



1 Stilling chamber
2 Effluent weir
3 Circular trough
4 Sludge discharge valve

FIGURE 3
Pilot Plant
Sedimentation Tank
Elevation

3.3.1.7 Flow Measurement System

A tee-joint ball valve was fitted to each tank effluent outlet pipe allowing effluent to be directed either to waste or into a 50.0 l stainless steel measuring tank. Flow rate was determined by the time taken for the tank to be filled.

3.3.1.8 Sludge Discharge System

On completion of each experiment and termination of flow, the entire contents of the sedimentation tanks were emptied in turn: efficient extraction of sludge alone was not possible. The sludge slurry remaining in the suspended solids loading system (Section 3.3.1.4) was pumped by a mutrator unit (Model D 30, Mono-Pumps Ltd., UK) to waste, and a diaphragm valve in the sludge discharge line from the base of the sedimentation tank was opened. The sludge and sewage supernatant were transferred by the same pump to the emptied storage tank and to an identical tank adjacent to it. Homogenisation of the sludge suspension was accomplished by pumping between the two storage tanks and operation of the paddle stirrer in one. The procedure was repeated for the second sedimentation tank after collection of sample and emptying of storage tanks.

3.3.1.9 Sampling System

The influent sampling point on each stream was located midway between the mixing chamber system exit and the sedimentation tank system entry. A 90° reducing tee-joint in the line held a rubber bung and glass tube of 10 mm i.d., bent through a smooth curve of 90° into pipe flow and along pipe axis. A length of silicone rubber tubing (10 mm i.d.) with a screw clamp was secured at the other end. The effluent sampling point on each stream was the tank effluent outlet pipe, and the sludge sampling point one of the two storage tanks (via the surface) following operation of the sludge discharge system (Section 3.3.1.8).

3.3.2 Experimental Design

3.3.2.1 Process Parameter Selection

A programme was undertaken to evaluate PAH removal during primary sedimentation as influenced by the two major process parameters of hydraulic loading and SS loading determining unit process performance in terms of SS removal efficiency (Section 1.8.2). The primary sedimentation pilot plant tanks were operated at four SS loadings at each of four hydraulic loadings. The four values of surface loading rate selected with corresponding theoretical hydraulic retention times (Table 20) covered typical ranges associated with full-scale tanks (Section 1.8.2). Flow rate (1 s^{-1}) and thus retention time were calculated from tank surface area (0.785 m^2) and volume (0.915 m^3) respectively; the latter fixed quantities producing a direct inverse proportionality between the former. The four values of SS loading attempted were by way of mean nominal increases in SS concentration of approximately 150, 300 and 450 mg l^{-1} (i.e. 150 mg l^{-1} increments) above a mean raw influent concentration of approximately 400 mg l^{-1}, producing four SS loadings of 400 mg l^{-1} (unamended, designated SS_0), 550 mg l^{-1} (SS_1), 700 mg l^{-1} (SS_2) and 850 mg l^{-1} (SS_3).

TABLE 20
Flow Conditions
and Corresponding Retention Times
Adopted for the Primary Sedimentation
Pilot Plant[a]

DWF	Surface loading rate (m^3 m^{-2} d^{-1})	Flow rate (1 s^{-1})	Retention time (h)
0.5	6.10	0.0555	4.58
1.0	12.2	0.111	2.29
3.0	36.6	0.333	0.76
5.0	61.0	0.555	0.46

[a] Per tank; based on a design surface loading rate of 36.6 m^3 m^{-2} d^{-1} and theoretical hydraulic retention time of 0.76 h at 3 DWF (dry weather flows).

Each experiment consisted in operation of a tank at a particular hydraulic and SS loading. The combination of four values of each process parameter therefore constituted 16 experiments (Table 21). As the pilot plant possessed twin sedimentation tanks, they were operated in parallel at a common hydraulic loading (Table 21; expressed as DWF equivalent) but with differing SS loadings. Experiments were therefore performed in pairs.

TABLE 21
Experimentation Programme for the Primary Sedimentation Pilot Plant

Experiment no.	Process parameters	
	Hydraulic loading[a]	SS loading[b]
1 and 2	1.0 DWF	SS_0 and SS_1
3 and 4	1.0 DWF	SS_2 and SS_3
5 and 6	5.0 DWF	SS_0 and SS_2
7 and 8	5.0 DWF	SS_1 and SS_3
9 and 10	3.0 DWF	SS_0 and SS_3
11 and 12	3.0 DWF	SS_1 and SS_2
13 and 14	0.5 DWF	SS_0 and SS_3
15 and 16	0.5 DWF	SS_1 and SS_2

[a] Surface loading rates given in Table 20.
[b] Approximate values: SS_0 400, SS_1 550, SS_2 700, SS_3 850 mg l^{-1}. Exact values achieved given in Table 71.

3.3.2.2 Sampling

The sampling frequency for each experiment was flow proportional and thus depended on tank hydraulic loading (Table 22). Single grab samples of influent and effluent were collected simultaneously at regular intervals of exactly 60, 30, 10 and 6 min for hydraulic loadings of 0.5, 1.0, 3.0 and 5.0 DWF respectively. Influent and effluent composite samples of six consecutive grab samples each were formed, with sampling continued for a total of ten influent and ten effluent composite samples. Thus for an experiment at 0.5 DWF, samples were collected at intervals of 60 min, six samples being composited over a 6 h period, and a total

TABLE 22
Sampling Programme
for the Primary Sedimentation Pilot Plant

Hydraulic loading	Sampling frequency[a]	Composite period[b]	Sampling period[c]	Experiment period[d]
0.5 DWF	60 min	6 h	60 h	71 h
1.0 DWF	30 min	3 h	30 h	35 h 30 min
3.0 DWF	10 min	1 h	10 h	11 h 50 min
5.0 DWF	6 min	36 min	6 h	7 h 6 min

[a] Per grab sample per tank, of influent and effluent.
[b] Six consecutive grab samples.
[c] Ten composite periods, generating ten composite samples for both influent and effluent.
[d] Including initial two equilibration composite periods. Total flow: ca. 14200 l in each experiment.

of ten composite samples generated over a period of 60 h, for both influent and effluent (Table 22). The total experimentation period included, on each occasion, a pre-sampling equilibration interval equivalent to two composite periods, resulting in a total flow of ca. 14200 l for each experiment. Furthermore, the composite period at each hydraulic loading (Table 22) approximated the respective tank retention time (Table 20). The sampling programme provided for each experiment, therefore, an identical number of composite samples obtained over an identical number of tank retention times (13). One grab sample of sludge was collected per experiment for computation of a mass balance.

3.3.3 Experimental Execution

3.3.3.1 Start-Up

The start-up procedure for a pair of experiments (Table 21) comprised operation of the sewage intake system (Section 3.3.1.2), and full lowering of the V-notch on the hydraulic loading system (Section 3.3.1.3) so as to fill both sedimentation tank systems (Section 3.3.1.6) rapidly. Once full, hydraulic and suspended solids loading systems (Section 3.3.1.4) were initiated as below, followed immediately by a pre-sampling equilibration period (for

both tanks), equivalent to two composite periods appropriate to the particular hydraulic loading under test (Table 22), for systems adjustment.

3.3.3.2 Equilibration Period

3.3.3.2.1 Adjustment of Hydraulic Loading

Hydraulic loading adjustment was achieved by means of the hydraulic loading system (Section 3.3.1.3.) in conjunction with the flow measurement system (Section 3.3.1.7). The V-notch weir in the former system was initially adjusted (manually) to the desired flow rate via an adjacent graduated scale. The effluents from both sedimentation tanks were directed into the flow measurement system for accurate measurement of total pilot plant flow (twice the desired flow rate for one tank; Table 20) and fine adjustment of the V-notch weir. To ensure equality of flow through the two sedimentation tanks, effluents were subsequently measured separately in the flow measurement system, and balance achieved through adjustment of the two rectangular weirs in the second compartment of the hydraulic loading system. The flows through both tanks were checked frequently for adjustment throughout the equilibration period and subsequent sampling period.

3.3.3.2.2 Adjustment of Suspended Solids Loading

SS loading adjustment was accomplished by the suspended solids loading system (Section 3.3.1.4) through steady pumping of sludge slurry into the influent stream. The concentration of the sludge slurry and its initial pumping rate at start-up (2-12 ml s^{-1}) were determined by the particular SS loading required (Table 21) and assuming a SS concentration of 400 mg l^{-1} for raw influent (SS_0). The hydraulic loading system was adjusted (Section 3.3.3.2.1) to account for the additional flow. Suspended solids loading system efficiency was determined by on-site measurement of influent SS concentration at the appropriate sampling point (Section 3.3.1.9). Samples from both streams were collected simultaneously throughout the equilibration period at approximately the sampling frequency for the particular hydraulic loading (Table 22).

A sample was obtained by gently unscrewing the clamp at the end of the rubber tubing, releasing the first ca. 100 ml of influent to waste, and collecting a subsequent 50.0 ml for immediate measurement. Adjustments to SS loading were made by altering the sludge slurry pumping rate. The desired loading was assisted by maintaining a rolling mean. Suspended solids loading system efficiency was monitored throughout the following sampling period by SS determination of each completed influent composite sample (Section 3.3.3.3), and appropriate adjustments made.

3.3.3.3 Sampling Period

Upon completion of the equilibration period single samples of influent and effluent from both sedimentation tanks were collected simultaneously from the appropriate sampling points (Section 3.3.1.9). Each influent sample was collected by gently unscrewing the clamp at the end of the rubber tubing, allowing the first ca. 100 ml to escape to waste, and subsequently collecting ca. 500 ml in a 500 ml polypropylene beaker. A 500 ml polypropylene measuring cylinder was rinsed with 3 x 20 ml portions of this, and thence used to measure 400.0 ml into a 2.5 l amber glass sample bottle. Each effluent sample was collected in an identical manner, with the beaker placed directly beneath the tank effluent outlet pipe. Subsequent samples of influent and effluent were collected simultaneously at the frequency appropriate to the hydraulic loading (Section 3.3.2.2. and Table 22), and composited with the previously obtained samples in the appropriate sample bottles. After compositing six samples in each case, subsequent samples were placed in fresh sample bottles to collect per sedimentation tank a total of ten influent and ten effluent composite samples. One sample of sludge was obtained per tank following operation of the sludge discharge system on completion of experiment. A ca. 1 l grab sample of the homogenised sludge suspension was collected in a sample bottle.

The ten influent and ten effluent composite samples and one sludge sample for each experiment/tank were each measured for five co-determinands: SS, NVSS, VSS, COD_{tot} and COD_{sol}. For each experiment, samples were further composited to

yield overall five influent and five effluent composite samples for determinand (PAH) analysis. This was achieved by pairing composite samples adjacent in the collection sequence through combining 500.0 ml of each member of the pair in a 1 l sample bottle. These hybrid composite samples were preserved, as was a 50.0 ml portion of sludge sample.

3.3.3.4 Termination

Upon completion of each pair of experiments, pilot plant systems and interconnecting pipework were drained and hosed out.

4. RESULTS

4.1 Development of an Analytical Procedure for PAH

4.1.1 Capillary Column GC Determination

4.1.1.1 Resolution

The adopted FID and injection port gas flow rates, and injector and detector temperatures, balanced determinand chromatogram peak profile (Gaussian) against sensitivity (as measured by peak height). The oven temperature programme selected provided optimum separation of the PAH within a reasonable analysis time (Figure 4). The compounds eluted in order of increasing molecular weight except for DBahA (MW 278) which eluted before BghiP (MW 276). DBahA eluted immediately after IP, with adequate separation for reliable determination. Resolution of the isomers BbF and BkF could not adequately be achieved, even with an extended temperature programme, rendering individual determination of the isomers (including BjF) impracticable. The analytical response was measured as BkF in consequence. Calibration standards and determinand dosing operations subsequently utilised this isomer only.

4.1.1.2 Instrument Precision, Calibration Curve Data and Detection Limits

Instrument precision with respect to analytical response ranged from an RSD of 2.6% (PA) to 8.7% (DBahA) (Table 23). Precision with respect to determinand retention time was a uniform ± 3 s, permitting confident assignation of peaks in complex chromatograms. The linear range of calibration curve for each PAH was sustained for sample concentrations of 0.05-4.0 $\mu g\ l^{-1}$. Detection limits ranged from 0.004 $\mu g\ l^{-1}$ (AY, AE) to 0.030 $\mu g\ l^{-1}$ (IP, BghiP, DBahA), and were non-statistical estimates based on twice signal-to-noise ratio. Sensitivity, as defined by rate of change of analytical response with concentration of determinand, decreased with increase in molecular weight of determinand.

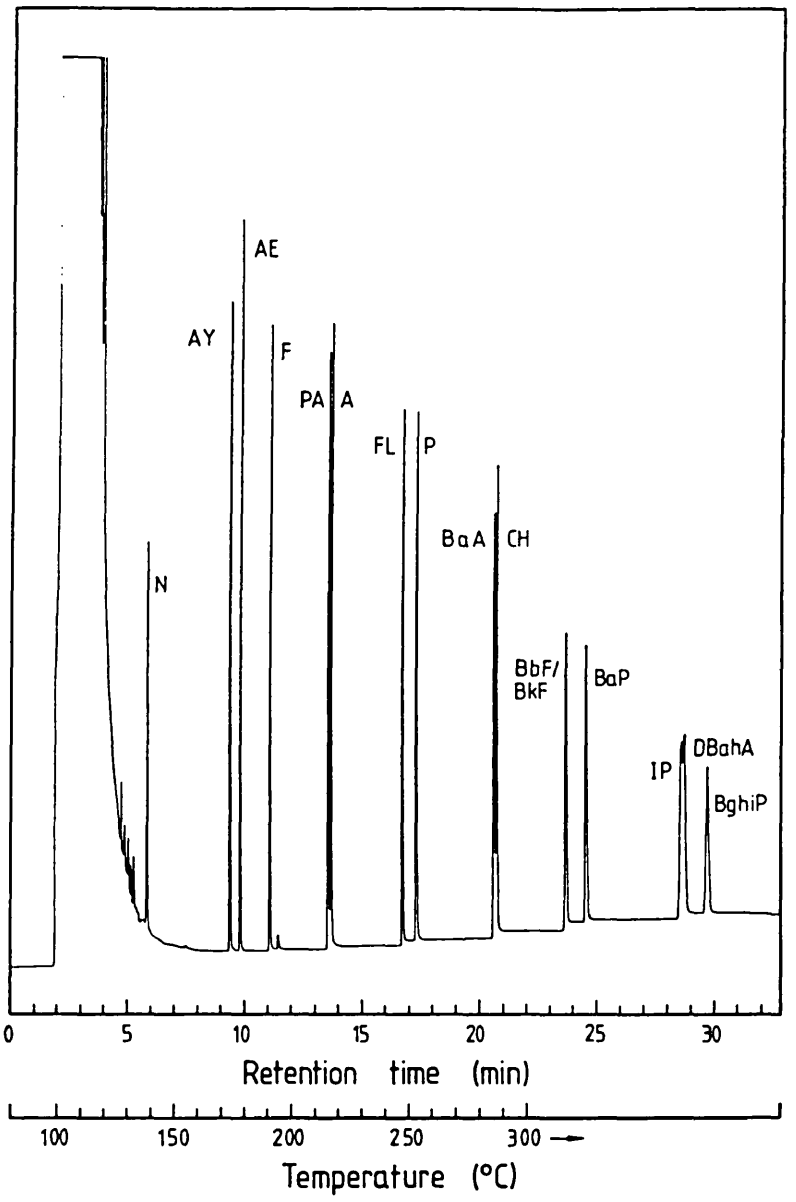


FIGURE 4
GC-FID Chromatogram
of a Mixed Standard Solution of PAH
(10.0 µg ml^{-1}, Attenuation 1 x 32;
Instrumental Conditions Given
in Section 3.1.1.10.1.1)

4.1.2 Sample Extraction

Sample to extractant (cyclohexane) ratios adopted allowed extractions free of emulsification. The extraction procedure was judged to be of adequate efficiency until such time as it could be more properly evaluated (Section 4.1.8). The centrifugation conditions provided solvent extracts of satisfactory clarity within a reasonable centrifugation time.

TABLE 23
GC Instrument Precision, Calibration Curve Data, Detection Limits and Sensitivity for PAH Determination by Flame Ionisation Detection

PAH	Precn.[a] RSD (%)	Linear range[b] (ng)	Linear range[c] (µg l^{-1})	Detn. limit[b] (ng)	Detn. limit[c] (µg l^{-1})	Sensitivity[d]
AY	4.0	0.5-40	0.05-4.0	0.04	0.004	1180
AE	3.5	0.5-40	0.05-4.0	0.04	0.004	1250
F	4.5	0.5-40	0.05-4.0	0.10	0.010	1090
PA	2.6	0.5-40	0.05-4.0	0.10	0.010	1060
A	5.3	0.5-40	0.05-4.0	0.10	0.010	1070
FL	3.7	0.5-40	0.05-4.0	0.10	0.010	990
P	4.3	0.5-40	0.05-4.0	0.10	0.010	900
BaA	4.5	0.5-40	0.05-4.0	0.10	0.010	860
CH	5.1	0.5-40	0.05-4.0	0.10	0.010	820
BkF	4.6	0.5-40	0.05-4.0	0.16	0.016	620
BaP	5.1	0.5-40	0.05-4.0	0.16	0.016	670
IP	2.9	0.5-40	0.05-4.0	0.30	0.030	470
BghiP	6.0	0.5-40	0.05-4.0	0.30	0.030	380
DBahA	8.7	0.5-40	0.05-4.0	0.30	0.030	490

[a] Precision of analytical response (peak height of determinand) for eight consecutive injections of a 10.0 µg ml^{-1} calibration standard; RSD = relative standard deviation.
[b] Per 2.00 µl injection.
[c] For 1.00 l sample and 0.200 ml treated sample.
[d] Approximate analytical response (peak height (mm) x attenuation) for 0.500 µg l^{-1}.

Rotary evaporation of standard mixtures of PAH exactly 1 min past dryness revealed a mean loss of N of 61% (RSD = 28.8%, n = 4), as determined by GC. Recoveries of all other PAH were quantitative, as when standard mixtures were evaporated just to dryness. Slight variability in rotary evaporator operation was considered such that reliable determination of N could not be made on a routine basis.

4.1.3 Sample Cleanup Selection

Evaluation of cleanup steps was judged on two criteria:

1. Efficiency of cleanup with respect to complexity of resulting chromatograms and presence of determinand interferences.
2. Efficiency and repeatability of recovery of determinand.

4.1.3.1 Preparative Thin Layer Chromatography

GC chromatograms of the four sludge extracts subjected to TLC cleanup with the solvent system of McIntyre et al. (1981), consisting of diethyl ether and hexane (1+19 V/V), revealed the presence of certain low molecular weight PAH, notably AE, F, PA, FL and P in readily measurable concentrations, but expected high molecular weight PAH peak positions were obscured by large, broad interferences.

Chromatograms of four blank isolates displayed no significant interferences arising from the procedure. Treatment of standard mixtures of PAH quantified recoveries which ranged from 50% (DBahA) to 79% (P), with a mean of 64% (Table 24). RSD were good ranging from 3.2% (BaA) to 12.0% (IP). The recoveries did not appear to display any particular trend, but did reveal that substantial losses of PAH were occuring, particularly with the high molecular weight compounds BaP, IP, BghiP and DBahA (nearly 50% in each case). Losses may be attributed to photodegradation (Inscoe, 1964) or volatilisation.

TABLE 24
Efficiency of Recovery
of Determinand from TLC Plate

PAH	Recovery[a] (µg)	Recovery[a] (%)	RSD (%)
AY	6.05	61	10.8
AE	6.44	64	7.4
F	7.06	71	7.9
PA	6.83	68	8.5
A	6.58	66	9.9
FL	7.47	75	6.1
P	7.94	79	6.7
BaA	7.09	71	3.2
CH	6.97	70	3.3
BkF	6.47	65	8.4
BaP	5.48	55	6.2
IP	5.23	52	12.0
BghiP	5.20	52	9.7
DBahA	5.03	50	7.3
		Mean: 64	

[a] Mean for four plates, 10.0 µg application; analysis by GC.

The four extracts treated with the solvent system of Thompson & Eglinton (1978), consisting of diethyl ether and light petroleum (b.p. 40-60°C) (1+8 V/V), produced very similar chromatograms. Thus changes in the solvent system proved largely ineffective in improving cleanup efficiency.

The problems of interferences, low determinand recoveries and the substantial time required for extract application to plate were considered to render preparative TLC an unfavourable first-step cleanup.

4.1.3.2 Liquid-Liquid Partition

GC chromatograms of four sludge isolates were very complex and included several major peaks of asymmetric (non-Gaussian) profile due to column overloading of the components concerned. Substantial dilution of isolates prior to re-injection was necessary, but major interferences remained in all regions of the chromatogram and no PAH could be identified.

Chromatograms of four treated blanks revealed only one non-interfering peak with a retention time intermediate to that of CH and BkF. Efficiency of recovery of determinand evaluated through treatment of standard mixtures ranged from 25% (AE) to 72% (BkF), with a mean of 59% (Table 25). A general increase in recovery with increase in determinand molecular weight was apparent up to BkF, after which there was a slight decrease. Repeatability of recovery was generally lower than that of TLC and ranged from an RSD of 9.4% (BkF) to 13.5% (IP, BghiP).

As with TLC cleanup, poor efficiencies of recovery and slowness of the procedure weighed against its use. Phase separation during back extraction was particularly time consuming and occasionally emulsification occurred which could only be broken by addition of further cyclohexane. The most important drawback of the procedure was its apparent inability to remove sufficient unwanted material. It was concluded that liquid-liquid partition was an inappropriate first-step cleanup operation.

TABLE 25
Efficiency of Recovery
of Determinand
from DMF Liquid-Liquid Partition

PAH	Recovery[a] (µg)	Recovery[a] (%)	RSD (%)
AY	4.64	46	9.9
AE	2.50	25	12.6
F	4.10	41	11.0
PA	5.98	60	10.1
A	5.15	52	12.5
FL	6.40	64	11.1
P	6.63	66	12.0
BaA	6.90	69	12.2
CH	7.00	70	12.5
BkF	7.19	72	9.4
BaP	6.58	66	11.5
IP	6.50	65	13.5
BghiP	6.54	65	13.5
DBahA	6.20	62	12.7
		Mean: 59	

[a] Mean for four replicates, 10.0 µg application; analysis by GC.

4.1.3.3 Aluminium Oxide Preparative Column Chromatography

Preparative TLC employing plates of silica gel did appear to offer a moderate degree of cleanup and it was postulated that silica gel in column form might present an efficient cleanup step. In column form the opportunity for PAH loss through photodegradation and volatilisation would be substantially reduced and the relative ease of extract application to column would result in a substantially improved analysis time. However, in preparative column chromatography it is customary to employ the less polar adsorbent aluminium oxide prior to silica gel (Lee et al., 1981) for effective use of the latter. Although Grimmer et al. (1978), Searl et al. (1979) and Schössner et al. (1983) employed aluminium oxide column chromatography as a cleanup step in their analytical schemes for PAH in municipal waste waters, it was used late in the respective treatment sequences, and thus rather than follow one of these

procedures directly it was deemed prudent to adapt use of the adsorbent for the present circumstances.

4.1.3.3.1 Selection of Adsorbent Mass

Calibration of columns (four in each case) containing 11.0, 8.0 and 5.0 g of adsorbent at 5.0% deactivation, with respect to PAH fraction elution volume, was accomplished by elution (with cyclohexane) of standard mixtures of determinand with fractionation and subsequent GC analysis of eluate. Elution volumes in columns containing 11.0 and 8.0 g of adsorbent were excessive, but with 5.0 g PAH eluted almost immediately, with complete elution of fraction within a total eluate volume of 15.0 ml.

Chromatograms of four sludge extracts isolated with 5.0 g of aluminium oxide displayed a series of peaks superimposed on a broad hump, diagnostic of an 'unresolved complex mixture.' However, superficial examination of columns suggested that the adsorbent effected substantial removal of material. The upper portions of the adsorbent beds had aquired a deep colouration and the residues of the eluates upon evaporation were much smaller in volume compared to the original sludge extracts. Considerably greater removal of material was achieved by this procedure compared with the liquid-liquid partition procedure attempted previously, as confirmed by the degree of dilution of isolate necessary prior to injection into the GC. Analysis of post-PAH fraction eluate for continued elution of material showed a small amount in the 15.0-25.0 ml eluate fraction and no appreciable trace with 25.0 ml and over. An adsorbent mass of 5.0 g was therefore judged sufficient.

Chromatograms of four blanks treated as for the sludge extracts revealed no procedural contribution towards contamination. Efficiency of recovery of determinand assessed through treatment of standard mixtures was generally high and essentially quantitative except for the high molecular weight compounds BaP (84%), IP (89%), BghiP (82%) and DBahA (70%) (Table 26). Mean recovery was 97%. Repeatability of recovery was good, only two PAH, BkF and DBahA, displaying higher RSD (15.4 and 14.4% respectively).

TABLE 26
Efficiency of Recovery
of Determinand
from Aluminium Oxide Column

PAH	Recovery[a] (µg)	Recovery[a] (%)	RSD (%)
AY	10.2	102	4.9
AE	11.0	110	5.1
F	10.1	101	5.0
PA	10.7	107	6.5
A	9.95	100	5.5
FL	10.1	101	5.3
P	10.6	106	5.9
BaA	9.81	98	5.6
CH	9.55	96	3.3
BkF	11.6	116	15.4
BaP	8.36	84	3.4
IP	8.94	89	7.3
BghiP	8.18	82	1.5
DBahA	7.01	70	14.4
		Mean: 97	

[a] Mean for four columns, 10.0 µg application; analysis by GC.

4.1.3.3.2 Selection of Adsorbent Deactivation

Calibration of columns (single) containing adsorbent (5.0 g) at 4.0%, 3.5% and 3.0% deactivation with respect to PAH fraction elution volume gave total eluate volumes of ca. 35, 50 and 70 ml respectively. Evaluations were performed singly and not in quadruplicate as component eluate volume repeatability was found to be high (Section 4.1.3.3.1).

Chromatograms of single sludge extracts isolated in this manner showed no marked improvement in cleanup efficiency achieved by adsorbent at 5.0% deactivation (Section 4.1.3.3.1). An adsorbent mass of 5.0 g at 5.0% deactivation with collection of the first ca. 30 ml of eluate (embodying a safety allowance) was adopted provisionally as a promising first-step cleanup in terms of the quantity of material removed and the high efficiencies of recovery of PAH.

4.1.3.4 Silica Gel Preparative Column Chromatography

4.1.3.4.1 Selection of Adsorbent Mass

Column calibrations, performed in quadruplicate, were initially performed with 11.0 g of adsorbent at 5.0% deactivation with hexane as eluent. Hexane is customarily employed in silica gel column chromatography (Lee et al., 1981). Elution volumes under these conditions were excessive and in order to reduce the PAH fraction elution volume, eluent polarity was subsequently increased. Column elution with 5% (V/V) diethyl ether in hexane proved too drastic in terms of PAH elution rates as did 2%. Adsorbent mass was subsequently reduced to 5.0 g, and with hexane only as eluent a satisfactory PAH fraction elution volume was achieved. AE was the first PAH to elute after an initial ca. 14 ml of eluate, and DBahA the last, within a total eluate volume of ca. 115 ml, the PAH fraction elution volume thus being approximately 100 ml.

Four sludge extracts, previously subjected to aluminium oxide cleanup, were isolated under these conditions (5.0 g of adsorbent and hexane as eluent) with the first 14 ml of eluate set aside and collection of the subsequent 100 ml. Chromatograms permitted identification of low molecular weight PAH with the high molecular weight region free from major interferences except for a large broad peak and an associated minor one with retention times approximating to those of BaP and BkF. Analysis of pre-PAH fraction eluate afforded evidence of substantial elution of aliphatic hydrocarbons, and analysis of post-PAH fraction eluate the continued elution of material responsible for interfering with the above PAH. GC-MS analysis, under repetitive scanning (RS) mode identified the mass spectrum of the major interference as that of squalene.

4.1.3.4.2 Selection of Adsorbent Deactivation

In an attempt to remove the interferences associated with PAH of MW 252, adsorbent activation was increased. Column calibrations, executed in quadruplicate, were performed on adsorbent (5.0 g) deactivated to 2.5% and 1.0%. PAH fraction elution volumes were ca. 130 ml after discarding

of first 20 ml of eluate, and ca. 150 ml after discarding of first 25 ml of eluate respectively.

Chromatograms of four sludge aluminium oxide isolates treated with adsorbent deactivated to 2.5% showed no marked improvement in cleanup efficiency over that achieved by adsorbent at 5.0% deactivation (Section 4.1.3.4.1). However, chromatograms of four isolates subjected to treatment by 1.0% deactivated adsorbent displayed no interferences.

4.1.3.4.3 Column Calibration at 15°C

Although within-batch PAH fraction elution volume repeatability was found to be high (Section 4.1.3.4.2), between-batch (day-to-day) repeatability was not so good: squalene was occasionally observed to contaminate the silica gel isolates. Repeatability was found to be improved by performing elutions at a constant ambient temperature (15°C±2°C). This finding is consistent with the phenomenon of temperature dependence of adsorption; silica gel chromatography being characteristic of the adsorption type.

Careful column calibration (5.0 g of adsorbent at 1.0% deactivation) was performed in quadruplicate at 15°C (±2°C). The PAH fraction elution volume was found to be 160 ml after discarding of first 25 ml of eluate.

Chromatograms of four sludge aluminium oxide isolates treated under these conditions were substantially interference free. Analysis of post-PAH fraction eluate showed elution of interfering material only after a gap of 50 ml.

Chromatograms of four blanks treated as for the sludge isolates revealed no procedural contribution towards interferences. Efficiency of recovery of determinand evaluated through treatment of standard mixtures in the same manner was, as for aluminium oxide cleanup, generally high and essentially quantitative, ranging from 87% (DBahA) to 122% (P), with a mean of 104% (Table 27). However, repeatability of recovery was somewhat lower here and ranged from an RSD of 6.7% (PA) to 20.2% (DBahA).

TABLE 27
Efficiency of Recovery
of Determinand
from Silica Gel Column

PAH	Recovery[a] (µg)	Recovery[a] (%)	RSD (%)
AY	10.3	103	10.2
AE	11.0	110	7.5
F	10.7	107	7.6
PA	10.8	108	6.7
A	10.6	106	8.8
FL	11.2	112	14.6
P	12.2	122	10.6
BaA	10.4	104	14.6
CH	10.8	108	14.7
BkF	11.1	111	9.5
BaP	9.44	94	13.6
IP	9.31	93	16.8
BghiP	9.08	91	19.3
DBahA	8.68	87	20.2
	Mean:	104	

[a] Mean for four columns, 10.0 µg application; analysis by GC.

An adsorbent mass of 5.0 g at 1.0% (±0.1%) deactivation, utilised at an ambient temperature of 15°C (±2°C), with the first 24 ml of eluate discarded and the subsequent 190 ml collected (the volumes embodying safety allowances) therefore provided an efficient second-step cleanup. The mass and deactivation of silica gel permitted an effective isolation of the PAH fraction from the aliphatic hydrocarbon fraction first to elute and from squalene and other interferences eluting last, in a reasonably economic elution volume and elution time. Furthermore, the high efficiencies of recovery of determinand (Table 27) confirmed the utility of the column form of the adsorbent in effectively eliminating losses through photodegradation and volatilisation.

Low molecular weight PAH were readily identified in chromatograms of treated samples (Figure 5), but identification and subsequent quantification of high molecular weight compounds was not so confident (Figure 6).

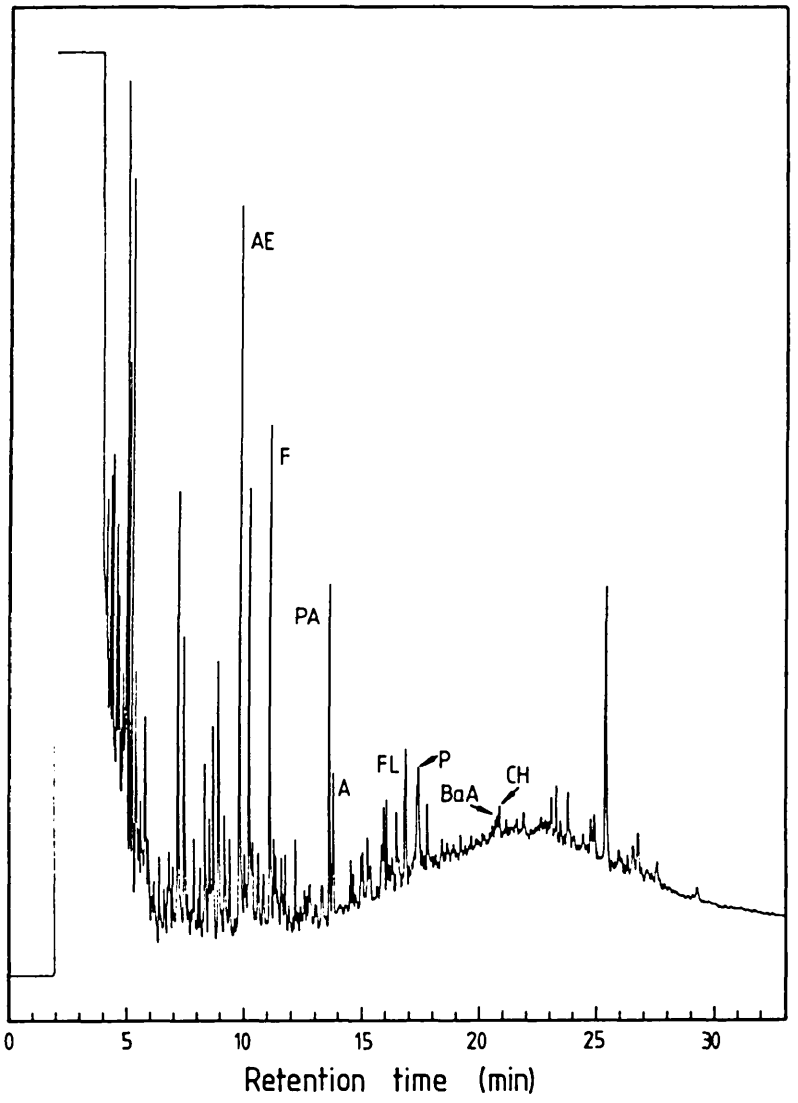


FIGURE 5
GC-FID Chromatogram
of a Treated Sample of Raw Sewage
(Attenuation 1 x 32; Instrumental
Conditions Given in Section 3.1.1.10.1.1)

However, it was judged that samples treated by the column chromatographic procedure were cleaned up as much as reasonably could be expected. GC-MS RS analysis revealed background peaks to be largely alkylated PAH.

4.1.4 Validation of Column Chromatographic Procedure by GC

The overall efficiency and repeatability of recovery of PAH for the procedure (extraction, cleanup with 5.0 g of aluminium oxide deactivated to 5.0%, and final cleanup with 5.0 g of silica gel deactivated to 1.0% and utilised at 15°C) were assessed to quantify procedure accuracy and

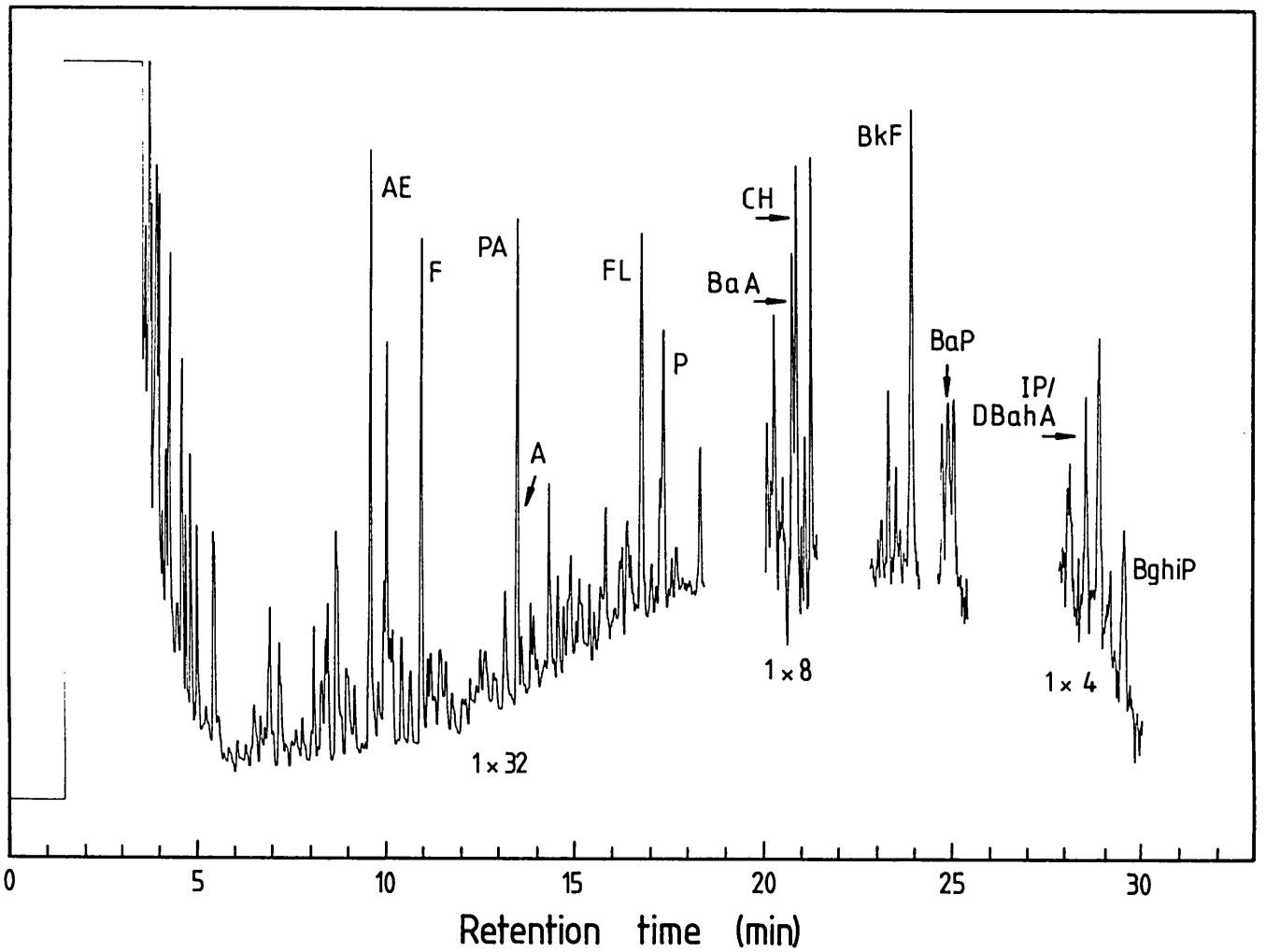


FIGURE 6
GC-FID Chromatogram
of the Treated Sample of Raw Sewage (Figure 5)
Under Variable Attenuation

precision. Samples of primary sludge and raw sewage were spiked with known masses of PAH, and the proportions remaining in the treated samples determined after subtraction of mean background (indigenous) masses.

Analysis of the sludge sample for background PAH identified all determinands except AY (Table 28). Determination of BaA and CH and PAH of higher molecular weight was less confident due to the relatively low abundancies of these compounds in the sample and the presence of background peaks in the chromatograms. Poor resolution of BaA and CH, and IP and DBahA, compounded the problem. These difficulties were reflected in the relatively high RSD of these high molecular weight determinands. Efficiency of recovery of determinand spiked the equivalent of the mean background concentration (1x) was high, except for BkF (19%), BaP (30%) and IP/DBahA (39%). Spiking at this low level was not sufficient to overcome the interfering effect of background peaks on these determinands and this was reflected in the relatively high RSD associated (42.5%, 30.1% and 16.9% respectively). Recovery at the 3x spike level was again high, ranging from 74% (AY) to 90% (A), except for BkF (54%, RSD 30.7%) and BaP (59%, RSD 8.8%). At the 9x spike level, and thus well above the interfering effect of background components, an overall high recovery was obtained ranging from 75% (IP/DBahA) to 100% (P). RSD was low and the range narrow (1.6% (A) to 10.3% (BghiP)).

Analysis of the sewage sample for background PAH included the preliminary assessment of the effect of the preserving agent, formaldehyde, on the analytical procedure (Table 29). Application of a t test showed, for each PAH, no significant difference at the 95% confidence level between mean mass determined for the four unpreserved and mean mass determined for the four preserved subsamples. Background interferences, however, prohibited the determination of BkF and BaP and the confident determination of the other high molecular weight PAH. As with the sludge sample, poor resolution of IP and DBahA necessitated their combined determination with consequent high RSD. For each PAH the overall mean value for all eight subsamples was taken as the mean background mass for subsequent spiking operations. Determinand efficiency of

TABLE 28
GC Analysis of Sludge Sample
and Evaluation of Efficiency of Recovery of Determinand

PAH	Mass[a] (µg)	RSD (%)	Spiked subsamples: Spike level	Spike (µg)	Recovery[a] (µg)	Recovery[a] (%)	RSD (%)
AY	ND[b]	----	1x	10.0[c]	8.14	81	4.7
			3x	30.0	22.1	74	3.5
			9x	90.0	79.8	89	4.2
AE	10.3	4.3	1x	10.3	9.67	94	12.2
			3x	30.9	25.7	83	8.9
			9x	92.7	89.1	96	2.9
F	7.94	4.7	1x	7.94	7.19	91	5.1
			3x	23.8	20.3	85	5.8
			9x	71.5	68.1	95	1.9
PA	5.95	4.3	1x	5.95	6.21	104	5.1
			3x	17.9	15.2	85	9.0
			9x	53.6	52.4	98	2.2
A	1.81	5.1	1x	1.81	1.25	69	13.2
			3x	5.43	4.91	90	5.3
			9x	16.3	14.5	89	1.6
FL	2.93	6.5	1x	2.93	2.18	74	8.9
			3x	8.79	6.65	76	4.1
			9x	26.4	25.0	95	2.2
P	2.31	8.5	1x	2.31	2.30	100	12.5
			3x	6.93	6.08	88	7.3
			9x	20.8	20.7	100	6.9
BaA	0.680	12.2	1x	0.680	0.383	56	4.5
			3x	2.04	1.59	78	10.4
			9x	6.12	5.78	94	5.4
CH	0.610	4.2	1x	0.610	0.483	79	6.2
			3x	1.83	1.60	87	3.8
			9x	5.49	5.37	98	4.7
BkF	1.04	10.7	1x	1.04	0.193	19	42.5
			3x	3.12	1.69	54	30.7
			9x	9.36	8.13	87	7.9
BaP	1.36	17.1	1x	1.36	0.410	30	30.1
			3x	4.08	2.39	59	8.8
			9x	12.2	10.3	84	5.0
IP/ DBahA[d]	0.800	11.2	1x	0.800[e]	0.310	39	16.9
			3x	2.40[e]	1.85	77	3.9
			9x	7.20[e]	5.40	75	6.4
BghiP	0.340	16.2	1x	0.340	0.320	94	29.6
			3x	1.02	0.815	80	10.7
			9x	3.06	2.77	91	10.3

[a] Mean for four 50.0 ml subsamples.
[b] ND = non-detectable.
[c] Arbitrary spike mass.
[d] Not resolved: analytical response measured as IP.
[e] Spike mass for both determinands.

TABLE 29
GC Analysis of Sewage Sample
and Evaluation of Efficiency of Recovery of Determinand

PAH	*Mass (µg)	RSD (%)	Spiked subsamples: Spike level	Spike (µg)	Recovery[a] (µg)	Recovery[a] (%)	RSD (%)
AY	0.378	7.4	1x	0.378	0.344	91	1.5
			3x	1.13	0.837	74	5.6
			9x	3.40	2.73	80	3.3
AE	0.856	8.2	1x	0.856	0.762	89	8.7
			3x	2.57	1.96	76	5.1
			9x	7.70	6.20	81	3.1
F	1.01	7.0	1x	1.01	0.940	93	10.7
			3x	3.03	2.85	94	8.4
			9x	9.09	8.45	93	4.3
PA	1.21	6.4	1x	1.21	1.17	97	8.9
			3x	3.63	3.41	94	8.1
			9x	10.9	10.7	98	1.2
A	0.173	9.6	1x	0.173	0.140	81	15.8
			3x	0.519	0.346	67	12.7
			9x	1.56	1.15	74	7.0
FL	0.860	6.1	1x	0.860	0.823	96	9.6
			3x	2.58	2.42	94	7.1
			9x	7.74	7.40	96	4.2
P	0.991	6.1	1x	0.991	0.929	94	8.5
			3x	2.97	2.90	98	6.9
			9x	8.92	9.37	105	3.9
BaA	0.368	7.5	1x	0.368	0.345	94	8.0
			3x	1.10	1.01	92	7.9
			9x	3.31	2.93	89	8.4
CH	0.327	13.4	1x	0.327	0.246	75	16.8
			3x	0.981	0.813	83	4.4
			9x	2.94	2.74	93	3.3
BkF	NQ[b]	----	1x	0.556[c]	NQ	---	----
			3x	1.67	NQ	---	----
			9x	5.00	4.87	97	5.9
BaP	NQ	----	1x	0.556[c]	NQ	---	----
			3x	1.67	1.76	105	4.5
			9x	5.00	4.74	95	6.2
IP/ DBahA[d]	0.197	30.2	1x	0.197[e]	0.184	93	10.7
			3x	0.591[e]	0.653	110	10.4
			9x	1.77[e]	1.91	108	5.4
BghiP	0.259	11.4	1x	0.259	0.208	80	20.4
			3x	0.777	0.685	88	11.7
			9x	2.33	1.99	85	2.4

/Continued overleaf

TABLE 29/Continued

* Mean mass of:

PAH	Unpreserved subsample Mass[a] (µg)	RSD (%)	Preserved subsample Mass[a] (µg)	RSD (%)
AY	0.361	3.4	0.395	7.5
AE	0.823	2.1	0.888	10.4
F	0.965	3.8	1.05	7.0
PA	1.17	4.7	1.24	7.0
A	0.171	9.8	0.175	10.8
FL	0.865	6.1	0.855	7.0
P	0.973	4.4	1.01	7.7
BaA	0.372	8.8	0.363	6.9
CH	0.344	15.3	0.309	9.8
BkF	NQ	----	NQ	----
BaP	NQ	----	NQ	----
IP/DBahA[d]	0.182	15.7	0.211	39.2
BghiP	0.267	7.2	0.250	15.4

[a] Mean for four 1.00 l subsamples.
[b] NQ = non-quantifiable due to presence of interferences.
[c] Arbitrary spike mass.
[d] Not resolved: analytical response measured as IP.
[e] Spike mass for both determinands.

recovery at the 1x spike level was high, ranging from 75% (CH) to 97% (PA), and repeatability of recovery generally good, except for A (15.8%), CH (16.8%) and BghiP (20.4%). At the 3x spike level recoveries ranged from 67% (A) to 110% (IP/DBahA) with low RSD. The relatively high level of spike permitted the determination of BaP for which a recovery of 105% was obtained. The highest level of spike (9x) admitted the determination of all PAH, including BkF. Recoveries ranged from 74% (A) to 108% (IP/DBahA) and RSD were low.

Procedure precision was expressed by the values of RSD for the analysis of the (unspiked) sample of sludge and sewage (column 3, Table 28 and 29). Procedure accuracy was expressed by determinand efficiencies of recovery which are

summarised (Table 30). For a given sample type, variation in mean recovery for all spike levels between PAH was not great, and no trend with respect to molecular weight was apparent. Mean recovery for all PAH at each spike level was uniform for the sewage sample (90%, 91% and 93% for 1x, 3x and 9x spike levels respectively), but appeared to increase with increasing level of spike for the sludge sample (69%, 78% and 90% for 1x, 3x and 9x spike levels). A contributory cause in the latter case may have been the low recoveries obtained for high molecular weight PAH at low spike levels due to the background interferences. The overall mean recovery for all spike levels for the sample of sludge was 79% and for the sample of sewage 91%. Four blanks in the form of 1.00 l samples of distilled deionised water underwent treatment by the procedure but no significant interferences or PAH arising from the method were detected. The distilled deionised water itself was shown to be free of detectable contamination.

TABLE 30
Summary of Results for Efficiency of Recovery (%) of Determinand from Sludge and Sewage Sample Determined by GC

	Sludge sample spike level				Sewage sample spike level			
PAH	1x	3x	9x	Mean	1x	3x	9x	Mean
AY	81	74	89	81	91	74	80	82
AE	94	83	96	91	89	76	81	82
F	91	85	95	90	93	94	93	93
PA	104	85	98	96	97	94	98	96
A	69	90	89	83	81	67	74	74
FL	74	76	95	82	96	94	96	95
P	100	88	100	96	94	98	105	99
BaA	56	78	94	76	94	92	89	92
CH	79	87	98	88	75	83	93	84
BkF	19	54	87	53	---	---	97	97
BaP	30	59	84	58	---	105	95	100
IP/DBahA	39	77	75	64	93	110	108	104
BghiP	94	80	91	88	80	88	85	84
Mean[a]:	69	78	90	79	90	91	93	91

[a] With IP and DBahA counted individually with values shown.

4.1.5 Capillary Column GC-MS Determination

4.1.5.1 Resolution

As the GC-MS system was equipped with a column identical to that utilised in the GC, resolution of the isomers BbF and BkF was not possible. Their common m/z and column retention time values necessitated measurement of analytical response as BkF.

4.1.5.2 Instrument Precision, Calibration Curve Data and Detection Limits

Instrument precision with respect to analytical response constant ranged from an RSD of 2.1% (PA) to 15.3% (BkF) (Table 31). Precision with respect to determinand

TABLE 31
GC-MS Instrument Precision, Calibration Curve Data, Detection Limits and Sensitivity for PAH Determination by Selected Ion Monitoring

PAH	Precn.[a] RSD (%)	Linear range[b] (ng)	Linear range[c] (µg l^{-1})	Detn. limit[b] (ng)	Detn. limit[c] (µg l^{-1})	Sensitivity[d]
AY	3.0	0.2-40	0.02-4.0	0.1	0.01	19.1
AE	2.9	0.2-40	0.02-4.0	0.1	0.01	9.6
F	3.6	0.2-40	0.02-4.0	0.1	0.01	9.5
PA	2.1	0.2-40	0.02-4.0	0.1	0.01	14.7
A	15.2	0.2-40	0.02-4.0	0.1	0.01	8.2
FL	2.9	0.5-40	0.05-4.0	0.2	0.02	6.8
P	14.3	0.5-40	0.05-4.0	0.2	0.02	4.1
BaA	15.2	1.0-40	0.10-4.0	0.5	0.05	1.1
CH	11.4	1.0-40	0.10-4.0	0.5	0.05	2.3
BkF	15.3	1.0-40	0.10-4.0	0.5	0.05	1.2
BaP	8.5	1.0-40	0.10-4.0	0.5	0.05	1.0
IP	10.0	1.0-40	0.10-4.0	0.5	0.05	0.9
BghiP	7.7	1.0-40	0.10-4.0	0.5	0.05	0.8
DBahA	11.2	1.0-40	0.10-4.0	0.5	0.05	0.8

[a] Precision of analytical response constant (ratio of peak area of characteristic ion of determinand over peak area of characteristic ion of internal standard) for eight consecutive injections of a 10.0 µg ml^{-1} calibration standard.
[b] Per 2.00 µl injection.
[c] For 1.00 l sample and 0.200 ml treated sample.
[d] Approximate analytical response (peak area, dimensionless) for 0.500 µg l^{-1}.

retention time ranged from ±1 s to ±4 s, the variation generally greater for the higher molecular weight PAH. The linear range of calibration curve decreased with increase in molecular weight of determinand: 0.02-4.0 μg l^{-1} (MW 152-178), 0.05-4.0 μg l^{-1} (MW 202) and 0.10-4.0 μg l^{-1} (MW 228-278). Ranges defined regions of approximate linearity as calibration curves were found to exhibit slight curvilinearity (convex to the concentration axis) which increased in pronounciation with decrease in determinand concentration and with increase in molecular weight. Detection limits, which were non-statistical estimates based on twice signal-to-noise ratio, ranged from 0.01 μg l^{-1} (MW 152-178) to 0.05 μg l^{-1} (MW 228-278). Sensitivity decreased with increase in molecular weight of determinand.

4.1.5.3 Accuracy and Precision of Calibration Procedure

The validity in terms of accuracy and precision of the daily calibration procedure employing three calibration standards was assessed by performing four replicate determinations of a 1.00 μg l^{-1} calibration standard, as test sample, on each of four consecutive days (Table 69, Appendix 1). The mean concentration, with 95% confidence limits, for all 16 determinations of each PAH ranged from 0.894±0.041 μg l^{-1} (PA) to 1.113±0.081 μg l^{-1} (BaP). Determinations employing the calibration procedure were judged to be of satisfactory accuracy and precision.

4.1.6 Validation of Column Chromatographic Procedure by GC-MS

All primary sludge and raw sewage treated subsamples and associated spikes (Section 4.1.4) were re-determined by GC-MS. The proportions of spiked hydrocarbon remaining in the treated subsamples were quantified after subtraction of mean background masses as determined by this instrumental method.

GC-MS analysis of the sludge sample for background PAH identified AY (Table 32), a compound undetected by GC. However, no DBahA could be detected. All other PAH were determined in readily measurable amounts with generally

good precision ranging from an RSD of 1.7% (PA) to 12.1% (BaP). Analysis of the spiked subsamples produced unexpected results. Efficiency of recovery of low molecular weight determinand at the 1x spike level was as expected by GC, but recovery of high molecular weight determinand (MW 228-278) was very high, ranging from 248% (CH) to 571% (BghiP). A similar trend was observed for recoveries at the 3x spike level, where for the same high molecular weight PAH they ranged from 203% (CH) to 450% (BghiP), and again for the 9x spike level where the corresponding range was 175% (DBahA) to 454% (BghiP). Repeatability of recovery of all PAH at all spike levels generally remained high: 3.2-23.0% (1x), 1.9-12.8% (3x) and 1.6-11.1% (9x).

Analysis of the sewage sample for background PAH enabled determination of BkF and BaP (Table 33), a condition which could not be met by GC because of background interferences. Furthermore, GC-MS analysis permitted individual quantification of IP and DBahA. Reassessment of the effect of the preserving agent on the analytical procedure revealed, by application of a t test, a significant difference at the 95% confidence level for PA and IP between mean mass determined for the four unpreserved and mean mass determined for the four preserved subsamples. This result, considered in conjunction with that obtained by GC (Section 4.1.4), was not deemed to be of practical consequence. It was concluded that the preserving agent had no significant effect on analytical accuracy in terms of mass of PAH determined nor to have a significant effect on precision (mean RSD for the unpreserved subsample was 5.5% (range 2.0-11.6%) and for the preserved subsample 6.0% (range 1.3-13.9%)). For each PAH the overall mean mass for all eight subsamples was taken as the mean background value for purposes of calculating recoveries. Analysis of the spiked subsamples produced a pattern of results similar to that of the sludge sample. Recovery efficiencies of low molecular weight determinand were credible, but those of high molecular weight PAH (MW 228-278) were again high, ranging from 65% (DBahA) to 284% (BaP) for the 1x spike level, 150% (CH) to 316% (BaP) for the 3x spike, and 126% (BaA) to 194% (BaP) for the 9x spike. Repeatability of recovery of all PAH remained high at the elevated spike levels: 4.8-27.9% (1x), 1.9-16.6% (3x) and 0.9-12.5% (9x).

TABLE 32
GC-MS Analysis of Sludge Sample
and Evaluation of Efficiency of Recovery of Determinand

PAH	Mass[a] (µg)	RSD (%)	Spiked subsamples: Spike level	Spike (µg)	Recovery[a] (µg)	Recovery[a] (%)	RSD (%)
AY	0.500	10.9	1x	10.0	5.65	57	10.2
			3x	30.0	17.4	58	5.2
			9x	90.0	65.1	72	9.0
AE	11.4	5.2	1x	10.3	6.43	62	11.5
			3x	30.9	18.8	61	2.4
			9x	92.7	69.2	75	9.6
F	7.31	3.7	1x	7.94	5.84	74	23.0
			3x	23.8	16.7	70	7.6
			9x	71.5	60.9	85	3.1
PA	6.35	1.7	1x	5.95	4.93	83	19.4
			3x	17.9	13.8	77	9.6
			9x	53.6	49.8	93	1.6
A	1.13	6.3	1x	1.81	2.28	126	11.0
			3x	5.43	4.64	85	9.6
			9x	16.3	17.9	110	7.6
FL	2.45	5.4	1x	2.93	3.21	110	15.0
			3x	8.79	8.45	96	8.6
			9x	26.4	29.7	113	2.8
P	3.58	2.8	1x	2.31	3.38	146	10.6
			3x	6.93	8.05	116	6.4
			9x	20.8	25.6	123	7.1
BaA	3.83	7.4	1x	0.680	2.21	325	12.2
			3x	2.04	5.49	269	3.5
			9x	6.12	16.4	268	9.5
CH	1.78	8.3	1x	0.610	1.51	248	6.8
			3x	1.83	3.71	203	9.2
			9x	5.49	11.1	202	6.7
BkF	3.85	7.1	1x	1.04	2.87	276	4.0
			3x	3.12	6.73	216	12.8
			9x	9.36	21.5	230	5.7
BaP	3.44	12.1	1x	1.36	7.11	523	5.4
			3x	4.08	12.9	317	8.7
			9x	12.2	40.8	334	11.1
IP	1.84	5.7	1x	0.800	2.59	324	6.5
			3x	2.40	6.27	261	7.3
			9x	7.20	15.8	219	7.5
BghiP	2.37	3.6	1x	0.340	1.94	571	15.2
			3x	1.02	4.59	450	6.5
			9x	3.06	13.9	454	4.7
DBahA	ND	----	1x	0.800	3.52	440	3.2
			3x	2.40	6.67	278	1.9
			9x	7.20	12.6	175	4.7

[a] Mean for four 50.0 ml subsamples.

TABLE 33
GC-MS Analysis of Sewage Sample
and Evaluation of Efficiency of Recovery of Determinand

PAH	*Mass (µg)	RSD (%)	Spiked subsamples: Spike level	Spike (µg)	Recovery[a] (µg)	Recovery[a] (%)	RSD (%)
AY	0.111	8.4	1x	0.378	0.246	65	4.8
			3x	1.13	0.709	63	5.3
			9x	3.40	2.42	71	2.0
AE	0.718	3.4	1x	0.856	0.575	67	12.9
			3x	2.57	1.72	67	7.8
			9x	7.70	5.14	67	3.8
F	1.15	3.6	1x	1.01	0.550	54	7.7
			3x	3.03	2.60	86	4.6
			9x	9.09	8.83	97	0.9
PA	1.50	2.9	1x	1.21	1.34	111	11.6
			3x	3.63	3.49	96	3.4
			9x	10.9	11.9	109	4.9
A	0.263	5.3	1x	0.173	0.213	123	11.3
			3x	0.519	0.446	86	16.6
			9x	1.56	1.51	97	4.6
FL	0.919	3.6	1x	0.860	0.779	91	7.6
			3x	2.58	2.72	105	1.9
			9x	7.74	9.14	118	4.6
P	1.54	3.5	1x	0.991	0.795	80	4.9
			3x	2.97	3.75	126	3.2
			9x	8.92	11.7	131	2.0
BaA	0.454	7.9	1x	0.368	0.557	151	24.9
			3x	1.10	2.01	183	5.1
			9x	3.31	4.16	126	11.0
CH	0.810	4.2	1x	0.327	0.370	113	8.8
			3x	0.981	1.47	150	3.1
			9x	2.94	4.53	154	4.1
BkF	1.16	5.4	1x	0.556	0.768	138	23.7
			3x	1.67	3.45	207	5.0
			9x	5.00	9.14	183	3.8
BaP	0.539	10.6	1x	0.556	1.58	284	13.0
			3x	1.67	5.28	316	4.0
			9x	5.00	9.68	194	12.5
IP	0.304	12.1	1x	0.197	0.256	130	17.4
			3x	0.591	1.41	239	6.6
			9x	1.77	3.22	182	6.9
BghiP	0.551	9.7	1x	0.259	0.439	169	25.5
			3x	0.777	2.02	260	6.8
			9x	2.33	4.05	174	12.5
DBahA	0.388	7.5	1x	0.197	0.128	65	27.9
			3x	0.591	0.972	164	5.2
			9x	1.77	2.63	149	10.0

/Continued overleaf

TABLE 33/Continued

* Mean mass of:

PAH	Unpreserved subsample Mass[a] (µg)	RSD (%)	Preserved subsample Mass[a] (µg)	RSD (%)
AY	0.113	4.4	0.108	11.7
AE	0.725	3.5	0.711	3.5
F	1.13	4.1	1.16	2.8
PA	1.46	2.0	1.53	1.9
A	0.263	6.5	0.263	4.8
FL	0.920	4.7	0.918	2.9
P	1.55	4.5	1.52	2.5
BaA	0.475	3.9	0.433	8.7
CH	0.825	5.4	0.795	1.3
BkF	1.18	4.0	1.13	6.4
BaP	0.546	8.2	0.531	13.9
IP	0.333	6.7	0.274	6.9
BghiP	0.544	11.6	0.558	9.1
DBahA	0.385	8.1	0.390	8.1

[a] Mean for four 1.00 l subsamples.

Procedure precision, as expressed by RSD for the GC-MS analysis of the (unspiked) sample of sludge and sewage (column 3, Table 32 and 33) was high. Procedure accuracy, however, as expressed by determinand efficiencies of recovery and as summarised (Table 34), was evidently suffering from systematic error. This error appeared to be present in the GC-MS measurement stage of the procedure and to cause bias (positive) in the measurement of high molecular weight PAH analytical response constants. Re-determination by GC-MS of the four treated blanks showed no detectable PAH or significant interferences arising through procedural contamination. Furthermore, it did not appear that background interferences in the treated samples were contributing directly towards bias: recoveries would have decreased with increase in level of spike under these circumstances. Two major sources of system bias had already been identified and rectified. The first, defined after a prolonged instrumental test of the type described in Section 3.1.1.10.2.3 and 4.1.5.3, was an insufficiently wide mass sweep range which did not permit confirmation of

TABLE 34
Summary of Results for Efficiency of Recovery (%) of Determinand from Sludge and Sewage Sample Determined by GC-MS

	Sludge sample spike level			Sewage sample spike level		
PAH	1x	3x	9x	1x	3x	9x
AY	57	58	72	65	63	71
AE	62	61	75	67	67	67
F	74	70	85	54	86	97
PA	83	77	93	111	96	109
A	126	85	110	123	86	97
FL	110	96	113	91	105	118
P	146	116	123	80	126	131
BaA	325	269	268	151	183	126
CH	248	203	202	113	150	154
BkF	276	216	230	138	207	183
BaP	523	317	334	284	316	194
IP	324	261	219	130	239	182
BghiP	571	450	454	169	260	174
DBahA	440	278	175	65	164	149

detection of correct ion (molecular ion, M). During SIM, the electrostatic analyzer of the MS sweeps (monitors) a narrow mass range around each selected ion mass. Occasional inadvertent monitoring of a secondary ion (M+1 or M-1) of diminished intensity was causing a large apparent change in instrument sensitivity. The problem was remedied by increasing the mass sweep range to 1.50 atomic mass units. The second source of bias was an insufficient temporal hold for the preset GC oven temperature maximum of 300°C, which prevented adequate capillary column equilibration for the subsequent injection. Determination herein of PAH of molecular weight 252 and above was subject to bias and this was eliminated by extending the hold from 9 to 23 min.

4.1.7 Evaluation of Systematic Error of GC-MS Column Chromatographic Procedure

4.1.7.1 Evidence for a Matrix Effect Mediated by Determinand Sorption

Evidence for sorption of PAH on active sites in the capillary column was obtained from the aforementioned slight curvilinearity of calibration curves (Section 4.1.5.2) and a small but noted amount of determinand peak tailing, both of which were observed to increase in pronounciation with decrease in determinand concentration and with increase in determinand molecular weight. Both curvilinearity of calibration curve and chromatogram peak tailing are symptomatic of determinand sorption, and the increase in these with high molecular weight PAH, with their noted tendency toward sorption, lent further evidence.

Evidence for sorption of PAH giving rise to bias was supplied by the injection of co-eluting PAH into the GC-MS. Mean (n = 4) analytical response constant for DBahA (2.00 µg) in octane (0.200 ml, with internal standard) was increased by 44% with the addition of IP (2.00 µg) to the solution. The increase was due to an increase in determinand peak area rather than to a decrease in peak area of internal standard, and was accompanied by a substantial reduction in IP peak tailing. IP and DBahA are both high molecular weight PAH and virtual co-elutants, and it appeared that the addition of DBahA assisted in the chromatographic transference of IP along the column probably by acting as a sorption site 'masker', that is, by occupying a proportion of the active sites that would otherwise have been occupied by IP, and thereby reducing the loss of this determinand. By this reasoning it was presumed that in the treated samples of raw sewage and primary sludge, as opposed to the calibration standards, unresolved background components acted as 'maskers', permitting elevated masses of high molecular weight PAH to reach the detector, and therefore increased analytical responses to be recorded. Such a treated sample matrix effect mediated by sorption can be invoked to explain the observation noted previously (Section 4.1.6) whereby an

insufficient capillary column equilibration at 300°C caused bias in the determination of high molecular weight PAH. The inadequate equilibration time resulted in the trapping of late-eluting treated sample background components (of presumably high molecular weight) on the column, which served to act as 'maskers' for high molecular weight PAH in the subsequent injection.

It was not exactly clear where the active sites might have been located, but the GC-MS interface was a probable candidate. The matrix effect was not encountered in GC analysis alone (Section 4.1.4) which employed an identical instrument and capillary column. Upon commissioning of the GC-MS system, extremely poor resolution and detection of high molecular weight PAH (MW 252 and above) was traced to a small column cold spot in that part of the heated interface in contact with the GC oven wall cavity. Although column active sites rather than cold spots were presently suspected as the cause of determinand sorption, the observation illustrated the critical importance of column integrity in this section of the system. Furthermore, the column equilibration time phenomenon, in entailing the probable trapping of late-eluting components, suggested sorption on active sites to be taking place toward the end of the column and therefore near or in the interface.

4.1.7.2 Quantification of Bias

The bias arising from the matrix effect was formally demonstrated and quantified by a method of standard additions performed on treated samples. The mean GC-MS analytical response constant (A_S) for each PAH was recorded for the four replicate unspiked treated samples of primary sludge obtained previously (Section 4.1.4; and each diluted to 0.500 ml). Mean analytical response constants (A_{SA}) were re-recorded after the addition of PAH (5.00 µg each) to each treated sample. Identical additions were made to four blanks (0.500 ml octane with internal standard) and the mean analytical response constants (A_{BA}) determined. The same operation was repeated on a subsequent occasion for the four replicate unspiked treated samples of raw sewage (unpreserved). For each PAH and for both sample

types a factor was derived with 95% confidence limits representing the factorial increase in mean analytical response constant of added determinand due to treated sample matrix:

$$\text{Factor} = \frac{A_{SA}-A_S}{A_{BA}} \qquad (6)$$

The factors confirmed the association of high molecular weight PAH with bias arising from a matrix effect (Table 35 and 36), a confidence interval excluding the value 1.00 demonstrating significant bias. A fundamental definition of bias could now be given as increase (absolute) in analytical response constant for determinand due to treated sample matrix, a measure of which is given by the aforementioned factor. Factors associated with significant

TABLE 35
Demonstration and Estimation of Bias
in GC-MS Determination of Treated Sample of Sludge

PAH	A_S[a]	RSD (%)	A_{SA}[b]	RSD (%)	A_{BA}[c]	RSD (%)	Factor[d]
AY	0.149	5.1	3.42	14.5	2.88	6.2	1.14±0.30
AE	2.28	3.8	3.24	7.0	1.89	7.3	0.81±0.34
F	2.28	4.0	3.40	11.9	1.35	13.9	0.83±0.52
PA	2.26	5.2	4.08	16.5	1.78	2.7	1.02±0.61
A	0.268	12.1	1.21	12.7	0.786	3.4	1.20±0.32
FL	0.392	4.6	1.85	21.1	0.818	3.1	1.78±0.76*
P	0.376	3.7	1.66	13.8	0.693	4.0	1.85±0.54*
BaA	0.0513	13.4	0.615	16.9	0.140	3.4	4.03±1.20*
CH	0.114	5.4	0.650	13.3	0.256	8.5	2.09±0.61*
BkF	0.0715	6.3	0.790	15.0	0.215	7.8	3.34±0.97*
BaP	0.0240	6.9	0.273	10.7	0.0695	8.4	3.58±0.82*
IP	0.0142	19.4	0.167	21.9	0.0547	6.0	2.79±1.10*
BghiP	0.0151	16.4	0.102	11.3	0.0393	4.9	2.21±0.51*
DBahA	ND[e]	----	0.170	50.4	0.0490	11.0	3.47±2.85

[a] Mean analytical response constant for four replicate treated samples.
[b] Mean analytical response constant for four replicate treated samples with addition of 5.00 µg of each PAH.
[c] Mean analytical response constant for four blanks with addition of 5.00 µg of each PAH.
[d] Factor = $(A_{SA}-A_S)/A_{BA}$ (with 95% confidence limits).
[e] ND = non-detectable.
* Significant bias (95% confidence interval not including 1.00).

TABLE 36
Demonstration and Estimation of Bias
in GC-MS Determination of Treated Sample of Sewage

PAH	A_S[a]	RSD (%)	A_{SA}[b]	RSD (%)	A_{BA}[c]	RSD (%)	Factor[d]
AY	0.0427	5.6	3.25	8.1	2.74	6.0	1.17±0.19
AE	0.123	2.0	2.25	5.8	1.90	4.9	1.12±0.14
F	0.160	4.4	2.25	6.9	1.53	3.6	1.37±0.18*
PA	0.291	6.7	3.04	5.6	1.95	2.1	1.41±0.15*
A	0.0509	6.4	1.06	6.5	0.860	4.5	1.17±0.15*
FL	0.0702	12.6	1.49	4.4	0.847	4.0	1.68±0.17*
P	0.0816	4.4	1.30	7.2	0.759	2.5	1.61±0.21*
BaA	0.0109	39.3	0.427	0.6	0.159	7.9	2.62±0.33*
CH	0.0272	15.5	0.511	6.1	0.256	8.0	1.89±0.31*
BkF	0.0172	2.3	0.566	5.1	0.225	9.7	2.44±0.43*
BaP	0.00496	17.6	0.168	5.3	0.0614	7.1	2.66±0.38*
IP	0.00405	42.4	0.112	5.6	0.0531	10.2	2.03±0.38*
BghiP	0.00478	43.6	0.0758	2.5	0.0391	7.2	1.82±0.24*
DBahA	ND[e]	----	0.105	6.2	0.0523	9.4	2.01±0.36*

[a] Mean analytical response constant for four replicate treated samples.
[b] Mean analytical response constant for four replicate treated samples with addition of 5.00 µg of each PAH.
[c] Mean analytical response constant for four blanks with addition of 5.00 µg of each PAH.
[d] Factor = $(A_{SA}-A_S)/A_{BA}$ (with 95% confidence limits).
[e] ND = non-detectable.
* Significant bias (95% confidence interval not including 1.00).

bias ranged from 1.78 (FL) to 4.03 (BaA) for the treated sample of sludge, and from 1.17 (A) to 2.66 (BaP) for the treated sample of sewage.

4.1.7.3 Dependence of Bias on Sample

Comparing factors in Table 35 with those in Table 36 suggested that bias for a given PAH may have depended on sample. F, PA and A were subject to bias in the treated sample of sewage but not in that of sludge, and application of a t test showed a significant difference at the 95% confidence level between factors for the two samples for BaA, BkF and BaP. The hypothesis was tested on six treated samples for three PAH representative of the high molecular weight determinands suffering bias, BaA (MW 228), BaP (MW 252) and IP (MW 276). The internal standard was also

TABLE 37
Evaluation of Dependency
of GC-MS Bias on Sample

PAH	Treated sample no.[a]	A_S[b]	A_{SA}[c]	$A_{SA}-A_S$
A-d_{10}	1	0.0690	0.313	0.244
	2	0.0605	0.302	0.242
	3	0.110	0.334	0.224
	4	0.0939	0.335	0.241
	5	0.0973	0.334	0.237
	6	0.0917	0.319	0.227
			Mean	0.236
			RSD (%)	3.6
BaA	1	0.00489	0.214	0.209
	2	0.00319	0.189	0.186
	3	0.0224	0.215	0.193
	4	0.0244	0.221	0.197
	5	0.0128	0.200	0.187
	6	0.0281	0.209	0.181
			Mean	0.192
			RSD (%)	5.2
BaP	1	0.00270	0.143	0.140
	2	0.00166	0.124	0.122
	3	0.00579	0.157	0.151
	4	0.00901	0.155	0.146
	5	0.00455	0.135	0.130
	6	0.0103	0.138	0.128
			Mean	0.136
			RSD (%)	8.3
IP	1	0.00174	0.0422	0.0405
	2	0.00115	0.0391	0.0380
	3	0.00337	0.0495	0.0461
	4	0.00409	0.0454	0.0413
	5	0.00211	0.0408	0.0387
	6	0.00447	0.0435	0.0390
			Mean	0.0406
			RSD (%)	7.3

[a] Consult Section 3.1.1.11.2 for details.
[b] Analytical response constant for treated sample.
[c] Analytical response constant for treated sample with addition of 2.28 µg A-d_{10}, 3.48 µg BaA, 3.81 µg BaP and 3.18 µg IP.

tested to confirm formally the independence of analytical response for this compound on treated sample: analytical response for A-d_{10} (peak area) was observed to vary little between treated samples and between these and calibration

standards. The GC-MS analytical response constant (A_S), relative to AY (10.0 μg ml^{-1}) as temporary internal standard, was recorded for the three PAH and A-d_{10} in each treated sample (diluted to 0.400 ml). Use of AY as an internal standard was valid: it was not subject to bias and natural background concentration in samples was very low. Analytical response constants (A_{SA}) were re-recorded after the addition of determinand (2.28 μg A-d_{10}, 3.48 μg BaA, 3.81 μg BaP and 3.18 μg IP) to each treated sample, and analytical response constant due to added determinand calculated (A_{SA}-A_S) for each sample. If magnitude of bias depended on sample, A_{SA}-A_S for a given PAH would have varied according to sample. For each PAH tested, variation in A_{SA}-A_S was found to be inconsequential (Table 37): RSD (BaA 5.2%, BaP 8.3% and IP 7.3%) were within instrument precisional error for these determinands (Table 31). RSD for A-d_{10} (3.6%) was judged to be inconsequential.

4.1.7.4 Dependence of Bias on Determinand Concentration

Dependence of bias on determinand concentration was ascertained by recording of GC-MS analytical response constant (A_S) (relative to A-d_{10}) for the previous three representative PAH in a treated sample (0.200 ml) of raw sewage. Analytical response constants (A_{SA}) were re-recorded after the addition of determinand (0.464 μg BaA, 0.508 μg BaP and 0.424 μg IP), to a total of four identical sets of additions. Analytical response constant due to total incremental addition was calculated (A_{SA}-A_S) for each PAH (Table 38), and plotted (Figure 7; regression lines unweighted). The good linear relationships obtained therefore demonstrated proportionality between analytical response constant and concentration of added determinand and hence, by inference, between bias and concentration of determinand. The proportionality thus signified the systematic error type as relative (i.e. constant percentage error), and the absence of an appreciable intercept (Figure 7) denoted the absence of any notable fixed systematic error.

TABLE 38
Evaluation of Dependency
of GC-MS Bias on Determinand Concentration

PAH	A_S[a]	Total addition (µl stock soln.)	Total addition (µg)	A_{SA}[b]	$A_{SA}-A_S$
BaA	0.143	0.40	0.464	0.696	0.553
		0.80	0.928	1.25	1.11
		1.20	1.39	1.70	1.56
		1.60	1.86	2.26	2.12
BaP	0.0580	0.40	0.508	0.338	0.280
		0.80	1.02	0.609	0.551
		1.20	1.52	0.781	0.723
		1.60	2.03	1.08	1.02
IP	0.0351	0.40	0.424	0.114	0.0789
		0.80	0.848	0.191	0.156
		1.20	1.27	0.269	0.234
		1.60	1.70	0.335	0.300

[a] Analytical response constant for treated sample.
[b] Analytical response constant for treated sample with additions.

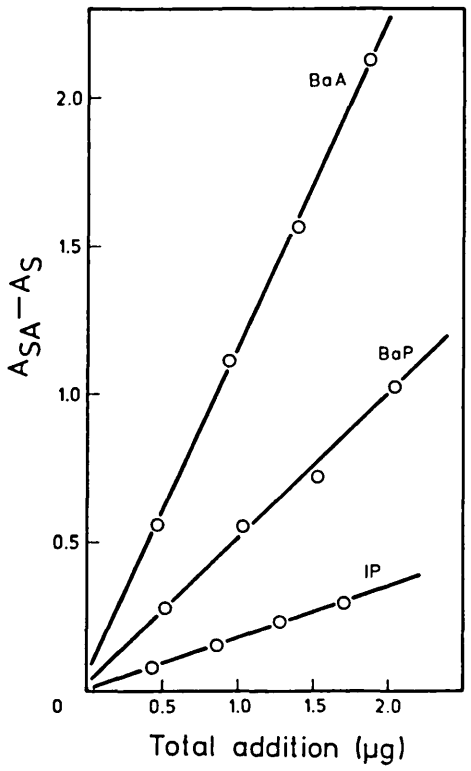


FIGURE 7
Dependence of GC-MS
Analytical Response Constant
on Determinand
Standard Addition Concentration

4.1.7.5 Correction for Bias

The relative nature of the bias enabled a straightforward correction to be made for it. The effect of the bias was essentially to change the slope of the calibration functions; the calculated factors (Table 35 and 36) equating the factorial increase in the slope of the calibration function for the appropriate determinand. As calibration curves derived from the calibration standards generally, within error, bisected the origin (see also Figure 7), the factors could be employed directly as correction factors after calculation of analytical result (i.e. after utilisation of calibration function). All mean masses determined in the primary sludge and raw sewage treated subsamples and associated spikes (Table 32 and 33, Section 4.1.6) were divided by the factor appropriate to the PAH and sample (whether significant or not; Table 35 and 36) to give corrected efficiencies of recovery (Table 39, RSD remaining unchanged and satisfactory). It

TABLE 39
Corrected Results for Efficiency of Recovery (%) of Determinand from Sludge and Sewage Sample Determined by GC-MS

	Sludge sample spike level				Sewage sample spike level			
PAH	1x	3x	9x	Mean	1x	3x	9x	Mean
AY	50	51	63	55	56	54	61	57
AE	77	75	92	81	60	60	60	60
F	89	84	103	92	40	63	71	58
PA	81	75	91	82	79	68	78	75
A	105	71	91	89	105	73	83	87
FL	61	54	63	59	54	63	70	62
P	79	63	66	69	50	78	82	70
BaA	81	67	67	72	58	70	48	59
CH	118	97	97	104	60	79	82	74
BkF	83	64	69	72	57	84	75	72
BaP	146	88	93	109	107	119	73	100
IP	116	94	79	96	64	118	90	91
BghiP	258	204	206	223	93	143	96	111
DBahA	126	80	50	85	32	82	74	63
Mean:	105	83	88	92	65	82	75	74

was readily apparent that the recoveries were now more realistic in the sense that few were appreciably greater than 100% (the most notable exception being BghiP in the sludge sample). The generally high recoveries determined by GC (Section 4.1.4) were confirmed, including separate quantification of IP and DBahA, and a complete set of recovery data for BkF and BaP in the sewage sample. The apparently low recoveries obtained by GC for the sludge sample for BaA, BkF and BaP at the 1x spike level, and for BkF and BaP at the 3x spike level, were assigned higher values by GC-MS. Mean recovery for all spike levels for the sludge sample ranged from 55% (AY) to 109% (BaP) (excluding BghiP), and for the sewage sample ranged from 57% (AY) to 111% (BghiP), with no apparent relationship between recovery and molecular weight of determinand in evidence. Mean recovery for all PAH at each spike level for the sludge sample was 105% (1x), 83% (3x) and 88% (9x), and for the sewage sample 65% (1x), 82% (3x) and 75% (9x), and the overall mean recovery for all spike levels was 92% and 74% respectively. These results, considered in conjunction with those obtained by GC (Table 30, bottom row), suggested no consistent relationship between mean recovery and spike level or between mean recovery and sample type (i.e. sewage or sludge). Hence it was concluded that there was no definite influence of determinand concentration or of sample total solids (TS) concentration on determinand recovery. Results would be expected to be comparable for a sample of primary effluent. The inclusive mean recovery of 85% determined by GC and 83% by GC-MS confirmed the overall high and repeatable efficiency of the column chromatographic procedure.

4.1.8 Validation of Efficiency of Extraction Procedure

The efficiency of the extraction procedure on indigenous (unspiked) PAH was confirmed by performing four successive extractions on each of four subsamples (1.00 l) of a sample of raw sewage. Sample treatment of each sequential extract by the column chromatographic procedure was followed by GC-MS determination (corrected for bias (using Table 36) but not for efficiency) (Table 40). The mean proportion of mean total mass of (individual) determinand extracted was 81.3% for the first extraction, 8.7% for the second, 7.1%

TABLE 40
Assessment of Efficiency of Extraction Procedure for Indigenous Determinand in a Sample of Sewage

PAH	Extract no.	Mass extracted[a] (µg)	RSD (%)	Proportion[b] (%)	1+2[c] (%)
AY	1	0.0791	10.3	51.4	
	2	0.0256	10.3	16.6	68.0
	3	0.0251	35.6	16.3	
	4	0.0240	21.6	15.6	
AE	1	1.24	4.3	79.0	
	2	0.123	14.6	7.8	86.8
	3	0.112	16.6	7.1	
	4	0.0941	16.1	6.0	
F	1	0.910	5.0	80.3	
	2	0.0811	3.4	7.2	87.5
	3	0.0779	15.9	6.9	
	4	0.0647	9.4	5.7	
PA	1	0.902	5.4	74.6	
	2	0.117	10.1	9.7	84.3
	3	0.103	12.3	8.5	
	4	0.0874	17.3	7.2	
A	1	0.183	5.6	92.3	
	2	0.0152	12.9	7.7	100.0
	3	ND	----	----	
	4	ND	----	----	
FL	1	0.431	7.0	84.6	
	2	0.0357	14.0	7.0	91.6
	3	0.0253	16.7	5.0	
	4	0.0177	26.3	3.5	
P	1	0.595	4.1	88.7	
	2	0.0369	9.4	5.5	94.2
	3	0.0220	20.4	3.3	
	4	0.0166	25.7	2.5	
BaA	1	0.275	9.2	93.8	
	2	0.0115[d]	34.4	3.9	97.7
	3	0.00675[e]	48.4	2.3	
	4	ND	----	----	
CH	1	0.252	4.1	93.2	
	2	0.0115[d]	34.4	4.3	97.5
	3	0.00675[e]	48.4	2.5	
	4	ND	----	----	
BkF	1	0.474	9.5	81.7	
	2	0.0509	18.6	8.8	90.5
	3	0.0550	24.7	9.5	
	4	ND	----	----	
BaP	1	0.247	12.4	69.1	
	2	0.0574	36.0	16.1	85.2
	3	0.0531	10.2	14.9	
	4	ND	----	----	
IP	1	0.157	12.2	75.3	
	2	0.0276	18.7	13.2	88.5
	3	0.0240	27.1	11.5	
	4	ND	----	----	

/Continued overleaf

TABLE 40/Continued

PAH	Extract no.	Mass extracted[a] (µg)	RSD (%)	Proportion[b] (%)	1+2[c] (%)
BghiP	1	0.223	16.5	74.6	
	2	0.0401	10.0	13.4	88.0
	3	0.0357	35.2	11.9	
	4	ND	----	----	
DBahA	1	0.0891	13.7	100.0	
	2	ND	----	----	100.0
	3	ND	----	----	
	4	ND	----	----	
			Mean[f]: 1	81.3	
			2	8.7	90.0
			3	7.1	
			4	2.9	

[a] Mean for four treated extracts from original four 1.00 l subsamples.
[b] Proportion of total mass of determinand extracted.
[c] Sum of proportions for extracts 1 and 2.
[d,e] BaA and CH not resolved: analytical response constant measured as CH and result halved.
[f] Mean proportion for each extract number (taking ND = 0% and including values of 100%).

for the third and 2.9% for the fourth. Thus the first two extractions combined (i.e. as per method) recovered a mean proportion of 90.0% (ranging from 68.0% (AY) to 100.0% (A, DBahA)). The high efficiency of the first extraction step suggested that the two-step extraction technique was adequately robust to extract efficiently samples of a wide range of TS concentrations.

4.1.9 Overall Assessment of GC-MS Column Chromatographic Procedure

4.1.9.1 Comparison With GC Determination

Mean masses determined in the sludge and sewage sample and mean masses recovered from the associated spiked subsamples quantified by GC (Table 28 and 29) and GC-MS (Table 32 and 33, corrected for bias as in Section 4.1.7.5 but not for efficiency) were compared (Table 41 and 42). In most cases agreements were good, but data for the unspiked samples, as unadulterated samples, merited the closest attention. GC-MS here permitted individual determination of IP and DBahA in both sample types, and determination of BkF and BaP in the sewage sample, unattainable by GC. It was evident that although both GC and GC-MS were capable of measuring low molecular weight PAH with satisfactory accuracy and precision, the greater specificity of GC-MS

TABLE 41
Comparison Between GC and GC-MS Determination (µg) of Sludge Sample and Associated Spiked Subsamples[a]

			Spiked subsamples spike level					
			1x		3x		9x	
PAH	GC	GC-MS	GC	GC-MS	GC	GC-MS	GC	GC-MS
AY	ND	0.439	8.14	4.96	22.1	15.3	79.8	57.1
AE	10.3	14.1	9.67	7.94	25.7	23.2	89.1	85.4
F	7.94	8.81	7.19	7.04	20.3	20.1	68.1	73.4
PA	5.95	6.23	6.21	4.83	15.2	13.5	52.4	48.8
A	1.81	0.942	1.25	1.90	4.91	3.87	14.5	14.9
FL	2.93	1.38	2.18	1.80	6.65	4.75	25.0	16.7
P	2.31	1.94	2.30	1.83	6.08	4.35	20.7	13.8
BaA	0.680	0.950	0.383	0.548	1.59	1.36	5.78	4.07
CH	0.610	0.852	0.483	0.722	1.60	1.78	5.37	5.31
BkF	1.04	1.15	0.193	0.859	1.69	2.01	8.13	6.44
BaP	1.36	0.961	0.410	1.99	2.39	3.61	10.3	11.4
IP	0.800[b]	0.659	0.310[b]	0.928	1.85[b]	2.25	5.40[b]	5.66
BghiP	0.340	1.07	0.320	0.878	0.815	2.08	2.77	6.29
DBahA	-----	ND	-----	1.01	-----	1.92	-----	3.63

[a] Masses from Table 28 and 32 (means for four 50.0 ml subsamples).
[b] Including DBahA (unresolved).

TABLE 42
Comparison Between GC and GC-MS Determination (µg) of Sewage Sample and Associated Spiked Subsamples[a]

			Spiked subsamples spike level					
			1x		3x		9x	
PAH	GC[b]	GC-MS[b]	GC	GC-MS	GC	GC-MS	GC	GC-MS
AY	0.378	0.0945	0.344	0.210	0.837	0.606	2.73	2.07
AE	0.856	0.641	0.762	0.513	1.96	1.54	6.20	4.59
F	1.01	0.836	0.940	0.401	2.85	1.90	8.45	6.45
PA	1.21	1.07	1.17	0.950	3.41	2.48	10.7	8.44
A	0.173	0.225	0.140	0.182	0.346	0.381	1.15	1.29
FL	0.860	0.547	0.823	0.464	2.42	1.62	7.40	5.44
P	0.991	0.954	0.929	0.494	2.90	2.33	9.37	7.27
BaA	0.368	0.173	0.345	0.213	1.01	0.767	2.93	1.59
CH	0.327	0.429	0.246	0.196	0.813	0.778	2.74	2.40
BkF	ND	0.474	ND	0.315	ND	1.41	4.87	3.75
BaP	ND	0.203	ND	0.594	1.76	1.98	4.74	3.64
IP	0.197[c]	0.150	0.184[c]	0.126	0.653[c]	0.695	1.91[c]	1.59
BghiP	0.259	0.303	0.208	0.241	0.685	1.11	1.99	2.23
DBahA	-----	0.193	-----	0.0637	-----	0.484	----	1.31

[a] Masses from Table 29 and 33 (means for four 1.00 l subsamples).
[b] (Means for eight 1.00 l subsamples).
[c] Including DBahA (unresolved).

permitted more satisfactory determination of high molecular weight PAH. This can be appreciated by comparing the GC-MS mass chromatograms (Figure 8) with the GC chromatogram (Figure 6) of a typical sample. The former were essentially interference free, as verified by GC-MS RS analysis which also confirmed peak identities. GC-MS enabled confident peak identification, and more accurate peak measurement, of high molecular weight PAH (MW 228 and above), conditions that were difficult and, on occasions, impossible to achieve by GC. Whereas the GC FID distinguished hydrocarbons only on the basis of column retention time, the higher specificity of GC-MS under SIM was due to its additional distinguishing facility on the basis of ion m/z value. This permitted PAH to be distinguished from background alkylated PAH and other GC interferences. The higher specificity of GC-MS was the deciding factor in its selection over GC as the preferred

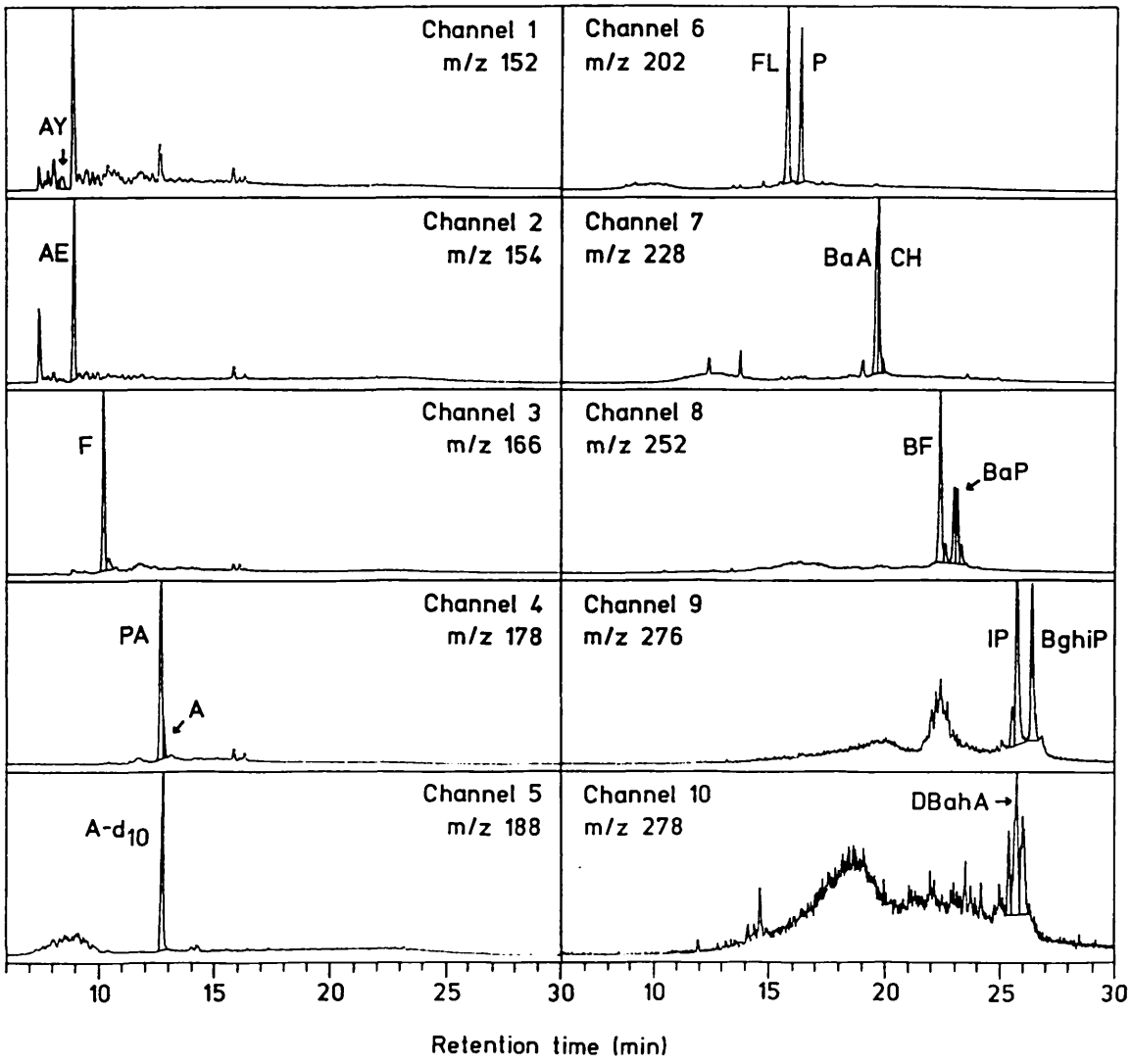


FIGURE 8
GC-MS SIM Mass Chromatograms
of a Treated Sample of Raw Sewage
(Instrumental Conditions Given in Section 3.1.1.10.2.1)

instrumental method of determination for the column chromatographic procedure.

4.1.9.2 Characterisation of Procedure Performance Characteristics

The performance characteristics of the GC-MS column chromatographic procedure were characterised, fulfilling the minimum requirements for an adequately validated analytical method (Table 16). Accuracy, as expressed by determinand efficiency of recovery and assessed for each PAH at three determinand concentrations (spike levels) on a sample of sludge and a sample of sewage, has already been shown to be independent of determinand concentration and

sample type (Section 4.1.7.5). Mean recovery of each PAH for all spike levels in both sample types quantified by GC (Table 30) and GC-MS (Table 39) was: AY 69%, AE 79%, F 83%, PA 87%, A 83%, FL 75%, P 84%, BaA 75%, CH 87%, BkF 69%, BaP 91%, IP 89%, BghiP 127% and DBahA 79%. In order to report accurate analytical results these should be corrected for procedure efficiency using these values, although such correction is not normal practice (Keith et al., 1983).

Procedure precision, as expressed by statistical estimate of error (random and systematic) (Table 16), more properly includes accuracy. An estimate of the random error (quoted separately from systematic error according to the recommendation of Hunt & Wilson (1986)) for each PAH at two determinand concentrations, was expressed by the values of RSD for the analysis of the (unspiked) sample of sludge (column 3, Table 32) and sample of sewage (column 3, Table 33). For a given PAH, RSD values for the two sample types, and hence for the determinand at two differing concentrations (column 2 of each table; typically near lower and upper limits routinely determined) were comparable, demonstrating that standard deviation of results was proportional to determinand concentration and hence that random error, as expressed by RSD, was independent of determinand concentration and sample type. (Mean RSD for the sludge sample was 6.2% and for the sewage sample 6.3%). RSD for the sewage sample representing seven degrees of freedom (n = 8) was adopted as the random error of the procedure, and values converted to 95% confidence limits and expressed as a percentage of analytical result C ($\mu g\ l^{-1}$, Table 43).

The nature of the bias, that is its relativity (Section 4.1.7.4) and independence of sample (Section 4.1.7.3), was such that a straightforward correction for the systematic error could be made to each analytical result on a regular basis by utilisation of factors in the manner described (Section 4.1.7.5). The factors in this context were a direct measure of the systematic error, and the estimate of the error adopted to characterise the procedure was that of the sample of sewage (Table 36); the age of the treated samples of sludge at the time of determination of the factors was such that the

TABLE 43
Random, Systematic and Total Errors, and Detection and Quantification Limits for Analytical Procedure

PAH	Random error[a]	Systematic error[b]	Total error[c]	Detn. limit[d] (μg l^{-1})	Quant. limit[e] (μg l^{-1})
AY	C (± 7.0%)	x 0.854 (±16.2%)	$C_{corr.}$ (±17.6%)	0.01	0.02
AE	C (± 2.8%)	x 0.893 (±12.6%)	$C_{corr.}$ (±12.9%)	0.01	0.02
F	C (± 3.0%)	x 0.732 (±13.0%)	$C_{corr.}$ (±13.3%)	0.01	0.02
PA	C (± 2.4%)	x 0.709 (±10.3%)	$C_{corr.}$ (±10.6%)	0.01	0.02
A	C (± 4.4%)	x 0.852 (±13.0%)	$C_{corr.}$ (±13.7%)	0.01	0.02
FL	C (± 3.0%)	x 0.597 (± 9.9%)	$C_{corr.}$ (±10.3%)	0.02	0.05
P	C (± 2.9%)	x 0.623 (±12.9%)	$C_{corr.}$ (±13.2%)	0.02	0.05
BaA	C (± 6.6%)	x 0.382 (±12.7%)	$C_{corr.}$ (±14.3%)	0.05	0.10
CH	C (± 3.5%)	x 0.529 (±16.4%)	$C_{corr.}$ (±16.8%)	0.05	0.10
BkF	C (± 4.5%)	x 0.410 (±17.6%)	$C_{corr.}$ (±18.2%)	0.05	0.10
BaP	C (± 8.9%)	x 0.377 (±14.3%)	$C_{corr.}$ (±16.8%)	0.05	0.10
IP	C (±10.1%)	x 0.492 (±18.8%)	$C_{corr.}$ (±21.3%)	0.05	0.10
BghiP	C (± 8.1%)	x 0.551 (±13.0%)	$C_{corr.}$ (±15.3%)	0.05	0.10
DBahA	C (± 6.3%)	x 0.498 (±18.0%)	$C_{corr.}$ (±19.1%)	0.05	0.10

[a] 'Within-batch' estimate based on seven degrees of freedom for analytical result C (μg l^{-1}).
[b] 'Within-batch' estimate based on three degrees of freedom. Factors inversed for computation of corrected result $C_{corr.}$
[c] Total error after correction for systematic error (= C x factor).
[d] Detection limit, defined as instrument detection limit (Table 31) for 1.00 l sample and 0.200 ml treated sample.
[e] Quantification limit, defined as lower limit of instrument calibration curve linear range (Table 31) for 1.00 l sample and 0.200 ml treated sample.

results for this sample were judged to be of doubtful integrity. Each factor was inversed, and 95% confidence limits expressed as a percentage re-calculated (Table 43). A correct analytical result ($C_{corr.}$) was obtained by conversion of analytical response constant to concentration (C) by means of the calibration function in the normal manner, followed by correction for systematic error by multiplication by the appropriate inversed factor. A result (C) for P (pyrene), for example, was multiplied by 0.623.

It is evident that as the determination of the systematic error was also itself subject to random error, the consequence of correcting for bias was to introduce extra random error variation with a consequent loss of overall precision. In the case of P, the random error (95%

confidence limits) associated with the systematic error was ±12.9% (Table 43). An individual result (C) for P was subject to a random error of ±2.9%, but after multiplication by the inversed factor to correct for the systematic error, the total (random) error for the individual result ($C_{corr.}$) became, by propagation of errors, ±13.2% (again, 95% confidence limits). The precision for the overall procedure of an individual analytical result thus ranged from ±10.3% (FL) to ±21.3% (IP) (Table 43, 'Total error' column). An assumption, considered valid, was that the random error of the systematic error factors, expressed as RSD, were independent of determinand concentration and sample type.

Procedure sensitivity, as measured by detection limit for each determinand, was estimated (non-statistically) from data gained (Section 4.1.8 and others), and was found to approximate instrumental detection limit (Table 31). The detection limit of the procedure was defined as equal to instrumental detection limit (Table 43), and the 'quantification limit' defined as the lower limit of instrument calibration curve linear range (Table 31). An analytical result less than the quantification limit was treated with caution.

The finalised GC-MS column chromatographic procedure and performance characteristics are summarised (Appendix 2), and are published elsewhere (Bedding et al., 1988a,b). The procedure was utilised for all subsequent determinations of PAH in waste water.

4.1.10 Sampling and Storage

4.1.10.1 Sample Integrity Over Time

Sample integrity over an extended period of time was evaluated as an integral part of method validation. A sample of raw sewage was distributed between two vessels (50 l tin-plated drums), the contents of one of which were preserved (1% V/V formaldehyde solution). Analyses were performed promptly, and subsequently after 7, 28 and 56 days. The data (Table 44) were plotted (Figure 9) and revealed that the concentrations of low molecular weight

TABLE 44
Evaluation of Sample Integrity
Through Analysis of a Sample of Raw Sewage
Over an Extended Time Period

PAH	Cond.[a]	Sample age (d) 0 Mass[b] (µg)	0 RSD (%)	7 Mass[b] (µg)	7 RSD (%)	28 Mass[b] (µg)	28 RSD (%)	56 Mass[b] (µg)	56 RSD (%)
AY	UP	0.242	14.3	0.213	3.8	0.149	11.5	ND	----
	P	0.206	3.9	0.168	12.6	0.185	15.5	0.166	13.6
AE	UP	1.74	8.1	1.32	4.8	0.530	4.7	ND	----
	P	1.60	3.1	1.26	4.7	1.42	9.4	1.31	8.7
F	UP	1.40	8.6	1.36	3.4	0.540	5.4	ND	----
	P	1.27	4.9	1.23	4.9	1.14	9.0	1.13	9.2
PA	UP	1.39	8.5	1.30	4.8	0.858	4.7	0.240	12.0
	P	1.20	6.4	1.15	4.3	1.08	10.3	1.12	9.9
A	UP	0.186	6.9	0.166	3.2	0.124	6.1	0.0591	5.2
	P	0.173	2.9	0.159	6.8	0.160	7.8	0.144	6.4
FL	UP	0.960	5.6	0.905	4.8	0.993	11.1	0.625	8.1
	P	0.913	3.6	0.893	6.1	0.865	4.7	0.940	4.7
P	UP	0.865	6.4	0.795	5.2	0.813	7.7	0.585	7.3
	P	0.800	4.1	0.790	7.7	0.703	9.7	0.760	7.8
BaA	UP	0.325	4.6	0.297	5.7	0.295	9.4	0.222	6.2
	P	0.266	7.0	0.279	11.6	0.268	3.8	0.264	9.6
CH	UP	0.380	6.5	0.342	2.8	0.346	7.0	0.251	6.1
	P	0.315	5.6	0.314	8.7	0.325	4.6	0.312	5.0
BkF	UP	NQ[c]	----	NQ	----	NQ	----	NQ	----
	P	NQ	----	NQ	----	NQ	----	NQ	----
BaP	UP	0.210	5.2	0.234	6.9	0.208	13.9	0.160	17.7
	P	0.160	14.9	0.194	19.7	0.203	7.0	0.160	19.2
IP/	UP	0.176	7.1	0.157	15.0	0.176	3.0	0.133	3.2
DBahA[d]	P	0.139	6.6	0.135	10.1	0.146	11.7	0.128	8.3
BghiP	UP	0.164	7.5	0.153	16.5	0.181	15.9	0.157	12.8
	P	0.152	15.9	0.150	16.1	0.159	13.1	0.132	13.0

[a] Condition: UP = unpreserved
P = preserved.
[b] Mean for four 1.00 l subsamples; analysis by GC.
[c] NQ = non-quantifiable due to presence of interferences.
[d] Not resolved: analytical response measured as IP.

PAH decreased steadily with time in the unpreserved sample. Furthermore, there was evidence that the rate of decrease diminished with increase in molecular weight. The preserving agent appeared to arrest concentration decline in all cases. Upon completion of the experiment, sorption of PAH on the inner surfaces of the emptied vessel containing the unpreserved sample was tested, but no determinand was detected.

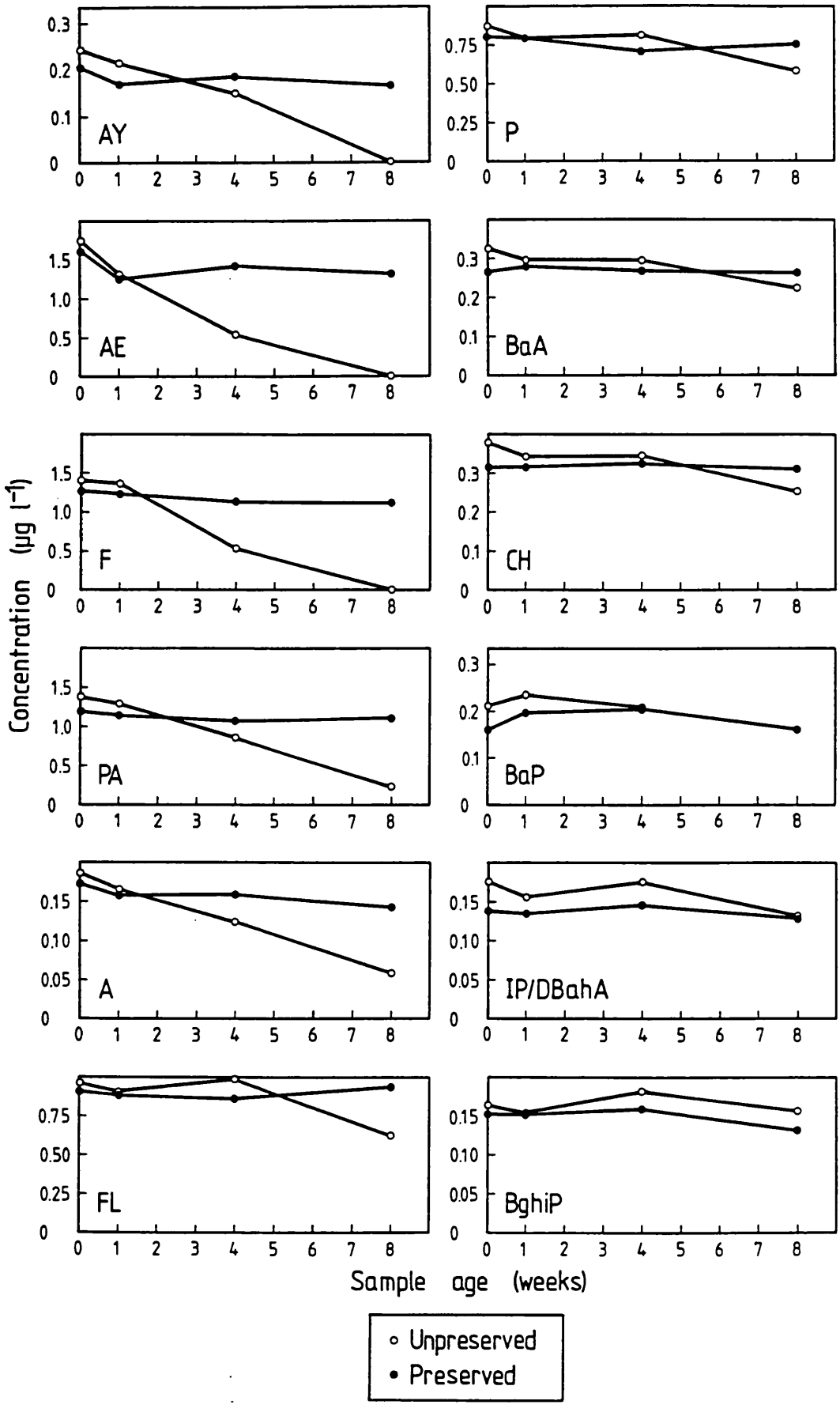


FIGURE 9
Integrity of a Sample of Raw Sewage
Over an Extended Time Period

4.1.10.2 Influence of Matrix on Sample Integrity

The effect was re-determined for influence of sample matrix after just one time interval of 28 d. A sample of raw sewage was divided into eight subsamples (1.00 l each), four of which were preserved. Each subsample was stored in a stoppered separating funnel (1.5 l), as used for sample extraction (Section 4.1.2), and placed in the dark. After 28 d, subsamples were extracted *in situ* and determined for PAH (Table 45). A parallel determination was performed with PAH spiked into glass-distilled deionised water at typical indigenous background concentrations (1.00 μg l^{-1} for PAH MW 152-228, 0.250 μg l^{-1} MW 252-278) and stored in identical vessels under identical conditions for the same period (Table 46). Application of a t test to each pair of

TABLE 45
Effect of Absence of Preservation on Analysis of a Sample of Raw Sewage After 28 Days

	Preserved subsample		Unpreserved subsample		
PAH	Mass[a] (μg)	RSD (%)	Mass[a] (μg)	RSD (%)	Propn.[b] (%)
AY	0.0572	15.3	0.0337	10.9	58.9*
AE	0.473	16.3	0.207	32.3	43.8*
F	0.261	15.8	0.146	33.1	55.9*
PA	0.323	9.3	0.235	18.7	72.8*
A	0.0676	7.1	0.0528	10.0	78.1*
FL	0.150	3.9	0.151	7.7	100.7
P	0.361	6.3	0.348	13.5	96.4
BaA	0.308	19.1	0.259	29.6	84.1
CH	0.137	8.0	0.138	8.7	100.7
BkF	0.494	4.0	0.293	31.8	59.3*
BaP	0.386	8.4	0.397	24.3	102.8
IP	0.174	11.6	0.0711	20.3	40.9*
BghiP	0.216	5.9	0.197	9.7	91.2
DBahA	ND	----	ND	----	----

[a] Mean for four 1.00 l subsamples; analysis by GC-MS.
[b] Mean mass in unpreserved subsample as a proportion of mean mass in preserved subsample.
* Significantly less than 100% at 95% confidence level.

TABLE 46
Effect of Absence of Preservation on Analysis of a Sample of Distilled Deionised Water, Containing Determinand, After 28 Days

	Preserved subsample		Unpreserved subsample		
PAH	Mass[a] (µg)	RSD (%)	Mass[a] (µg)	RSD (%)	Propn.[b] (%)
AY	0.691	10.4	0.717	9.3	103.8
AE	0.696	11.0	0.683	8.2	98.1
F	0.864	9.2	1.01	10.4	116.9
PA	0.875	9.2	0.849	7.5	97.0
A	0.815	10.6	0.789	7.0	96.8
FL	0.860	3.2	0.908	7.8	105.6
P	0.894	10.6	0.911	10.0	101.9
BaA	0.871	10.4	0.880	8.4	101.0
CH	0.887	8.3	0.856	6.3	96.5
BkF	0.248	7.8	0.263	9.0	106.0
BaP	0.235	8.5	0.262	5.7	111.5
IP	0.238	10.7	0.212	8.4	89.1
BghiP	0.194	11.5	0.202	5.4	104.1
DBahA	0.221	5.1	0.215	8.1	97.3

[a] Mean for four 1.00 l subsamples; analysis by GC.
[b] Mean mass in unpreserved subsample as a proportion of mean mass in preserved subsample. No proportion significantly less than 100% at 95% confidence level.

mean masses obtained for the sewage sample showed a significant decrease at the 95% confidence level in the unpreserved subsample for the low molecular weight PAH AY, AE, F, PA and A, as well as for the high molecular weight PAH BkF and IP. The result for IP should be treated with caution as determinand mass was below the quantification limit. Application of a t test to results for the sample of distilled deionised water containing determinand showed no significant decrease for any of the PAH in the unpreserved batch, thus confirming the presence of a slow process operating via the sewage matrix.

Extraction (*in situ*) and determination of dosed distilled deionised water was performed as for the direct determination of distilled deionised water by GC reported previously (Section 3.1.1.9). These and similar 'clean'

samples (Section 3.2.2 and 3.2.3) justified use of the shortened procedure with determination by GC for reasons of speed and economy. Absence of interferences (Section 4.1.4), simplicity of procedure, and repeatability (Table 46), were judged to permit satisfactory accuracy and precision. Mean efficiency of recovery of PAH for the preserved subsample was 85.7% and for the unpreserved subsample 87.3% (Table 46), reflecting incomplete partitioning of determinand during solvent extraction rather than incomplete extraction due to determinand loss by some process.

4.2 Physicochemical Behaviour of PAH in Raw and Settled Sewage

4.2.1 Assessment of Settleability of PAH

A preliminary investigation into the effect of sedimentation on PAH was performed in the laboratory. Four subsamples (1.00 l each) of a sample of raw sewage were promptly determined for PAH as were another four after settlement for 2.3 h (tank retention time at 1 DWF for primary sedimentation pilot plant; Section 3.3), and for a further four subsamples after centrifugation (Table 47). Sedimentation achieved removal of PAH ranging from 35.1% (AY) to 86.1% (BaA), the figures tending towards those of the solids (SS, NVSS, VSS; approximately 81%) with increase in molecular weight. Only a modest increase in removal of PAH was brought about by centrifugation; the fraction

TABLE 47
Assessment of the Effect of Sedimentation and Centrifugation on PAH in a Sample of Raw Sewage

	Raw subsample		Settled subsample			Centrifuged subsample			
PAH	Mass[a] (µg)	RSD (%)	Mass[a,b] (µg)	RSD (%)	R[c] (%)	Mass[a,b] (µg)	RSD (%)	R[d] (%)	100%-R (%)
AY	0.222	17.1	0.144	9.1	35.1	0.147	12.8	33.8	66.2
AE	7.54	12.8	4.29	9.3	43.1	3.50	15.6	53.6	46.4
F	5.04	11.9	2.57	15.7	49.0	2.41	15.8	52.2	47.8
PA	2.70	11.1	1.05	16.2	61.1	0.996	13.0	63.1	36.9
A	0.607	10.5	0.211	8.3	65.2	0.185	22.0	69.5	30.5
FL	1.31	7.8	0.314	14.1	76.0	0.262	15.9	80.0	20.0
P	1.59	6.8	0.363	14.0	77.2	0.288	16.4	81.9	18.1
BaA	0.823	12.3	0.114	22.6	86.1	0.0808	24.9	90.2	9.8
CH	0.729	6.5	0.174	11.8	76.1	0.134	15.1	81.6	18.4
BkF	1.36	5.6	0.245	12.2	82.0	0.168	18.6	87.6	12.4
BaP	0.852	2.8	0.143	11.5	83.2	0.0939	19.7	89.0	11.0
IP	0.313	7.8	0.0705	13.0	77.5	0.0531	29.2	83.0	17.0
BghiP	0.519	10.3	0.108	8.7	79.2	0.0704	20.4	86.4	13.6
DBahA	0.281	10.1	0.0759	14.1	73.0	0.0375	30.6	86.7	13.3

[a] Mean for four 1.00 l subsamples.
[b] Supernatants.
[c] R = removal (relative to raw subsample). Data for co-determinands (%): SS 80.7, NVSS 80.5, VSS 80.8, COD_{tot} 69.5, COD_{sol} 52.6.
[d] Data for co-determinands (%): SS 93.6, NVSS 93.8, VSS 93.5, COD_{tot} 81.6, COD_{sol} 44.0.

remaining, which ranged from 9.8% (BaA) to 66.2% (AY) and which decreased with increase in molecular weight of hydrocarbon, may be considered to represent PAH in the dissolved/colloidal/microparticulate state and thus to be effectively unamenable to settlement.

4.2.2 PAH Particle Size Distribution Analysis

4.2.2.1 Test of Determinand Sorption to Sieve Material

Due to reported losses of PAH through sorption during filtration of aqueous solutions of determinand (Inscoe, 1966), an initial experiment was conducted to test for sorption of PAH on sieve material used in the particle size distribution analysis. Four portions (1.00 l each) of glass-distilled deionised water each containing determinand (1.00 µg l^{-1} for PAH MW 152-228, 0.250 µg l^{-1} MW 252-278;

TABLE 48
Test of Determinand Sorption to Sieve Material Used in Particle Size Distribution Analysis

PAH	Recovery[a] (µg)	Recovery[a] (%)	RSD (%)
AY	0.908	90.8	9.5
AE	0.903	90.3	7.8
F	0.988	98.8	11.0
PA	1.02	102.0	8.3
A	0.979	97.9	8.4
FL	1.01	101.0	8.3
P	1.03	103.0	10.3
BaA	0.976	97.6	9.4
CH	1.01	101.0	5.9
BkF	0.252	100.8	9.2
BaP	0.259	103.6	7.5
IP	0.192	76.8	7.7
BghiP	0.231	92.4	8.2
DBahA	0.257	102.8	8.0
		Mean: 97.1	

[a] Mean for filtrates of four 1.00 l samples of distilled deionised water containing 1.00 µg AY-CH and 0.250 µg BkF-DBahA; analysis by GC.

as in Section 4.1.10.2) were filtered through a sieve (53 µm mesh) and subsequently determined (Table 48). Recovery of PAH, excepting IP (76.8%), was high, ranging from 90.3% (AE) to 103.6% (BaP) with an overall mean of 97.1%. No appreciable sorption was considered to be taking place.

4.2.2.2 Distribution Analysis of Raw Sewage

Four subsamples (1.00 l each) of a sample of raw sewage were determined for PAH as were sets of four after filtration through sieves of mesh size 253, 150, 106 and 53 µm (Table 49). A satisfactory gradation in SS was achieved: a mean of 74.4% of unfiltered SS was present in the filtrate from the 253 µm sieve, 65.9% from the 150 µm sieve, 55.0% from the 106 µm sieve and 37.0% from the 53 µm sieve.

TABLE 49
PAH and Particle Size Distribution Analysis of a Sample of Raw Sewage

PAH	Mesh size[a] (µm)	Mass[b] (µg)	RSD (%)	Propn.[c] (%)
AY	UF	0.151	7.5	
	253	0.138	5.9	91.4
	150	0.122	7.8	80.8
	106	0.122	9.0	80.8
	53	0.112	19.9	74.2
AE	UF	2.64	11.0	
	253	2.27	4.9	86.0
	150	2.08	3.5	78.8
	106	1.97	8.6	74.6
	53	1.68	14.2	63.6
F	UF	1.48	6.2	
	253	1.20	3.6	81.1
	150	1.08	2.5	73.0
	106	0.972	6.9	65.7
	53	0.864	14.2	58.4
PA	UF	1.09	3.1	
	253	0.883	2.3	81.0
	150	0.847	5.8	77.7
	106	0.730	12.9	67.0
	53	0.667	14.7	61.2
A	UF	0.298	13.7	
	253	0.229	16.5	76.8
	150	0.216	8.9	72.5
	106	0.181	22.0	60.7
	53	0.171	17.6	57.4

/Continued overleaf

TABLE 49/Continued

PAH	Mesh size[a] (μm)	Mass[b] (μg)	RSD (%)	Propn.[c] (%)
FL	UF	0.480	7.2	
	253	0.394	3.7	82.1
	150	0.375	8.8	78.1
	106	0.290	21.4	60.4
	53	0.232	21.2	48.3
P	UF	0.629	5.4	
	253	0.519	5.7	82.5
	150	0.483	6.6	76.8
	106	0.364	22.1	57.9
	53	0.300	22.2	47.7
BaA	UF	0.348	7.3	
	253	0.320	10.5	92.0
	150	0.318	21.1	91.4
	106	0.277	23.7	79.6
	53	0.179	27.2	51.4
CH	UF	0.272	9.4	
	253	0.216	3.9	79.4
	150	0.236	9.0	86.8
	106	0.150	24.8	55.1
	53	0.125	24.9	46.0
BkF	UF	0.584	10.5	
	253	0.486	5.7	83.2
	150	0.512	7.2	87.7
	106	0.372	22.1	63.7
	53	0.264	21.5	45.2
BaP	UF	0.500	13.1	
	253	0.335	23.7	67.0
	150	0.471	10.3	94.2
	106	0.277	37.6	55.4
	53	0.209	50.0	41.8
IP	UF	0.203	15.0	
	253	0.180	3.8	88.7
	150	0.189	2.3	93.1
	106	0.142	19.5	70.0
	53	0.104	16.8	51.2
BghiP	UF	0.316	20.0	
	253	0.314	10.8	99.4
	150	0.311	4.5	98.4
	106	0.233	16.6	73.7
	53	0.163	20.0	51.6
DBahA	UF	ND	----	
	253	ND	----	----
	150	ND	----	----
	106	ND	----	----
	53	ND	----	----

[a] UF = unfiltered.
[b] Mean for filtrates of four 1.00 l subsamples. Data for SS (mg l^{-1}): unfiltered 703, 253 μm 523, 150 μm 463, 106 μm 387, 53 μm 260.
[c] Proportion of mean unfiltered mass.

4.2.2.2.1 PAH Particle Size Distribution on a Sample Volume Basis

Data (Table 49) were expressed as microgram PAH per litre of sample associated with each particle size fraction (Table 50), and relative proportions displayed as a bar chart (Figure 10). Data for the size fraction <0.45 µm was obtained by performing a linear regression analysis of

TABLE 50
PAH Particle Size Distribution in Sample of Raw Sewage Expressed as Microgram PAH per Litre Sample

PAH	Concentration (µg l^{-1}) and proportion (%, in parentheses) in particle size fraction					
	>253 µm	150-253 µm	106-150 µm	53-106 µm	0.45-53 µm	<0.45 µm[a]
AY	0.013 (8.6)	0.016 (10.6)	0 (0)	0.010 (6.6)	0.024 (15.7)	0.088 (58.5)
AE	0.370 (14.0)	0.190 (7.2)	0.110 (4.2)	0.290 (11.0)	0.560 (21.2)	1.12 (42.4)
F	0.280 (18.9)	0.120 (8.1)	0.108 (7.3)	0.108 (7.3)	0.344 (23.3)	0.520 (35.1)
PA	0.207 (19.0)	0.036 (3.3)	0.117 (10.7)	0.063 (5.8)	0.238 (21.8)	0.429 (39.4)
A	0.069 (23.2)	0.013 (4.4)	0.035 (11.7)	0.010 (3.4)	0.066 (22.1)	0.105 (35.2)
FL	0.086 (17.9)	0.019 (4.0)	0.085 (17.7)	0.058 (12.1)	0.176 (36.6)	0.056 (11.7)
P	0.110 (17.5)	0.036 (5.7)	0.119 (18.9)	0.064 (10.2)	0.241 (38.3)	0.059 (9.4)
BaA	0.028 (8.0)	0.002 (0.6)	0.041 (11.8)	0.098 (28.2)	0.135 (38.8)	0.044 (12.6)
CH	0.056 (20.6)	-0.020[b] (-7.4)	0.086 (31.6)	0.025 (9.2)	0.112 (41.4)	0.013 (4.6)
BkF	0.098 (16.8)	-0.026[b] (-4.5)	0.140 (24.0)	0.108 (18.5)	0.244 (41.8)	0.020 (3.4)
BaP	0.165 (33.0)	-0.136[b] (-27.2)	0.194 (38.8)	0.068 (13.6)	0.175 (35.1)	0.034 (6.7)
IP	0.023 (11.3)	-0.009[b] (-4.4)	0.047 (23.2)	0.038 (18.7)	0.083 (41.0)	0.021 (10.2)
BghiP	0.002 (0.6)	0.003 (0.9)	0.078 (24.7)	0.070 (22.2)	0.161 (51.0)	0.002 (0.6)
DBahA	---- ----	---- ----	---- ----	---- ----	---- ----	---- ----

[a] Data from Table 51.
[b] Mean mass for filtrates from 150 µm sieve greater than that from 253 µm sieve (Table 49).

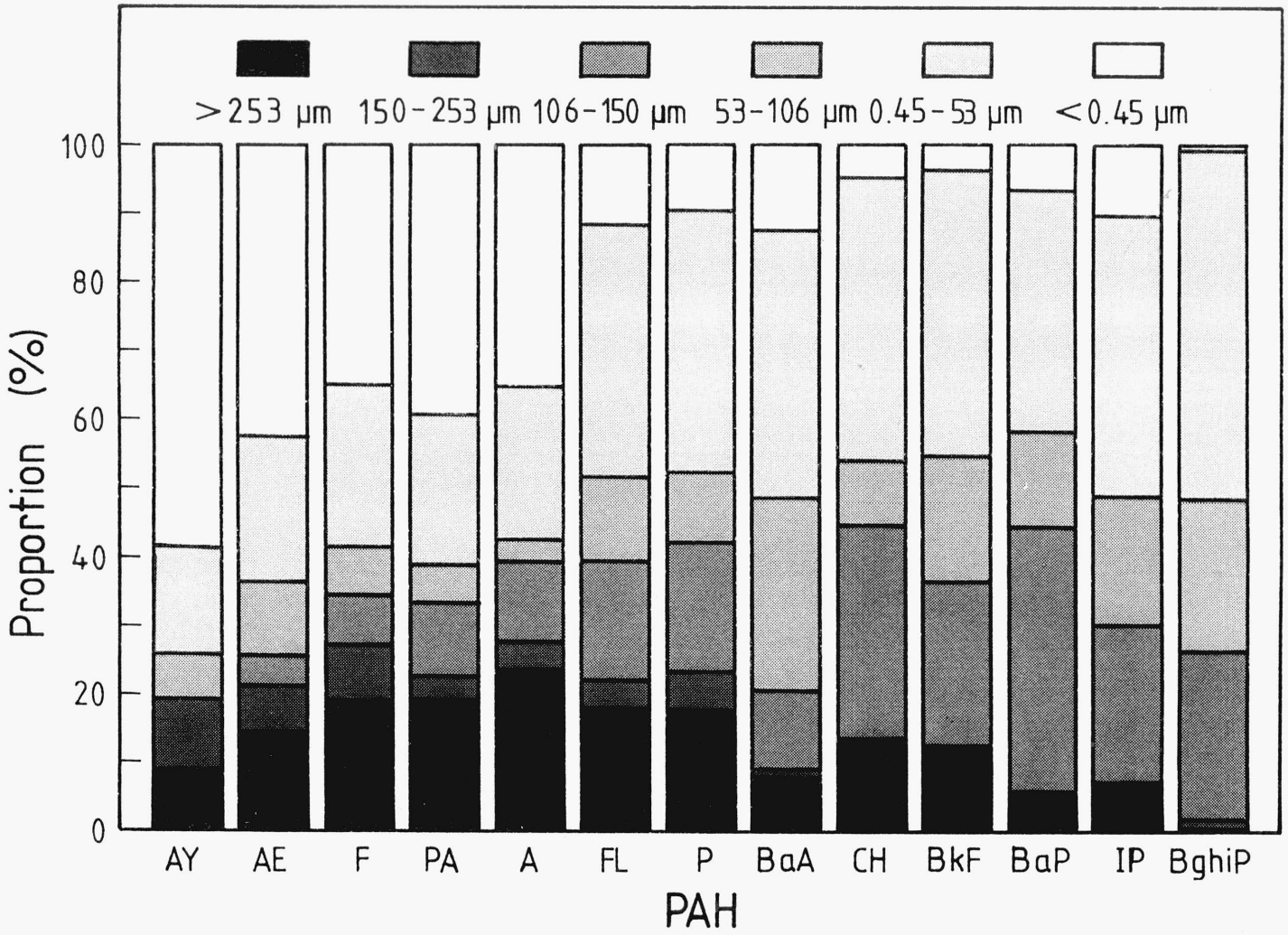


FIGURE 10
PAH Particle Size Distribution of a Sample of Raw Sewage
(Sample Volume Basis)

filtrate PAH mass on filtrate SS mass (Table 51). Statistically significant correlations, and linearity confirmed by scatter plots, permitted linear extrapolation of PAH mass (A) for zero mg SS, equivalent to filtrate from a 0.45 µm sieve (as used in the standard filtration procedure for SS; Section 3.1.2.2). The poor correlation for BaP may have been due to high values of RSD obtained for filtrate masses for this determinand (Table 49). Association of PAH with the particle size fraction >253 µm ranged from 0.6% (BghiP) to 33.0% (BaP) (Table 50), but with the fraction 150-253 µm proportions were small and tended to zero. Association with the fraction 106-150 µm ranged from 0% (AY) to 38.8% (BaP), a distinct trend of increase in proportion with increase in molecular weight of

TABLE 51
Linear Regression Analysis
of Filtrate PAH Mass on Filtrate SS Mass
Obtained in Particle Size Distribution Analysis

	Mass (µg) in filtrate from sieve[a]					
PAH	253 µm	150 µm	106 µm	53 µm	r[c]	A[d]
SS[b]	523	463	387	260		
AY	0.138	0.122	0.122	0.112	0.907*	0.088
AE	2.27	2.08	1.97	1.68	0.994*	1.12
F	1.20	1.08	0.972	0.864	0.981*	0.520
PA	0.883	0.847	0.730	0.667	0.973*	0.429
A	0.229	0.216	0.181	0.171	0.946*	0.105
FL	0.394	0.375	0.290	0.232	0.980*	0.056
P	0.519	0.483	0.364	0.300	0.973*	0.059
BaA	0.320	0.318	0.277	0.179	0.966*	0.044
CH	0.216	0.236	0.150	0.125	0.891*	0.013
BkF	0.486	0.512	0.372	0.264	0.948*	0.020
BaP	0.335	0.471	0.277	0.209	0.722	0.034
IP	0.180	0.189	0.142	0.104	0.949*	0.021
BghiP	0.314	0.311	0.233	0.163	0.977*	0.002
DBahA	-----	-----	-----	-----	-----	-----

[a] Data from Table 49 (means for four 1.00 l subsamples).
[b] Data in mg.
[c] Correlation coefficient.
[d] Constant term A: intercept for 0 mg SS, equivalent to filtrate (PAH, µg) from a 0.45 µm sieve.
* Correlation statistically significant at 95% confidence level. Scatter plots linear.

determinand in evidence. Variable proportions of PAH were associated with the size fraction 53-106 µm, ranging from 3.4% (A) to 28.2% (BaA), but association with SS (i.e. fractions >0.45 µm) was generally greatest for the smallest particle size fraction 0.45-53 µm, ranging from 15.7% (AY) to 51.0% (BghiP), the figures showing a trend of increasing proportion with increase in molecular weight. Association of PAH with the fraction <0.45 µm, representing the dissolved/colloidal phase, ranged from 3.4% (BkF) to 58.5% (AY), and exhibited a clear trend of rapidly decreasing proportion with increase in molecular weight. The values obtained for this phase agreed favourably with those attempted by centrifugation (Table 47).

4.2.2.2.2 PAH Particle Size Distribution on a Particle Mass Basis

The same data (Table 49) were expressed in terms of microgram PAH per gram (dry weight) of SS associated with each particle size fraction (Table 52). Relative proportions in each size fraction demonstrated no marked and consistent enrichment of PAH on a mass basis for any fraction, although there was evidence for enrichment of the low molecular weight PAH AY (52.5%), AE (28.6%) and F (27.9%) in the size fraction 150-253 µm, and enrichment of the remaining determinands in the next smallest class size (105-150 µm; ranging from 26.7% (BaA) to 65.1% (BaP)).

TABLE 52
PAH Particle Size Distribution in Sample of Raw Sewage Expressed as Microgram PAH per Gram, Dry Weight, SS

	Concentration (µg g^{-1}) and proportion (%, in parentheses) in particle size fraction				
PAH	>253 µm	150-253 µm	106-150 µm	53-106 µm	0.45-53 µm
AY	0.0722 (14.2)	0.267 (52.5)	0 ----	0.0787 (15.5)	0.0910 (17.9)
AE	2.06 (18.6)	3.17 (28.6)	1.45 (13.1)	2.28 (20.5)	2.16 (19.5)
F	1.56 (21.8)	2.00 (27.9)	1.42 (19.8)	0.850 (11.9)	1.33 (18.6)
PA	1.15 (24.5)	0.600 (12.8)	1.54 (32.8)	0.496 (10.6)	0.914 (19.4)
A	0.383 (27.6)	0.217 (15.6)	0.461 (33.2)	0.0787 (5.7)	0.254 (18.3)
FL	0.478 (15.7)	0.317 (10.4)	1.12 (36.7)	0.457 (15.0)	0.676 (22.2)
P	0.611 (14.5)	0.600 (14.3)	1.57 (37.3)	0.504 (12.0)	0.926 (22.0)
BaA	0.156 (7.7)	0.0333 (1.6)	0.539 (26.7)	0.772 (38.2)	0.520 (25.7)
CH	0.200 (10.2)	0 ----	1.13 (57.7)	0.197 (10.1)	0.433 (22.1)
BkF	0.400 (9.9)	0 ----	1.84 (45.7)	0.850 (21.1)	0.939 (23.3)
BaP	0.161 (4.1)	0 ----	2.55 (65.1)	0.535 (13.6)	0.675 (17.2)
IP	0.0778 (5.9)	0 ----	0.618 (47.2)	0.299 (22.8)	0.320 (24.4)
BghiP	0.0111 (0.5)	0.0500 (2.2)	1.03 (45.6)	0.551 (24.4)	0.620 (27.4)
DBahA	---- ----	---- ----	---- ----	---- ----	---- ----

4.2.3 Stability of PAH During Sedimentation

PAH removal via volatilisation and photodegradation, as potential removal mechanisms additional to sedimentation, was assessed on a sample of primary effluent. Four subsamples (1.00 l each) were each placed in a separating funnel as used for sample extraction, stoppered, and posited in the dark as control. A set of four subsamples were each placed in a tall-form beaker (1.5 l) and stored in the dark and in the absence of draughts to test for volatilisation, and a further set of four subsamples in stoppered separating funnels, as for the control, were exposed to light to test for photodegradation. After 48 h, subsamples were extracted *in situ* and determined (Table 53). Preservation of sample with formaldehyde solution was not performed in order to avoid the introduction of an unintentionable variable; determinand loss (Section 4.1.10) was assumed to be negligible. A

TABLE 53
Assessment of the Influence
of Volatilisation and Photodegradation
on Removal of PAH in a Sample of Settled Sewage Over 48 h

	Control subsample		Atmosphere-exposed subsample			Light-exposed subsample		
PAH	Mass[a] (µg)	RSD (%)	Mass[a] (µg)	RSD (%)	R[b] (%)	Mass[a] (µg)	RSD (%)	R[b] (%)
AY	0.0829	12.7	0.0487	14.4	41.3*	0.0407	2.2	50.9*
AE	1.19	9.5	0.588	8.6	50.6*	1.02	6.5	14.3*
F	0.669	10.1	0.409	7.3	38.9*	0.603	3.8	9.9
PA	0.522	8.8	0.453	4.8	13.2*	0.431	10.9	17.4*
A	0.128	7.0	0.0932	21.5	27.2*	0.0356	32.8	72.2*
FL	0.185	8.0	0.169	3.5	8.6*	0.118	30.9	36.2*
P	0.236	6.7	0.227	2.0	3.8	0.154	32.1	34.7*
BaA	0.0936	16.5	0.0821	13.7	12.3	0.0856	43.6	8.5
CH	0.0953	10.2	0.0897	4.4	5.9	0.0555	37.2	41.8*
BkF	0.152	22.3	0.146	7.7	3.9	0.108	30.6	28.9
BaP	0.157	18.0	0.147	3.4	6.4	0.106	22.9	32.5*
IP	0.0993	15.5	0.0710	8.4	28.5*	0.0690	33.1	30.5*
BghiP	0.192	12.9	0.165	13.5	14.1	0.163	34.6	15.1
DBahA	ND	----	ND	----	----	ND	----	----

[a] Mean for four 1.00 l subsamples.
[b] R = removal (relative to control subsample).
* Statistically significant at 95% confidence level.

parallel and simultaneous determination was performed with PAH spiked into each of three sets of four portions (1.00 l each) of glass-distilled deionised water, at concentrations employed previously (Section 4.1.10.2 and 4.2.2.1), and in vessels as above. These were stored alongside the corresponding subsamples of primary effluent, and extracted in situ and determined after the same time interval (Table 54). For the settled sewage experiment, application of a t test demonstrated significant removal in the subsamples testing volatilisation for the low molecular weight PAH AY (41.3%), AE (50.6%), F (38.9%), PA (13.2%), A (27.2%), FL (8.6%), and for one high molecular weight PAH IP (28.5%), although the result for this hydrocarbon should be treated with caution as mass determined in the test subsample was below the quantification limit. In the subsamples testing photodegradation significant removal was observed for AY (50.9%), AE (14.3%), PA (17.4%), A (72.2%), FL (36.2%), P (34.7%), CH (41.8%), BaP (32.5%) and IP

TABLE 54
Assessment of the Influence of Volatilisation and Photodegradation on Removal of PAH in a Sample of Distilled Water Over 48 h

	Control subsample		Atmosphere-exposed subsample			Light-exposed subsample		
PAH	Mass[a] (µg)	RSD (%)	Mass[a] (µg)	RSD (%)	R[b] (%)	Mass[a] (µg)	RSD (%)	R[b] (%)
AY	0.842	9.9	0.276	4.9	67.2*	0.783	8.6	7.0
AE	0.850	8.8	0.260	3.4	69.4*	0.663	10.1	22.0*
F	0.934	8.9	0.351	6.2	62.4*	0.841	5.0	10.0*
PA	0.920	7.0	0.534	5.1	42.0*	0.910	6.1	1.1
A	0.902	6.9	0.392	10.0	56.5*	ND	----	100.0*
FL	1.01	9.2	0.772	5.4	23.2*	0.830	4.5	17.4*
P	1.05	5.1	0.808	5.9	23.1*	0.318	8.6	69.7*
BaA	1.03	8.0	0.907	5.0	11.7*	ND	----	100.0*
CH	1.02	5.2	0.960	7.5	5.4	0.790	6.0	22.2*
BkF	0.246	6.5	0.256	11.2	-4.1	0.152	9.4	38.2*
BaP	0.274	6.7	0.185	7.2	32.5*	ND	----	100.0*
IP	0.206	8.5	0.197	10.4	4.4	0.144	10.6	30.1*
BghiP	0.234	5.4	0.241	4.6	-3.0	0.0888	6.3	62.1*
DBahA	0.266	10.2	0.266	9.9	0	0.130	9.0	51.1*

[a] Mean for four 1.00 l subsamples; analysis by GC.
[b] R = removal (relative to control subsample).
* Statistically significant at 95% confidence level.

(30.5%). Values of RSD were generally high for these subsamples. For the distilled water experiment, significant removal in the subsamples testing volatilisation was observed for AY (67.2%), AE (69.4%), F (62.4%), PA (42.0%), A (56.5%), FL (23.2%), P (23.1%), BaA (11.7%) and BaP (32.5%), a distinct trend (BaP excepting) of increase in removal with decrease in molecular weight of PAH in evidence. In the subsamples testing photodegradation removals of significance occured with AE (22.0%), F (10.0%), A (100.0%), FL (17.4%), P (69.7%), BaA (100.0%), CH (22.2%), BkF (38.2%), BaP (100.0%), IP (30.1%), BghiP (62.1%) and DBahA (51.1%), that is all PAH excepting AY and PA.

It was evident that the processes operating in the distilled water matrix were generally more rapid than those operating in the sewage matrix. In the case of volatilisation, it was probable that the reduced rates observed in the sample of settled sewage were due to PAH sorption onto solids accompanied by some sedimentation. With regard to photodegradation, suspended solids considerably reduced the susceptibility of the hydrocarbons to degradation by light by probable reduction of the attenuation and dispersion characteristics of the medium. However, possible sensitization of PAH by suspended solids and dissolved matter leading to increased photodegradation rates may have occured with AY (no significant removal in distilled water matrix, but 50.9% removal in sewage matrix), PA (0%, 17.4%), FL (17.4%, 36.2%) and CH (22.2%, 41.8%). Nevertheless, these increased removals together with those obtained generally for the sewage matrix over the 48 h experimentation period, suggest that the contribution of volatilisation and photodegradation to the removal of PAH during the comparatively rapid process of primary sedimentation would be minimal.

4.3 Removal Behaviour of PAH During Primary Sedimentation

Removal of PAH during primary sedimentation was formally evaluated by means of the primary sedimentation pilot plant. The experimental programme was designed to assess removal as influenced by the two major process parameters of hydraulic loading and SS loading determining unit process performance in terms of SS removal efficiency. The primary sedimentation pilot plant tanks were operated at four SS loadings at each of four hydraulic loadings. The four values of hydraulic loading, expressed as tank surface loading rate ($m^3\ m^{-2}\ d^{-1}$), were 6.10 (equivalent to 0.5 DWF), 12.2 (1.0 DWF), 36.6 (3.0 DWF) and 61.0 (5.0 DWF) (Table 20). The respective theoretical tank hydraulic retention times were 4.58, 2.29, 0.76 and 0.46 h, and were directly inversely proportional to hydraulic loading. The four values of SS loading attempted were by way of mean nominal increases in SS concentration of approximately 150, 300 and 450 mg l^{-1} (i.e. 150 mg l^{-1} increments) above a mean raw influent concentration of approximately 400 mg l^{-1}, to effect four SS loadings of 400 mg l^{-1} (unamended, designated SS_0), 550 mg l^{-1} (SS_1), 700 mg l^{-1} (SS_2) and 850 mg l^{-1} (SS_3). Each experiment consisted in operation of a tank at a particular hydraulic and SS loading. The total combination of four values of each process parameter therefore constituted 16 experiments (Table 21). The twin sedimentation tanks of the pilot plant were operated in parallel at a common hydraulic loading but with differing SS loading, thus enabling experiments to be executed in pairs (Table 21).

The sampling frequency for each experiment was flow proportional (Table 22), but a total of ten successive influent and ten successive effluent composite samples (each of six consecutive grab samples) were collected per experiment/tank. The sampling programme therefore provided for each experiment an identical number of composite samples obtained over an identical number of tank retention times (13) and total flow (14200 l). One grab sample of sludge was collected per experiment for computation of a mass balance. Each sample was determined for SS, NVSS, VSS, COD_{tot} and COD_{sol}. For each experiment, samples were

further composited to yield overall five influent and five effluent composite samples for PAH determination by pairing composite samples adjacent in the collection sequence. An experiment thus consisted in fixing two process parameters (hydraulic loading and SS loading) and subsequently measuring for determinands (PAH) and co-determinands (SS, NVSS, VSS, COD_{tot} and COD_{sol}). Measurement of co-determinands permitted:

1. The performance of the pilot plant to be monitored and assessed.
2. The influence of the co-determinands on PAH removal to be determined to facilitate a greater understanding of PAH removal behaviour during primary sedimentation.

4.3.1 Evaluation of Primary Sedimentation Pilot Plant Performance

4.3.1.1 Removal of Co-Determinands

4.3.1.1.1 Range of Removals Observed

Mean influent (n = 10), mean effluent (n = 10) and sludge concentration (n = 1) of SS, NVSS, VSS, COD_{tot} and COD_{sol} were calculated for each experiment (Table 71, Appendix 3). Based on a precision of measurement for a single result of ±7.5% for SS, ±15.3% NVSS, ±10.0% VSS, ±28.8% COD_{tot} and ±30.7% COD_{sol} (95% confidence limits, n = 8), errors associated with values of mean influent and mean effluent concentration were ±2.4% for SS, ±4.8% NVSS, ±3.2% VSS, ±9.1% COD_{tot} and ±9.7% COD_{sol}. Values of mean influent SS concentration represented the actual SS loadings achieved at each hydraulic loading of the pilot plant. SS_0 ranged from 322 to 442 mg l^{-1}, SS_1 464-792 mg l^{-1}, SS_2 651-822 mg l^{-1}, and SS_3 767-981 mg l^{-1}. However, mean values for SS_0 were 402 mg l^{-1}, SS_1 575 mg l^{-1}, SS_2 733 mg l^{-1} and SS_3 888 mg l^{-1}, and approximated the intended SS loadings of 400 mg l^{-1} (for SS_0), 550 mg l^{-1} (SS_1), 700 mg l^{-1} (SS_2) and 850 mg l^{-1} (SS_3). The difficulty of amending raw sewage of continuously varying SS concentration in a feed-back mode was responsible for deviation from target values.

The data (Table 71) were utilised to calculate a removal efficiency and a mass balance for each co-determinand for each experiment (Table 55) using equations (7) and (8):

$$R = \frac{100(C_I - C_E)}{C_I} \quad (7)$$

where R = removal efficiency (%)
C_I = mean influent concentration (mg l^{-1})
C_E = mean effluent concentration (mg l^{-1})

$$MB = \frac{100C_I}{C_E + \frac{C_S V_T}{V_F}} \quad (8)$$

where MB = mass balance (%) (approx.)
C_I = mean influent concentration (mg l^{-1})
C_E = mean effluent concentration (mg l^{-1})
C_S = sludge concentration (mg l^{-1})
V_T = tank volume (915 l)
V_F = total flow (14200 l)

Mass balances, representing the ratio of influent mass to combined effluent and sludge mass, were calculated to permit an indication of the reliability of the computed removal efficiencies. They were generally acceptable: mean mass balance for SS was 109%, NVSS 95%, VSS 114%, COD_{tot} 96% and COD_{sol} 90%. Mass balances of 100% would be expected assuming conservative partitioning of co-determinand between influent, effluent and sludge and assuming perfect techniques of sampling, but variations herein may largely be ascribed to unrepresentativeness of the single sample of sludge obtained for each experiment and whose result is employed in the mass balance calculation.

Ranges of removals were 47.3-78.7% (overall mean 65.0%) for SS, 27.1-62.9% (47.0%) NVSS, 50.0-82.8% (70.5%) VSS, 26.5-66.8% (51.1%) COD_{tot} and 0-37.7% (14.5%) COD_{sol}. The approximate errors associated with each removal were (for 50.0% removal) ±3.0% for SS, ±5.9% NVSS, ±4.0% VSS, ±11.1% COD_{tot} and ±11.9% COD_{sol} (95% confidence limits;

TABLE 55
Removal Efficiency and Mass Balance of SS, NVSS, VSS, Total and Soluble COD Obtained at Each Hydraulic and SS Loading of the Primary Sedimentation Pilot Plant

Hydraulic loading	SS loading[a]		Removal (R, %) and mass balance (MB, %)[b] SS	NVSS	VSS	COD_{tot}	COD_{sol}
0.5 DWF	SS_0	R	70.3	42.0	77.4	52.2	0
		MB	147	101	166	124	84
	SS_1	R	74.2	52.5	80.0	56.6	4.3
		MB	146	119	156	131	91
	SS_2	R	78.7	62.9	82.8	63.6	7.5
		MB	155	133	162	131	78
	SS_3	R	76.9	62.9	80.3	66.8	0
		MB	121	108	125	113	72
1.0 DWF	SS_0	R	58.4	48.3	60.7	50.1	3.0
		MB	97	82	102	89	83
	SS_1	R	67.0	57.5	68.9	63.4	2.8
		MB	88	83	89	78	78
	SS_2	R	64.3	37.7	75.7	60.4	31.9
		MB	123	100	136	104	83
	SS_3	R	64.6	30.1	77.1	58.3	34.7
		MB	98	86	103	76	79
3.0 DWF	SS_0	R	47.3	38.0	50.0	26.5	9.0
		MB	87	85	88	74	78
	SS_1	R	69.1	61.1	71.0	38.1	14.2
		MB	93	84	96	77	91
	SS_2	R	67.5	51.6	71.2	42.5	11.2
		MB	90	73	96	55	80
	SS_3	R	64.8	59.1	66.1	46.7	13.5
		MB	124	127	123	102	94
5.0 DWF	SS_0	R	55.7	36.5	61.5	57.9	24.6
		MB	90	82	93	122	103
	SS_1	R	55.2	27.1	66.0	40.1	16.6
		MB	85	73	90	93	105
	SS_2	R	59.6	28.7	70.2	47.3	37.7
		MB	88	75	93	87	128
	SS_3	R	66.4	55.0	69.1	47.2	19.8
		MB	106	105	106	80	111

[a] Mean SS_0 = 402, SS_1 = 575, SS_2 = 733, SS_3 = 888 mg l^{-1}. Individual values given in Table 71.
[b] Calculation based on data in Table 71.

absolute). Data (SS, COD_{tot}) relating to sedimentation of the influent raw sewage (unamended) in the adjacent Hogsmill Valley Water Pollution Control Works during pilot plant operation are presented (Table 72, Appendix 4).

4.3.1.1.2 Influence of Hydraulic Loading and SS Loading on Removals

Removal efficiency data (Table 55) were so arranged to assess the overall influence of hydraulic loading and SS loading, separately, on co-determinand removal (Table 56). Mean removals at hydraulic loadings of 0.5, 1.0, 3.0 and 5.0 DWF respectively were 75.0, 63.6, 62.2 and 59.2% for SS, 55.1, 43.4, 52.5 and 36.8% for NVSS, 80.1, 70.6, 64.6 and 66.7% for VSS, 59.8, 58.1, 38.5 and 48.1% for COD_{tot}.

TABLE 56
Influence of Hydraulic and SS Loading on Removal Efficiency (%) of SS, NVSS, VSS, Total and Soluble COD

Co-determinand	Hydraulic loading	SS loading[a]				
		SS_0	SS_1	SS_2	SS_3	Mean
SS	0.5 DWF	70.3	74.2	78.7	76.9	75.0
	1.0 DWF	58.4	67.0	64.3	64.6	63.6
	3.0 DWF	47.3	69.1	67.5	64.8	62.2
	5.0 DWF	55.7	55.2	59.6	66.4	59.2
	Mean	57.9	66.4	67.5	68.2	65.0
NVSS	0.5 DWF	42.0	52.5	62.9	62.9	55.1
	1.0 DWF	48.3	57.5	37.7	30.1	43.4
	3.0 DWF	38.0	61.1	51.6	59.1	52.5
	5.0 DWF	36.5	27.1	28.7	55.0	36.8
	Mean	41.2	49.6	45.2	51.8	47.0
VSS	0.5 DWF	77.4	80.0	82.8	80.3	80.1
	1.0 DWF	60.7	68.9	75.7	77.1	70.6
	3.0 DWF	50.0	71.0	71.2	66.1	64.6
	5.0 DWF	61.5	66.0	70.2	69.1	66.7
	Mean	62.4	71.5	75.0	73.2	70.5
COD_{tot}	0.5 DWF	52.2	56.6	63.6	66.8	59.8
	1.0 DWF	50.1	63.4	60.4	58.3	58.1
	3.0 DWF	26.5	38.1	42.5	46.7	38.5
	5.0 DWF	57.9	40.1	47.3	47.2	48.1
	Mean	46.7	49.6	53.5	54.8	51.1
COD_{sol}	0.5 DWF	0	4.3	7.5	0	3.0
	1.0 DWF	3.0	2.8	31.9	34.7	18.1
	3.0 DWF	9.0	14.2	11.2	13.5	12.0
	5.0 DWF	24.6	16.6	37.7	19.8	24.7
	Mean	9.2	9.5	22.1	17.0	14.5

[a] Mean SS_0 = 402, SS_1 = 575, SS_2 = 733, SS_3 = 888 mg l^{-1}.

and 3.0, 18.1, 12.0 and 24.7% for COD_{sol}. Mean removals at SS loadings of SS_0 (402 mg l^{-1}), SS_1 (575 mg l^{-1}), SS_2 (733 mg l^{-1}) and SS_3 (888 mg l^{-1}) respectively were 57.9, 66.4, 67.5 and 68.2% for SS, 41.2, 49.6, 45.2 and 51.8% for NVSS, 62.4, 71.5, 75.0 and 73.2% for VSS, 46.7, 49.6, 53.5 and 54.8% for COD_{tot}, and 9.2, 9.5, 22.1 and 17.0% for COD_{sol}. Considering the approximate errors associated with each mean removal value which were ±1.5% for SS, ±3.0% NVSS, ±2.0% VSS, ±5.6% COD_{tot} and ±6.0% COD_{sol} (95% confidence limits for 50.0% removal; absolute), mean removals generally increased with increase in SS loading but decreased with increase in hydraulic loading. The major exception was for COD_{sol} where removals, which tended toward zero at low hydraulic loadings, generally increased with increase in hydraulic load; a not unexpected result in view of the essentially soluble nature of the constituents measured by this pollutant parameter. The similar removal behaviour of the co-determinands under the influence of the two process parameters was a consequence of the inter-relatedness of the pollutant parameters. A linear relationship has been shown between SS and VSS concentration of raw sewage (Tebbutt & Christoulas, 1975), and a linear dependence of COD_{tot} removal on SS removal during primary sedimentation (Tebbutt, 1979; Tebbutt & Christoulas, 1975). In the present study, mean ratio (expressed as a percentage) of mean influent NVSS concentration to mean influent SS concentration was 21.8% (RSD 17.8%, n = 16), VSS to SS 78.2% (RSD 5.0%), COD_{sol} to COD_{tot} 18.0% (RSD 19.7%) and SS to COD_{tot} 70.5% (RSD 15.2%).

4.3.1.2 Assessment of Removal of SS

Removal behaviour of SS is of special importance as sedimentation tank design and tank performance are expressed in terms of removal efficiency of SS (Section 1.8.2).

4.3.1.2.1 Influence of Hydraulic Loading on Removal

Mean removal of SS at each hydraulic loading (Table 56) was plotted (Figure 11). The increase in loading from 0.5 to 1.0 DWF effected a relatively large decrease in mean SS removal of 11.4% (absolute), whereas the continued increase to 5.0 DWF brought about only a modest reduction in mean removal of 4.4% (absolute), the overall reduction being 15.8%.

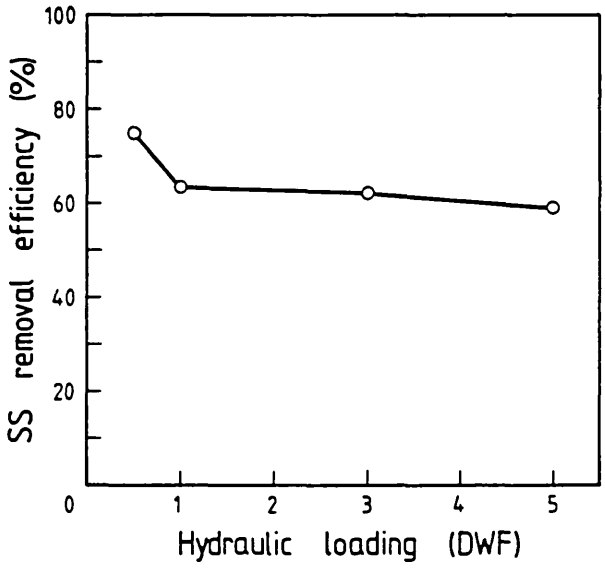


FIGURE 11
Influence of
Pilot Plant Hydraulic Loading
on Mean Removal of SS

4.3.1.2.2 Influence of SS Loading on Removal

A plot of mean SS removal against SS loading (Figure 12) showed a relatively large increase in mean SS removal of 8.5% (absolute) with increase in loading from 402 mg l^{-1} (SS_0) to 575 mg l^{-1} (SS_1), but a relatively small increase of 1.8% in mean removal with loading increased to 888 mg l^{-1} (SS_3). However, the overall increase in removal of 10.3% was less than the corresponding change effected by hydraulic loading (15.8%), thus demonstrating the greater influence of the latter process parameter under the range of conditions studied (mean SS loading 402-888 mg l^{-1}, an approximate two-fold range; hydraulic loading 0.5-5.0 DWF, a ten-fold range).

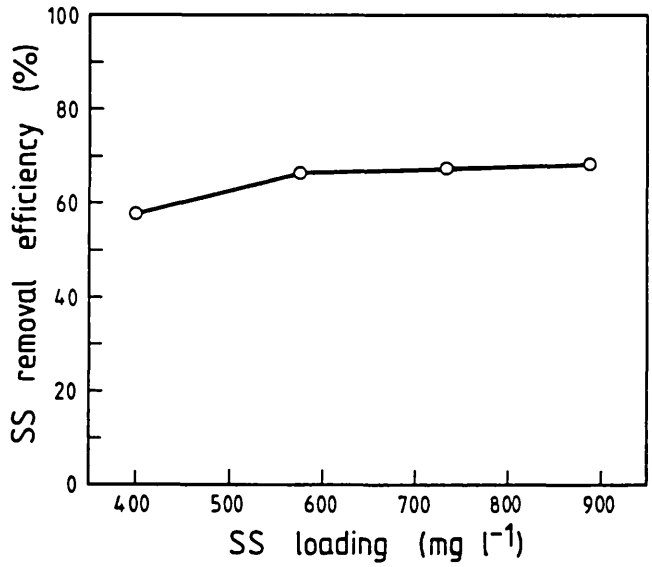


FIGURE 12
Influence of
Pilot Plant SS Loading
on Mean Removal of SS

4.3.2 Removal of PAH

4.3.2.1 Range of Removals Observed

Results for the determination of PAH in each of the five influent and five effluent composite samples and one sludge sample generated for each experiment, together with values of mean influent and mean effluent concentration in each case, are presented (Table 73-88, Appendix 5). The errors for single results are those already reported (Table 43, 'Total error' column), but errors associated with mean values of influent and effluent concentration were (by propagation) ±7.9% for AY, ±5.8% AE, ±5.9% F, ±4.7% PA, ±6.1% A, ±4.6% FL, ±5.9% P, ±6.4% BaA, ±7.5% CH, ±8.1% BkF, ±7.5% BaP, ±9.5% IP, ±6.8% BghiP and ±8.5% DBahA (95% confidence limits).

The data were employed to calculate a removal efficiency (Table 57) and a mass balance (Table 58) for each PAH for each experiment from equations (7) and (8). Mass balances were generally acceptable. Mean mass balance for each PAH ranged from 81% (BghiP) to 99% (BaA) and mean mass balance per experiment ranged from 68% (5.0 DWF, SS_1 (575 mg l^{-1})) to 128% (0.5 DWF, SS_2 (733 mg l^{-1})), with an overall mean of 88%.

Ranges of removal of PAH (Table 57; data expressed as in Table 56) were 0-47.4% (overall mean 21.3%) for AY, 3.6-55.2% (34.9%) AE, 9.7-61.4% (37.6%) F, 17.6-64.9% (44.3%) PA, 30.3-66.5% (42.5%) A, 30.5-67.5% (52.9%) FL, 31.7-71.2% (54.1%) P, 44.7-80.5% (63.0%) BaA, 36.0-73.0% (54.9%) CH, 42.5-79.6% (59.4%) BkF, 44.2-78.8% (59.3%) BaP, 34.0-78.2% (54.3%) IP, 27.6-76.4% (50.5%) BghiP, and 29.6-79.2% (52.1%) DBahA. The approximate errors associated with each removal were (for 50.0% removal) ±9.7% for AY, ±7.1% AE, ±7.3% F, ±5.8% PA, ±7.5% A, ±5.7% FL, ±7.3% P, ±7.9% BaA, ±9.2% CH, ±9.9% BkF, ±9.2% BaP, ±11.6% IP, ±8.4% BghiP and ±10.4% DBahA (95% confidence limits; absolute). Removal ranges, in terms of absolute percentages, were bounded by a minimum of 34.6% (BaP) and a maximum of 51.7% (F), with a mean of 42.7%. Overall mean removals of PAH generally increased with increase in molecular weight of determinand up to BaA, after which

TABLE 57
Influence of Hydraulic and SS Loading
on Removal Efficiency (%) of PAH[a]

PAH	Hydraulic loading	SS loading[b] SS_0	SS_1	SS_2	SS_3	Mean
AY	0.5 DWF	0	47.4	47.2	18.6	28.3
	1.0 DWF	3.7	5.6	32.9	36.5	19.7
	3.0 DWF	18.1	0	0	34.8	13.2
	5.0 DWF	24.9	21.2	23.3	26.9	24.1
	Mean	11.7	18.6	25.9	29.2	21.3
AE	0.5 DWF	3.6	40.7	55.2	51.7	37.8
	1.0 DWF	32.1	41.0	44.2	44.4	40.4
	3.0 DWF	27.0	26.3	31.2	42.9	31.9
	5.0 DWF	22.9	22.7	26.9	44.9	29.4
	Mean	21.4	32.7	39.4	46.0	34.9
F	0.5 DWF	19.0	46.2	61.4	50.8	44.4
	1.0 DWF	40.9	43.8	42.3	49.2	44.1
	3.0 DWF	33.0	29.6	35.6	46.2	36.1
	5.0 DWF	9.7	25.1	26.5	41.9	25.8
	Mean	25.7	36.2	41.5	47.0	37.6
PA	0.5 DWF	42.5	57.0	64.9	57.3	55.4
	1.0 DWF	38.3	46.7	44.0	53.2	45.6
	3.0 DWF	37.2	42.6	46.0	51.6	44.4
	5.0 DWF	17.6	32.0	32.1	45.9	31.9
	Mean	33.9	44.6	46.8	52.0	44.3
A	0.5 DWF	40.9	43.2	66.5	57.0	51.9
	1.0 DWF	30.3	33.8	41.3	51.4	39.2
	3.0 DWF	31.9	31.9	45.5	45.6	38.7
	5.0 DWF	31.1	34.7	40.7	54.7	40.3
	Mean	33.6	35.9	48.5	52.2	42.5
FL	0.5 DWF	58.0	62.0	66.8	67.5	63.6
	1.0 DWF	42.1	51.2	51.6	60.8	51.4
	3.0 DWF	42.6	53.2	56.9	56.0	52.2
	5.0 DWF	30.5	42.5	47.4	56.6	44.3
	Mean	43.3	52.2	55.7	60.2	52.9
P	0.5 DWF	64.3	65.0	67.4	71.2	67.0
	1.0 DWF	40.7	52.1	53.6	59.8	51.6
	3.0 DWF	42.8	53.2	56.5	54.9	51.9
	5.0 DWF	31.7	45.3	48.7	57.1	45.7
	Mean	44.9	53.9	56.6	60.8	54.1
BaA	0.5 DWF	79.6	68.9	72.2	80.5	75.3
	1.0 DWF	59.0	67.7	64.4	69.8	65.2
	3.0 DWF	44.9	56.0	61.6	60.9	55.9
	5.0 DWF	44.7	56.0	56.1	66.1	55.7
	Mean	57.1	62.2	63.6	69.3	63.0

/Continued overleaf

TABLE 57/Continued

PAH	Hydraulic loading	SS loading[b] SS_0	SS_1	SS_2	SS_3	Mean
CH	0.5 DWF	65.7	64.2	63.3	73.0	66.6
	1.0 DWF	39.5	47.6	53.5	58.0	49.7
	3.0 DWF	47.5	58.9	60.5	57.0	56.0
	5.0 DWF	36.0	45.9	47.5	60.0	47.4
	Mean	47.2	54.2	56.2	62.0	54.9
BkF	0.5 DWF	75.8	63.0	59.7	79.6	69.5
	1.0 DWF	53.4	58.0	60.8	64.4	59.2
	3.0 DWF	50.6	56.3	58.6	60.2	56.4
	5.0 DWF	42.5	51.7	53.6	62.6	52.6
	Mean	55.6	57.3	58.2	66.7	59.4
BaP	0.5 DWF	74.8	63.6	58.2	78.8	68.9
	1.0 DWF	48.8	49.1	61.6	67.5	56.8
	3.0 DWF	52.8	53.5	61.8	62.5	57.7
	5.0 DWF	44.2	50.6	53.7	66.3	53.7
	Mean	55.2	54.2	58.8	68.8	59.3
IP	0.5 DWF	69.6	49.1	47.7	78.2	61.2
	1.0 DWF	59.8	48.1	57.4	63.5	57.2
	3.0 DWF	50.9	50.3	52.4	61.3	53.7
	5.0 DWF	34.3	53.0	34.0	59.2	45.1
	Mean	53.7	50.1	47.9	65.6	54.3
BghiP	0.5 DWF	63.3	51.9	48.6	76.4	60.1
	1.0 DWF	47.5	28.3	53.8	57.8	46.9
	3.0 DWF	48.8	49.6	53.6	59.1	52.8
	5.0 DWF	27.6	43.1	43.0	55.8	42.4
	Mean	46.8	43.2	49.8	62.3	50.5
DBahA	0.5 DWF	60.7	47.9	46.5	79.2	58.6
	1.0 DWF	----	----	56.9	65.1	61.0
	3.0 DWF	48.2	50.6	40.1	59.2	49.5
	5.0 DWF	29.6	48.8	45.0	51.1	43.6
	Mean	46.2	49.1	47.1	63.7	52.1

[a] Removal efficiencies calculated from mean values in Table 73 to 88.
[b] Mean SS_0 = 402, SS_1 = 575, SS_2 = 733, SS_3 = 888 mg l^{-1}.

removals decreased (Figure 13). This trend could be observed in the results of any one experiment.

TABLE 58
Mass Balance of PAH Obtained During the
Primary Sedimentation Pilot Plant Experimentation Programme

	Mass balance (%)[a] at each hydraulic and SS loading[b]																
	0.5 DWF				1.0 DWF				3.0 DWF				5.0 DWF				
PAH	SS_0	SS_1	SS_2	SS_3	SS_0	SS_1	SS_2	SS_3	SS_0	SS_1	SS_2	SS_3	SS_0	SS_1	SS_2	SS_3	Mean
AY	60	125	121	83	87	88	88	75	94	59	53	115	101	80	82	86	87
AE	76	91	121	96	84	89	87	71	106	71	68	122	91	80	78	99	89
F	83	88	120	90	89	90	86	78	102	71	70	117	76	77	72	89	87
PA	99	89	129	94	81	88	81	80	97	74	71	119	74	72	68	85	88
A	80	73	152	68	77	75	77	76	97	60	73	113	86	73	76	87	84
FL	112	102	133	97	75	83	77	79	95	74	70	120	77	69	70	79	88
P	111	129	153	90	72	80	83	82	96	74	73	117	77	67	73	79	91
BaA	145	182	207	93	68	76	85	91	84	73	74	120	80	61	74	75	99
CH	118	124	122	100	76	79	79	79	102	78	74	119	75	68	69	82	90
BkF	125	127	120	99	77	79	80	79	93	74	71	118	74	59	66	64	88
BaP	114	151	137	94	74	77	78	79	90	69	69	111	75	58	70	65	88
IP	112	102	92	104	95	92	76	79	86	72	69	118	69	58	50	61	83
BghiP	107	96	93	99	88	74	78	73	89	71	69	110	69	61	65	59	81
DBahA	105	96	98	115	---	---	81	77	82	73	65	113	68	65	65	59	83
Mean:	103	113	128	94	80	82	81	78	94	71	69	117	78	68	70	76	88

[a] Calculation based on data in Table 73 to 88.
[b] Mean SS_0 = 402, SS_1 = 575, SS_2 = 733, SS_3 = 888 mg l^{-1}. Individual values given in Table 71.

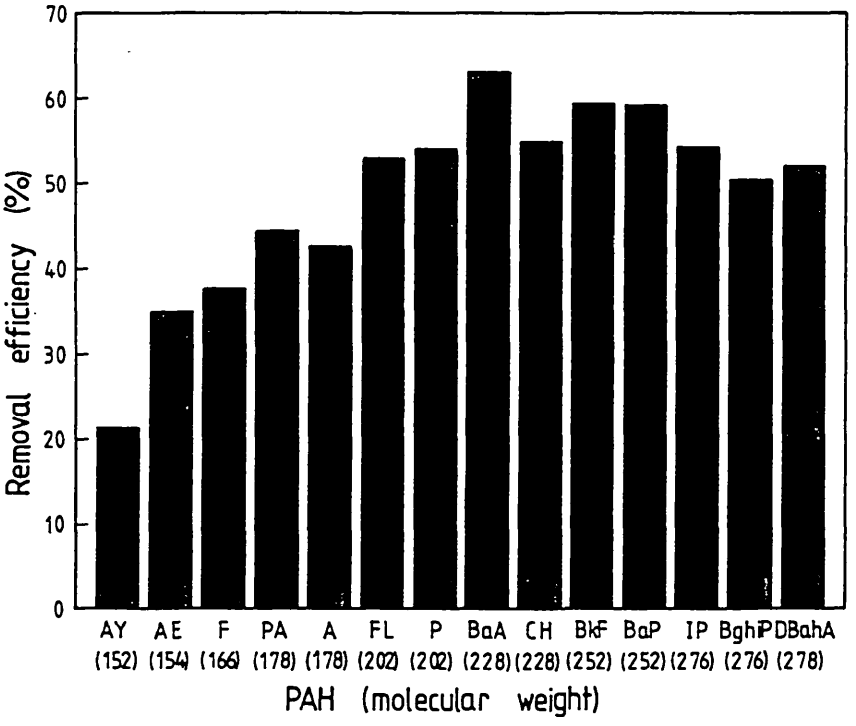


FIGURE 13
Overall Mean Removals of PAH
Achieved During the Pilot Plant
Experimentation Programme

4.3.2.2 Influence of Hydraulic Loading on Removals

The SS-averaged and flow-averaged mean removals (Table 57) permitted assessment of the influence of hydraulic loading and SS loading respectively on PAH removal. The approximate errors associated with each mean removal value ranged from ±2.9% (PA, FL) to ±5.8% (IP), a mean for all PAH of ±4.2% (95% confidence limits for 50.0% removal; absolute). The SS-averaged mean removals revealed that hydraulic loading exerted a modest influence. Mean removals decreased with increase in loading from 0.5 to 5.0 DWF for F (from 44.4 to 25.8%), PA (55.4-31.9%), BaA (75.3-55.7%), BkF (69.5-52.6%) and IP (61.2-45.1%). Small variances in mean removals, within error, at loadings of 1.0 and 3.0 DWF disrupted the trend for FL (63.6, 51.4, 52.2 and 44.3% for loadings of 0.5, 1.0, 3.0 and 5.0 DWF respectively), P (67.0, 51.6, 51.9, 45.7%) and BaP (68.9, 56.8, 57.7, 53.7%); and at 0.5 and 1.0 DWF for AE (37.8, 40.4, 31.9, 29.4%) and DBahA (58.6, 61.0, 49.5, 43.6%); and at 1.0, 3.0 and 5.0 DWF for A (51.9, 39.2, 38.7, 40.3%). No distinct trend was apparent for the remaining PAH: AY (28.3, 19.7, 13.2, 24.1%), CH (66.6, 49.7, 56.0, 47.4%) and BghiP (60.1, 46.9, 52.8, 42.4%).

The influence of hydraulic loading on removal of PAH was evaluated more rigourously by performing a correlation analysis (Table 59). Correlation of mean removals of each PAH against corresponding hydraulic loading (column 2) resulted in statistically significant correlations only for AE, F, PA, IP and DBahA. The poor correlations were confirmed by repeating the analysis for removals at each SS loading (SS_0, SS_1, SS_2, SS_3, Table 57; column 3-6, Table 59). The inconsistency of correlations here may be partly attributable to the inequality of individual SS loadings embraced by each of SS_0, SS_1, etc (Section 4.3.1.1.1), but the general lack of correlation with the SS-averaged mean removals (column 2), where mean SS loadings were similar at each hydraulic loading (691 mg l^{-1} at 0.5 DWF, 584 mg l^{-1} at 1.0 DWF, 742 mg l^{-1} at 3.0 DWF, and 581 mg l^{-1} at 5.0 DWF), confirmed that the influence of hydraulic loading on PAH removal was essentially weak.

TABLE 59
Correlation of Removal Efficiency of PAH on Hydraulic Loading

PAH	Correlation coefficient (r) at SS loading[a]				
	All SS[b]	SS_0	SS_1	SS_2	SS_3
AY	-0.210	0.940*	-0.247	-0.462	0.170
AE	-0.935*	0.410	-0.964*	-0.940*	-0.551
F	-0.991*	-0.565	-0.976*	-0.899*	-0.996*
PA	-0.928*	-0.914*	-0.949*	-0.829	-0.955*
A	-0.546	-0.547	-0.531	-0.615	-0.178
FL	-0.831	-0.865	-0.847	-0.700	-0.812
P	-0.785	-0.784	-0.817	-0.754	-0.703
BaA	-0.860	-0.828	-0.917*	-0.917*	-0.692
CH	-0.638	-0.653	-0.524	-0.677	-0.516
BkF	-0.854	-0.816	-0.935*	-0.928*	-0.660
BaP	-0.736	-0.694	-0.510	-0.605	-0.635
IP	-0.980*	-0.981*	0.947*	-0.749	-0.748
BghiP	-0.696	-0.897*	0.131	-0.596	-0.667
DBahA	-0.970*	-0.983*	0.385	-0.510	-0.903*

[a] Calculated from data in Table 57, assuming normal distribution of hydraulic loading. Removal efficiency data arcsin transformed. Mean SS_0 = 402, SS_1 = 575, SS_2 = 733, SS_3 = 888 mg l^{-1}.
[b] Calculated from means in Table 57.
* Correlation statistically significant at 95% confidence level.

4.3.2.3 Influence of SS Loading on Removals

The flow-averaged mean removals revealed a noted influence of SS loading on PAH removal (Table 57). Mean removals increased with increase in loading from SS_0 (402 mg l^{-1}) to SS_3 (888 mg l^{-1}) for AY (from 11.7 to 29.2%), AE (21.4-46.0%), F (25.7-47.0%), PA (33.9-52.0%), A (33.6-52.2%), FL (43.3-60.2%), P (44.9-60.8%), BaA (57.1-69.3%), CH (47.2-62.0%) and BkF (55.6-66.7%). Only for four of the highest molecular weight PAH did small variances in mean removals, within error, disrupt the trend: at loadings of SS_0 and SS_1 for BaP (55.2, 54.2, 58.8 and 68.8% for loadings of SS_0 (402 mg l^{-1}), SS_1 (575 mg l^{-1}), SS_2 (733 mg l^{-1}) and SS_3 (888 mg l^{-1}) respectively) and BghiP (46.8, 43.2, 49.8, 62.3%); at SS_1 and SS_2 for DBahA (46.2, 49.1, 47.1, 63.7%); and at SS_0,

SS_1 and SS_2 for IP (53.7, 50.1, 47.9, 65.6%). Ranges of mean removals, in terms of absolute percentages, for those PAH exhibiting the trend, were similar: 17.5% for AY, 24.6% AE, 21.3% F, 18.1% PA, 18.6% A, 16.9% FL, 15.9% P, 12.2% BaA, 14.8% CH and 11.1% BkF.

Correlation analysis confirmed the influence of SS loading on removal of PAH (Table 60). Correlation of mean removals of each PAH against corresponding mean SS loading (402, 575, 733, 888 mg l^{-1}) (column 2) produced statistically significant correlations for PAH of molecular weight 152 to 252 (BaP excepting). Analysis of removals at each hydraulic loading (Table 57) against the appropriate individual SS loading (Table 71) resulted in less consistent correlations (column 3-6, Table 59); the greater accuracy afforded by averaging can be taken to be responsible for the consistent correlations obtained with the flow-averaged mean removals (column 2).

TABLE 60
Correlation of Removal Efficiency of PAH on SS Loading

	Correlation coefficient (r) at hydraulic loading[a]				
PAH	All DWF[b]	0.5 DWF	1.0 DWF	3.0 DWF	5.0 DWF
AY	0.987*	0.394	0.945*	-0.085	0.612
AE	0.990*	0.800	0.880*	0.661	0.901*
F	0.985*	0.740	0.826	0.539	0.856
PA	0.963*	0.664	0.861	0.929*	0.843
A	0.959*	0.767	0.986*	0.706	0.960*
FL	0.983*	0.952*	0.945*	0.962*	0.910*
P	0.973*	0.977*	0.939*	0.948*	0.874
BaA	0.977*	0.232	0.773	0.958*	0.849
CH	0.983*	0.663	0.986*	0.873	0.894*
BkF	0.881*	0.199	0.991*	0.984*	0.895*
BaP	0.866	0.175	0.963*	0.751	0.929*
IP	0.535	0.304	0.442	0.615	0.401
BghiP	0.811	0.450	0.586	0.766	0.834
DBahA	0.785	0.541	-----	0.309	0.627

[a] Calculated from data in Table 57 and 71. Removal efficiency data arcsin transformed.
[b] Calculated from means in Table 57.
* Correlation statistically significant at 95% confidence level.

4.3.2.4 Influence of Co-Determinand Removals on PAH Removals

Having investigated the influence on PAH removal of process parameter (hydraulic loading and SS loading), the influence on hydrocarbon removal of removal of SS (Table 61), NVSS (Table 62), VSS (Table 63), COD_{tot} (Table 64) and COD_{sol} (Table 65) achieved during sedimentation was evaluated. In each case, two sets of calculations were performed. Flow-averaged and SS-averaged mean removals of PAH (Table 57) were correlated against the corresponding flow-averaged and SS-averaged mean removals of co-determinand (Table 56) respectively, permitting correlation at variable SS loading (i.e. constant hydraulic loading (mean of 2.4 DWF)) and at variable hydraulic loading (i.e. constant SS loading (mean of 650 mg l^{-1})). Secondly, each mean removal value of determinand was normalised with respect to corresponding mean removal of co-determinand.

4.3.2.4.1 Influence of SS Removal

Correlation of mean removal of PAH on mean removal of SS (Table 61) was statistically significant for low to medium molecular weight PAH, AY, AE, F, PA, FL, P and CH, at variable SS loading, and for medium to high molecular weight PAH, PA, A, FL, P, BaA, CH, BkF, BaP and BghiP, at variable hydraulic loading. Ranges of mean removals of PAH, in terms of absolute percentages, for the two groups under the respective conditions, were similar: for PAH of molecular weight 152 to 228, the increases associated with the increase in mean removal of SS from 57.9% at the loading of 402 mg l^{-1} (SS_0) to 68.2% at 888 mg l^{-1} (SS_3) were 17.5% for AY, 24.6% AE, 21.3% F, 18.1% PA, 18.6% A, 16.9% FL, 15.9% P, 12.2% BaA, 14.8% CH (as noted in Section 4.3.2.3 with respect to correlation with SS loading); and for PAH of molecular weight 202 to 278, the decreases associated with the decrease in mean removal of SS from 75.0% at the loading of 0.5 DWF to 59.2% at 5.0 DWF were 19.3% for FL, 21.3% P, 19.6% BaA, 19.2% CH, 16.9% BkF, 15.2% BaP, 16.1% IP, 17.7% BghiP and 15.0% DBahA. Ratios of mean removals of PAH to mean removals of SS increased from AY (mean of 0.325, n = 8) to BaA (0.969) and

thereafter decreased slightly, in accordance with the pattern of PAH removal noted previously (Section 4.3.2.1). For a given PAH, ratios were essentially independent of mean removal of SS under both variable SS and variable hydraulic loading conditions, but for PAH of molecular weight 152 to 202 it was noteworthy that ratios increased with increase in mean removal of SS under variable SS loading, indicating increasing removal efficiencies of the PAH proportionately greater than those of SS. Ratios for mean removal of SS of 57.9% at the loading of 402 mg l^{-1} (SS_0) to mean removal of 68.2% at 888 mg l^{-1} (SS_3) increased from 0.202 to 0.428 for AY, 0.370-0.674 AE, 0.444-0.689 F, 0.585-0.762 PA, 0.580-0.765 A, 0.748-0.883 FL and 0.775-0.891 P. The factorial increases in ratios for the PAH were, respectively, 2.12, 1.82, 1.55, 1.30, 1.32, 1.18 and 1.15, thus showing that the effect of enhanced PAH removal decreased with increase in molecular weight of determinand.

TABLE 61
Correlation of Removal Efficiency of PAH on Removal Efficiency of SS

Removal (%)[a], correlation coefficient (r)[b], and ratio of PAH removal to SS removal (in parentheses) at variable SS loading and variable hydraulic loading

	SS loading[c]					Hydraulic loading				
PAH	SS_0	SS_1	SS_2	SS_3	r	0.5 DWF	1.0 DWF	3.0 DWF	5.0 DWF	r
SS	57.9	66.4	67.5	68.2		75.0	63.6	62.2	59.2	
AY	11.7 (0.202)	18.6 (0.280)	25.9 (0.384)	29.2 (0.428)	0.921*	28.3 (0.377)	19.7 (0.310)	13.2 (0.212)	24.1 (0.407)	0.572
AE	21.4 (0.370)	32.7 (0.492)	39.4 (0.584)	46.0 (0.674)	0.937*	37.8 (0.504)	40.4 (0.635)	31.9 (0.513)	29.4 (0.497)	0.579
F	25.7 (0.444)	36.2 (0.545)	41.5 (0.615)	47.0 (0.689)	0.946*	44.4 (0.592)	44.1 (0.693)	36.1 (0.580)	25.8 (0.436)	0.712
PA	33.9 (0.585)	44.6 (0.672)	46.8 (0.693)	52.0 (0.762)	0.964*	55.4 (0.739)	45.6 (0.717)	44.4 (0.714)	31.9 (0.539)	0.895*
A	33.6 (0.580)	35.9 (0.541)	48.5 (0.719)	52.2 (0.765)	0.763	51.9 (0.692)	39.2 (0.616)	38.7 (0.622)	40.3 (0.681)	0.939*
FL	43.3 (0.748)	52.2 (0.786)	55.7 (0.825)	60.2 (0.883)	0.948*	63.6 (0.848)	51.4 (0.808)	52.2 (0.839)	44.3 (0.748)	0.971*
P	44.9 (0.775)	53.9 (0.812)	56.6 (0.839)	60.8 (0.891)	0.959*	67.0 (0.893)	51.6 (0.811)	51.9 (0.834)	45.7 (0.772)	0.993*
BaA	57.1 (0.986)	62.2 (0.937)	63.6 (0.942)	69.3 (1.02)	0.862	75.3 (1.00)	65.2 (1.03)	55.9 (0.899)	55.7 (0.941)	0.947*
CH	47.2 (0.815)	54.2 (0.816)	56.2 (0.833)	62.0 (0.909)	0.908*	66.6 (0.888)	49.7 (0.781)	56.0 (0.900)	47.4 (0.801)	0.927*
BkF	55.6 (0.960)	57.3 (0.863)	58.2 (0.862)	66.7 (0.978)	0.623	69.5 (0.927)	59.2 (0.931)	56.4 (0.907)	52.6 (0.889)	0.993*
BaP	55.2 (0.953)	54.2 (0.816)	58.8 (0.871)	68.8 (1.01)	0.537	68.9 (0.919)	56.8 (0.893)	57.7 (0.928)	53.7 (0.907)	0.991*
IP	53.7 (0.927)	50.1 (0.755)	47.9 (0.710)	65.6 (0.962)	0.172	61.2 (0.816)	57.2 (0.899)	53.7 (0.863)	45.1 (0.762)	0.839
BghiP	46.8 (0.808)	43.2 (0.651)	49.8 (0.738)	62.3 (0.913)	0.440	60.1 (0.801)	46.9 (0.737)	52.8 (0.849)	42.4 (0.716)	0.890*
DBahA	46.2 (0.798)	49.1 (0.739)	47.1 (0.698)	63.7 (0.934)	0.531	58.6 (0.781)	61.0 (0.959)	49.5 (0.796)	43.6 (0.736)	0.642

[a] Mean values from Table 56 and 57.
[b] Based on arcsin transformation.
[c] Mean SS_0 = 402, SS_1 = 575, SS_2 = 733, SS_3 = 888 mg l^{-1}.
* Correlation statistically significant at 95% confidence level.

4.3.2.4.2 Influence of NVSS Removal

Correlation of mean removal of PAH on mean removal of NVSS (Table 62) was statistically significant only for CH and BghiP at variable hydraulic loading. Ratios of mean removals of PAH to mean removals of NVSS ranged from a mean of 0.459 (AY) to 1.35 (BaA).

TABLE 62
Correlation of Removal Efficiency of PAH on Removal Efficiency of NVSS

Removal (%)[a], correlation coefficient (r)[b], and ratio of PAH removal to NVSS removal (in parentheses) at variable SS loading and variable hydraulic loading

	SS loading[c]					Hydraulic loading				
PAH	SS_0	SS_1	SS_2	SS_3	r	0.5 DWF	1.0 DWF	3.0 DWF	5.0 DWF	r
NVSS	41.2	49.6	45.2	51.8		55.1	43.4	52.5	36.8	
AY	11.7 (0.284)	18.6 (0.375)	25.9 (0.573)	29.2 (0.564)	0.723	28.3 (0.514)	19.7 (0.454)	13.2 (0.251)	24.1 (0.655)	-0.102
AE	21.4 (0.519)	32.7 (0.659)	39.4 (0.872)	46.0 (0.888)	0.799	37.8 (0.686)	40.4 (0.931)	31.9 (0.608)	29.4 (0.799)	0.348
F	25.7 (0.624)	36.2 (0.730)	41.5 (0.918)	47.0 (0.907)	0.810	44.4 (0.806)	44.1 (1.02)	36.1 (0.688)	25.8 (0.701)	0.660
PA	33.9 (0.823)	44.6 (0.899)	46.8 (1.04)	52.0 (1.00)	0.870	55.4 (1.01)	45.6 (1.05)	44.4 (0.846)	31.9 (0.867)	0.874
A	33.6 (0.816)	35.9 (0.724)	48.5 (1.07)	52.2 (1.01)	0.543	51.9 (0.942)	39.2 (0.903)	38.7 (0.737)	40.3 (1.10)	0.561
FL	43.3 (1.05)	52.2 (1.05)	55.7 (1.23)	60.2 (1.16)	0.830	63.6 (1.15)	51.4 (1.18)	52.2 (0.994)	44.3 (1.20)	0.871
P	44.9 (1.09)	53.9 (1.09)	56.6 (1.25)	60.8 (1.17)	0.848	67.0 (1.22)	51.6 (1.19)	51.9 (0.989)	45.7 (1.24)	0.812
BaA	57.1 (1.39)	62.2 (1.25)	63.6 (1.41)	69.3 (1.34)	0.863	75.3 (1.37)	65.2 (1.50)	55.9 (1.06)	55.7 (1.51)	0.548
CH	47.2 (1.15)	54.2 (1.09)	56.2 (1.24)	62.0 (1.20)	0.864	66.6 (1.21)	49.7 (1.15)	56.0 (1.07)	47.4 (1.29)	0.899*
BkF	55.6 (1.35)	57.3 (1.16)	58.2 (1.29)	66.7 (1.29)	0.766	69.5 (1.26)	59.2 (1.36)	56.4 (1.07)	52.6 (1.43)	0.739
BaP	55.2 (1.34)	54.2 (1.09)	58.8 (1.30)	68.8 (1.33)	0.607	68.9 (1.25)	56.8 (1.31)	57.7 (1.10)	53.7 (1.46)	0.801
IP	53.7 (1.30)	50.1 (1.01)	47.9 (1.06)	65.6 (1.27)	0.524	61.2 (1.11)	57.2 (1.32)	53.7 (1.02)	45.1 (1.23)	0.787
BghiP	46.8 (1.14)	43.2 (0.871)	49.8 (1.10)	62.3 (1.20)	0.514	60.1 (1.09)	46.9 (1.08)	52.8 (1.01)	42.4 (1.15)	0.960*
DBahA	46.2 (1.12)	49.1 (0.990)	47.1 (1.04)	63.7 (1.23)	0.782	58.6 (1.06)	61.0 (1.41)	49.5 (0.943)	43.6 (1.18)	0.458

[a] Mean values from Table 56 and 57.
[b] Based on arcsin transformation.
[c] Mean SS_0 = 402, SS_1 = 575, SS_2 = 733, SS_3 = 888 mg l^{-1}.
* Correlation statistically significant at 95% confidence level.

4.3.2.4.3 Influence of VSS Removal

Correlations and ratios obtained for removals of VSS (Table 63) were similar to those obtained for SS, both with regard to numerical value and apparent trend. Statistically significant correlations were observed for low to medium molecular weight PAH, AY, AE, F, PA, FL and P at variable SS loading, and for medium to high molecular weight PAH, A, P, BaA, BkF and BaP at variable hydraulic loading. Mean ratios ranged from 0.299 (AY) to 0.893 (BaA), and as with SS, individual ratios were found to increase with increase in mean removal of co-determinand for low molecular weight PAH under conditions of variable SS loading.

TABLE 63
Correlation of Removal Efficiency of PAH on Removal Efficiency of VSS

Removal (%)[a], correlation coefficient (r)[b], and ratio of PAH removal to VSS removal (in parentheses) at variable SS loading and variable hydraulic loading

	SS loading[c]					Hydraulic loading				
PAH	SS_0	SS_1	SS_2	SS_3	r	0.5 DWF	1.0 DWF	3.0 DWF	5.0 DWF	r
VSS	62.4	71.5	75.0	73.2		80.1	70.6	64.6	66.7	
AY	11.7 (0.188)	18.6 (0.260)	25.9 (0.345)	29.2 (0.399)	0.912*	28.3 (0.353)	19.7 (0.279)	13.2 (0.204)	24.1 (0.361)	0.768
AE	21.4 (0.343)	32.7 (0.457)	39.4 (0.525)	46.0 (0.628)	0.903*	37.8 (0.472)	40.4 (0.572)	31.9 (0.494)	29.4 (0.441)	0.629
F	25.7 (0.412)	36.2 (0.506)	41.5 (0.553)	47.0 (0.642)	0.911*	44.4 (0.554)	44.1 (0.625)	36.1 (0.559)	25.8 (0.387)	0.650
PA	33.9 (0.543)	44.6 (0.624)	46.8 (0.624)	52.0 (0.710)	0.911*	55.4 (0.692)	45.6 (0.646)	44.4 (0.687)	31.9 (0.478)	0.770
A	33.6 (0.538)	35.9 (0.502)	48.5 (0.647)	52.2 (0.713)	0.776	51.9 (0.648)	39.2 (0.555)	38.7 (0.599)	40.3 (0.604)	0.939*
FL	43.3 (0.694)	52.2 (0.730)	55.7 (0.743)	60.2 (0.822)	0.906*	63.6 (0.794)	51.4 (0.728)	52.2 (0.808)	44.3 (0.664)	0.856
P	44.9 (0.720)	53.9 (0.754)	56.6 (0.755)	60.8 (0.831)	0.914*	67.0 (0.836)	51.6 (0.731)	51.9 (0.803)	45.7 (0.685)	0.908*
BaA	57.1 (0.915)	62.2 (0.870)	63.6 (0.848)	69.3 (0.947)	0.782	75.3 (0.940)	65.2 (0.924)	55.9 (0.865)	55.7 (0.835)	0.981*
CH	47.2 (0.756)	54.2 (0.758)	56.2 (0.749)	62.0 (0.847)	0.840	66.6 (0.831)	49.7 (0.704)	56.0 (0.867)	47.4 (0.711)	0.772
BkF	55.6 (0.891)	57.3 (0.801)	58.2 (0.776)	66.7 (0.911)	0.510	69.5 (0.868)	59.2 (0.839)	56.4 (0.873)	52.6 (0.789)	0.947*
BaP	55.2 (0.885)	54.2 (0.758)	58.8 (0.784)	68.8 (0.940)	0.458	68.9 (0.860)	56.8 (0.805)	57.7 (0.893)	53.7 (0.805)	0.906*
IP	53.7 (0.861)	50.1 (0.701)	47.9 (0.639)	65.6 (0.896)	0.020	61.2 (0.764)	57.2 (0.810)	53.7 (0.831)	45.1 (0.676)	0.746
BghiP	46.8 (0.750)	43.2 (0.604)	49.8 (0.664)	62.3 (0.851)	0.369	60.1 (0.750)	46.9 (0.664)	52.8 (0.817)	42.4 (0.636)	0.703
DBahA	46.2 (0.740)	49.1 (0.687)	47.1 (0.628)	63.7 (0.870)	0.384	58.6 (0.732)	61.0 (0.864)	49.5 (0.766)	43.6 (0.654)	0.657

[a] Mean values from Table 56 and 57.
[b] Based on arcsin transformation.
[c] Mean SS_0 = 402, SS_1 = 575, SS_2 = 733, SS_3 = 888 mg l^{-1}.
* Correlation statistically significant at 95% confidence level.

4.3.2.4.4 Influence of Total COD Removal

Correlation of mean removal of PAH on mean removal of COD_{tot} (Table 64) was significant for PAH of molecular weight 152 to 228 at variable SS loading only. Mean ratios ranged from 0.412 (AY) to 1.24 (BaA), and individual ratios for low molecular weight PAH at variable SS loading again exhibited the trend noted with SS and VSS.

TABLE 64
Correlation of Removal Efficiency of PAH on Removal Efficiency of Total COD

Removal (%)[a], correlation coefficient (r)[b], and ratio of PAH removal to total COD removal (in parentheses) at variable SS loading and variable hydraulic loading

	SS loading[c]					Hydraulic loading				
PAH	SS_0	SS_1	SS_2	SS_3	r	0.5 DWF	1.0 DWF	3.0 DWF	5.0 DWF	r
COD_{tot}	46.7	49.6	53.5	54.8		59.8	58.1	38.5	48.1	
AY	11.7 (0.251)	18.6 (0.375)	25.9 (0.484)	29.2 (0.533)	0.996*	28.3 (0.473)	19.7 (0.339)	13.2 (0.343)	24.1 (0.501)	0.762
AE	21.4 (0.458)	32.7 (0.659)	39.4 (0.736)	46.0 (0.839)	0.982*	37.8 (0.632)	40.4 (0.695)	31.9 (0.829)	29.4 (0.611)	0.778
F	25.7 (0.550)	36.2 (0.730)	41.5 (0.776)	47.0 (0.858)	0.977*	44.4 (0.742)	44.1 (0.759)	36.1 (0.938)	25.8 (0.536)	0.599
PA	33.9 (0.726)	44.6 (0.899)	46.8 (0.875)	52.0 (0.949)	0.944*	55.4 (0.926)	45.6 (0.785)	44.4 (1.15)	31.9 (0.663)	0.491
A	33.6 (0.719)	35.9 (0.724)	48.5 (0.907)	52.2 (0.953)	0.976*	51.9 (0.868)	39.2 (0.675)	38.7 (1.01)	40.3 (0.838)	0.608
FL	43.3 (0.927)	52.2 (1.05)	55.7 (1.04)	60.2 (1.10)	0.969*	63.6 (1.06)	51.4 (0.885)	52.2 (1.36)	44.3 (0.921)	0.496
P	44.9 (0.961)	53.9 (1.09)	56.6 (1.06)	60.8 (1.11)	0.958*	67.0 (1.12)	51.6 (0.888)	51.9 (1.35)	45.7 (0.950)	0.549
BaA	57.1 (1.22)	62.2 (1.25)	63.6 (1.19)	69.3 (1.26)	0.930*	75.3 (1.26)	65.2 (1.12)	55.9 (1.45)	55.7 (1.16)	0.842
CH	47.2 (1.01)	54.2 (1.09)	56.2 (1.05)	62.0 (1.13)	0.948*	66.6 (1.11)	49.7 (0.855)	56.0 (1.45)	47.4 (0.985)	0.296
BkF	55.6 (1.19)	57.3 (1.16)	58.2 (1.09)	66.7 (1.22)	0.797	69.5 (1.16)	59.2 (1.02)	56.4 (1.46)	52.6 (1.09)	0.673
BaP	55.2 (1.18)	54.2 (1.09)	58.8 (1.10)	68.8 (1.26)	0.804	68.9 (1.15)	56.8 (0.978)	57.7 (1.50)	53.7 (1.12)	0.525
IP	53.7 (1.15)	50.1 (1.01)	47.9 (0.895)	65.6 (1.20)	0.408	61.2 (1.02)	57.2 (0.985)	53.7 (1.39)	45.1 (0.938)	0.569
BghiP	46.8 (1.00)	43.2 (0.871)	49.8 (0.931)	62.3 (1.14)	0.750	60.1 (1.01)	46.9 (0.807)	52.8 (1.37)	42.4 (0.881)	0.237
DBahA	46.2 (0.989)	49.1 (0.990)	47.1 (0.880)	63.7 (1.16)	0.675	58.6 (0.980)	61.0 (1.05)	49.5 (1.29)	43.6 (0.906)	0.739

[a] Mean values from Table 56 and 57.
[b] Based on arcsin transformation.
[c] Mean SS_0 = 402, SS_1 = 575, SS_2 = 733, SS_3 = 888 mg l^{-1}.
* Correlation statistically significant at 95% confidence level.

4.3.2.4.5 Influence of Soluble COD Removal

Correlations and ratios obtained for removals of COD_{sol} (Table 65) were inconsistent. A significant correlation was found only for A under variable SS loading conditions, and for some medium to high molecular weight PAH, PA, FL, P, CH, BkF, BaP and BghiP, under variable hydraulic loading conditions (negative correlations here). Ratios for a given PAH varied considerably, with mean values ranging from 2.34 (AY) to 6.92 (BaA).

TABLE 65
Correlation of Removal Efficiency of PAH on Removal Efficiency of Soluble COD

Removal (%)[a], correlation coefficient (r)[b], and ratio of PAH removal to soluble COD removal (in parentheses) at variable SS loading and variable hydraulic loading

	SS loading[c]					Hydraulic loading				
PAH	SS_0	SS_1	SS_2	SS_3	r	0.5 DWF	1.0 DWF	3.0 DWF	5.0 DWF	r
COD_{sol}	9.2	9.5	22.1	17.0		3.0	18.1	12.0	24.7	
AY	11.7 (1.27)	18.6 (1.96)	25.9 (1.17)	29.2 (1.72)	0.827	28.3 (9.43)	19.7 (1.09)	13.2 (1.10)	24.1 (0.976)	-0.291
AE	21.4 (2.33)	32.7 (3.44)	39.4 (1.78)	46.0 (2.71)	0.754	37.8 (12.6)	40.4 (2.23)	31.9 (2.66)	29.4 (1.19)	-0.431
F	25.7 (2.79)	36.2 (3.81)	41.5 (1.88)	47.0 (2.76)	0.744	44.4 (14.8)	44.1 (2.44)	36.1 (3.01)	25.8 (1.04)	-0.676
PA	33.9 (3.68)	44.6 (4.69)	46.8 (2.12)	52.0 (3.06)	0.665	55.4 (18.5)	45.6 (2.52)	44.4 (3.70)	31.9 (1.29)	-0.918*
A	33.6 (3.65)	35.9 (3.78)	48.5 (2.19)	52.2 (3.07)	0.891*	51.9 (17.3)	39.2 (2.17)	38.7 (3.23)	40.3 (1.63)	-0.836
FL	43.3 (4.71)	52.2 (5.49)	55.7 (2.52)	60.2 (3.54)	0.720	63.6 (21.2)	51.4 (2.84)	52.2 (4.35)	44.3 (1.79)	-0.980*
P	44.9 (4.88)	53.9 (5.67)	56.6 (2.56)	60.8 (3.58)	0.698	67.0 (22.3)	51.6 (2.85)	51.9 (4.33)	45.7 (1.85)	-0.970*
BaA	57.1 (6.21)	62.2 (6.55)	63.6 (2.88)	69.3 (4.08)	0.616	75.3 (25.1)	65.2 (3.60)	55.9 (4.66)	55.7 (2.26)	-0.789
CH	47.2 (5.13)	54.2 (5.71)	56.2 (2.54)	62.0 (3.65)	0.653	66.6 (22.2)	49.7 (2.75)	56.0 (4.67)	47.4 (1.92)	-0.993*
BkF	55.6 (6.04)	57.3 (6.03)	58.2 (2.63)	66.7 (3.92)	0.460	69.5 (23.2)	59.2 (3.27)	56.4 (4.70)	52.6 (2.13)	-0.921*
BaP	55.2 (6.00)	54.2 (5.71)	58.8 (2.66)	68.8 (4.05)	0.564	68.9 (23.0)	56.8 (3.14)	57.7 (4.81)	53.7 (2.17)	-0.970*
IP	53.7 (5.84)	50.1 (5.27)	47.9 (2.17)	65.6 (3.86)	0.067	61.2 (20.4)	57.2 (3.16)	53.7 (4.48)	45.1 (1.83)	-0.828
BghiP	46.8 (5.09)	43.2 (4.55)	49.8 (2.25)	62.3 (3.66)	0.546	60.1 (20.0)	46.9 (2.59)	52.8 (4.40)	42.4 (1.72)	-0.993*
DBahA	46.2 (5.02)	49.1 (5.17)	47.1 (2.13)	63.7 (3.75)	0.280	58.6 (19.5)	61.0 (3.37)	49.5 (4.13)	43.6 (1.77)	-0.526

[a] Mean values from Table 56 and 57.
[b] Based on arcsin transformation.
[c] Mean SS_0 = 402, SS_1 = 575, SS_2 = 733, SS_3 = 888 mg l^{-1}.
* Correlation statistically significant at 95% confidence level.

4.3.2.4.6 Relative Influence of Co-Determinand Removals

The relative influence of co-determinand removals on removal of PAH was confirmed by performing a correlation analysis, for each co-determinand, for removal efficiency of PAH for each experiment (Table 57) against corresponding removal efficiency of co-determinand (Table 56). The results (Table 66) demonstrated for SS, statistically significant correlations for PAH of molecular weight 166 to 252, for NVSS correlation for F, PA, FL, P and CH, for VSS correlation for hydrocarbons of molecular weight 178 to 252, for COD_{tot} correlation for BaA only, and for COD_{sol} correlation (negative) for BaA, BkF and IP. Considered in conjunction with Table 61 to 65, the most consistent overall correlation was with SS; correlation with VSS was nearly as good. (The significant correlations observed for PAH of molecular weight 152 to 228 for mean removal of PAH on mean removal of COD_{tot} at variable SS loading (Table 64)

TABLE 66
Correlation of Removal Efficiency of PAH on Removal Efficiency of SS, NVSS, VSS, Total and Soluble COD Over All Hydraulic and SS Loadings

	Correlation coefficient (r) for co-determinand[a]				
PAH	SS	NVSS	VSS	COD_{tot}	COD_{sol}
AY	0.066	-0.131	0.212	0.333	0.384
AE	0.387	0.446	0.310	0.438	0.148
F	0.559*	0.533*	0.467	0.372	-0.168
PA	0.787*	0.621*	0.688*	0.385	-0.362
A	0.705*	0.384	0.708*	0.471	-0.059
FL	0.868*	0.553*	0.817*	0.407	-0.344
P	0.878*	0.502*	0.853*	0.437	-0.413
BaA	0.825*	0.405	0.830*	0.641*	-0.527*
CH	0.820*	0.527*	0.758*	0.271	-0.414
BkF	0.704*	0.373	0.690*	0.432	-0.545*
BaP	0.613*	0.261	0.641*	0.314	-0.359
IP	0.373	0.294	0.325	0.198	-0.525*
BghiP	0.468	0.275	0.459	0.075	-0.333
DBahA	0.416	0.241	0.442	0.341	-0.405

[a] Calculated from data, arcsin transformed, in Table 56 and 57.
* Correlation statistically significant at 95% confidence level.

may have been due to the marked dependence of the flow-averaged mean removals of COD_{tot} on SS loading (Table 56), the latter having been shown to influence mean removal of low to medium molecular weight PAH (Table 60, column 2)).

4.3.3 Formulation of Regression Functions Relating PAH Removal to Plant Performance

The good correlations obtained for PAH removal on SS removal (Table 66) permitted meaningful formulation of empirical regression functions from the correlation analysis (n = 16), and hence for convenient expressions to be obtained, from a practical engineering standpoint, for PAH removal as a function of tank performance. Functions were formulated both from non-arcsin (Table 67) and arcsin transformed data (Table 89, Appendix 6); the latter are more strictly correct but give very similar results to the former, except for the function for AY. The former functions are represented graphically (Figure 14).

TABLE 67
Linear Regression Function
for Removal Efficiency of PAH
on Removal Efficiency of SS
Achieved During Primary Sedimentation

PAH	Regression function[a]
AY	$R = 0.383\ R_{SS} - 3.6$
AE	$R = 0.738\ R_{SS} - 13.1$
F	$R = 0.900\ R_{SS} - 20.9$
PA	$R = 1.10\ R_{SS} - 27.2$
A	$R = 0.884\ R_{SS} - 15.0$
FL	$R = 1.04\ R_{SS} - 14.5$
P	$R = 1.11\ R_{SS} - 18.0$
BaA	$R = 1.04\ R_{SS} - 4.3$
CH	$R = 0.992\ R_{SS} - 9.6$
BkF	$R = 0.776\ R_{SS} + 9.0$
BaP	$R = 0.716\ R_{SS} + 12.7$
IP	$R = 0.505\ R_{SS} + 21.5$
BghiP	$R = 0.672\ R_{SS} + 6.8$
DBahA	$R = 0.559\ R_{SS} + 15.5$

[a] Where R = removal efficiency (%) of PAH
R_{SS} = removal efficiency (%) of SS.
Range of application of functions: surface loading rate 6.10-61.0 $m^3\ m^{-2}\ d^{-1}$; SS loading *ca.* 300-1000 mg l^{-1}; hydraulic retention time 0.46-4.58 h.

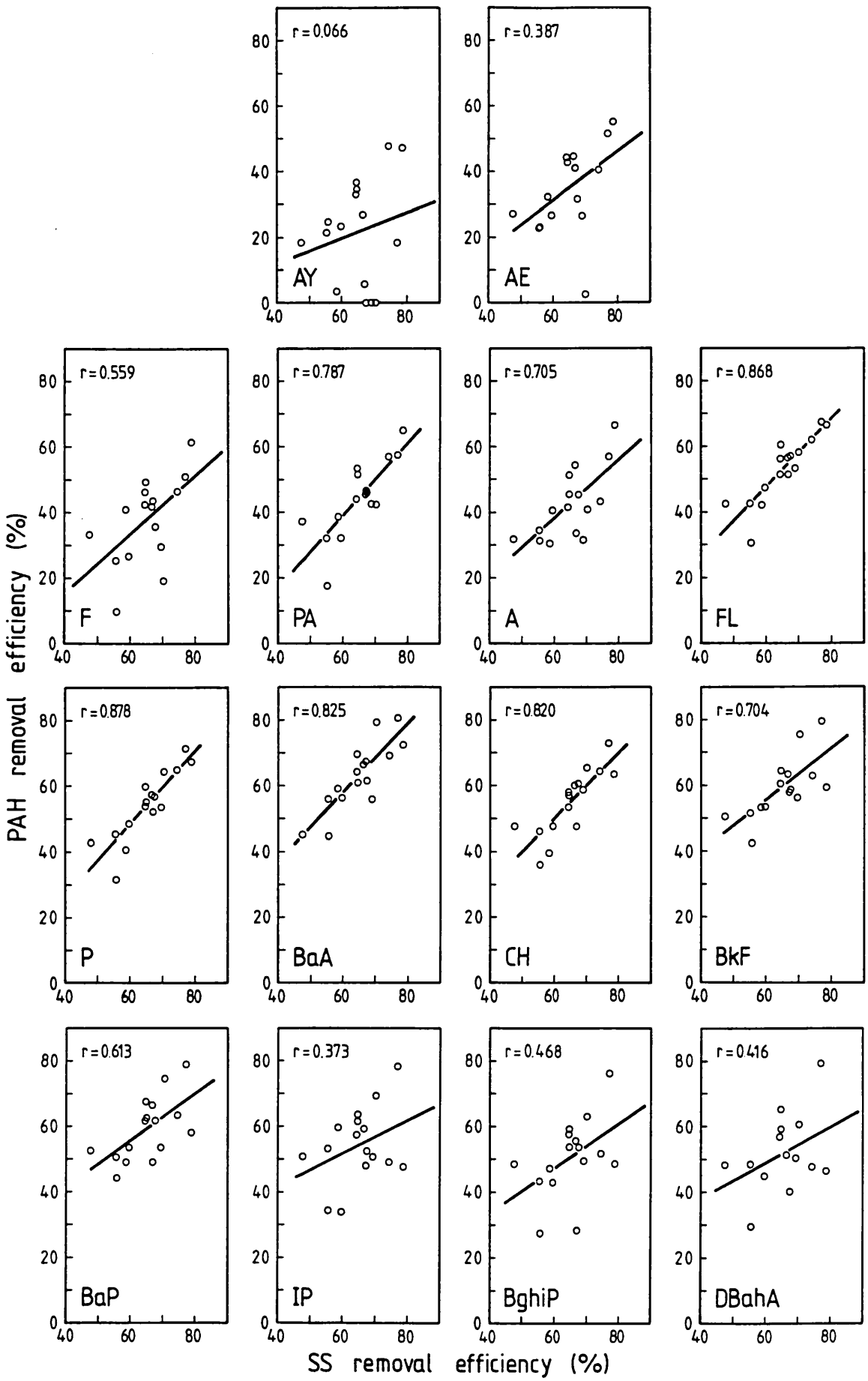


FIGURE 14
Dependence of PAH Removal on SS Removal Achieved During Primary Sedimentation

Correlations improved with increase in determinand molecular weight to reach an optimum for the medium molecular weight PAH FL, P, BaA and CH (regression lines essentially unity), and thereafter deteriorated. Correlation coefficients (for data arcsin transformed) were not statistically significant for the lowest molecular weight PAH studied (AY, AE) nor for the highest (IP, BghiP, DBahA) (Table 66).

5. DISCUSSION

Knowledge of analytical procedure performance characteristics is essential for the correct interpretation of measurement data necessary for the effective monitoring and control of the pollutants concerned. The results obtained by GC (Table 28-30) and GC-MS (Table 32, 33 and 39) confirmed the efficiency of the analytical method, that is, the high and repeatable determinand recoveries at the three concentrations (three spike levels) by the whole procedure. The overall mean recovery of 84% agreed favourably with the overall mean of 90% for the efficiency of the two-step extraction procedure on indigenous PAH (Table 40). This suggested that the modest losses were principally incurred for most determinands at the extraction stage, as the efficiencies of the two cleanup steps (Table 26 and 27) were generally quantitative. Indeed, this is supported from the recoveries obtained for the direct determinations of distilled deionised water samples (Table 46 and as alluded to in Section 4.1.10.2, Table 48 and Table 54 (control subsample)).

Recovery efficiency tests do not assess accuracy directly as is commonly believed, but rather procedure efficiency. They indicate analytical accuracy only when the analytical response for determinand in an unspiked sample is due to the determinand alone (i.e. no interferences) and is not subject to any bias. Analytical accuracy is ideally measured directly by analysis of certified reference materials, which are largely unavailable for aqueous samples, or by 'confirmatory testing', together with circumstantial evidence. Confirmatory testing consists in applying two inherently different analytical procedures to the same set of samples containing a range of determinand concentrations and comparing the resulting data statistically, in particular by regression methods (Thompson, 1982). A positive relative bias (+30%) was shown in a screening method for PAH by this means (Riggin & Strup, 1984). Although not strictly used in the present circumstances, in the sense that a second inherently dissimilar procedure was not applied, the GC determinations did provide a good cross-check and confirmed immediately the presence of positive relative bias in the initial

results for the GC-MS determination of procedure efficiency.

Additional evidence of satisfactory analytical accuracy for the GC-MS procedure after correction for bias was provided by a comparison of the GC and GC-MS results for determination of background concentrations of PAH in the sludge sample (Table 41, column 2 and 3) and for those for the sewage sample (Table 42, column 2 and 3). Low molecular weight PAH determinations were in good agreement by the two methods of measurement; the discrepencies for the higher molecular weight PAH were ascribed to the more inaccurate GC measurement of these determinands in the presence of interferences (Section 4.1.9.1), and were not unusually large when compared with the results of interlaboratory PAH analyses (Hilpert et al., 1978, on marine sediments).

The GC-MS mass chromatograms (Figure 8) provided good circumstantial evidence for analytical responses for determinands being essentially free of interferences and hence permitting accurate analyses.

It is evident from Table 43 that the most dominant source of analytical error was that arising from the measurement of the systematic error. The random error component of the systematic error was for each determinand much larger than the associated random error (column 2) which was generally modest. As the systematic error was shown to be associated with the measurement stage of the procedure, and the effect of the bias essentially to change the slope of the calibration functions, it implied that the accuracy of the analytical procedure developed was very largely dependent on the calibration procedure employed.

The linearity of the bias (Figure 7) and more particularly its independence of sample (Table 37), both of which were assumed to apply over the concentration ranges regularly measured (including the random error associated with its measurement, expressed as RSD), made determination of the bias for each sample unnecessary. Furthermore, the bias was not measured daily as it was considered that the existing calibration procedure would accomodate any

variations in it. Nevertheless, the calibration procedure can be modified according to the degree of accuracy of results required, and any one of a variety of procedures utilised, for example multiple standard additions, or single standard additions performed on each sample without external calibration. In any case, as it is strongly suspected that the bias experienced is critically dependent on the measuring instrument used, the magnitude of the bias (if any) should be determined in each application of the procedure. This can be done very simply by the method of single standard additions performed on the treated sample matrix in the manner described (Section 4.1.7.2; Table 35 and 36). Indeed, this test is strongly recommended in any GC-MS work involving the determination of high molecular weight and high boiling point compounds.

It should be emphasised that the often practised, and recommended, technique of regularly carrying the internal standard through the whole procedure (from extraction to final determination) would still lead to bias in the method unless there was an internal standard for each of the determinands affected, a most unlikely circumstance. Hence statements of the form 'it is assumed there is no bias... because any losses of analytes should be compensated with the internal standard' (Eichelberger et al., 1983) should be treated with extreme caution. Furthermore it should be noted that the bias was not due to determinand discrimination by the sample introduction device (the injector) as an identical device was used successfully on the GC-FID system; Eichelberger et al. (1983) reported that high molecular weight PAH may not be transferred efficiently and consistently to the column in the splitless injection system. Neither was the bias due to a mass cycling error (Matthews & Hayes, 1976): the MS executed at least eight measurement cycles per GC peak.

It has been said that 'the control and estimation of bias is one of the key problems of modern water analysis' (Hunt & Wilson, 1986) and bias arising from calibration procedure giving rise to analytical inaccuracy, although reported (Kirchmer et al., 1983), may be more widespread than is acknowledged, and may belie poor interlaboratory comparison exercise results. A recent study involving 20 water

industry laboratories (Gardner et al., 1986) analysing cadmium and lead by graphite furnace atomic absorption spectrometry demonstrated a very poor overall standard of accuracy. Many of the largest errors observed were ascribed to simple calibration bias. Use of standard methods is no guarantee of accuracy and precision if descriptions of calibration procedures are lacking. These problems of calibration and instrument contribution to procedure inaccuracy may be among factors that have prompted legislation in this area. An EC directive (Council of the European Communities, 1979) specifies the accuracy, precision and detection limit for the measurement in surface waters of many determinands, including PAH (accuracy ±50%, precision ±50%, limit of detection 0.04 μg l^{-1}). Such legislation is likely, and justifiably, to increase in the future.

The detection limits of the procedure were estimated, and not determined statistically to give 'method detection limits' (MDL) (Glaser et al., 1981) or limits alternatively defined (Hunt & Wilson, 1986), as it appeared that inter-sample variation in detection limit as defined by twice signal-to-noise ratio was appreciable (varying by up to a factor of three or four) and rendered elaborate analytical and statistical treatment of one sample inappropriate. Although it is acknowledged that 'the MDL for an analytical procedure may vary as a function of the sample type' (Glaser et al., 1981) for example between raw and settled sewage, inter-sample variation within a given sample type does not appear to be widely appreciated. Given that 'the detection limit is one of the most important performance characteristics of an analytical procedure' (Glaser et al., 1981) this is an area which necessitates further statistical study. It is of even greater significance in the UK where, as a result of EC pollution legislation, very low concentrations in water are required to be determined, and where the monitoring needed to sustain a policy based on EQO/EQS as advocated by the UK requires the measurement of much lower concentrations of pollutants than one based on ES. This consequence is not widely recognised and entails significant technical and economic aspects.

The developed procedure fulfils all the minimum requirements for method validation as laid down in Table 16 and displays satisfactory numerical performance characteristics for accuracy, precision and sensitivity. The method therefore compares very favourably with schemes reported in the literature (Table 15) and compares well, too, in terms of scope, that is the numbers of PAH and variety of sample types (raw sewage, primary effluent and raw primary sludge) for which the method has been characterised.

A procedure (McIntyre et al., 1981) for the determination of the six WHO PAH (FL, BbF, BkF, BaP, IP and BghiP) in sludge samples of 50 ml involves extraction with cyclohexane, silica gel TLC cleanup followed by two dimensional TLC. The procedure is semiquantitative only, based on visual comparison of fluorescence of sample chromatograms with that of standard chromatographic plates under UV light.

Another TLC procedure (Aichberger & Reifenauer, 1984) determines BaP in sludge down to 0.05 p.p.m. Soxhlet extraction with hexane of 5 to 10 g samples with subsequent silica gel microcolumn cleanup is followed by TLC with fluorescence detection. No other procedure performance characteristics were reported.

A profile analysis method (Grimmer et al., 1978) for 19 PAH in sludge consists of extraction with methanolic potassium hydroxide, partitioning into a mixture of DMF and water with back extraction into cyclohexane, followed by chromatographic cleanup on Sephadex LH 20 and subsequently aluminium oxide, with determination by GC (with FID). The precision of the method, expressed as RSD, for five determinations of 5 g samples (and thus for one determinand concentration) ranged from 1.6 to 11.3%, with detection limits ranging from 0.5 to 5 ng. No data on the accuracy of the procedure were provided, being a profile analysis method.

An HPLC procedure requiring no cleanup was reported (Hagenmaier & Jäger, 1979) for the determination of the six WHO PAH in sludge samples of 5 to 10 g, extracted with

cyclohexane. Although the procedure was designed for drinking water analysis, it is claimed to be suitable for sludges and sediments. Accuracy was assessed by means of a comparison of analytical results with those obtained by other procedures but, together with other performance characteristics, was not reported.

A further HPLC procedure (Mertens & Rittmann, 1983) for water and sludge samples requiring no cleanup was compared with a capillary column GC method primarily designed for the profile analysis of PAH in air particulate matter. The comparison was qualitative only, based on visual inspection of chromatograms. The HPLC method is applicable for the six WHO compounds but performance data were supplied for BaP only: for a 1 l sample the detection limit for the analyte is 0.3 ng with a precision of measurement (evaluated at one determinand concentration) of 25% (RSD).

A method developed by Schössner et al. (1983) for the determination of the WHO PAH in drinking, surface and 'waste water' consists of sample extraction with cyclohexane, cleanup by aluminium oxide or Sephadex LH 20 column chromatography, followed by TLC separation (one dimensional) and spectrofluorometric detection. Method precision, determined only by means of analysis of a mixed standard solution at one concentration, ranged from 3.3 to 5.9% (RSD). Recovery tests at three concentrations determined on a sample of drinking water only revealed quantitative (100%) recoveries. No detection limits were reported.

Grzybowski et al. (1983) for an HPLC procedure for the determination of 16 PAH in sewage effluent described extraction of 2 l samples with cyclohexane, partitioning into DMSO-cyclohexane and DMF-water-cyclohexane, with final cleanup by Florisil column chromatography. Limited method validation yielded a mean precision estimate only of 3.6% (RSD; one determinand concentration) and a mean procedure efficiency, based on spiking of doubly distilled water at one concentration, of 90%. No detection limits were reported.

A more satisfactorily characterised but laborious procedure (Searl et al., 1979) for the measurement of 23 PAH in industrial and municipal waste water effluent involves methylene chloride extraction of 3 l samples followed by DMSO-isooctane partitioning, aluminium oxide column chromatography (optional) and measurement by GC-UV spectrophotometry. Only mean values were reported for precision and accuracy. The precision of the procedure (including variation in sampling) for real samples was reported to be within a RSD of 27% of the mean for the concentration range 0-30 μg l^{-1} and 18% for the range 30-200 μg l^{-1}. Accuracy was reported to be ±0.3 μg l^{-1} (1 σ) for the range 0-2.0 μg l^{-1} and within 20% (relative error, 1 σ) for the range 2.0-20 μg l^{-1}. Again, no detection limits were presented.

A carefully validated method is that of EPA's 'Method 610' for the GC or HPLC determination of priority pollutant PAH in industrial and municipal waste water effluents (Longbottom & Lichtenberg, 1982). Samples of 1 l are manually extracted with methylene chloride with cleanup (if necessary) by silica gel column chromatography. A legislative procedure, the cleanup stage and methods of detection (FID, UV and fluorescence) are optional as long as certain method performance 'acceptance criteria' are met for accuracy, precision and MDL. The MDL for reagent water by HPLC was reported (Cole et al., 1981) as ranging from 0.013 μg l^{-1} for BaA to 2.3 μg l^{-1} for AY, for a refinery effluent ranging from 0.010 μg l^{-1} for BaA to 2.4 μg l^{-1} for AY, and for a coke plant effluent ranging from 0.011 μg l^{-1} for BaP to 4.0 μg l^{-1} for AY. The analytical curve (linearity of spike recovery) for reagent water was demonstrated to be applicable for the concentration range 8x MDL to 800x MDL for all PAH except BghiP (at 80x and 800x MDL) (Cole et al., 1981). An interlaboratory study (Kinzer et al., 1984) involving 16 establishments tested procedure accuracy and precision for Method 610 with HPLC on reagent water, a tap water, a surface water, and three industrial waste water effluents spiked at six concentrations over the range 0.1-463 μg l^{-1}. Method accuracy, single analyst precision and overall interlaboratory precision, defined absolutely, were found, through recovery tests, to be directly related to the

concentration of the determinand and to be essentially independent of sample type. For the three waste water samples, mean recoveries ranged from 53 to 122%, single analyst precision from 11 to 46% (RSD), and overall precision from 23 to 69% (RSD).

Given that the present procedure cannot analyse for N nor quantify separately the benzofluoranthene (BF) isomers, accuracy is comparable to the EPA HPLC procedure but displays higher (single analyst) precision and, for the low molecular weight PAH, appreciably lower detection limits. Furthermore, the developed method was specifically validated with respect to raw sewage, primary effluent and primary sludge whereas the EPA procedure was chiefly validated with respect to industrial waste water sample types containing relatively high concentrations of PAH.

The studies of sample integrity demonstrated the utility of formaldehyde solution (at 1% V/V) in maintaining integrity for at least 56 d. This simple preservation technique has a very useful field application and obviates the need for refrigeration (4°C), immediate extraction or other restrictive sampling requirements. The studies also suggested that without preservation, accurate analysis of samples can be accomplished up to 24 h after collection. The experiments confirmed the presence of a process or processes operating in the sewage matrix accounting for a gradual reduction in the concentration of low molecular weight PAH including, possibly, BkF and IP. PAH are subject to loss and degradation through five potential mechanisms: photodegradation, chemical degradation, sorption (irreversible), volatilisation and biodegradation. There was no opportunity for photodegradation. The results for the pure water matrix confirmed the general stability and resistance to chemical degradation of PAH in aqueous solution and furthermore proved that irreversible sorption to container walls was not a cause. The observed decay pattern, comprising an increase in decay rate with decrease in molecular weight (Table 44 and 45), was consistent with relative volatilisation rates predicted by Southworth (1979) (Section 1.7.1) for a clear stream, H (Table 2) and results obtained herein (Table 53 and 54), and was also consistent with relative biodegradation rates for PAH in

aqueous matrices as reported by Heitkamp & Cerniglia (1987) and Tabak et al. (1981) (Section 1.7.3). Volatilisation may have been occurring into sample container headspace but no such process appeared to be operating in the pure water matrix and furthermore the preventative effect of formaldehyde would not be readily explained. Biodegradation therefore appeared to be operative with formaldehyde acting in a biocidal capacity.

The sample integrity and extraction results stand at variance with a previous study (Acheson et al., 1976) where substantial reductions in PAH extraction efficiencies due to suspended solids and storage (6 h) were reported. The study, limited in scope, utilised extraction by Ultra-Turrax high speed blending which has been shown by McIntyre et al. (1981) to be inferior as a mixer-homogenizer device to use of a laboratory disperser for the extraction of PAH from aqueous samples. The apparent reductions in extraction efficiencies could well be ascribed to the poorer efficiency of the mixing device used.

The MS system remains one of the most complex of analytical machines. It is costly to maintain and is traditionally of great value in compound identification, structure elucidation and survey/search work. Routine analysis and monitoring of organic pollutants can sometimes be more ideally served by simpler and cheaper analytical systems in the form of GC and HPLC. Although the very complex sample types studied herein demanded determination by GC-MS instead of GC, use of HPLC in PAH analysis is likely to increase in the future. A relatively low cost combined with high analyte sensitivity and specificity account for major advantages and, furthermore, very high molecular weight PAH (MW 300 such as that of coronene, and above) not amenable to analysis by GC and GC-MS, are so by HPLC. It is showing considerable promise in the examination of the non-volatile high molecular weight fraction of general organic substances which constitutes 80-90% of the total organic carbon (TOC) of raw waters (Fielding et al., 1981).

Additional future developments and improvements in PAH analysis may be expected with capillary GC and GC-MS where improvements in column technology (stationery phase) may provide for greater selectivity of PAH isomers. The development of capillary HPLC and capillary HPLC-MS, still in their infancy, may be expected to offer major advantages in the form of greatly improved resolution over existing HPLC systems. As mentioned previously, contemporary PAH analytical practice is characterised by a preoccupation with new technology and 'high-tech' instrumentation at the expense of basic method validation. The water industry would benefit most from a proper attention to the latter area and to improvements to the well established and more simple systems. The renaissance in high performance TLC (HPTLC), for example, would offer very attractive specifications. However, an exception to this imbalance should be allowed for in the search for systems offering improved sensitivity and hence lower detection limits the lack of which so often limit the quantity and quality of environmental data obtained. In this context the use of lasers (of modest cost) as excitation sources in spectroscopic methods of detection (Table 15; e.g. with HPLC) should bring about dramatic increases in sensitivity and specificity.

Quite apart from the importance of the study of pollutants in sewage effluents in so far as they may impact upon the quality of surface waters abstracted for potable supply, the quality of sewage effluent itself is worthy of detailed study as it represents a valuable water resource. This resource will become increasingly important in the future as water demand increases and primary sources of supply are fully exploited. Taylor & Denner (1987) distinguished four use areas of sewage effluent: agriculture, industry, amenity and potable supply (via river and via artificial ground water recharge).

The performance of the primary sedimentation pilot plant in terms of SS removal efficiency compared well with predictions by five performance relationships relating removal efficiency to hydraulic loading and SS loading derived from pilot- and full-scale settlement units (Table 68). Removal efficiencies, in agreement with all

TABLE 68
Removal Efficiency (%) of SS for Pilot Plant Predicted by Five Performance Relationships for Primary Sedimentation Tanks

Pilot plant loading	This study[c]	A	B	C	D	E
Variable SS Loading[a]						
SS_0 402 mg l^{-1}	57.9	64.0	----	71.2	52.6	46.5
SS_1 575 mg l^{-1}	66.4	65.9	----	73.2	58.3	56.7
SS_2 733 mg l^{-1}	67.5	66.9	----	74.4	63.5	62.6[d]
SS_3 888 mg l^{-1}	68.2	67.6	----	75.2	68.7	66.7[d]
Variable Hydraulic Ldng.[b]						
0.5 DWF 6.1 m^3 m^{-2} d^{-1}	75.0	74.3	77.7[d]	79.2	77.5	64.2[d]
1.0 DWF 12.2 m^3 m^{-2} d^{-1}	63.6	71.4	73.7[d]	74.0	60.9	59.1[d]
3.0 DWF 36.6 m^3 m^{-2} d^{-1}	62.2	64.6	59.4	66.2	35.6[d]	61.9[d]
5.0 DWF 61.0 m^3 m^{-2} d^{-1}	59.2	56.8	47.9	60.2	22.4[d]	53.3

A Steel (1960); relationship derived (Tebbutt & Christoulas, 1975) from full-scale tanks; loading ranges applicable of original data not given.
B Smith (1969); relationship derived from full-scale tanks; applicable for range 20-90 m^3 m^{-2} d^{-1} (no term for SS loading).
C Escritt (1972); relationship derived from full-scale tanks; loading ranges applicable not given.
D Construction Industry Research and Information Association (1975); relationship derived from full-scale tanks; applicable for retention time of 2-10 h.
E Tebbutt & Christoulas (1975); relationship derived from pilot-scale tanks; applicable for range 200-600 mg l^{-1}, 25-150 m^3 m^{-2} d^{-1} and retention time of 20 min - 2 h.
[a] Mean surface loading rate 29.0 m^3 m^{-2} d^{-1}.
[b] Mean SS loading (mg l^{-1}) at 0.5 DWF 691, 1.0 DWF 584, 3.0 DWF 742, 5.0 DWF 581. (Data from Table 71).
[c] Means from Table 56.
[d] Associated loading or hydraulic retention time outside range applicable of relationship.

predictions, increased with decreasing hydraulic loading and hence with increasing theoretical hydraulic retention time and, furthermore, increased with increasing SS loading commensurate with increasing flocculation (Class II settlement), as expected (Section 1.8.2). Numerical values for various hydraulic and SS loadings agreed well with predictions by performance relationships derived from full-scale units by Steel (1960), Escritt (1972) and Construction Industry Research and Information Association (1975), and furthermore agreed on the relative influence of the two process parameters on removal efficiency. Appreciable disagreements, however, occured with the

predictions based on the pilot-scale work of Tebbutt & Christoulas (1975). Numerical differences were especially apparent for low hydraulic and SS loadings and in the relative influence of the two parameters. For the present work, and under the range of conditions studied, hydraulic loading was found to be more important in controlling SS removal than SS loading (Section 4.3.1.2.2), in direct contrast to Tebbutt & Christoulas. This was most probably due to the latter's range of applicability of performance relationship from which the predictions were made. The range for surface loading rate, 25-150 $m^3 m^{-2} d^{-1}$ (corresponding to retention times of 20-120 min), displays a relatively high lower limit. It is noteworthy that the present study obtained higher removals at the low hydraulic loadings falling outside Tebbutt & Christoulas' range of applicability. The authors noted, furthermore, that their relationship predicted a relatively low maximum removal efficiency, indicating a relatively high proportion of non-settleable solids in the plant influent utilised.

The nature of the raw sewage, as a property additional to concentration as expressed by SS, can be responsible for observed deviation from predictions. The removal-hydraulic loading relationship is typically exponential (Steel, 1960; Smith, 1969; Escritt, 1972; Construction Industry Research and Information Association, 1975; Tebbutt & Christoulas, 1975) and the removal-SS loading relationship exponential (Steel, 1960; Escritt, 1972; Tebbutt & Christoulas, 1975) or linear (Construction Industry Research and Information Association, 1975). The limited data of the present study suggested exponential relationships (Figure 11 and 12) but particular variances (Table 56) can be ascribed to the nature of the raw feed and to a consideration of the SS determination employed to quantify sedimentation efficiency.

The main process objective of primary sedimentation is removal of settleable solids. The SS determination, however, entails filtration of sample through glass fibre filter paper with a nominal pore diameter of 0.45 μm (Department of the Environment, 1984), thereby including measurement of particles normally considered non-settleable (<100 μm diameter according to Tebbutt (1983) and Valioulis

& List (1984a)). Frequently no relationship is found between SS and settleable solids (as determined by a settleable solids test) in raw sewage (Tebbutt, 1969). Hence, for a given SS and hydraulic loading, a tank can display quite different removal efficiencies as determined by the SS test on separate occasions because of varying proportions of settleable solids in the influent.

Notwithstanding the direct inverse proportionality between hydraulic loading and theoretical hydraulic retention time (for a tank of fixed depth and surface area), actual flow-through time for a given hydraulic loading can be variable and significantly less than the theoretical time (Section 1.8.2). Uniform and ideal plug flow distribution can be severely limited by two phenomena (March & Hamlin, 1966; Hamlin & Abdul Wahab, 1970; Price & Clements, 1974): short-circuiting due to density currents arising from differences in density (temperature, mass, ionic strength) between the influent and tank contents, and mixing due to hydraulic turbulence caused by inlet and outlet structures and surface wind. Thus variations in retention time may cause deviations from the removal-hydraulic loading relationship as variations in influent settleability cause deviations from the removal-SS loading relationship.

The sampling regime adopted for the pilot plant experimentation programme, consisting of the summation of composite samples, was designed to provide a more accurate determination of sedimentation efficiency than one attempting instantaneous measurements of removal efficiency with attendant problems of varying flow-through times and varying influent settleability. Sample compositing for determining removal efficiency is well documented (Tebbutt & Christoulas, 1975; Reichert et al., 1971; Petrasek et al., 1983; Hannah et al., 1986), and the validity of sample compositing for the pilot plant has been confirmed by Kempton et al. (1987a) who compared results from both composite and a series of discrete (grab) samples for influent SS and copper concentration. The concentration obtained from the determination of a composite sample accurately reflected the mean concentration determined by a corresponding series of discrete samples.

A major qualification as to the veracity of the pilot plant approach adopted concerned the soundness of amending plant feed with sludge slurry in order to control SS loading. Kempton et al. (1987b) were able to show that the particle size distribution of raw sewage at the Hogsmill Valley Water Pollution Control Works was essentially unaffected by amendment with a sludge slurry constituted from primary sludge diluted with primary effluent.

The range and quality of the pilot plant results for PAH behaviour and removal during primary sedimentation in comparison with published results are high due to good analytical and sampling integrity (including measurement of native PAH only), the wide range of conditions (SS and hydraulic loading) examined, and the characterisation of accompanying plant performance in terms of SS and COD removal.

The very limited examination of three full-scale units reported by Borneff & Kunte (1967) comprised taking single grab samples (one influent, one effluent) from each unit, taking approximate account of retention time, and reporting mean removals for two groups of PAH only: Σ5 'carcinogenic' and high molecular weight compounds BaA, BbF, BjF, BaP, IP, and Σ10 consisting of Σ5 with FL, P, BkF, BghiP and perylene. Removals of the former ranged from 32 to 80% and the latter 0 to 78%.

The subsequent extension of this study carried out by Reichert et al. (1971) utilised more elaborate sampling methods (Table 8) on two full-scale tanks. 'Mixed sampling' performed on 'Plant A' consisted of taking one influent and subsequently one mixed (i.e. composite) effluent sample 65 to 90 min later, corresponding to the tank retention time. Removal of Σ5 was 31% and Σ10 16%. Removals determined from one influent and one effluent 24 h composite sample from the same plant were halved to Σ5 15% and Σ10 8%. 'Single sampling' was performed on both plants, comprising in each case the collection of three pairs of influent and effluent samples each separated by one tank retention time (Plant A 170 min, Plant B 180-210 min). Removals achieved by Plant A were Σ5 90% and Σ10 89%, and by Plant B 81% and 75% respectively. The

removals determined from mixed and composite samples were very low and questionable. Although possibly representative, only single determinations were performed on one influent and one effluent sample in each case, thereby placing heavy emphasis on the integrity of the analysis. Furthermore, the ratio of Σ5 to Σ10 removals (2:1) was very large. All Σ10 removals reported were less than those of Σ5, as would be predicted from present results where removals of low molecular weight PAH were less than those of high molecular weight compounds (Σ5 restricted to high molecular weight PAH only), but the large ratios suggested simultaneous near-zero removal of the three high and two low molecular weight PAH characterising Σ10, a most unlikely consequence. Removals determined from the 'single samples' were computed from the mean concentrations in three influent and three effluent samples and therefore were more likely to represent true removals. Values for both plants were very high, but the relatively high influent concentrations of Σ5 and Σ10 recorded (Table 8) may be indicative of high influent SS concentrations and therefore of high SS removals. The absence of plant performance data makes interpretation difficult.

The pilot plant results of Petrasek et al. (1983) (Table 9) were in agreement with present results with respect to the general increase in removal of PAH with increase in molecular weight. Removal maximum appeared to occur with MW 202, in contrast to the presently reported MW 228. The study confirmed the low removal efficiency for N which would be predicted on the basis of its molecular weight (128). Percentage removals approximated those obtained for 0.5 DWF, SS_1 (575 mg l^{-1}) and SS_3 (888 mg l^{-1}) (Table 57), but differed markedly for FL and P which Petrasek and co-workers observed to be very high. Although composite samples were taken, plant feed had to be spiked with each PAH at 50 µg l^{-1}. This approached the aqueous solubility of A (73 µg l^{-1}, Table 2) and greatly exceeded that of BaA (14 µg l^{-1}) and CH (2 µg l^{-1}). This oversight would automatically result in a high degree of sorption with the possibility of an erroneously high removal efficiency for the PAH concerned. The very high removals for FL (84.0%) and P (107.0%) may have been a consequence of determinand

aqueous phase concentration falling outside the range for linear sorption because of the high spike level (Section 1.6.1). The authors reported PAH detection limit problems notwithstanding the high spike levels employed. These shortcomings, together with an absence of plant performance data (reporting only that the median influent SS concentration was 430 mg l^{-1} and flow variation 6.1%), preclude meaningful interpretation of results.

Hannah et al. (1986) utilised a pilot-scale circular tank of 0.91 m i.d. and 1.5 m depth, with 45° conical bottom, and design surface loading rate of 12.4 m^3 m^{-2} d^{-1} (retention time 3.2 h). PAH were spiked at 100 µg l^{-1}, which although not exceeding the aqueous solubility of any determinand studied (Table 10), approached that of FL (260 µg l^{-1}) and P (135 µg l^{-1}). Composite samples were taken. Sedimentation achieved removal efficiencies of 13% for N, 21% PA, 22% FL and 18% P and were very low; those for FL and P were not achieved at Hogsmill under any conditions. Again, no data were supplied on plant performance, only that the mean influent SS was 244 mg l^{-1} and tank retention time ranged from 1.2 to 5.6 h.

PAH sedimentation and removal with sludge permitted determination of PAH waste water/sludge phase 'concentration factors' in a manner analogous to that of Petrasek et al. (1983). A concentration factor for each PAH, equivalent to the ratio of sludge to influent concentration on a weight by weight basis, was calculated from the overall mean removal of hydrocarbon achieved by the pilot plant (Table 57) and an overall mean sludge concentration of 6110 mg l^{-1} SS (Table 71). Factors were plotted against log K_{OW} of the appropriate PAH (Table 2) and the data subjected to linear regression analysis (unweighted) (Figure 15) as performed by Petrasek and co-workers. Although the concentration factors were not directly comparable the correlation was slightly better than that of Petrasek et al. It should be noted that a measure of the scatter may have been due to inaccuracies in literature values of log K_{OW} which are acknowledged by many workers.

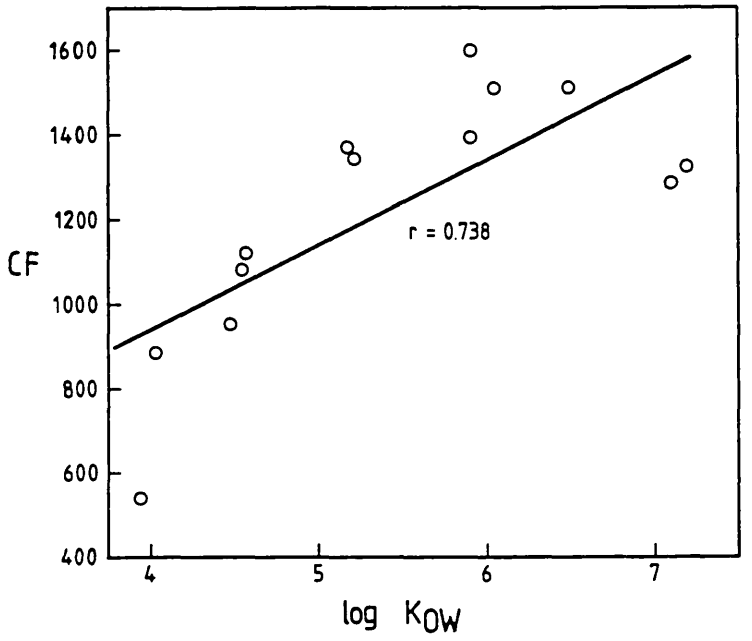


FIGURE 15
Relationship Between PAH
Waste Water/Sludge Phase Concentration Factor (CF)
and Octanol/Water Partition Coefficient (K_{OW})
for Pilot Plant Data

A major assumption implicit in the pilot plant experimentation programme was that PAH removal efficiency was independent of PAH influent concentration and, by implication, that isotherms for PAH sorption to the sewage particulate phase were linear (i.e. constant fraction sorbed) (Section 1.6.1). Weber et al. (1983) warned that 'assumptions of linear partitioning... should be used with extreme caution, and only after substantiation for the specific sorbate/sorbent combination and concentration range in question.' It is argued that this is adequately substantiated in the pilot plant investigations. The concentrations of dissolved and suspended solids in raw sewage were far in excess of the $\mu g\ l^{-1}$ and sub-$\mu g\ l^{-1}$ concentrations of PAH in coexistence, thereby excluding the possibility that active sites for sorption by PAH may be limiting. Herbes (1977) in a study of PAH sorption to autoclaved yeast cells reported marked non-linearity only at low sorbent concentrations. Karickhoff et al. (1979) observed linear sorption for a number of PAH on three natural sediments for PAH aqueous phase concentrations up to approximately 50% of the compound's aqueous solubility; total concentrations of each PAH in pilot plant influent

(Table 73-88) were usually well below the hydrocarbon's solubility. Landrum et al. (1984) reported that the partition coefficient for PAH sorption to humic acid was independent of sorbate concentration in the range investigated and, furthermore, Karickhoff et al. (1979) observed that sorbates in a binary mixture (PA and P) sorbed independently. EPA, in its extensive investigation of the fate of priority pollutants in 50 municipal waste water treatment works, concluded that removal efficiencies were essentially independent of pollutant influent concentration. (A consequence of the assumption maintained was that amendment of plant feed with sludge slurry, although contributing to an extra load of PAH in the influent, remained a valid practice.)

The results for PAH fractionation in the sample of raw sewage (Table 50 and 52) appear to be the first for this matrix; PAH particle size distribution analysis of aqueous-based samples has only been reported for fluvial sediment (Hellmann, 1983), coastal sediment (Prahl & Carpenter, 1983), urban runoff (Hoffman et al., 1984) and estuarine particulates (Readman et al., 1984b). Hellmann (1983) reported results for the sum of the six WHO PAH in sediment from the River Elbe, W. Germany. On a weight by weight basis, <0.7% was associated with the particle size fraction 60-200 μm, 1.7% with the fraction 20-60 μm, and the vast bulk, 97.6%, with the fraction <20 μm. Prahl & Carpenter (1983), in their study of coastal sediment off Washington, D.C., USA ('Station 5'), obtained very different results with fractions distinguished on the basis of particle density as well as size. On a weight by weight representation, and for priority pollutant PAH of MW 178-276, a mean of 95.9% was associated with the particle fraction >64 μm in size but <1.9 g cm^{-3} in density (termed 'low density'). A mean of 0.6% was associated with the fraction >64 μm but >1.9 g cm^{-3} (termed 'sand'). Only 3.5% was associated with the fraction <64 μm ('silt/clay'). The relative proportions corresponded to the percentage organic carbon by weight in each fraction. On a weight by volume representation, a mean of 23.5% was associated with the low density fraction, 9.8% with the sand, and 66% with the silt/clay fraction, the maxima associated with this fraction (<64 μm) in approximate agreement with those

obtained for high molecular weight PAH for the equivalent fraction in the raw sewage sample (Table 50).

Greater correspondence was obtained with the two studies of the more similar matrices to waste water, namely urban runoff and estuarine particulates. Hoffman et al. (1984) reported results for PA, FL and P in a first flush sample of urban runoff. On a weight by weight basis a mean of 24.6% was associated with the particle size fraction >250 μm, 23.6% 125-250 μm, 11.2% 63-125 μm, 13.4% 45-63 μm and 27.2% <45 μm. On a weight by volume basis the corresponding proportions were 24.6, 11.0, 10.1, 18.5 and 24.2%, with a mean of 11.7% soluble. The most important classes on the weight (>250, 125-250 and <45 μm) and volume bases (>250 and <45 μm) corresponded approximately to those of raw sewage (Table 52 and 50 respectively). Suspended particulates from the turbidity maximum of the Tamar Estuary, UK, were examined by Readman et al. (1984b). For priority pollutant PAH of MW 178-252 but excluding MW 228, and on a weight by weight calculation, a mean of 77.6% was associated with the particle size fraction >100 μm, 18.6% 53-100 μm, 1.5% 10-53 μm and 2.4% 0.45-10 μm (Readman, 1988). The proportion maximum at >100 μm was in agreement with that of raw sewage (Table 52) but the proportion associated with fractions <53 μm was very low. On a $\mu g\ l^{-1}$ comparison, a mean of 9.0% was associated with the fraction >100 μm, 36.7% 53-100 μm, 27.4% 10-53 μm and 27.0% 0.45-10 μm; the combined proportion for the 10-53 μm and 0.45-10 μm fractions formed a proportion maximum for this class which agreed roughly with that of raw sewage (Table 50).

It was evident from Table 52 that particulate surface area controlled PAH distribution to a negligible extent as shown by Prahl & Carpenter (1983) and Readman et al. (1984b), the former workers demonstrating the dominance of fraction f_{OC} as a controlling factor and as emphasised by other workers (Section 1.6.1).

The PAH particle size distribution data (Table 50) are important in the interpretation of the overall mean removals of PAH achieved during the pilot plant experimentation programme (Figure 13). The general

increase in overall mean removal of PAH with increase in molecular weight of hydrocarbon can be attributed to the increasing proportion of PAH associated with the sewage particulate phase (fractions >0.45 μm; Table 50) with increasing molecular weight (from 41.5% for AY to 99.4% for BghiP). This is as expected on the basis of PAH log K_{OW} (Table 2). On the basis of proportion of particulate PAH (Table 50), dissolved/particulate phase partition coefficients (K_p, equation (1)) were calculated for each PAH for the raw sewage sample and plotted against log K_{OW} by linear regression analysis (unweighted) (Figure 16). The good correlation was in accord with theory (Section 1.6.1). The slight decrease in overall mean

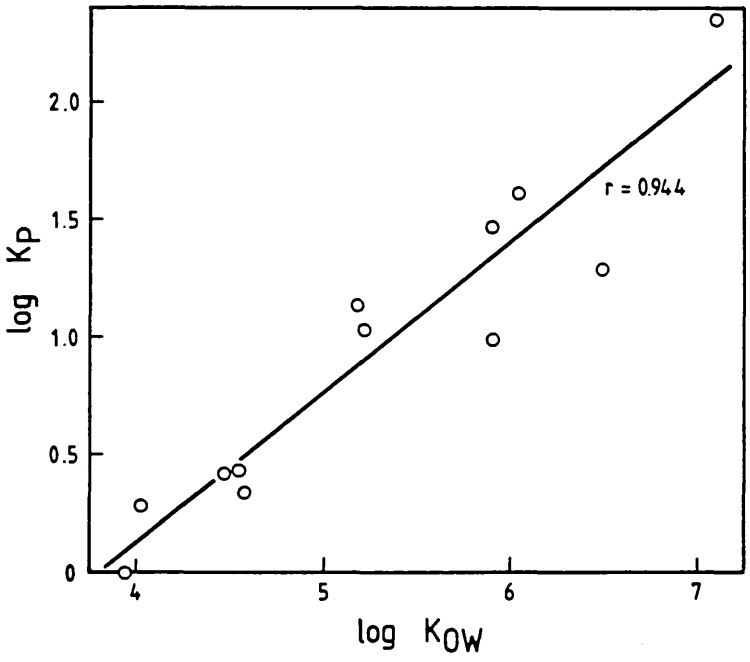


FIGURE 16
Relationship Between PAH
Dissolved/Particulate Phase Partition Coefficient (K_p)
and Octanol/Water Partition Coefficient (K_{OW})
for Raw Sewage Sample

removal of PAH after MW 228 (BaA) (Figure 13) may be attributed to the increasing proportion of PAH associated with the smallest particle size fraction 0.45-53 μm (Table 50) with increase in molecular weight (from 15.7% for AY to 51.0% for BghiP). The slightly poorer removals of the highest molecular weight PAH may have been a consequence of their relatively high association with this fraction of smallest particles of low settleability. The

two effects may thus have concurred to produce the PAH removal pattern observed.

Support for preferential association of high molecular weight PAH with small particle size fractions can be found in the reports of several workers. Walters & Luthy (1984b) examined the dissolved/particulate phase partitioning of PAH in coal coking waste waters undergoing treatment by ammonia stripping, biological oxidation and filtration (by sand). Eleven of the 16 priority pollutant PAH were sampled, but this included the whole molecular weight range from N (MW 128) to DBahA (MW 278). Although the fraction of the total waste water concentration of each PAH associated with the SS phase increased with increasing molecular weight from approximately 50% to greater than 99% in various plant streams, relatively low removals of the high molecular weight PAH (BaP, BghiP and DBahA, i.e. MW 252 and above) were observed in the final oxidation and filtration stage. It was postulated that these high molecular weight compounds may have been selectively enriched in smaller particles less amenable to removal. Readman et al. (1984b) in their study discussed previously, observed relative enrichment of high molecular weight homologs in <10 μm particles, and there was evidence of the same in particles <45 μm in the sample of urban runoff examined by Hoffman et al. (1984). In a controlled ecosystem enclosure Lee et al. (1978) noted that N and dimethyl-N settled at a faster rate than the high molecular weight PAH studied (A, FL, BaA and BaP) and suggested that the settlement mechanism for the former must be different. It was noteworthy of the investigations conducted by Hannah et al. (1986) (Table 10) that with the higher removals of PAH achieved by primary sedimentation with filtration, the benefit increased with increase in molecular weight, as was evident with chemical clarification. Garcia Gutierrez (1983) reported poor and variable removal, independent of SS removal, of polychlorinated biphenyls (PCB) during pilot plant primary sedimentation. PCB possess high hydrophobicity and K_{OW} in common with high molecular weight PAH and may, too, have been preferentially associated with fine SS.

Although correlation of removal efficiency of PAH on the process parameters of hydraulic loading (Table 59) and SS loading (Table 60) was significant particularly for the latter, the correlation of PAH removal on actual SS removal achieved (Table 61) emphasised the importance of influent settleability in controlling the removal of hydrocarbon. The most consistent overall correlation was on SS removal rather than on the removal of the other four co-determinands (Table 62-65, and as summarised in Table 66), but the correlation on VSS removal was nearly as good. This demonstrated the influence of the organic solids subfraction of SS over that of the inorganic solids (NVSS) and total (COD_{tot}) and soluble (COD_{sol}) organic compound components of the raw sewage; previous workers have emphasised the importance of the mass fractional organic carbon content (f_{OC}) of suspended solids and sediments in determining the extent of PAH sorption (Section 1.6.1). Table 61 and Figure 14, where the dependence of PAH removal on SS removal is represented graphically, provide information on the more precise pollutant removal mechanisms involved.

Correlation of mean removal of PAH on mean removal of SS (Table 61) was statistically significant for low to medium molecular weight PAH (MW 152-228) at variable SS loading, and for medium to high molecular weight PAH (MW 178-278) at variable hydraulic loading. The behaviour of the second group of PAH is best interpreted in terms of the removal of the smallest particles. Kempton *et al.* (1987b) in parallel studies performed on the pilot plant observed that hydraulic loading and not SS loading had a regular effect on removal of suspended solids <64 μm: increasing hydraulic loading resulted in a regular decrease in the mean removal of this particle size fraction. Under conditions of variable SS loading, variations in hydraulic retention time due to short-circuiting and mixing effects may well have caused irregular removal of the size fraction leading to a lack of correlation of PAH removal on total SS removal.

Information as to the removal mechanism of the former group of PAH (MW 152-228), where mean removals correlated on mean removal of SS under variable SS loading conditions, may be derived from the observation of increasing ratio of mean

removal of PAH to mean removal of SS with increase in mean removal of SS for the group under these loading conditions, indicating increasing removal efficiencies of the PAH proportionately greater than those of SS (Section 4.3.2.4.1). Ratios for mean removal of SS of 57.9% at the loading of 402 mg l^{-1} (SS_0) to mean removal of 68.2% at 888 mg l^{-1} (SS_3) increased from 0.202 to 0.428 for AY, 0.370-0.674 AE, 0.444-0.689 F, 0.585-0.762 PA, 0.580-0.765 A, 0.748-0.883 FL and 0.775-0.891 P (Table 61). A linear dependence of ratio on SS loading is apparent as an example shows (Figure 17), suggesting that the fractional increase

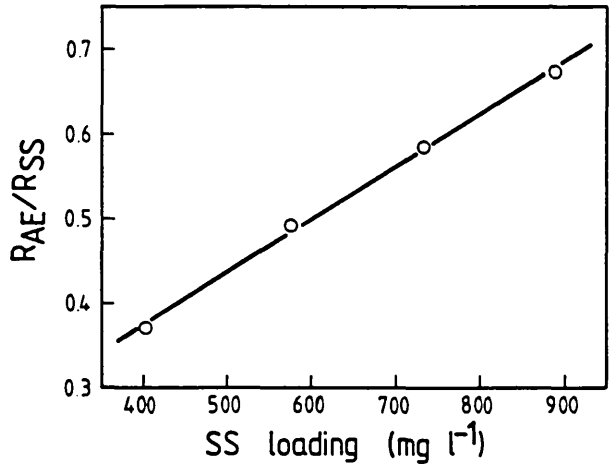


FIGURE 17
Influence of
Pilot Plant SS Loading on Ratio
of Mean Removal of AE (R_{AE})
to Mean Removal of SS (R_{SS})

in mean removal of PAH above that brought about by extra flocculation is proportional to SS loading. The result would be broadly consistent with equilibrium partitioning theory for a solute in a two-phase system. Increasing SS phase concentrations would result in increasing near-linear partitioning of PAH to this phase giving rise to regularly increasing PAH removals over and above those caused by SS-induced flocculation. The factorial increases in ratios for the PAH were 2.12 for AY, 1.82 AE, 1.55 F, 1.30 PA, 1.32 A, 1.18 FL and 1.15 P showing that the effect of enhanced PAH removal decreased with increase in molecular weight of hydrocarbon to a point of insignificance. This may be explained in terms of the proportion of PAH in raw sewage present in the dissolved state, and thus available

for further sorption, which decreases with increase in molecular weight from ca. 60% (μg l^{-1} basis) for MW 152 to <10% around MW 202/228 (Table 50). SS loading thus controls removal of the MW 152-228 group of PAH via SS removal through two probable mechanisms: simple partitioning and flocculation. The weaker influence of hydraulic loading (evident, too, in the comparison of Table 59 and 60) may be a consequence of a preferential association (on a weight by volume basis) of low molecular weight PAH, in contradistinction to that of high molecular weight PAH, for larger particle size fractions (Table 50).

It would therefore appear that for low molecular weight PAH, SS loading is the main controlling influence for SS-mediated PAH removal and hydraulic loading of minor, variable influence, whereas the reverse is apparent for high molecular weight PAH. For medium molecular weight PAH (MW 178-228) both process parameters exert a controlling influence. The absence of statistically significant correlations for certain individual PAH within the above groupings (Table 61) can be ascribed to small differences, within experimental error, between mean removals of a given PAH (Section 4.3.2.2.), and particularly between mean removals of SS (Section 4.3.1.1.2), used in the correlation analyses. The correlation of PAH removal on SS removal over all hydraulic and SS loadings (Figure 14) improved with increase in determinand molecular weight to reach an optimum for the medium molecular weight PAH FL, P, BaA and CH (regression line gradients essentially unity), and thereafter deteriorated steadily. By the above findings it may be considered that low molecular weight PAH data point scatter under this representation is flow variation-induced, and that for high molecular weight PAH SS variation-induced. It is noteworthy that three of these medium molecular weight PAH (FL, P, BaA) are also the priority pollutant PAH whose particle size distributions in raw sewage on a weight by volume basis (Table 50) most closely resemble that of SS itself (Table 49; 25.6, 8.5, 10.8, 18.1 and 37.0% present in particle size fractions >253, 150-253, 106-150, 53-106 and 0.45-53 μm respectively). A similar removal behaviour to SS and thus a similar susceptibility to influence by both process parameters would be expected. Numerically, BaA removal was

closest to that of SS (Figure 14). The implications of this analysis of PAH removal mechanisms for clarifier operation are as follows: to optimize low molecular weight PAH removal tanks should be operated at high SS loadings, and to optimize removal of high molecular weight PAH low hydraulic loading operation is required in hydraulically efficient tanks.

Three sets of evidence exist for the preferential association of high molecular weight PAH with small particle size fractions in raw sewage and thus for the potential importance of fine SS removal in influencing the removal of this important group of PAH: data for the particle size fraction 0.45-53 μm (Table 50), the overall mean PAH removal trend with respect to molecular weight (Figure 13), and the statistically significant correlations of mean removals of high molecular weight PAH on mean removal of SS at variable hydraulic loading (Table 61). It was evident from the findings of Kempton et al. (1987b), and from the PAH removals observed (Table 57) compared against the PAH particle size distribution results (Table 50), that removal of particles <100 μm, and normally considered non-settleable by Class I sedimentation (Tebbutt, 1983; Valioulis & List, 1984a), undoubtedly accounted for appreciable removals of PAH during the pilot plant experimentation programme. From Table 50 it can be determined that the proportion of each PAH associated with the particle size fraction 0.45-106 μm ranged from 22.3% for AY to 73.2% for BghiP, a steady increase with molecular weight. From an examination of the ranges of PAH removals observed, and particularly of the maxima, these proportions were evidently subject to appreciable removal, the importance of which was potentially greatest for the high molecular weight PAH. It would seem therefore that Class II settlement (flocculation) brought about notable sedimentation of PAH and that it assumed added significance for the removal of high molecular weight PAH. However, the relative importance of Class I and Class II settlement on removal of a given PAH under any given conditions cannot be determined precisely: particles >100 μm are subject to both types of settlement during primary sedimentation and the relative proportions of discrete and flocculent particles in raw sewage are variable and to a large extent unknown.

Moreover, sedimentation is not just related to particle size and settling class type.

Sedimentation is determined by particle settleability which is dependent on particle density as well as size (Section 1.8.2). The limitations of the particle size distribution analysis performed should be appreciated, not only because it was performed on just one sample, but that the basis of the fractionation was particle size and not density and a fractionation based on the latter may have resulted in a somewhat different distribution. Prahl & Carpenter (1983) showed that PAH could be preferentially enriched in particles of low density. Furthermore, Class I settling, which is adequately described by Stoke's Law, favours denser, bigger particles during primary sedimentation, but Class II settling can occur with all particle densities and sizes, including colloidal/ microparticulate matter, and is enhanced by factors which increase particle collision (increased retention time, increased SS). O'Melia (1987) provided a succinct modern summary of particle-particle interaction theories. Particle transport (collision) is brought about by three mechanisms: Brownian diffusion (perikinetic flocculation), which is rapid (<1 min); fluid shear, both laminar and turbulent (orthokinetic flocculation), where particles are brought together by velocity gradients; and differential settlement under gravity, where particles with high settling velocities overtake and thus collide with those with lower velocities (O'Melia, 1987; Valioulis & List, 1984a). Particle attachment is dependent upon particle surface characteristics (especially electric charge density) and the fluid medium chemistry (especially pH and ionic strength). With regard to particle transport, the 'collision rate' is strongly dependent on the number-concentration of particles, and with respect to particle attachment, the 'collision efficiency' is defined as equivalent to the fraction of particle-particle collisions that results in attachment. Floc shear may be brought about by a high (fluid) shear stress. The mechanisms and factors affecting flocculation of settling sewage, however, are poorly understood in comparison with the body of data now existing on flocculation in water and activated sludge treatment.

Although it was shown that the principle PAH removal mechanism was physicochemical sorption to SS and removal with settleable solids, a further mechanism in the form of solute partitioning into non-polar (insoluble) fat and lipid material present in liquid globular form in the raw sewage may have mediated removal. An appropriate measure of this material would be an oil and grease determination, but Barrick (1982) in a study of full-scale primary settlement units reported that oil and grease effluent concentration did not correlate with PAH effluent concentration. The internal consistency of the present results with respect to PAH and SS removal imply, however, that if this was a valid mechanism its effect was minor.

It is not clear how dissolved organic matter (DOM) in the form of humic acid, colloids and other materials to which PAH are known to sorb extensively (Section 1.6.1) affects PAH sorption to SS and hence PAH settleability. DOM present in raw and waste waters may be expected to decrease the proportion of pollutant that sorbs to SS and to increase the proportion 'stabilized' in the water column. This has been demonstrated in the laboratory by Hassett & Anderson (1979, 1982) in investigations of the effect of DOM on sorption to fluvial and secondary effluent particulates by cholesterol and 2,2',5,5'-tetra-chlorobiphenyl. Varying concentrations of DOM in raw sewage, which are not measured by the SS determination, could modulate PAH removal. PAH sorption to DOM is sensitive to pH (Wijayaratne & Means, 1984).

Effect of PAH sorption kinetics and reversibility on PAH removal is difficult to assess because data in this field are only just appearing. Assuming steady state conditions and absence of chemical or biological changes in tank contents on sedimentation no shift in the PAH distribution between dissolved and particulate phases would be expected. However, under dynamic conditions of varying influent SS, flow and PAH concentration, sorption equilibrium theory should predict no overall effect on PAH removal but only a dampening of short-term PAH effluent concentration fluctuations (additional to the dampening of short-term SS effluent concentration variations noted for primary units (March & Hamlin, 1966; Valioulis & List, 1984b)). The work

of Karickhoff (Section 1.6.1) suggests that the effect may be limited: only 50% of sorption may be labile (rapid). Morozzi & Scardazza (1988), however, noted of BaP sorption to activated sludge, that ca. 60% sorbed after 5 min and virtual equilibrium was reached after 30 min. Readman et al. (1984b) presented important empirical evidence for occlusion of estuarine particle-sorbed PAH, that is for irreversibly sorbed PAH, subsequently reinforced by predictions by a calibrated PAH sediment-water exchange model (Readman et al., 1987). Such a phenomenon would be expected to modify PAH particle size distributions and to produce unexpected removals during sedimentation. Clearly, more work is needed on sorption kinetics and reversibility to account fully for PAH behaviour during waste water treatment.

In summary, PAH removal during primary sedimentation has been shown to be principally a function of PAH physicochemical property (molecular weight) and unit process performance (SS removal efficiency) (Table 67 and 89). The significance of the regression functions lies with the following:

- -The expressions enable prediction of mean removals and removal ranges of PAH on the basis of tank performance, and thus permit prediction of primary effluent and sludge quality.
- -They define load on the subsequent secondary treatment and sludge treatment processes.
- -They aid definition of tank design requirements (via SS removal) to achieve a specified PAH removal.
- -The functions are suitable for use by regulatory agencies in the calculation of consent conditions for industrial discharges of PAH to sewers to meet receiving water and sludge quality criteria at minimal overall cost.

PAH effluent concentration will, in addition to being a function of the above two parameters, be related to PAH influent concentration. For a given removal efficiency, effluent concentration should be proportional to influent concentration. Influent data from the four experiments involving unamended SS loading (SS_0; Table 73, 77, 81 and 85) indicated that concentrations of individual PAH generally varied at least four-fold.

Further examination of influent data from the same experiments revealed no clear or consistent correlation of (composite sample) individual PAH influent concentration on SS influent concentration, in contrast to the findings of Rump (1981) who, over a 24 h period, found four PAH (FL, BaP, BghiP and 3,4-(o-phenylene)pyrene) to correlate on SS in a works influent. Hagenmaier et al. (1986), however, reported that the sum of the six WHO PAH correlated on daily inflow and furthermore ranged at least nineteen-fold. Influent concentrations approximated those commonly reported (Borneff & Kunte, 1965). Relative abundancies ('profiles', on a mol l^{-1} basis, based on the mean for the four experiments) were AY 1.4%, AE 36.0%, F 20.6%, PA 14.5%, A 3.6%, FL 4.8%, P 6.1%, BaA 2.2%, CH 2.3%, BkF 3.2%, BaP 2.5%, IP 1.0%, BghiP 1.3% and DBahA 0.4%. The general decrease in relative abundance with molecular weight has been observed for other raw sewages (Borneff & Kunte, 1965; Readman et al., 1984b) and sludges (Grimmer et al., 1980; Hagenmaier et al., 1986; Dierckxsens et al., 1987). Values for AY and A were relatively low, though. Pilot plant sludge concentrations could not be compared directly with literature values (Table 11) because sampling was performed after mixing sludge with tank contents.

PAH removal behaviour observed in the pilot plant would be expected to be similar in full-scale units, due to the established dependence of PAH removal on SS removal (Table 67) and the favourable comparison of pilot plant performance with that of full-scale tanks with respect to SS removal (Table 68). A possible difference may exist in respect to high molecular weight PAH, where the increased depth of works tanks (1.5-4 m: Institute of Water Pollution Control, 1973; Barnes et al., 1981) in comparison to that of the pilot plant (1.46 m) may favour slightly increased removals through increased flocculation of fine SS.

If it is wished to consider PAH removal in sedimentation tank design then the regression functions provide the appropriate means for this. The previous analysis of PAH removal mechanisms suggests that if removal of high molecular weight PAH is required to be optimized, tanks should be designed with adequate depth or retention time and have satisfactory hydraulic efficiency. Tank design is

more realistically subject to optimization for more conventional (SS) reasons. Tebbutt & Christoulas (1975) claimed that conventional settlement design criteria are very conservative and underutilised. The relatively modest dependence of SS removal efficiency on hydraulic loading compared with the appreciably greater dependence on SS loading under the range of conditions normally encountered (and as verified by numerous investigators; Section 1.8.2) suggested that shorter tank retention times could be adopted with little loss in removal efficiency. Tank design optimization for new works and for the hydraulic upgrading of existing ones could be based on discharge consents appropriate to the EQO of the receiving water (Lester, 1979; Robinson, 1980). Bowden & Young (1984) noted that rule-of-thumb plant design based on treatment of flows up to 3 DWF, with excess flows diverted to storm tanks and flows in excess of 6 DWF directed to a nearby watercourse, results in a less than 50% utilisation of plant hydraulic capacity in dry weather (in a fully combined drainage catchment). They noted, furthermore, that it is rare even for the full capacity to be used in wet months, and reported that modelling techniques are evolving for effective prediction of urban runoff and behaviour of sewerage network which should provide the means for replacing current semi-arbitrary hydraulic specification by a basis for design optimized to local conditions.

It is important to assess correctly the contribution of flocculation to sedimentation in the design of tanks. In early pilot-scale studies, Tebbutt (1969) observed, over a wide range of hydraulic loading, a lack of correlation of SS removal on tank hydraulic efficiency (ratio of actual to theoretical retention time). It was previously mentioned that the actual flow-through time for a given hydraulic loading can vary and be significantly less than the theoretical time because of short-circuiting (due to density currents) and mixing (due to hydraulic turbulence). It was postulated by Tebbutt that the lack of correlation resulted from the flocculent nature of sewage particulates which caused the formation of more readily settleable solids within the velocity gradients associated with density currents and turbulence. Reduction in hydraulic

efficiency may thus have been offset by an increase in flocculation. Hamlin and co-workers in full-scale (March & Hamlin, 1966) and laboratory studies (Hamlin & Abdul Wahab, 1970) of the effect of tank density gradients (mass and temperature), presented good evidence of density current induction of flocculation as giving rise to improved SS removal efficiencies. Furthermore, Tebbutt (1969) noted that higher flow rates appeared to overcome density currents, but March & Hamlin (1966), although reporting that lower flow rates tended to encourage the formation of density currents, at higher flow rates they observed that hydraulic turbulence became pronounced. The apparent contribution of density currents and hydraulic turbulence to increased flocculation through velocity gradient induced particle collision is a major reason for the growing belief that, despite continuing investigations, attempts to improve sedimentation tank hydraulic flow patterns and thus hydraulic efficiency are likely to be met with very limited success in terms of removal of SS (Tebbutt, 1969; March & Hamlin, 1966; White & Allos, 1976). Now, in the scale-up of tank design parameters from the results of settling column tests, surface loading rates are divided, and retention times multiplied, by a factor in the range 1.25-2.50 to account principally for short-circuiting and mixing effects in full-scale tanks (Section 1.8.2). Thus, in order to avoid an arbitrary selection of factor and instead to select one as low as possible to reduce tank construction costs, it is necessary to estimate carefully Class II settling contribution to sedimentation. This is also important in the incorporation of the later, but related, findings of Tebbutt & Christoulas (1975), referred to previously, in which the greater importance of SS loading over hydraulic loading in controlling removal of sewage led to the recommendation of shorter retention times and hence smaller tank capacities. It is important, too, for assessing removal of high molecular weight pollutants preferentially associated with small particle size fractions non-settleable by Class I sedimentation (<100 μm). However, current settling column practice suggests that measurement of flocculation and thus importance of SS concentration on sedimentation may be inadequate.

A single test employing a settling column with a number of sampling ports effectively determines the effect of depth and retention time on combined discrete and flocculent removal. The contribution of flocculation itself to removal is not readily quantified, although an approximate indication may be obtained by inspection of SS isopercentage removal line curvature (Figure 1). It is more appropriately measured via its dependence on SS concentration but although good estimates of the influence of flow rate and thus hydraulic loading on removal can be computed from the results of one settling column test (from retention time), the influence of SS concentration and thus SS loading on removal cannot be so judged. This can only be done by repeating the test on samples of differing SS concentration, and where texts do suggest this they fail to give clear guidance on the practice required. Samples of differing SS concentration collected separately would fail to distinguish between the two effects of SS concentration and sample representativeness on flocculent removal; serial dilution of a single sample with tap or distilled water would modify fluid medium chemistry (pH and ionic strength) which is known to affect flocculation; dilution of a sample with secondary effluent could introduce a similar problem. A logical answer would be to successively dilute a sample (of high SS concentration) with filtrate (0.45 μm) from the same sample. Unfortunately, filtration through such a mesh size is extremely slow. A satisfactory compromise could suffice whereby a portion of the original sample is allowed to settle in a spare column and a non-settleable aliquot drawn off for use as diluent when required. A maximum SS concentration for the diluent should be advised. This simple procedure does not appear to have been delineated in any text or laboratory manual.

Further evidence exists to show that settling column practice has not been fully optimized and principles not fully appreciated. Only very recently (Agrawal & Bewtra, 1985) has a modification been proposed for the calculation of particle settling velocity from the settling column test to permit an improved determination of particle removal. An attempt at developing a standard procedure (Zanoni & Blomquist, 1975) in terms of column length and width, number of sampling ports and number of SS determinations at

each port, involved serial dilution of the test sample with tap water. To encourage and to ease the correct assessment of the effect of SS concentration on sedimentation in the settling column test, it would be of value if users of the test were able to resort to an empirically derived function of the kind developed by Wahlberg & Keinath (1988) for the sludge volume index (SVI) test, enabling assessment of the effect from the results of a single settling test on the basis of a series of tests executed properly. The authors developed an empirical regression function relating SVI to settling flux and SS concentration, the two parameters describing activated sludge interface settling velocity, from data collected from 21 full-scale activated sludge plants. The function permitted the development of a settling flux curve (settling flux versus SS concentration) from a single SVI test, thus avoiding the time-consuming task of determining flux at a number of SS concentrations. Similarly, for primary sedimentation, correct dilution of a series of flocculent sewages from a statistically valid data set may permit formulation of an equation for SS removal as a function of SS concentration, column depth and time, which can be related to some parameter measuring curvature of the SS isopercentage removal curves (Figure 1; for example, that of the 60% removal curve, a ratio of two points on the curve). Such a relationship should lead to the basis of a more rational selection of scale-up factor; the greater the dependence of removal on SS concentration the greater the flocculation and thus the less detrimental the effect of short-circuiting and mixing is likely to be, and hence the smaller the factor which may fittingly be selected. Correct execution of the dilution method would also clarify the speculation (Tebbutt & Christoulas, 1975) that the higher SS removals observed for sewages of high SS may not be due entirely to flocculation but to a greater proportion of settleable solids (i.e. settleable by Class I sedimentation), as there is some evidence that for sewages in the UK the non-settleable solids concentration is approximately constant (ca. 150-200 mg l^{-1}) (Anderson, 1981; Tebbutt & Christoulas, 1975). A further aid for the settling column test would be the formulation of a function relating SS concentration to depth for a suspension undergoing both Class I and Class II settlement. Panjan (1988) recently attempted three such functions for

laboratory vessels (0.3 m), tanks (3.0 m) and lakes (30.0 m). The relationship would potentially allow the use of a shorter and more manageable column by requiring only limited data on SS isopercentage removal curve shape, as outlined above, for purposes of extrapolation.

Concerning the accuracy of the settling column test itself (i.e. scale-up factors aside), White & Allos (1976) stated that the test gives a useful first approximation to tank performance only. Clements (1976), on the basis of column test studies of a full-scale tank, proposed an empirical correction factor for the test but warned, ironically, of the danger of its general applicability. It would seem extraordinary that no statistical analysis has been performed to quantify formally the error associated with the settling column test and which may thus be expected with its use. A data base should be maintained of settling column test results, with scale-up factors employed, against subsequent performance of tanks. This would permit a statistical analysis of overall procedure accuracy and precision, ensuring that future selection of scale-up factors is based on properly quantified random and systematic errors. Maintenance of the data base would encourage better engineering practice in the form of a proper execution of a minimum number of column tests and would permit identification and warning of troublesome sample types. Much valuable data are currently being discarded.

The complexities of Class II settlement are such that, until such time as it is possible to predict the performance of sedimentation tanks from purely theoretical relationships, satisfactory tank design will continue to require a substantially empirical (settling column test) approach. The work of Panjan (1988) and Valioulis & List (1984a,b) represent notable first attempts at modelling Class II settlement, although they are for simple homogeneous systems and entail diverse assumptions. Numerical simulation models of the sedimentation process invariably assume Class I type settlement only (Curtis & McCuen, 1977; Larock et al., 1983). It is now widely believed that primary tanks are frequently oversized and the retention times at many works excessive (Black, 1988;

Tebbutt & Christoulas, 1975; Valioulis & List, 1984a), undoubtedly for some of the reasons outlined above. Black (1988) suggested that a proportion of capacity at those works could be usefully removed from use, and the spare capacity converted into flow balancing tanks. Lowe & Sidwick (1987) proposed a dual-function use of sedimentation tanks as storm tanks at large works, whereby incremental increases in tank capacity are brought on stream as the flow increases. Achieving correct tank design is important not only for minimizing tank construction (and maintenance) costs, but also for fulfilling the required tank objectives and performance targets. The latter is particularly important as once constructed, sedimentation tanks are subject to limited control. 'Fines', the sedimentation of which is favoured by long retention times, can be deleterious to sludge dewaterability and filterability (Barnes & Wilson, 1978).

The deficient attention paid to effect of SS concentration on flocculation and therefore settlement in the laboratory column test may account for the only very recent realisation (by Tebbutt & Christoulas (1975)) of its importance in relation to flow in controlling tank performance, and for the related observation (by Tebbutt (1969)) of lack of correlation of SS removal efficiency on tank hydraulic efficiency. The true importance of SS concentration would only be appreciated by performing the settling column dilution technique described or, as done by Tebbutt and in the present study, by deliberately controlling tank influent SS concentration or measuring its effect independent of flow (practices difficult to perform and rarely achieved).

That the influence of SS concentration and thus flocculation on settlement is not fully appreciated in environmental engineering is evident when an examination is made of the method of determining the percentage by mass of incoming sediment trapped, termed 'trap efficiency', of reservoirs receiving direct surface runoff (i.e. not pumped storage). Although flocculation is deemed significant enough to determine for tanks of only a few metres in depth, this does not seem to be the case for reservoirs. It is reported that an empirical relationship derived by

Brune (1953) is used extensively for determining reservoir trap efficiencies (Gottschalk, 1964; Vanoni, 1975; Golzé, 1977; Gill, 1978, 1988; Annandale, 1987; Mahmood, 1987; Linsley et al., 1982). In the design of a dam it is frequently important to consider the volume of sediment that will deposit, in order to avoid a subsequent premature loss of storage dedicated to a specific purpose. Dam height and position of outlets can depend on deposits and their distribution, and latterly turbine design has involved consideration of the nature and concentration of suspended particles (Xue-Zhong, 1985). The Brune curve (Figure 18) relates the trap efficiency of some US normally

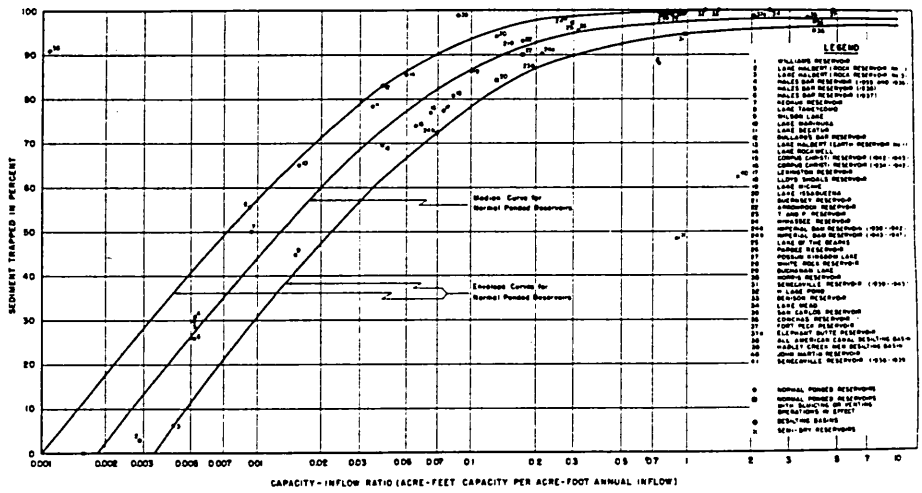


FIGURE 18
Reservoir Sediment Trap Efficiency Curve
After Brune (1953)

ponded reservoirs to 'capacity-inflow ratio' (mean capacity in acre-feet divided by mean annual inflow in the same units). This index is effectively a measure of retention time and hence of flow but it is noteworthy in that it does not include a term for inflow SS concentration. There is a considerable scatter of the datum points, which number 40, as bounded by the two 'envelope curves' about the regression line ('median curve'). It is evident straightaway that the capacity-inflow ratio is a somewhat incomplete index for the relation because of the width of the envelope: for a trap efficiency of 40%, for example, the associated error defined by the envelope curves is approximately ±15%, giving a range of 25-55%.

A more critical examination of the relation reveals further serious shortcomings. Apart from the age of the data upon which the relationship rests (pre-1953), the 40 datum points, corresponding to nearly the same number of reservoirs, were obtained by no less than seven different sampling methods, only one of which was essentially reliable (reservoir bed survey with downstream SS measurements) as was acknowledged by the author. Although this method was the one most commonly employed, the utilisation of so many different sampling methods to produce a single relation is a bad practice by modern standards. Now, above a capacity-inflow ratio of approximately 0.15, corresponding to just over 6.5 reservoir 'turnovers' per annum, the trap efficiency levels off from 90% to approach 100% asymptotically. The narrowness of the envelope curves shows that the error here is relatively small. The 'critical' region, for ratios <0.15 where incomplete removals (>0-<90%) can be expected, is served by 18 of the 40 datum points, only six of the 18 having been obtained by the only arguably valid sampling method. Three of the six points incorporate data collected in the 1920s. The relation between these six datum points on the graph is a visibly tenuous one. A most unfortunate error has, in addition, been associated with the use of the Brune graph. It would appear that the median and two envelope curves have been mistakenly interpreted as three curves for fine, medium and coarse sediments that predominate in the influent (the lower curve for fine, the upper for coarse). This can be seen, for example, in Szechowycz & Qureshi (1973), in the standard text on sedimentation engineering by Vanoni (1975) and in Gill (1988), the latter, as with Linsley et al. (1982), presenting three precise algebraic equations for the curves. It would appear that use of the Brune relation has not been accompanied by a critical re-examination of the underlying data.

Although it would seem that the critical region of the graph only applies to relatively small reservoirs with high inflows, such schemes are common in humid and tropical areas. However, the relation is also used for small sections of large reservoirs as in the case of the Mangla Reservoir, Pakistan, where the critical part of the graph

was used to determine sediment deposition in important sections (Szechowycz & Qureshi, 1973). Furthermore, in the determination of reservoir storage life, the calculation involving Brune is performed incrementally on increasing volumes of deposit and hence decreasing capacities of reservoir and thus involves, for large reservoirs, employment of the critical region of the relation for later years of reservoir life. A new sediment trap efficiency curve has been developed for small reservoirs serving a drainage area of less than 39 km^2 (Heinemann, 1981). The Brune capacity-inflow ratio is again used but the overall function is significantly different. That part of the curve representing trap efficiencies of 0-80% is defined by only four of the 20 datum points. Mahmood (1987) distinguishes two types of method for predicting reservoir sedimentation: empirical models based on inductive analysis of field data of which Brune is the principle and which are used for small projects, projects with limited funds and the detailing of large projects, and mathematical models based on numerical simulation analysis of sediment transport processes. The latter require particle size distributions as raw data but it is questionable whether the determination of these is entirely satisfactory.

Particle size distributions for mathematical models are determined on the basis of particle settling velocity distributions (Vanoni, 1975; Mahmood, 1987; Ackers & Thompson, 1985). A settling velocity is converted to an equivalent particle 'sedimentation (fall) diameter' which is the diameter of a sphere of a particular specific gravity that has the same terminal settling velocity in quiescent water at 24°C as the original particle (Vanoni, 1975; Mahmood, 1987). Use is made of standard settling velocity curves for a wide range of theoretical particle sizes. Settling velocities are determined in three types of tube (Vanoni, 1975): the VA Tube (120-180 cm in length) for sands (0.062-2.0 mm), the Pipet (5-15 cm) and BW Tube (up to ca. 100 cm) for combined silts and clays (0.002-0.062 mm) (although the latter can also include sands). The Pipet enjoys routine use for fines. The design of the tubes, and practice associated with them, appear to assume Class I type settlement only. The short lengths of the tubes do not allow a realistic assessment of

the effect of depth on settling velocity, and the recommended separation of size classes before analysis (usually be wet sieving) assumes absence of interparticulate interaction. It is acknowledged that mathematical models are sensitive to particle size distribution data (Mahmood, 1987).

It may be argued that flocculation and thus influence of SS concentration are unimportant in surface fresh water sedimentation and that the Brune index involving a retention time consideration only is of sufficient validity. This may be so for capacity-inflow ratios >0.15, but for lesser critical ratios representing incomplete removals and with the aforementioned shortcomings, this is more tenuous. It is well known that clays are subject to flocculation (Håkanson & Jansson, 1983) and that 'the bulk of sediment transported to reservoirs is, at least in the humid agricultural areas... in the silt and clay range' (Gottschalk, 1964), this same author acknowledging that 'in some areas, clays and colloids are aggregated into clusters which have settling properties similar to larger grains.' Vanoni (1975) stated that 'in many cases, (flocculation) may be the major factor in determining the settling velocity and the specific weight of a deposit,' and O'Melia (1987) summarised recently obtained evidence for flocculation in lakes. That flocculation is considered absent or negligible in sedimentation is implicit in another practice. Physical models (hydraulic scale models), which are used for detailed work on hydraulic and sediment behaviour (Ackers & Thompson, 1985) are, in their reduced scale, valid for Class I settlement but not for Class II where depth cannot validly be scaled down any more than a short settling column can at present be used to model Class II settlement in a primary sedimentation tank. Class II contribution to sedimentation cannot be assumed to be absent unless specifically proven for the particular suspension concerned. A simple test for flocculation is proposed based on the settling column test dilution technique described and exploiting the SS concentration dependence of Class II settlement. A sample is allowed to settle for just one time interval in a short column possessing a single lower sampling port and percentage removal calculated. The test is repeated after a correct

dilution of the sample using settled suspension from a spare, second column. If flocculation is absent, an identical value for percentage removal should be obtained, Class I settlement being independent of sample SS concentration. If, however, flocculation is present, then a significantly reduced removal would be recorded for the less concentrated sample. Testing for flocculation in this manner would, if negative, at least secure confidence in measurements assuming Class I settlement only, and if positive, enable additional sampling and measurement requirements to be gauged. A simple field kit could be developed based on turbidity rather than gravimetric measurements of SS concentration: a relative calibration could be performed in the field by a serial dilution of a portion of the original sample. Such a useful and simple test, in this or in any related form, does not appear to have been advocated.

In view of the current world siltation problem and the high cost of even the smallest scheme, it is evident that a more rational approach for assessing environmental sedimentation is urgently required and a clearer set of guidelines on practice needed. The potentially large errors associated with the Brune relation, especially for reservoir capacity-inflow ratios <0.15, must be acknowledged. In particular, the engineering community must be made aware of the erroneous mis-labelling of the Brune curves. It is questionable whether, for these low ratios and thus high reservoir 'turnovers', more accurate predictions of trap efficiency might not be obtained from the application of settling column tests and sedimentation tank theory. Where mathematical models are used and where flocculation is shown to be operative, then particle settling velocity distributions should be determined in significantly longer tubes and ideally with no separation of class sizes. A much longer BW Tube may suffice. For a flocculent suspension, each SS isopercentage removal curve obtained from a traditional settling column analysis represents the settling behaviour of the given fraction of solids (Figure 1): curvilinearity is due to settling velocities changing (increasing) with depth (h) and time (t). An average settling velocity (h/t) may be determined for each solids fraction and for example, that for the fraction

represented by the 50% removal curve in the figure is equivalent to h_5/t_2 for this particular column depth. Similarly for a tube analysis of a flocculent reservoir suspension, the determination of average settling velocities of fractions over a larger depth should more accurately approach the settling velocity distributions liable to be attained in the high depth conditions of the reservoir. Furthermore, the effect of SS concentration on the settling velocity distribution should be quantified using the settling test dilution technique described. It should not be difficult to incorporate a term in the sediment transport functions of the mathematical models for particle size distribution dependency on SS concentration from the settling velocity distribution dependency. Concerning major reservoir studies it would be wise to test for flocculation in storm samples where SS concentrations can be high (1000-4000 mg l^{-1}) and when sediment delivery and therefore deposition rates can be large. When data are collected concerning seasonal effects on particle size distributions (Ackers & Thompson, 1985) it is important that these are not confused with SS concentration effects under current practice.

The discussion of PAH behaviour during primary sedimentation has largely considered PAH percentage removal but in terms of the quality regulation of surface waters abstracted for potable supply PAH effluent concentration is a more fundamentally significant parameter. PAH percentage removal has been shown to be a function of SS percentage removal (Table 67) and judged to be independent of PAH influent concentration. The relatively narrow range of SS removal efficiencies associated with the normal operation of full-scale units experiencing diurnal variations in flow and SS (typically 15%), imply that PAH effluent concentration is likely to be influenced at least as much by PAH influent concentration as by SS removal and hence tank performance. For a given PAH removal efficiency, effluent concentration should be proportional to influent concentration. A variation in influent concentration of at least four-fold, as previously noted and by other authors, should produce an equivalent variation in effluent concentration, and hence this variation represents a larger potential impact on the quality of subsequent potable

supplies than variation in tank performance, which is subject to limited control. Control and removal of PAH are thus more likely to be effectively secured through catchment management via selection of, and compliance with, appropriate quality standards (Section 1.5). This in turn calls for a careful monitoring programme.

Surface waters themselves require rigorous monitoring. In the case of PAH these water resources are subject to contamination not only from the more recognisable point and non-point sources (Table 3) but also from intentional and incidental fossil fuel spills. Furthermore, the UK EQO/EQS pollution control philosophy depends upon adequate monitoring of receiving waters. The role of the sewage treatment works as a major point of convergence for multi-source PAH entering surface waters suggests that plants should form effective monitoring locations in addition to selected catchment sites in a river basin monitoring programme.

Current recommendations for monitoring of PAH, considered collectively, are disparate and inadequate. The EC surface water directive (Council of the European Communities, 1975) stipulates a minimum of only one sample per year for all water categories even for over 100000 population served. The drinking water directive (Council of the European Communities, 1980) specifies no monitoring requirements. The World Health Organization (1984) incorrectly judges BaP (the sole determinand) to be a type '2b' contaminant, that is a substance for which the distribution system, rather than the raw water, provides the main source, and recommends sampling at the consumer tap. The UK Water Research Centre (Crane et al., 1981) stated that 'since water treatment has been shown to be so effective, there seems little value in routinely measuring PAHs in river waters (in relation to abstraction)'. Furthermore, the EC PAH and associated criterion (200 ng l^{-1}) embody major shortcomings.

The EC drinking water and surface water directive PAH (FL, BbF, BkF, BaP, IP and BghiP) and the criterion were taken directly from the former WHO standard for PAH (World Health Organization, 1970, 1971; Section 1.5.1) which in turn

derived from the work of Borneff & Kunte (1969). The selection of the PAH and associated limit were arbitrary, however, for a number of reasons. The limit was not based on a toxicological consideration but on the premise that tap water should contain no more PAH than that found in ground water. Borneff & Kunte (1969) obtained ground water and associated tap water PAH concentrations at 14 sites in the Rhine-Palatinate and Hesse region of W. Germany. The results indicated an overall mean concentration for the sum of the six PAH in ground water of approximately 50 ng l^{-1}, and in ground water derived tap water approximately 100 ng l^{-1}, the increase due to pick-up from distribution pipe linings. The final limit of 200 ng l^{-1} was obtained by multiplying the value for tap water by a factor of two to allow for potential variations in ground water concentrations and pipe pick-up. The analytical method employed (developed from the procedures of Kunte (1967) and Borneff & Kunte (1964)) consisted of a simple TLC procedure, which although regularly detected ten PAH (the above six with P, BaA, BjF and perylene), only the six occured at concentrations regularly in excess of the detection limit. Hence the selection of the six PAH was not based on any toxicological consideration but on what was readily detected. Concentrations of the six were summed to reduce errors due to sample contamination associated with the method. This practice should no longer be necessary in modern analytical methodology where contamination is controlled and, in any case, the practice is analytically inelegant as the summed results do not permit meaningful interpretation of individual PAH. The aforementioned leaching is due very largely to one of the 6, FL, shown in subsequent studies with respect to coal tar lined distribution systems (Section 1.3). The concentration of this PAH normally dominates the summation. Borneff & Kunte (1969) reported typical concentration ratios of 20:2:1:1:1:1 for FL:BbF:BkF:BaP:IP:BghiP. Hellmann (1987), summarising earlier work (Hellmann, 1980, 1981), noted that FL composed 80-90% of the dissolved fraction of WHO PAH in River Rhine water. Crane *et al.* (1981) in their survey of PAH in UK tap waters observed that some, derived from ground water, contained levels of PAH comparable to the EC limit, but that these levels were composed almost entirely of FL. The PAH has since been

shown to be non-carcinogenic (Table 6) and thus it is evident that the EC/former WHO summed determination is very markedly and deleteriously influenced by this non-toxic component.

The EC drinking water and surface water directives should therefore be revised to stipulate the reporting of individual PAH concentrations; to delete FL and replace it possibly with BaA (a known carcinogen, Table 6); and to replace the arbitrary 200 ng l^{-1} limit by limits based on toxicological considerations in the manner of the new World Health Organization (1984) limit for BaP (10 ng l^{-1}). Retention of the remaining PAH and inclusion of any further in a new list should be assessed on the basis of the latest knowledge of PAH occurrence and toxicology. The common origin of PAH (high temperature combustion processes) and the often observed approximate uniformity of homolog profiles suggests that monitoring of a reduced number (less than six) may be valid and representative. It is of crucial importance that serious consideration is given to reform of the EC PAH regulation. In a recent survey of tap waters conducted by Thames Water Authority (Anon., 1988), and widely reported in the press, approximately 1% of samples were found to be 'several times' above the EC PAH MAC due to distribution pipe leaching and/or shedding of particulates. Compliance failure was very probably due to non-toxic FL, and therefore to replace or re-line (e.g. with bitumen or cement mortar) the potentially troublesome 25000 km of iron mains in the Thames Water Authority region at a cost of many millions of pounds to comply with the EC regulation, as warned, could represent a huge waste of resources.

The pending EC daughter directive on PAH under the dangerous substances directive (Council of the European Communities, 1976) will consist of limits in the form of emission standards (ES) and in the form of EQS (favoured by the UK; Section 1.5.2). The directive should incorporate the revisions detailed above. Legislation pertaining to the EQO/EQS control philosophy should be made compatible with, and correspond to, that in the surface water directive which already contains PAH quality standards for three classes of surface water. The new directive should

extend EQO and corresponding PAH EQS to include further classes of water in the manner of the new National Water Council classification (Section 1.5.1). Legislation pertaining to the ES control approach is more problematic. The appreciable contribution of non-point sources of PAH to contamination of surface waters (Table 3) implies that ES laid down for industrial point sources would only be of limited effectiveness unless the sources concerned were very large. Application of equitable ES to particular industrial categories in the context of river basin management requires data which at present are lacking. As outlined earlier (Section 1.3) emission data are confined to large industrial concerns, and information on small to medium scale industrial enterprises, which may contribute a large PAH pollution load, is not available. The Environmental Protection Agency (1982) recorded very large (mg l^{-1}) concentrations of individual PAH in the effluent of a wood preserving plant. A study of small to medium enterprises could very profitably be initiated by conducting a 'desk study' of processes likely to emit PAH via high temperature combustion. A smokeless fuel plant, for example, will very probably discharge PAH as the process involves treating coal in a very high temperature furnace to drive off gases and tars. When assigning ES, consideration could usefully be given to programming or balancing discharges as suggested by Chalmers (1981).

In formulating a monitoring programme, objectives must be precisely defined. Present programmes are often arbitrary and confused in their design, causing generation of inferior data and eroding cost-effectiveness. Miller (1982) estimated that for the EC drinking water directive alone, the cost of monitoring the determinands in the UK ranges from £3 M to £17 M per annum depending upon the exact frequency of sampling and analysis. Rational, quantified sampling design and assessment theory in the form of systems analysis has been available for many years but has rarely been used. Leemans (1971) described a quantitative procedure, derived from control engineering theory, for the determination of optimum sampling frequency and illustrated its application to the control of a fertiliser production process. However, there do not appear to have been any applications of this type in the

field of water monitoring.

A monitoring programme must address five points (Steel, 1984): programme purpose, sampling determinands, sampling locations, sampling frequency, and expression of results. Hunt & Wilson (1986) distinguished two types of monitoring programme: quality control programmes ('feed-forward') and quality characterisation programmes ('feed-back'). This distinction is not widely appreciated. Current quality standards tend to be expressed in terms of probabilistic limits e.g. annual mean, median and 95th percentile. UK compliance criteria now adopt the 95th percentile for discharge consent conditions and for RQS (National Water Council, 1978) as do criteria in the EC surface water directive where, furthermore, the percentiles are coupled with absolute upper limits. The significance of this is that probabilistic limits, entailing a number of analyses over a period of time before (retrospective) determination of compliance achievement, imply (long-term) quality characterisation rather than quality control. Characterisation does not offer immediate or short-term protection. The poor appreciation of the two types of programme, especially in regard to monitoring of surface waters, may be due to inadequate definition of programme purpose and action required in the event of non-compliance with criterion.

A PAH monitoring programme for river basins subject to reuse is therefore proposed which is fundamentally different to EC and indeed WHO stipulations which imply quality characterisation or feed-back control rather than quality or feed-forward control (in the case of WHO by virtue of the recommendation that sampling should be exercised at the consumer tap). The programme purpose should be control of surface water quality and hence should be of the quality control type with 'threshold control' and expression of results in terms of absolute limits (in contrast to a second category of quality control programme 'process control' (Hunt & Wilson, 1986) for control of concentrations within narrow limits of specified value). The sampling determinands should be those included in the revised EC surface water directive. The sampling locations could usefully include rising mains of sewage and water

treatment works together with catchment (and trade effluent) sites. The sampling frequency requires prior baseline studies as in order to achieve optimum efficiency from a sampling programme it is necessary to have some knowledge of the system to be measured. This could be served (in the UK) by an examination of the data (six WHO PAH) appearing under the 'Harmonised Monitoring Scheme' for river waters (Simpson, 1978). The information can be used to assess probabilities of deviations beyond a given threshold concentration, and to assess system 'time constants.' Samples should be 'systematic' and not 'random' in order to allow for abnormal hydrological conditions such as storms giving rise to high flows and SS concentrations and hence high PAH concentrations.

On the basis of the suggestion by Steel (1984) in which it is considered desirable to undertake some basic monitoring frequently and some more advanced or specific monitoring at a lesser but reasonable frequency, and of the suggestion by Branson et al. (1981) of a 'tiered' approach to effluent monitoring, a scheme employing carefully defined action levels for non-compliance could be as follows. Frequent and inexpensive analyses could be performed utilising a semiquantitative or screening method (such as that of Riggin & Strup, 1984), amenable to automation. Samples failing compliance would then be subjected to a more precise and quantitative procedure or procedures in order to identify and arrest the polluting source. It is conventional to define samples in general according to three types: discrete, continuous ('on-line'), and integrative. This last has suffered neglect although reports of integrative sampling systems in the form of capillary inlets and solid adsorbents (such as activated carbon and macroreticular resins) are occasionally published. Black et al. (1982) described use of sheets of commercial oil-absorbing cloth (of a polypropylene substrate) for immersion in water (for a number of days) for integrative sampling of PAH. Such greatly under-utilised techniques could very profitably serve as cost-effective and efficient means for semiquantitative screening in the proposed monitoring programme. Furthermore, integrative sampling would overcome the traditional (and severe) problems associated with discrete

sample representativeness and detection limit.

In contrast to metal (inorganic) pollutants of limited and modest number the large and possibly increasing number of organic micropollutants demand, in the long-term, rationalisation with respect to river basin monitoring. A future aim of organic pollutant control should be the selection of a 'source-specific marker' for each polluting source, that is, a pollutant or pollutant combination characterising a particular source in a river basin, and where sample non-compliance for the particular determinand or determinand combination would immediately suggest the source responsible. Although this should be utilised alongside ordinary trade effluent control, the general thrust should be one of more thorough and effective monitoring of a modest number of pollutants rather than one of infrequent and inefficient monitoring of a large number. A monitoring scheme should, naturally, incorporate determinands which are limiting, that is occurring at concentrations near or on any quality limit. An effective means of appraising limiting determinands would be by application, resources permitting, of a type of 'Catchment Quality Control' scheme as utilised by Thames Water Authority (Richardson & Bowron, 1983). It is essentially a system for predicting the presence of non-biodegradable and toxic organic pollutants at river abstraction points at concentrations of, typically, at least 0.1 $\mu g\ l^{-1}$ from an inventory of all substances known to be used or produced in the catchment and potentially polluting via both point and non-point routes (domestic and agricultural included). The major advantage of such a scheme is that it aids appraisal of limiting pollutants (as well as placing pollutant sources in perspective) which could only otherwise be achieved by general survey type analyses with their attendant numerous shortcomings.

The current crisis of public confidence in the UK in the quality of water supplies amid charges of government and water authority complacency and ineptitude requires an urgent commitment to greater monitoring and control of water pollution.

6. CONCLUSIONS

6.1 The GC-MS column chromatographic procedure, developed for the determination of 14 PAH in raw sewage, primary effluent and raw primary sludge from municipal waste water treatment works, represented a reliable and well validated analytical method with satisfactory performance characteristics. Accuracy, in terms of determinand efficiency of recovery, was an overall mean of 84% and was independent of determinand concentration and sample type. Precision, in terms of total analytical error, ranged from ±10.3% (FL) to ±21.3% (IP) and was independent of determinand concentration and sample type. Sensitivity, as measured by detection limit, ranged from 0.01 to 0.05 $\mu g\ l^{-1}$.

6.2 The procedure compared very favourably with schemes reported in the literature in terms of method validation, performance characteristics and scope (numbers of PAH and variety of sample types applicable). It was matched only by the EPA HPLC procedure. Given that the GC-MS method could not analyse for N nor quantify separately the BF isomers, accuracy was comparable to the EPA procedure but displayed higher (single analyst) precision and, for the low molecular weight PAH, appreciably lower detection limits.

6.3 The studies of sample integrity (sampling and storage) are the first to be reported for municipal waste water. They demonstrated the utility of formaldehyde solution (at 1% V/V) in maintaining integrity for at least 56 d, thereby facilitating sample management and permitting accurate analyses after extended time periods. The preservation technique has a useful field application. The studies also suggested that, without preservation, accurate analyses can be accomplished up to 24 h after collection of sample, and that biodegradation was responsible for the slow loss of low molecular weight PAH.

6.4 The analytical procedure demonstrated that instrument calibration can be a major source of bias. Analytical inaccuracy by this means may well be more widespread than is appreciated, especially as calibration procedures are not normally described in published analytical methods. Complete and unambiguous details should always be recorded.

6.5 The nature of the bias experienced demonstrated the danger of placing reliance in the internal standard in the often practised, and recommended, technique of regularly carrying this through the whole procedure to compensate for any bias. Internal standards must be used and interpreted critically in any method in the knowledge of the extent of its validation.

6.6 It is recommended in any GC-MS work involving the determination of high molecular weight and high boiling point compounds that a preliminary test for instrument bias be undertaken by the method of single standard additions performed on a treated sample matrix, in order to avoid any subsequent difficulties and delays in interpretation of anomalous data.

6.7 Inter-sample variation in procedure detection limit requires addressing in the context of existing methods for determining detection limit which consider a single sample only. This is particularly important in the UK for the analysis and monitoring of low concentrations involved in the EQO/EQS pollution control approach.

6.8 Use of determinand recovery tests alone to measure analytical accuracy, as is so often practised, is subject to error and thus requires care. Use should be made of certified reference materials or of 'confirmatory testing.'

6.9 The multiple sources of error to which an analytical measurement is subject makes it highly unlikely that use of standard methods will guarantee accuracy and precision. It is anticipated that future legislation will increasingly specify method performance

characteristics in place of standard methods alongside quality standards.

6.10 The range and quality of the pilot plant results for PAH behaviour and removal during primary sedimentation in comparison with published results were high due to good analytical and sampling integrity (including measurement of native PAH only), the wide range of conditions (SS and hydraulic loading) examined, and the characterisation of accompanying plant performance in terms of SS and COD removal.

6.11 The performance of the primary sedimentation pilot plant in terms of SS removal efficiency compared well with predictions by five performance relationships relating removal efficiency to hydraulic loading and SS loading derived from pilot- and full-scale settlement units. The pilot plant therefore operated as an acceptable model of the full-scale process.

6.12 SS removal efficiencies, in agreement with all predictions, increased with decreasing hydraulic loading (and hence with increasing theoretical hydraulic retention time) and increased with increasing SS loading. The increase in mean removal of 15.8% (from 59.2 to 75.0%) with decrease in hydraulic loading from 5.0 DWF (61.0 m^3 m^{-2} d^{-1}) to 0.5 DWF (6.10 m^3 m^{-2} d^{-1}) was greater than the increase of 10.3% (from 57.9 to 68.2%) associated with the increase in SS loading from 402 to 888 mg l^{-1}, thus demonstrating the greater influence of the former process parameter in controlling SS removal under the range of conditions studied.

6.13 Mass balance analysis of determinand and co-determinand data obtained from the pilot plant experimentation programme exhibited good internal consistency indicating the reliability of the computed removal efficiencies.

6.14 The series of primary sedimentation experiments achieved an overall mean removal for AY of 21.3%, AE 34.9%, F 37.6%, PA 44.3%, A 42.5%, FL 52.9%, P 54.1%,

BaA 63.0%, CH 54.9%, BkF 59.4%, BaP 59.3%, IP 54.3%, BghiP 50.5% and DBahA 52.1%, a general increase in removal with increase in molecular weight of PAH up to BaA in evidence, after which removal decreased.

6.15 The influence of hydraulic loading on PAH removal was generally weak. A decrease in removal with increase in loading was statistically significant only for AE, F, PA, IP and DBahA. The influence of SS loading was more definite. A statistically significant increase in removal with increase in loading was true for PAH of molecular weight 152 to 252 (BaP excepting).

6.16 The consistent correlation of PAH removal on actual SS removal achieved emphasised the importance of influent settleability in controlling the removal of hydrocarbon. The principle PAH removal mechanism was thus judged to be physicochemical sorption to SS and removal with settleable solids. The good correlation of PAH removal on VSS removal demonstrated the influence of the organic solids subfraction of SS.

6.17 Volatilisation and photodegradation of PAH in the sewage matrix were shown to be sufficiently slow as to be of minimal importance as PAH removal mechanisms during the comparatively rapid process of primary sedimentation.

6.18 Influence of process parameter on PAH removal was via SS removal. For low molecular weight PAH (MW 152-228) SS loading was the main controlling influence for SS-mediated PAH removal and hydraulic loading of minor, variable influence. Increases (absolute) in mean removals of PAH associated with the increase in mean removal of SS from 57.9% at the loading of 402 mg l^{-1} to 68.2% at 888 mg l^{-1} were 17.5% for AY, 24.6% AE, 21.3% F, 18.1% PA, 18.6% A, 16.9% FL, 15.9% P, 12.2% BaA and 14.8% CH. For high molecular weight PAH (MW 178-278), hydraulic loading was the main controlling influence for SS-mediated PAH removal and SS loading of minor, variable influence. Decreases in mean removals of PAH associated with the decrease in mean removal of SS from 75.0% at the loading of

0.5 DWF to 59.2% at 5.0 DWF were 19.3% for FL, 21.3% P, 19.6% BaA, 19.2% CH, 16.9% BkF, 15.2% BaP, 16.1% IP, 17.7% BghiP and 15.0% DBahA. Thus for medium molecular weight PAH (MW 178-228) both process parameters exerted a controlling influence.

6.19 The PAH particle size distribution analysis of the sample of raw sewage provided data for size fractions >253, 150-253, 106-150, 53-106, 0.45-53 and <0.45 μm (representing the dissolved/colloidal phase). PAH were associated with all particle size fractions but important trends, on a weight by volume basis, were noted for fractions 0.45-53 and <0.45 μm. Association of PAH with the former smallest particle size fraction, containing generally the greatest proportion of particulate PAH, ranged from 15.7% (AY) to 51.0% (BghiP), a trend of increasing proportion with increase in molecular weight of hydrocarbon. Association of PAH with the fraction <0.45 μm ranged from 0.6% (BghiP) to 58.5% (AY), exhibiting a clear trend of rapidly decreasing proportion with increase in molecular weight. These results for PAH fractionation appear to be the first for this matrix.

6.20 The general increase in overall mean removal of PAH achieved during the pilot plant experimentation programme with increase in molecular weight of hydrocarbon can be attributed to the increasing proportion of PAH associated with the sewage particulate phase (fractions >0.45 μm) with increasing molecular weight, revealed by the PAH particle size distribution analysis, from 41.5% (AY) to 99.4% (BghiP). The slight decrease in overall mean removal of PAH after BaA may be attributed to the increasing proportion of PAH associated with the smallest particle size fraction 0.45-53 μm with increase in molecular weight. The slightly poorer removals of the highest molecular weight PAH may have been a consequence of their relatively high association with this fraction of smallest particles of low settleability.

6.21 Two components of the PAH fractionation data appeared to be important in determining for each PAH the precise pollutant removal mechanism involved: the proportion of PAH dissolved/colloidal and the PAH particle size distribution with respect to that of SS itself.

6.22 The removal mechanism of low molecular weight PAH (MW 152-166) was determined largely by the proportion of PAH dissolved/colloidal in raw sewage. Ratio of mean removal of PAH to mean removal of SS increased with increase in SS loading from 402 to 888 mg l^{-1} from 0.202 to 0.428 for AY, 0.370-0.674 AE and 0.444-0.689 F, indicating increasing removal efficiencies of the PAH proportionately greater than those of SS. The linear dependence of fractional increase in removal of PAH above that brought about by extra flocculation on SS loading was consistent with increasing solute partitioning to the SS phase. The factorial increases in ratios for the PAH decreased with increase in molecular weight from 2.12 (AY, MW 152) to 1.15 (P, MW 202), showing that the effect of enhanced PAH removal decreased to a point of insignificance due to the proportion of PAH present in the dissolved state, and thus available for further sorption, decreasing with increase in molecular weight (from ca. 60% (weight by volume basis) for MW 152 to <10% around MW 202/228 according to the fractionation data). SS loading thus controlled removal of the MW 152-166 group of PAH via SS removal through two probable mechanisms: simple partitioning and flocculation.

6.23 The removal mechanism of medium molecular weight PAH (MW 178-228) was determined by the close resemblence of their particle size distributions in raw sewage on a weight by volume basis to that of SS itself (with little dissolved, and true especially of MW 202 and 228). The removal mechanism was therefore similar to, and coincident with, that of SS, consisting of a dependence on both SS loading and hydraulic loading. Numerically, BaA (MW 228) removal was closest to that of SS.

6.24 The removal mechanism of high molecular weight PAH (MW 252-278) appeared to be determined by a preferential association of high molecular weight PAH with the small particle size fraction (0.45-53 μm), the removal of which hydraulic loading and not SS loading had a regular effect.

6.25 The PAH removal mechanisms indicate that to optimize low molecular weight PAH removal primary sedimentation tanks should be operated at high SS loadings, and to optimize removal of high molecular weight PAH low hydraulic loading operation is required in hydraulically efficient tanks. If it is wished to consider PAH removal in sedimentation tank design then the latter condition requires tanks to have adequate depth or retention time and be so designed that mixing effects due to hydraulic turbulence are minimized.

6.26 Regression functions were formulated relating PAH removal during primary sedimentation to PAH physicochemical property (molecular weight) and unit process performance (SS removal efficiency). The functions are significant for the following reasons: they enable prediction of mean removals and removal ranges of PAH on the basis of tank performance, and thus permit prediction of primary effluent and sludge quality; they define load on the subsequent secondary treatment and sludge treatment processes; they aid definition of tank design requirements (via SS removal) to achieve a specified PAH removal; and they are suitable for use by regulatory agencies in the calculation of consent conditions for industrial discharges of PAH to sewers to meet receiving water and sludge quality criteria at minimal overall cost.

6.27 The regression functions are suitable for modelling purposes and in this respect represent a major improvement over use of PAH log K_{OW} values hitherto the tendency. Although log K_{OW} was shown to be a good measure of proportion of PAH sorbed to SS in raw sewage, it was not so good as an indicator of PAH removal through sedimentation (as expressed by PAH waste water/sludge phase concentration factors), most

probably due, at least in part, to the shift in PAH particle size distribution with molecular weight.

6.28 There were three sets of evidence for the preferential association of high molecular weight PAH with small particle size fractions in raw sewage: fractionation data for the particle size class 0.45-53 μm, the overall mean PAH removal trend with respect to molecular weight showing a decrease in removal after MW 228, and the importance of hydraulic loading in controlling removal of the MW 252-278 group of PAH via SS removal. The consequent importance of flocculation in influencing the removal of this significant group of PAH was demonstrated.

6.29 The preferential association of higher molecular weight PAH with fine SS of poorer settleability has been tentatively suggested in, and inferred from, a number of published results. The present study, involving a continuous homologous series and indicating a trend with solute molecular weight, represents further and major empirical evidence for a phenomenon which is potentially of considerable importance to environmental engineering systems that separate phases. High molecular weight solutes which sorb strongly are typically recalcitrant and often toxic, and their removal from aqueous systems may therefore be of special concern.

6.30 The experimental approach adopted herein to study PAH removal during primary sedimentation should be utilised to include an investigation of secondary treatment. A similar investigation of PAH removal and transformation during water treatment is called for, including research on leaching of PAH from coal tar lined distribution mains. The latter phenomenon requires a more up-to-date survey of PAH in tap waters. Further studies of PAH sorption kinetics and reversibility and of PAH particle size distributions would be of value in the understanding of PAH behaviour in the various unit processes.

6.31 Current settling column practice suggests that measurement of flocculation and thus importance of SS concentration on sedimentation in primary clarifiers is inadequate. Estimation of the influence of flow rate and thus hydraulic loading on removal is favoured at the expense of that of SS concentration and thus SS loading on removal. Clear guidance is required for the correct assessment of SS concentration. The test should be repeated on samples of differing SS concentration obtained by successively diluting a sample (of high SS concentration) with settled suspension (of a certain maximum SS concentration) from the same sample, acquired by allowing a portion of the original to settle in a spare column. This practice is important to avoid design of tanks with unnecessarily long retention times and to provide a rational criterion for selection of factors for scale-up of tank design parameters from the results of the settling column tests.

6.32 A data base should be maintained of settling column test results, with scale-up factors employed, against subsequent performance of tanks. This would permit statistical determination, hitherto unperformed, of overall procedure accuracy and precision, ensuring that future selection of scale-up factors is based on properly quantified random and systematic errors. Maintenance of the data base would encourage better engineering practice in the form of a proper execution of a minimum number of settling column tests and would permit identification and warning of troublesome sample types. A similar approach could usefully apply to the analysis of raw waters required for the design of water treatment plant.

6.33 The Brune relation for determining the trap efficiencies of reservoirs embodies a number of major shortcomings. The potentially large errors associated with the relation, especially for reservoir capacity-inflow ratios <0.15, must be acknowledged. In particular, the engineering community must be made aware of the erroneous mis-labelling of the Brune curves. It is questionable whether, for these low

ratios and thus high reservoir turnovers, more accurate predictions of trap efficiency might not be obtained from the application of settling column tests and sedimentation tank theory.

6.34 A simple test for presence of flocculation in surface fresh water sedimentation is proposed based on the settling column test dilution technique advocated and exploiting the SS concentration dependence of Class II settlement. By allowing a sample to settle for just one time interval in a short column possessing a single lower sampling port and determining percentage removal, flocculation can be tested for by repeating the procedure after a correct dilution of the sample using settled suspension from a spare, second column and checking for a significant reduction in removal. Testing for flocculation in this manner would, if negative, at least secure confidence in situations assuming Class I settlement only, and if positive, enable additional sampling and measurement requirements to be gauged.

6.35 Where mathematical models are used for determining reservoir sedimentation and where flocculation is shown to be operative, then particle settling velocity distributions should be determined in significantly longer versions of the tubes used and ideally with no separation of class sizes. A much longer BW Tube may suffice. The determination of average settling velocities of solids fractions over a larger depth should more accurately approach the settling velocity distributions liable to be attained in the high depth conditions of the reservoir. The effect of SS concentration on the settling velocity distribution should be quantified using the recommended settling test dilution technique, and a term incorporated in the sediment transport functions of the mathematical models for particle size distribution dependency on SS concentration from the settling velocity distribution dependency.

6.36 Reform of the EC drinking water and surface water directives with regard to the PAH regulation is advised. Summation of the concentrations of the six PAH to express a total should be discontinued and concentrations reported individually. FL should be deleted from the list as it has now been shown to be non-carcinogenic and the EC determination as it stands can be very markedly and deleteriously influenced by leaching of this component from coal tar lined distribution mains; it could possibly be replaced with BaA, a known carcinogen. The arbitrary 200 ng l^{-1} limit should be replaced by limits based on toxicological considerations in the manner of the WHO limit for BaP. Retention of the remaining PAH and inclusion of any further in a new list should be assessed on the basis of the latest knowledge of PAH occurrence and toxicology. The common origin of PAH and the often observed approximate uniformity of homolog profiles suggests that monitoring of a reduced number may be valid and representative.

6.37 The pending EC daughter directive on PAH under the dangerous substances directive should incorporate the recommendations made above. Legislation pertaining to the EQO/EQS control philosophy should be made compatible with, and correspond to, that in the surface water directive which already contains PAH quality standards for three classes of surface water. The new directive should extend EQO and corresponding PAH EQS to include further classes of water in the manner of the new National Water Council classification. Legislation pertaining to the ES control approach requires further research before formulation. Selection of equitable numerical limits for industrial categories requires a clear knowledge of all industrial sources of PAH and discharge fluxes which is considerably incomplete at present.

6.38 The limited control which can be exercised over primary sedimentation tank performance and overall plant performance implies that PAH effluent concentrations, and thus the quality of surface waters abstracted for potable supply, are more effectively

subject to control through catchment management, via selection of, and compliance with, appropriate quality standards. This calls for a careful monitoring programme with a precisely defined purpose fundamentally different to EC and WHO stipulations which imply quality characterisation rather than quality control.

6.39 The purpose of the proposed PAH monitoring programme should be control of surface water quality and hence should be of the quality control programme type ('feed-forward') with 'threshold control' and expression of results in terms of absolute limits, with carefully defined action levels based on non-compliance of systematic samples. The approach should be one of frequent semiquantitative (screening) analyses, combined with infrequent accurate analyses of samples that fail compliance to identify and arrest the polluting source.

6.40 It is recommended that research be greatly increased on integrative (composite) sampling systems such as solid adsorbents and capillary inlets which are immersed in the water matrix for a prescribed time. Such greatly under-utilised techniques would very usefully serve as cost-effective and efficient means for semiquantitative screening in the proposed monitoring programme. Integrative sampling would overcome the traditional (and severe) problems associated with discrete sample representativeness and detection limit.

6.41 In contrast to metal (inorganic) pollutants of limited and modest number the large number of organic micropollutants demand rationalisation with respect to river basin monitoring. A long-term aim of organic pollutant control should be the selection of a 'source-specific marker' for each polluting source, that is, a pollutant or pollutant combination characterising a particular source in a river basin, and where sample non-compliance for the particular determinand or determinand combination would immediately suggest the source responsible. It is

preferable to monitor thoroughly and effectively a modest number of pollutants than to monitor infrequently and inefficiently a large number.

6.42 The current crisis of public confidence in the UK in the quality of water supplies requires an urgent commitment to greater monitoring and control of water pollution.

BIBLIOGRAPHY

Abdul, A.S. & Gibson, T.L. (1986). Equilibrium batch experiments with six polycyclic aromatic hydrocarbons and two aquifer materials. Hazard. Waste Hazard. Mater., 3, 125-137.

Abdul, A.S., Gibson, T.L. & Rai, D.N. (1986). The effect of organic carbon on the adsorption of fluorene by aquifer materials. Hazard. Waste Hazard. Mater., 3, 429-440.

Acheson, M.A., Harrison, R.M., Perry, R. & Wellings, R.A. (1976). Factors affecting the extraction and analysis of polynuclear aromatic hydrocarbons in water. Water Res., 10, 207-212.

Ackers, A. & Thompson, G. (1985). Reservoir sedimentation and influence of flushing. Paper presented to the International Conference Problems of Sediment Transport in Gravel Bed Rivers, Colorado, USA, August 1985.

Agrawal, S.K. & Bewtra, J.K. (1985). Modified approach to evaluate column test data. J. Environ. Eng. (N.Y.), 111, 231-234.

Aichberger, K. & Reifenauer, D. (1984). Determination of polycyclic aromatic hydrocarbons in sewage sludge. In L'Hermite, P. & Ott, H. (Eds.), Processing and Use of Sewage Sludge: Proceedings of the Third International Symposium, Brighton, UK, September 27-30, 1983, Commission of the European Communities, D. Reidel, Dordrecht, Holland, pp. 161-163.

Alben, K. (1980). Coal tar coatings of storage tanks. A source of contamination of the potable water supply. Environ. Sci. Technol., 14, 468-470.

Alexander, M. (1985). Biodegradation of organic chemicals. Environ. Sci. Technol., 19, 106-111.

Andelman, J.B. & Suess, M.J. (1970). Polynuclear aromatic hydrocarbons in the water environment. Bull. W.H.O., 43, 479-508.

Andelman, J.B. & Suess, M.J. (1971). The photo-decomposition of 3,4-benzpyrene sorbed on calcium carbonate. In Faust, S.J. & Hunter, J.V. (Eds.), Organic Compounds in Aquatic Environments, Marcel Dekker, New York, USA, Chap. 19, pp. 439-468.

Anderson, J.A. (1981). Primary sedimentation of sewage. Water Pollut. Control (Maidstone, Engl.), 80, 413-420.

Annandale, G.W. (1987). Reservoir Sedimentation, Elsevier, Amsterdam, Holland.

Annesini, M.C., Beccari, M. & Mininni, G. (1979). Solids removal efficiency of primary settling tanks in municipal wastewater treatment plants. Water, Air, Soil Pollut., 12, 441-447.

Anon. (1988). Water quality probed. Thames Water News, November, p. 12.

Anthony, R.M. & Breimhurst, L.H. (1981). Determining maximum influent concentrations of priority pollutants for treatment plants. J.-Water Pollut. Control Fed., 53, 1457-1468.

Baird, R., Selna, M., Haskins, J. & Chappelle, D. (1979). Analysis of selected trace organics in advanced wastewater treatment systems. Water Res., 13, 493-502.

Baralkiewicz, D., Gramowska, H. & Zerbe, J. (1988). Polycyclic aromatic hydrocarbons in water samples. Gospod. Wodna, 48, 41-43.

Barnes, D. & Wilson, F. (1978). Chemistry and Unit Operations in Sewage Treatment, Applied Science, Barking, UK.

Barnes, D., Bliss, P.J., Gould, B.W. & Vallentine, H.R. (1981). Water and Wastewater Engineering Systems, Longman, Harlow, UK.

Barrick, R.C. (1982). Flux of aliphatic and polycyclic aromatic hydrocarbons to Central Puget Sound from Seattle (Westpoint) primary sewage effluent. Environ. Sci. Technol., 16, 682-692.

Bartell, S.M., Landrum, P.F., Giesy, J.P. & Leversee, G.J. (1981). Simulated transport of polycyclic aromatic hydrocarbons in artificial streams. In Mitsch, W.J., Bosserman, R.W. & Klopatek, J.M. (Eds.), Energy and Ecological Modelling, Elsevier, Amsterdam, Holland, pp. 133-143.

Bartle, K.D., Lee, M.L. & Novotny, M. (1977). Identification of environmental polynuclear aromatic hydrocarbons by pulse Fourier-transform ^{1}H nuclear magnetic resonance spectroscopy. Analyst (London), 102, 731-738.

Basu, D.K. & Saxena, J. (1978a). Monitoring of polynuclear aromatic hydrocarbons in water. II. Extraction and recovery of six representative compounds with polyurethane foams. Environ. Sci. Technol., 12, 791-795.

Basu, D.K. & Saxena, J. (1978b). Polynuclear aromatic hydrocarbons in selected U.S. drinking waters and their raw water sources. Environ. Sci. Technol., 12, 795-798.

Bates, T.S., Hamilton, S.E. & Cline, J.D. (1984). Vertical transport and sedimentation of hydrocarbons in the Central Main Basin of Puget Sound, Washington. Environ. Sci. Technol., 18, 299-305.

Bates, T.S., Murphy, P.P., Curl, H.C. Jr. & Feely, R.A. (1987). Hydrocarbon distributions and transport in an urban estuary. Environ. Sci. Technol., 21, 193-198.

Baughman, G.L. & Lassiter, R.R. (1978). Prediction of environmental pollution concentration. In Cairns, J., Dickson, K.L. & Macki, A.W. (Eds.), Estimating the Hazard of Chemical Substances to Aquatic Life, American Society for Testing and Materials Special Technical Publication 657, American Society for Testing and Materials, Philadelphia, USA, pp. 35-54.

Bedding, N.D., McIntyre, A.E., Perry, R. & Lester, J.N. (1982). Organic contaminants in the aquatic environment I. Sources and occurrence. Sci. Total Environ., 25, 143-167.

Bedding, N.D., McIntyre, A.E., Perry, R. & Lester, J.N. (1983a). Organic contaminants in the aquatic environment II. Behaviour and fate in the hydrological cycle. Sci. Total Environ., 26, 255-312.

Bedding, N.D., McIntyre, A.E. & Lester, J.N. (1983b). Organic contaminants in the aquatic environment III. Public health aspects, quality standards and legislation. Sci. Total Environ., 27, 163-200.

Bedding, N.D., McIntyre, A.E., Lester, J.N. & Perry, R. (1988a). Analysis of waste waters for polynuclear aromatic hydrocarbons I. Method development and validation. J. Chromatogr. Sci., 26, 597-605.

Bedding, N.D., McIntyre, A.E., Lester, J.N. & Perry, R. (1988b). Analysis of waste waters for polynuclear aromatic hydrocarbons II. Errors, sampling, and storage. J. Chromatogr. Sci., 26, 606-615.

Bedient, P.B., Springer, N.K., Baca, E., Bouvette, T.C., Hutchins, S.R. & Tomson, M.B. (1983). Ground-water transport from wastewater infiltration. J. Environ. Eng. (N.Y.), 109, 485-501.

Benoit, F.M., LeBel, G.L. & Williams, D.T. (1979). Polycyclic aromatic hydrocarbon levels in Eastern Ontario drinking waters, 1978. Bull. Environ. Contam. Toxicol., 23, 774-778.

Beresford, S.A.A. (1981). The relationship between water quality and health in the London area. Int. J. Epidemiol., 10, 103-115.

Beresford, S.A.A. (1983). Cancer incidence and reuse of drinking water. Am. J. Epidemiol., 117, 258-268.

Beresford, S.A.A., Carpenter, L.M. & Powell, P. (1984). Epidemiological Studies of Water Reuse and Types of Water Supply, Water Research Centre Technical Report TR 216, Water Research Centre, Medmenham, UK.

Bierl, R., Kaa, W. & Thomas, W. (1984). Spatial and temporal concentration gradients of PAH (fluoranthene, benzo[a]pyrene), γ-BHC and 2,4-D in samples of soil, soil water and ground water in an agricultural research area. Fresenius' Z. Anal. Chem., 319, 172-179.

Bjørseth, A. (1977). Analysis of polycyclic aromatic hydrocarbons in particulate matter by glass capillary gas chromatography. Anal. Chim. Acta, 94, 21-27.

Bjørseth, A. (Ed.) (1983). Handbook of Polycyclic Aromatic Hydrocarbons, Marcel Dekker, New York, USA.

Bjørseth, A. & Eklund, G. (1979). Analysis of polynuclear aromatic hydrocarbons by glass capillary gas chromatography using simultaneous flame ionization and electron capture detection. J. High Resolut. Chromatogr. Chromatogr. Commun., 2, 22-26.

Bjørseth, A. & Olufsen, B.S. (1983). Long-range transport of polycyclic aromatic hydrocarbons. In Bjørseth, A. (Ed.), Handbook of Polycyclic Aromatic Hydrocarbons, Marcel Dekker, New York, USA, Chap. 12, pp. 507-524.

Black, D.W. (1988). COPA II - reasons for failure to comply with effluent consents. J. Inst. Water Environ. Manage., 2, 141-147.

Black, J.J., Hart, T.F. Jr. & Black, P.J. (1982). A novel integrative technique for locating and monitoring polynuclear aromatic hydrocarbon discharges to the aquatic environment. Environ. Sci. Technol., 16, 247-250.

Boehm, P.D. & Quinn, J.G. (1973). Solubilization of hydrocarbons by the dissolved organic matter in sea water. Geochim. Cosmochim. Acta, 37, 2459-2477.

Böhm-Gössl, T. & Krüger, R. (1965). Solubilization of 3,4-benzpyrene by alkylbenzenesulphonates. Kolloid. Z. Z. Polym., 206, 65-70.

Borneff, J. (1969). The removal of carcinogenic polycyclic aromatic hydrocarbons during water treatment. GWF, Gas-Wasserfach: Wasser/Abwasser, 110, 29-34.

Borneff, J. & Kunte, H. (1963). Carcinogenic substances in water and soil. XIV. Further investigations on polycyclic aromatic hydrocarbons in soil samples. Arch. Hyg. Bakteriol., 147, 401-409.

Borneff, J. & Kunte, H. (1964). Carcinogenic substances in water and soil. XVI. Evidence of polycyclic aromatic hydrocarbons in water samples through direct extraction. Arch. Hyg. Bakteriol., 148, 585-597.

Borneff, J. & Kunte, H. (1965). Carcinogenic substances in water and soil. XVII. About the origin and evaluation of polycyclic hydrocarbons in water. Arch. Hyg. Bakteriol., 149, 226-243.

Borneff, J. & Kunte, H. (1967). Carcinogenic substances in water and soil. XIX. Results of waste water treatment on polycyclic aromatic hydrocarbons. Arch. Hyg. Bakteriol., 151, 202-210.

Borneff, J. & Kunte, H. (1969). Carcinogenic substances in water and soil. XXVI. Routine method for the determination of polycyclic aromatic hydrocarbons in water. Arch. Hyg. Bakteriol., 153, 220-229.

Bossert, I., Kachel, W.M. & Bartha, R. (1984). Fate of hydrocarbons during oily sludge disposal in soil. Appl. Environ. Microbiol., 47, 763-767.

Boulos, B.M. (1978). High risks in exposure to polycyclic aromatic hydrocarbons. In Jones, P.W. & Freudenthal, R.I. (Eds.), Carcinogenesis - A Comprehensive Survey. Vol. 3: Polynuclear Aromatic Hydrocarbons, Second International Symposium, Raven Press, New York, USA, pp. 439-449.

Bouwer, E.J., McCarty, P.L., Bouwer, H. & Rice, R.C. (1984). Organic contaminant behaviour during rapid infiltration of secondary wastewater at the Phoenix 23rd Avenue project. Water Res., 18, 463-472.

Bowden, K. & Young, D.D. (1984). River quality and sewage effluent standards. J. Inst. Water Eng. Sci., 38, 511-523.

Branson, D.R., Armentrout, D.N., Parker, W.M., Van Hall, C. & Bone, L.I. (1981). Effluent monitoring step by step. Environ. Sci. Technol., 15, 513-518.

Brune, G.M. (1953). Trap efficiency of reservoirs. Trans., Am. Geophys. Union, 34, 407-418.

Brunner, P.H., Capri, S., Marcomini, A. & Giger, W. (1988). Occurrence and behaviour of linear alkylbenzenesulphonates, nonylphenol, nonylphenol mono- and nonylphenol diethoxylates in sewage and sewage sludge treatment. Water Res., 22, 1465-1472.

Bull, R.J. (1985). Carcinogenic and mutagenic properties of chemicals in drinking water. Sci. Total Environ., 47, 385-413.

Butkovič, V., Klasinc, L., Orhanovič, M., Turk, J. & Güsten, H. (1983). Reaction rates of polynuclear aromatic hydrocarbons with ozone in water. Environ Sci. Technol., 17, 546-548.

Calabrese, E.J. & Gilbert, C.E. (1986). Unresolved issues in risk assessment. In Ram, N.M., Calabrese, E.J. & Christman, R.F. (Eds.), Organic Carcinogens in Drinking Water: Detection, Treatment and Risk Assessment, Wiley, Chichester, UK, Chap. 17, pp. 437-460.

Calvert, J.T., Lees, E.A. & Thompson, H.F. (1959). The design and construction of the Hogsmill Valley Drainage Scheme. Proc.-Inst. Civ. Eng., 12, 269-288.

Camp, T.R. (1946). Sedimentation and the design of settling tanks. Trans. Am. Soc. Civ. Eng., 111, 895-958.

Carlberg, G.E. & Martinsen, K. (1982). Adsorption/complexation of organic micropollutants to aquatic humus. Sci. Total Environ., 25, 245-254.

Carpenter, L.M. & Beresford, S.A.A. (1986). Cancer mortality and type of water source: findings from a study in the U.K. Int. J. Epidemiol., 15, 312-320.

Chalmers, R. (1981). Amounts and effects of toxic materials discharged to sewers. Chem. Ind. (London), No. 8, 271-277.

Clements, M.S. (1976). The application of static column tests to sedimentation tank design. Water Pollut. Control (Maidstone, Engl.), 75, 360-376.

Cole, R.H., Frederick, R.E., Healy, R.P. & Rolan, R.G. (1984). Preliminary findings of the Priority Pollutant Monitoring Project of the Nationwide Urban Runoff Program. J.-Water Pollut. Control Fed., 56, 898-908.

Cole, T., Riggin, R. & Glaser, J. (1981). Evaluation of method detection limits and analytical curve for EPA Method 610-PAH. In Cooke, M. & Dennis, A.J. (Eds.), Polynuclear Aromatic Hydrocarbons: Chemical Analysis and Biological Fate, Fifth International Symposium, Battelle Press, Columbus, Ohio, USA, pp. 439-454.

Commission of the European Communities (1982). Communication from the Commission to the Council on Dangerous Substances Which Might be Included in List I of Council Directive 76/464/EEC, Report No. COM(82) 337 final, Commission of the European Communities, Brussels, Belgium.

Connell, D.W. & Miller, G.J. (1980). Petroleum hydrocarbons in aquatic ecosystems - behaviour and effects of sublethal concentrations: Part 1. CRC Crit. Rev. Environ. Control, 11, 37-104.

Connell, D.W. & Miller, G.J. (1981). Petroleum hydrocarbons in aquatic ecosystems - behaviour and effects of sublethal concentrations: Part 2. CRC Crit. Rev. Environ. Control, 11, 105-162.

Connor, M.S. (1984). Monitoring sludge-amended agricultural soils. BioCycle, 25, 47-48 & 50-51.

Constable, T.W., Taylor, L.J. & Rush, R.J. (1986). The effect of three sludge processing operations on the fate and leachability of trace organics in municipal sludges. Environ. Technol. Lett., 7, 129-140.

Construction Industry Research and Information Association (1975). Cost-Effective Sewage Treatment - The Creation of an Optimising Model, Report 46, Vol. 2 (Revised), Construction Industry Research and Information Association, London, UK.

Cotruvo, J.A., Goldhaber, S. & Vogt, C. (1986). Regulatory significance of organic contamination in the decade of the 1980s. In Ram, N.M., Calabrese, E.J. & Christman, R.F. (Eds.), Organic Carcinogens in Drinking Water: Detection, Treatment and Risk Assessment, Wiley, Chichester, UK, Chap. 20, pp. 511-530.

Council of the European Communities (1975). Council Directive of 16 June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the Member States, Directive 75/440/EEC. Off. J. Eur. Communities, L 194, 26-31.

Council of the European Communities (1976). Council Directive of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community, Directive 76/464/EEC. Off. J. Eur. Communities, L 129, 23-29.

Council of the European Communities (1979). Council Directive of 9 October 1979 concerning the methods of measurement and frequencies of sampling and analysis of surface water intended for the abstraction of drinking water in the Member States, Directive 79/869/EEC. Off. J. Eur. Communities, L 271, 44-53.

Council of the European Communities (1980). Council Directive of 15 July 1980 relating to the quality of water intended for human consumption, Directive 80/778/EEC. Off. J. Eur. Communities, L 229, 11-29.

Crane, R.I., Fielding, M., Gibson, T.M. & Steel, C.P. (1981). A Survey of Polycyclic Aromatic Hydrocarbon Levels in British Waters, Water Research Centre Technical Report TR 158, Water Research Centre, Medmenham, UK.

Crump, K.S. & Guess, H.A. (1982). Drinking water and cancer: review of recent epidemiological findings and assessment of risks. Am. Rev. Public Health, 3, 339-357.

Curtis, D.C. & McCuen, R.H. (1977). Design efficiency of stormwater detention basins. J. Water Resour. Plann. Manage. Div. (Am. Soc. Civ. Eng.), 103, 125-140.

Dean, R.B. & Suess, M.J. (1985). The risk to health of chemicals in sewage sludge applied to land. Waste Manage. Res., 3, 251-278.

DeLuca, S.J., Chao, A.C. & Smallwood, C. Jr. (1983). Removal of organic priority pollutants by oxidation-coagulation. J. Environ. Eng. (N.Y.), 109, 36-46.

Demirjian, Y.A., Joshi, A.M. & Westman, T.R. (1987). Fate of organic compounds in land application of contaminated municipal sludge. J.-Water Pollut. Control Fed., 59, 32-38.

Dennis, J.M., Massey, R.C., McWeeny, D.J. & Watson, D.H. (1983). Polycyclic aromatic hydrocarbons in the UK diet. In Cooke, M. & Dennis, A.J. (Eds), Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement, Seventh International Symposium, Battelle Press, Columbus, Ohio, USA, pp. 405-412.

Department of the Environment (1981). Report of the Sub-Committee on the Disposal of Sewage Sludge to Land, Standing Technical Committee Report No. 20, Department of the Environment/National Water Council Standing Committee on the Disposal of Sewage Sludge, London, UK.

Department of the Environment (1982). The Bacteriological Examination of Drinking Water Supplies, Reports on Public Health and Medical Subjects 71, Department of the Environment/Department of Health and Social Security/ Public Health Laboratory Service, Her Majesty's Stationery Office, London, UK.

Department of the Environment (1984). Suspended, Settleable, and Total Dissolved Solids in Waters and Effluents 1980, Methods for the Examination of Waters and Associated Materials, Her Majesty's Stationery Office, London, UK.

Department of the Environment (1987). Chemical Oxygen Demand (Dichromate Value) of Polluted and Waste Waters 1986 (Second Edition), Methods for the Examination of Waters and Associated Materials, Her Majesty's Stationery Office, London, UK.

Department of the Environment (1988a). Inputs of Dangerous Substances to Water: Proposals for a Unified System of Control, Department of the Environment, London, UK.

Department of the Environment (1988b). The Determination of 6 Specific Polynuclear Aromatic Hydrocarbons in Waters (with notes on the determination of other PAH) 1985, Methods for the Examination of Waters and Associated Materials, Her Majesty's Stationery Office, London, UK.

Diercxsens, Ph., Wegmann, M., Daniel, R., Haeni, H. & Tarradellas, J. (1987). The accumulation of organic micropollutants in soils and in cultures by sewage sludge spreading. Gas, Wasser, Abwasser, 67, 123-132.

Driscoll, J.N. (1982). Identification of hydrocarbons in complex mixtures using a variable energy PID and capillary column gas chromatography. J. Chromatogr. Sci., 20, 91-94.

Dzombak, D.A. & Luthy, R.G. (1984). Estimating adsorption of polycyclic aromatic hydrocarbons on soils. Soil Sci., 137, 292-308.

Edwards, N.T. (1983). Polycyclic aromatic hydrocarbons (PAH's) in the terrestrial environment - a review. J. Environ. Qual., 12, 427-441.

Eganhouse, R.P. & Calder, J.A. (1976). The solubility of medium molecular weight aromatic hydrocarbons and the effects of hydrocarbon co-solutes and salinity. Geochim. Cosmochim. Acta, 40, 555-561.

Eichelberger, J.W., Kerns, E.H., Olynyk, P. & Budde, W.L. (1983). Precision and accuracy in the determination of organics in water by fused silica capillary column gas chromatography/mass spectrometry and packed column gas chromatography/mass spectrometry. Anal. Chem., 55, 1471-1479.

Eisenbrand, J. (1971). On the water solubility of 3,4-benzopyrene and other aromatic hydrocarbons and its increase by solubilizers. Dtsch. Lebensm.-Rundsch., 67, 435-444.

Ekwall, P. & Sjöblom, L. (1952). Butyric acid and lactic acid in aqueous solutions as solubilizers for carcinogenic hydrocarbons. Acta Chem. Scand., 6, 96-100.

Ellis, J.B., Revitt, D.M. & Gavens, A. (1985). Polyaromatic hydrocarbon distributions in sediments of an urban catchment. Int. J. Environ. Anal. Chem., 21, 161-170.

Environmental Protection Agency (1979). Polynuclear Aromatic Hydrocarbons - Ambient Water Quality Criteria, United States Environmental Protection Agency, Office of Water Regulations and Standards, Criteria and Standards Division, Washington, D.C., USA.

Environmental Protection Agency (1980). Water Quality Criteria Documents; Availability. Fed. Regist., 45, 79318-79379.

Environmental Protection Agency (1982). Fate of Priority Pollutants in Publicly Owned Treatment Works - Final Report, Vols. I & II, Report No. EPA-440/1-82/303, United States Environmental Protection Agency, Office of Water Regulations and Standards, Effluent Guidelines Division, Washington, D.C., USA.

Environmental Protection Agency (1983). Research Outlook, United States Environmental Protection Agency, Office of Research and Development, Washington, D.C., USA.

Escritt, L.B. (1972). Public Health Engineering Practice. Volume II: Sewerage and Sewage Disposal, Macdonald & Evans, London, UK, 4th Edn.

Eves, E.G. (1981). Hogsmill Valley Works: twenty years on. Water Pollut. Control (Maidstone, Engl.), 80, 453-462.

Fair, G.M., Geyer, J.C. & Okun, D.A. (1966). Water and Wastewater Engineering. Volume 2: Water Purification and Wastewater Treatment, Wiley, New York, USA.

Fielding, M. & Packham, R.F. (1977). Organic compounds in drinking water and public health. J. Inst. Water Eng. Sci., 31, 353-375.

Fielding, M., Gibson, T.M., James, H.A., McLoughlin, K. & Steel, C.P. (1981). Organic Micropollutants in Drinking Water, Water Research Centre Technical Report TR 159, Water Research Centre, Medmenham, UK.

Forster, R. & Wilson, I. (1981). The application of mutagenicity testing to drinking water. J. Inst. Water Eng. Sci., 35, 259-274.

Futoma, D.J., Smith, S.R., Smith, T.E. & Tanaka, J. (1981). Polycyclic Aromatic Hydrocarbons in Water Systems, CRC Press, Boca Raton, Florida, USA.

Garcia Gutierrez, A. (1983). Significance and Removal of Organochlorine Micropollutants in Primary Sedimentation. A thesis submitted to the University of London in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Engineering. Public Health and Water Resource Engineering, Department of Civil Engineering, Imperial College of Science, Technology and Medicine, London, UK.

Gardner, M.J., Hunt, D.T.E. & Winnard, D.A. (1986). Graphite Furnace Atomic Absorption Spectrometry in Water Industry Laboratories - A Collaborative Study, Water Research Centre Technical Report TR 236, Water Research Centre, Medmenham, UK.

Gauthier, T.D., Seitz, W.R. & Grant, C.L. (1987). Effects of structural and compositional variations of dissolved humic materials on pyrene K_{OC} values. Environ. Sci. Technol., 21, 243-248.

Giger, W. & Blumer, M. (1974). Polycyclic aromatic hydrocarbons in the environment: isolation and characterization by chromatography, visible, ultraviolet, and mass spectrometry. Anal. Chem., 46, 1663-1671.

Giger, W. & Schaffner, C. (1978). Determination of polycyclic aromatic hydrocarbons in the environment by glass capillary gas chromatography. Anal. Chem., 50, 243-249.

Gill, M.A. (1978). Analysis of reservoir sedimentation. Water Power Dam Constr., 30, 29-31 & 53.

Gill, M.A. (1988). Planning the useful life of a reservoir. Water Power Dam Constr., 40, 46-47.

Gjessing, E.T. & Berglind, L. (1981). Adsorption of PAH to aquatic humus. Arch. Hydrobiol., 92, 24-30.

Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A. & Budde, W.L. (1981). Trace analyses for wastewaters. Environ. Sci. Technol., 15, 1426-1435.

Golzé, A.R. (Ed.) (1977). Handbook of Dam Engineering, Van Nostrand Reinhold, New York, USA.

Gottschalk, L.C. (1964). Reservoir sedimentation. In Chow, V.T. (Ed.), Handbook of Applied Hydrology, McGraw-Hill, New York, USA, Sectn. 17-I, Pt. I, pp. 17-1 - 17-34.

Gowda, T.P.H. & Lock, J.D. (1985). Volatilization rates of organic chemicals of public health concern. J. Environ. Eng. (N.Y.), 111, 755-776.

Griest, W.H., Kubota, H. & Guerin, M.R. (1975). Resolution of polynuclear aromatic hydrocarbons by packed column GLC. Anal. Lett., 8, 949-957.

Grimmer, G. & Böhnke, H. (1972). Determination of polycyclic aromatic hydrocarbons in automobile exhaust and air pollutants by capillary-GLC. Fresenius' Z. Anal. Chem., 261, 310-314.

Grimmer, G., Böhnke, H. & Borwitzky, H. (1978). Profile analysis of polycyclic aromatic hydrocarbons in sewage sludge by gas chromatography. Fresenius' Z. Anal. Chem., 289, 91-95.

Grimmer, G., Hilge, G. & Niemitz, W. (1980). Comparison of polycyclic aromatic hydrocarbon profiles in sludges from 25 sewage treatment works. Vom Wasser, 54, 255-272.

Grimmer, G., Schneider, D. & Dettbarn, G. (1981). The load of different rivers in the Federal Republic of Germany by PAH (PAH-profiles of surface water). Vom Wasser, 56, 131-144.

Grob, K. & Grob, K. Jr. (1974). Isothermal analysis on capillary columns without stream splitting. The role of the solvent. J. Chromatogr., 94, 53-64.

Grob, K. & Grob, K. Jr. (1978). Splitless injection and the solvent effect. J. High Resolut. Chromatogr. Chromatogr. Commun., 1, 57-64.

Groenewegen, D. & Stolp, H. (1976). Microbial breakdown of polycyclic aromatic hydrocarbons. Zentralbl. Bakteriol., Parasitenkd., Infektionskrankh. Hyg., Abt. 1: Orig., Reihe B, 162, 225-232.

Grzybowski, J., Radecki, A. & Rewkowska, G. (1983). Isolation, identification, and determination of polycyclic aromatic hydrocarbons in sewage. Environ. Sci. Technol., 17, 44-47.

Gschwend, P.M. & Hites, R.A. (1981). Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States. Geochim. Cosmochim. Acta, 45, 2359-2367.

Gschwend, P.M. & Wu, S. (1985). On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. Environ. Sci. Technol., 19, 90-96.

Hagenmaier, H. & Jäger, W. (1979). Latest results of the determination of polycyclic aromatic hydrocarbons in drinking water, sludge and sediment samples by high performance liquid chromatography. Vom Wasser, 53, 18-25.

Hagenmaier, H., Kaut, H. & Krauss, P. (1986). Analysis of polycyclic aromatic hydrocarbons in sediments, sewage sludges and composts from municipal refuse by HPLC. Int. J. Environ. Anal. Chem., 23, 331-345.

Håkanson, L. & Jansson, M. (1983). Principles of Lake Sedimentology, Springer-Verlag, Heidelberg, W. Germany.

Hamlin, M.J. & Abdul Wahab, A.H. (1970). Settling characteristics of sewage in density currents. Water Res., 4, 609-626.

Hannah, S.A., Austern, B.M., Eralp, A.E. & Wise, R.H. (1986). Comparative removal of toxic pollutants by six wastewater treatment processes. J.-Water Pollut. Control Fed., 58, 27-34.

Harms, H. & Sauerbeck, D.R. (1983). Toxic organic compounds in town waste materials: their origin, concentration and turnover in waste composts, soils and plants. In Davis, R.D., Hucker, G. & L'Hermite, P. (Eds.), Environmental Effects of Organic and Inorganic Contaminants in Sewage Sludge, Proceedings of a Workshop held at Stevenage, May 25-26, 1982, Commission of the European Communities, D. Reidel, Dordrecht, Holland, pp. 38-51.

Harrison, R.M. & Johnston, W.R. (1985). Deposition fluxes of lead, cadmium, copper and polynuclear aromatic hydrocarbons (PAH) on the verges of a major highway. Sci. Total Environ., 46, 121-135.

Harrison, R.M., Perry, R. & Wellings, R.A. (1975). Polynuclear aromatic hydrocarbons in raw, potable and waste waters. Water Res., 9, 331-346.

Harrison, R.M., Perry, R. & Wellings, R.A. (1976a). Effect of water chlorination upon levels of some polynuclear aromatic hydrocarbons in water. Environ. Sci. Technol., 10, 1151-1156.

Harrison, R.M., Perry, R. & Wellings, R.A. (1976b). Chemical kinetics of chlorination of some polynuclear aromatic hydrocarbons under conditions of water treatment processes. Environ. Sci. Technol., 10, 1156-1160.

Hassett, J.P. & Anderson, M.A. (1979). Association of hydrophobic organic compounds with dissolved organic matter in aquatic systems. Environ. Sci. Technol., 13, 1526-1529.

Hassett, J.P. & Anderson, M.A. (1982). Effects of dissolved organic matter on adsorption of hydrophobic organic compounds by river- and sewage-borne particles. Water Res., 16, 681-686.

Hazen, A. (1904). On sedimentation. Trans. Am. Soc. Civ. Eng., 53, 45-88.

Heinemann, H.G. (1981). A new sediment trap efficiency curve for small reservoirs. Water Resour. Bull., 17, 825-830.

Heitkamp, M.A. & Cerniglia, C.E. (1987). Effects of chemical structure and exposure on the microbial degradation of polycyclic aromatic hydrocarbons in freshwater and estuarine ecosystems. Environ. Toxicol. Chem., 6, 535-546.

Hellmann, H. (1980). Occurrence, origin and breakdown of polycyclic aromatic hydrocarbons in the Rhine. GWF, Gas-Wasserfach: Wasser/Abwasser, 121, 178-184.

Hellmann, H. (1981). Polycyclic aromatic hydrocarbons in the Mosel and Saar and their importance in the water economy. Haustech., Bauphys., Umwelttech.-Gesund.-Ing., 102, 75-89.

Hellmann, H. (1982). Polycyclic aromatic hydrocarbons in arable and forest soils and their contribution to pollution load of waters. Dtsch. Gewaesserkd. Mitt., 26, 63-69.

Hellmann, H. (1983). Grain size distributions and organic trace substances in fluvial sediments and soils. Fresenius' Z. Anal. Chem., 316, 286-289.

Hellmann, H. (1987). Analysis of Surface Waters, Ellis Horwood, Chichester, UK.

Hembree, D.M., Garrison, A.A., Crocombe, R.A., Yokley, R.A., Wehry, E.L. & Mamantov, G. (1981). Matrix isolation Fourier transform infrared spectrometric detection in the open tubular column gas chromatography of polycyclic aromatic hydrocarbons. Anal. Chem., 53, 1783-1788.

Herbes, S.E. (1977). Partitioning of polycyclic aromatic hydrocarbons between dissolved and particulate phases in natural waters. Water Res., 11, 493-496.

Herbes, S.E. (1981). Rates of microbial transformation of polycyclic aromatic hydrocarbons in water and sediments in the vicinity of a coal-coking wastewater discharge. Appl. Environ. Microbiol., 41, 20-28.

Herbes, S.E. & Schwall, L.R. (1978). Microbial transformation of polycyclic aromatic hydrocarbons in pristine and petroleum-contaminated sediments. Appl. Environ. Microbiol., 35, 306-316.

Herrmann, R. (1981). Transport of polycyclic aromatic hydrocarbons through a partly urbanised river basin. Water, Air, Soil Pollut., 16, 445-467.

Hilpert, L.R., May, W.E., Wise, S.A., Chesler, S.N. & Hertz, H.S. (1978). Interlaboratory comparison of determinations of trace level petroleum hydrocarbons in marine sediments. Anal. Chem., 50, 458-463.

Hoffman, E.J., Mills, G.L., Latimer, J.S. & Quinn, J.G. (1984). Urban runoff as a source of polycyclic aromatic hydrocarbons to coastal waters. Environ. Sci. Technol., 18, 580-587.

Hoffman, E.J., Latimer, J.S., Hunt, C.D., Mills, G.L. & Quinn, J.G. (1985). Stormwater runoff from highways. Water, Air, Soil Pollut., 25, 349-364.

Hoffmann, D. & Wynder, E.L. (1960). Short-term determination of carcinogenic aromatic hydrocarbons. Anal. Chem., 32, 295-296.

Hosmer, D.W. (1986). Principles of quantitative risk assessment and their application to drinking water. In Ram, N.M., Calabrese, E.J. & Christman, R.F. (Eds.), Organic Carcinogens in Drinking Water: Detection, Treatment and Risk Assessment, Wiley, Chichester, UK, Chap. 13, pp. 339-351.

Hrubec, J., van Kreijl, C.F., Morra, C.F.H. & Sloof, W. (1983). Treatment of municipal waste water by reverse osmosis and activated carbon removal of organic micropollutants and reduction of toxicity. Sci. Total Environ, 27, 71-88.

Hunt, D.T.E. & Wilson, A.L. (1986). The Chemical Analysis of Water, The Royal Society of Chemistry, London, UK, 2nd Edn.

Hunt, S.M. & Fawell, J.K. (1987). The toxicology of organic micropollutants in drinking water: estimating the risk. J. Inst. Water Eng. Sci., 41, 276-284.

Hutchins, S.R., Tomson, M.B., Wilson, J.T. & Ward, C.H. (1984). Fate of trace organics during rapid infiltration of primary wastewater at Fort Devens, Massachusetts. Water Res., 18, 1025-1036.

Il'nitskii, A.P. (1969). An experimental study of the effectiveness of removal of carcinogenic hydrocarbons in water during clarification and disinfection. Gig. Sanit., 34, 26-29.

Inscoe, M.N. (1964). Photochemical changes in thin layer chromatograms of polycyclic, aromatic hydrocarbons. Anal. Chem., 36, 2505-2506.

Inscoe, M.N. (1966). Losses due to adsorption during filtration of aqueous solutions of polycyclic aromatic hydrocarbons. Nature (London), 211, 1083-1085.

Institute of Water Pollution Control (1973). Manuals of British Practice in Water Pollution Control. Unit Processes: Primary Sedimentation, Institute of Water Pollution Control, Maidstone, UK.

Jamieson, D.G. & Nicolson, N.J. (1984). Water resources of the Thames Basin: quantitative and qualitative aspects. J. Inst. Water Eng. Sci., 38, 379-388.

Jenkins, T.F., Leggett, D.C., Parker, L.V. & Oliphant, J.L. (1985). Toxic organics removal kinetics in overland flow land treatment. Water Res., 19, 707-718.

Johnsen, S. & Gribbestad, I.S. (1988). Influence of humic substances on the formation of chlorinated polycyclic aromatic hydrocarbons during chlorination of polycyclic aromatic hydrocarbon polluted water. Environ. Sci. Technol., 22, 978-981.

Johnsen, S., Krane, J., Carlberg, G.E., Aamot, E. & Schou, L. (1986). PAH in water systems. Effect of aquatic humus and chlorination. In Bjørseth, A. & Angeletti, G. (Eds.), Organic Micropollutants in the Aquatic Environment: Proceedings of the Fourth European Symposium, Vienna, Austria, October 22-24, 1985, Commission of the European Communities, D. Reidel, Dordrecht, Holland, pp. 440-448.

Johnson, L.D. & Young, J.C. (1983). Inhibition of anaerobic digestion by organic priority pollutants. J.-Water Pollut. Control Fed., 55, 1441-1449.

Jones, K.C., Stratford, J.A., Tidridge, P., Waterhouse, K.S. & Johnston, A.E. (1989). Polynuclear aromatic hydrocarbons in an agricultural soil: long-term changes in profile distribution. Environ. Pollut., Ser. A, 56, 337-351.

Jordan, T.E. (1954). Vapour Pressure of Organic Compounds, Interscience, New York, USA.

Junk, G.A., Richard, J.J., Grieser, M.D., Witiak, D., Witiak, J.L., Arguello, M.D., Vick, R., Svec, H.J., Fritz, J.S. & Calder, G.V. (1974). Use of macroreticular resins in the analysis of water for trace organic contaminants. J. Chromatogr., 99, 745-762.

Karickhoff, S.W. (1980). Sorption kinetics of hydrophobic pollutants in natural sediments. In Baker, R.A. (Ed.), Contaminants and Sediments, Vol. 2, Ann Arbor, Michigan, USA, Chap. 11, pp. 193-205.

Karickhoff, S.W. (1984). Organic pollutant sorption in aquatic systems. J. Hydraul. Eng. (N.Y.), 110, 707-735.

Karickhoff, S.W. & Morris, K.R. (1985). Sorption dynamics of hydrophobic pollutants in sediment suspensions. Environ. Toxicol. Chem., 4, 469-479.

Karickhoff, S.W., Brown, D.S. & Scott, T.A. (1979). Sorption of hydrophobic pollutants on natural sediments. Water Res., 13, 241-248.

Keefer, L.K., Wallcave, L., Loo, J. & Peterson, R.S. (1971). Analysis of mixtures of isomeric polynuclear hydrocarbons by nuclear magnetic resonance spectrometry. Methylated derivatives of anthracene, benz[a]anthracene, benzo[c]phenanthrene, and pyrene. Anal. Chem., 43, 1411-1416.

Keith, L.H. & Telliard, W.A. (1979). Priority pollutants. I - a perspective view. Environ. Sci. Technol., 13, 416-423.

Keith, L.H., Crummett, W., Deegan, J. Jr., Libby, R.A., Taylor, J.K. & Wentler, G. (1983). Principles of environmental analysis. Anal. Chem., 55, 2210-2218.

Kempton, S., Sterritt, R.M. & Lester, J.N. (1987a). Heavy metal removal in primary sedimentation I. The influence of metal solubility. Sci. Total Environ., 63, 231-246.

Kempton, S., Sterritt, R.M. & Lester, J.N. (1987b). Heavy metal removal in primary sedimentation II. The influence of metal speciation and particle size distribution. Sci. Total. Environ., 63, 247-258.

Kinzer, G., Riggin, R., Bishop, T., Birts, M.A. & Strup, P. (1984). Project Summary: EPA Method Study 20, Method 610-PNA'S, Report No. EPA-600/S4-84-063, United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, USA.

Kirchmer, C.J., Winter, M.C. & Kelly, B.A. (1983). Factors affecting the accuracy of quantitative analyses of priority pollutants using GC/MS. Environ. Sci. Technol., 17, 396-401.

Kirkbright, G.F. & DeLima, C.G. (1974). The detection and determination of polynuclear aromatic hydrocarbons by luminescence spectrometry utilising the Shpol'skii effect at 77 K. Analyst (London), 99, 338-354.

Klevens, H.B. (1950). Solubilization of polycyclic hydrocarbons. J. Phys. Colloid Chem., 54, 283-298.

Kool, H.J., van Kreijl, C.F. & Zoeteman, B.C.J. (1982). Toxicology assessment of organic compounds in drinking water. CRC Crit. Rev. Environ. Control, 12, 307-357.

Krasnoschekova, R. & Goubergrits, M. (1983). The PAH hydrophobicity and solubilization in aqueous solutions of ionic surfactants. In Cooke, M. & Dennis, A.J. (Eds.), Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement, Seventh International Symposium, Battelle Press, Columbus, Ohio, USA, pp. 721-729.

Kunte, H. (1967). Carcinogenic substances in water and soil. XVIII. The determination of polycyclic aromatic hydrocarbons with mixed thin layer chromatography and fluorescence detection. Arch. Hyg. Bakteriol., 151, 193-201.

Laganà, A., Petronio, B.M. & Rotatori, M. (1980). Concentration and determination of polycyclic aromatic hydrocarbons in aqueous samples on graphitized carbon black. J. Chromatogr., 198, 143-149.

Landrum, P.F., Nihart, S.R., Eadie, B.J. & Gardner, W.S. (1984). Reverse-phase separation method for determining pollutant binding to Aldrich humic acid and dissolved organic carbon of natural waters. Environ. Sci. Technol., 18, 187-192.

Lao, R.C., Thomas, R.S. & Monkman, J.L. (1975). Computerized gas chromatographic-mass spectrometric analysis of polycyclic aromatic hydrocarbons in environmental samples. J. Chromatogr., 112, 681-700.

Larock, B.E., Chun, W.C.K. & Schamber, D.R. (1983). Computation of sedimentation basin behaviour. Water Res., 17, 861-867.

Lee, M.L. & Hites, R.A. (1977). Mixed charge exchange-chemical ionization mass spectrometry of polycyclic aromatic hydrocarbons. J. Am. Chem. Soc., 99, 2008-2009.

Lee, M.L. & Wright, B.W. (1980). Capillary column gas chromatography of polycyclic aromatic compounds: a review. J. Chromatogr. Sci., 18, 345-358.

Lee, M.L., Novotny, M.V. & Bartle, K.D. (1981). Analytical Chemistry of Polycyclic Aromatic Compounds, Academic Press, London, UK.

Lee, R.F. (1977). Fate of petroleum components in estuarine waters of the southeastern United States. In American Petroleum Institute, Proceedings of the 1977 Oil Spill Conference (Prevention, Behaviour, Control, Cleanup), American Petroleum Institute, Washington, D.C., USA, pp. 611-616.

Lee, R.F., Gardner, W.S., Anderson, J.W., Blaylock, J.W. & Barwell-Clarke, J. (1978). Fate of polycyclic aromatic hydrocarbons in controlled ecosystem enclosures. Environ. Sci. Technol., 12, 832-838.

Leemans, F.A. (1971). Selection of an optimum analytical technique for process control. Anal. Chem., 43, 36A-49A.

Leermakers, P.A. & Thomas, H.T. (1965). Electronic spectra and photochemistry of adsorbed organic molecules. I. Spectra of ketones on silica gel. J. Am. Chem. Soc., 87, 1620-1622.

Lester, J.N. (1983). Occurrence, behaviour and fate of organic micropollutants during waste water and sludge treatment processes. In Davis, R.D., Hucker, G. & L'Hermite, P. (Eds.), Environmental Effects of Organic and Inorganic Contaminants in Sewage Sludge, Proceedings of a Workshop held at Stevenage, UK, May 25-26, 1982, Commission of the European Communities, D. Reidel, Dordrecht, Holland, pp. 3-18.

Lester, J.N. (1984). Presence of organic micropollutants in sewage sludges. In L'Hermite, P. & Ott, H. (Eds.), Processing and Use of Sewage Sludge: Proceedings of the Third International Symposium, Brighton, UK, September 27-30, 1983, Commission of the European Communities, D. Reidel, Dordrecht, Holland, pp. 150-157.

Lester, W.F. (1979). River quality objectives. J. Inst. Water Eng. Sci., 33, 429-450.

Lewis, W.M. (1975). Polynuclear aromatic hydrocarbons in water. Water Treat. Exam., 24, 243-277.

Lewis, W.M. (1985). World Health Organization, Guidelines on Organic Micropollutants. Sci. Total Environ., 47, 83-91.

Liao, M.Y. & Randtke, S.J. (1986). Predicting the removal of soluble organic contaminants by lime softening. Water Res., 20, 27-35.

Linsley, R.K., Kohler, M.A. & Paulhus, L.H. (1982). Hydrology for Engineers, McGraw-Hill, New York, USA, 3rd Edn.

Liss, P.S. & Slater, P.G. (1974). Flux of gases across the air-sea interface. Nature (London), 247, 181-184.

Longbottom, J.E. & Lichtenberg, J.J. (Eds.) (1982). Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Report No. EPA-600/4-82-057, United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, USA.

Lowe, P. & Sidwick, J.M. (1987). Towards more efficient treatment - preliminary and primary treatment. Water Pollut. Control (Maidstone, Engl.), 86, 206-219.

Luin, van A.B. & Starkenburg, van W. (1985). Hazardous substances in waste water. Water Sci. Technol., 17, 843-853.

Mackay, D. & Shiu, W.Y. (1977). Aqueous solubility of polynuclear aromatic hydrocarbons. J. Chem. Eng. Data, 22, 399-402.

Mackay, D. & Wolkoff, A.W. (1973). Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol., 7, 611-614.

Mackay, D., Shiu, W.Y. & Sutherland, R.J. (1980). Estimating volatilization and water column diffusion rates of hydrophobic contaminants. In Haque, R. (Ed.), Dynamics, Exposure and Hazard Assessment of Toxic Chemicals, Ann Arbor, Michigan, USA, Chap. 11, pp. 127-142.

Mackay, D.M., Roberts, P.V. & Cherry, J.A. (1985). Transport of organic contaminants in groundwater. Environ. Sci. Technol., 19, 384-392.

Mahmood, K. (1987). Reservoir Sedimentation: Impact, Extent, and Mitigation, World Bank Technical Paper Number 71, The World Bank, Washington, D.C., USA.

Malaney, G.W., Lutin, P.A., Cibulka, J.J. & Hickerson, L.H. (1967). Resistance of carcinogenic organic compounds to oxidation by activated sludge. J.-Water Pollut. Control Fed., 39, 2020-2029.

March, R.P. & Hamlin, M.J. (1966). An investigation into the performance of a full-scale sedimentation tank. J. Proc. Inst. Sewage Purif., 2, 118-139.

Matter-Müller, C., Gujer, W. & Giger, W. (1981). Transfer of volatile substances from water to the atmosphere. Water Res., 15, 1271-1279.

Matthews, D.E. & Hayes, J.M. (1976). Systematic errors in gas chromatography-mass spectrometry isotope ratio measurements. Anal. Chem., 48, 1375-1382.

Matthews, P.J. (1983). The proposal for an EEC Directive on utilisation of sewage sludge in agriculture - An introductory review. Effluent Water Treat. J., 23, 94-99.

Matthews, P.J. (1985). Optimising sewage sludge treatment, disposal and utilisation - the British approach. Wastes Manage., 75, 557-570.

Matthews, P.J. (1987). COPA II: Interpretation and application. Public Health Eng., 14, 38-42.

May, W.E., Chesler, S.N., Cram, S.P., Gump, B.H., Hertz, H.S., Enagonio, D.P. & Dyszel, S.M. (1975). Chromatographic analysis of hydrocarbons in marine sediments and seawater. J. Chromatogr. Sci., 13, 535-540.

May, W.E., Wasik, S.P. & Freeman, D.H. (1978). Determination of the aqueous solubility of polynuclear aromatic hydrocarbons by a coupled column liquid chromatographic technique. Anal. Chem., 50, 175-179.

McCarthy, J.F. & Jimenez, B.D. (1985). Interactions between polycyclic aromatic hydrocarbons and dissolved humic material: binding and dissociation. Environ. Sci. Technol., 19, 1072-1076.

McCarty, P.L. (1980). Organics in water - an engineering challenge. J. Environ. Eng. Div. (Am. Soc. Civ. Eng.), 106, 1-17.

McIntyre, A.E., Perry, R. & Lester, J.N. (1981). Analysis of polynuclear aromatic hydrocarbons in sewage sludges. Anal. Lett., 14, 291-309.

McKenna, E.J. & Health, R.D. (1976). Biodegradation of Polynuclear Aromatic Hydrocarbon Pollutants by Soil and Water Microorganisms, Research Report 113, University of Illinois Urbana-Champaign Water Resources Center, University of Illinois, Urbana-Champaign, USA.

McVeety, B.D. & Hites, R.A. (1988). Atmospheric deposition of polycyclic aromatic hydrocarbons to water surfaces: a mass balance approach. Atmos. Environ., 22, 511-536.

Means, J.C., Wood, S.G., Hassett, J.J. & Banwart, W.L. (1980a). Sorption of polynuclear aromatic hydrocarbons by sediments and soils. Environ. Sci. Technol., 14, 1524-1528.

Means, J.C., Hassett, J.J., Wood, S.G., Banwart, W.L., Ali, S. & Khan, A. (1980b). Sorption properties of polynuclear aromatic hydrocarbons and sediments: heterocyclic and substituted compounds. In Bjørseth, A. & Dennis, A.J. (Eds.), Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, Fourth International Symposium, Battelle Press, Columbus, Ohio, USA, pp. 395-404.

Means, J.C., Wood, S.G., Hassett, J.J. & Banwart, W.L. (1982). Sorption of amino- and carboxy-substituted polynuclear aromatic hydrocarbons by sediments and soils. Environ. Sci. Technol., 16, 93-98.

Mertens, H. & Rittmann, R. (1983). Determination of polycyclic aromatic hydrocarbons in water and sludge samples by high performance liquid chromatography. Comparison of results with gas chromatographic analyses. Gewaesserschutz, Wasser, Abwasser, 67, 175-195.

Metcalf & Eddy (1979). Wastewater Engineering: Treatment, Disposal, Reuse, Tata McGraw-Hill, New Delhi, India, 2nd Edn.

Mill, T., Mabey, W.R., Lan, B.Y. & Baraze, A. (1981). Photolysis of polycyclic aromatic hydrocarbons in water. Chemosphere, 10, 1281-1290.

Miller, D.G. (1982). Further Evidence to the Royal Commission on Environmental Pollution Concerning the Appropriateness of EEC Directives and the Functional Problems of Implementation, Water Research Centre Report 381-M, Water Research Centre, Medmenham, UK.

Miller, G.C. & Zepp, R.G. (1979). Effects of suspended sediments on photolysis rates of dissolved pollutants. Water Res., 13, 453-459.

Miller, H.C., Barrett, W.J. & James, R.H. (1982). Investigating potential water contamination by petroleum-asphalt coatings in ductile-iron pipe. J.-Am. Water Works Assoc., 74, 151-156.

Moretti, C.J. & Neufeld, R.D. (1989). PAH partitioning mechanisms with activated sludge. Water Res., 23, 93-102.

Morozzi, G. & Scardazza, F. (1988). Adsorption of carcinogenic benz(a)pyrene on activated sludges. J. Environ. Sci. Health, Part A, 23, 169-180.

Namkung, E., Stratton, R.G. & Rittmann, B.E. (1983). Predicting removal of trace organic compounds by biofilms. J.-Water Pollut. Control Fed., 55, 1366-1372.

National Water Council (1978). River Water Quality - The Next Stage. Review of Discharge Consent Conditions, National Water Council, London, UK.

Navratil, J.D., Sievers, R.E. & Walton, H.F. (1977). Open-pore polyurethane columns for collection and preconcentration of polynuclear aromatic hydrocarbons from water. Anal. Chem., 49, 2260-2263.

Neff, J.M. (1979). Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Sources, Fates and Biological Effects, Applied Science, London, UK.

Nicholls, T.P., Perry, R. & Lester, J.N. (1979). The influence of heat treatment on the metallic and polycyclic aromatic hydrocarbon content of sewage sludge. Sci. Total Environ., 12, 137-150.

Nicholls, T.P., Lester, J.N. & Perry, R. (1980). The influence of heat treatment on the metallic and polycyclic aromatic hydrocarbon content of sewage sludge: a pilot plant study. Sci. Total Environ., 14, 19-30.

O'Connor, D.J. & Connolly, J.P. (1980). The effect of concentration of adsorbing solids on the partition coefficient. Water Res., 14, 1517-1523.

Office of Population Censuses and Survey (1985). OPCS Monitor, DH2, 85/3, Office of Population Censuses and Survey, London, UK.

Ogawa, I., Junk, G.A. & Svec, H.J. (1981). Degradation of aromatic compounds in ground-water, and methods of sample preservation. Talanta, 28, 725-729.

Oliver, B.G., Cosgrove, E.G. & Carey, J.H. (1979). Effect of suspended sediments on the photolysis of organics in water. Environ. Sci. Technol., 13, 1075-1077.

O'Melia, C.R. (1980). Aquasols: the behaviour of small particles in aquatic systems. Environ. Sci. Technol., 14, 1052-1060.

O'Melia, C.R. (1987). Particle-particle interactions. In Stumm, W. (Ed.), Aquatic Surface Chemistry, Chemical Processes at the Particle-Water Interface, Wiley, London, UK, Chap. 14, pp. 385-403.

Oyler, A.R., Liukkonen, R.J., Lukasewycz, M.K., Cox, D.A., Peake, D.A. & Carlson, R.M. (1982). Implications of treating water containing polynuclear aromatic hydrocarbons with chlorine: a gas chromatographic-mass spectrometric study. Environ. Health Perspect., 46, 73-86.

Oyler, A.R., Liukkonen, R.J., Lukasewycz, M.T., Heikkila, K.E., Cox, D.A. & Carlson, R.M. (1983). Chlorine 'disinfection' chemistry of aromatic compounds. Polynuclear aromatic hydrocarbons: rates, products, and mechanisms. Environ. Sci. Technol., 17, 334-342.

Packham, R.F., Beresford, S.A.A. & Fielding, M. (1981). Health related studies of organic compounds in relation to re-use in the United Kingdom. Sci. Total Environ., 18, 167-186.

Panjan, J. (1988). Analysis of the influences on sedimentation and flotation processes. Wasserwirtschaft, 78, 161-167.

Petrasek, A.C., Kugelman, I.J., Austern, B.M., Pressley, T.A., Winslow, L.A. & Wise, R.H. (1983). Fate of toxic organic compounds in wastewater treatment plants. J.-Water Pollut. Control Fed., 55, 1286-1296.

Ponsford, B. (1987). Her Majesty's Inspectorate of Pollution. Chem. Ind. (London), No. 18, 651-653.

Prahl, F.G. & Carpenter, R. (1983). Polycyclic aromatic hydrocarbon (PAH)-phase associations in Washington coastal sediment. Geochim. Cosmochim. Acta, 47, 1013-1023.

Price, G.A. & Clements, M.S. (1974). Some lessons from model and full-scale tests in rectangular sedimentation tanks. Water Pollut. Control (Maidstone, Engl.), 73, 102-113.

Pupp, C., Lao, R.C., Murray, J.J. & Pottie, R.F. (1974). Equilibrium vapour concentrations of some polycyclic aromatic hydrocarbons, As_4O_6 and SeO_2 and the collection efficiencies of these air pollutants. Atmos. Environ., 8, 915-925.

Quaghebeur, D. & De Wulf, E. (1978). Polynuclear aromatic hydrocarbons in the main Belgian aquifers. Sci. Total Environ., 10, 231-237.

Quaghebeur, D., De Wulf, E., Ravelingien, M.C. & Janssens, G. (1983). Polycyclic aromatic hydrocarbons in rainwater. Sci. Total Environ., 32, 35-54.

Radding, S.B., Mill, T., Gould, C.W., Liu, D.H., Johnson, H.L., Bomberger, D.C. & Fojo, C.V. (1976). The Environmental Fate of Selected Polynuclear Aromatic Hydrocarbons, Report No. EPA-560/5-75-009, United States Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia, USA.

Ramalho, R.S. (1983). Introduction to Wastewater Treatment Processes, Academic Press, New York, USA, 2nd Edn.

Rav-Acha, Ch. & Blits, R. (1985). The different reaction mechanisms by which chlorine and chlorine dioxide react with polycyclic aromatic hydrocarbons (PAH) in water. Water Res., 19, 1273-1281.

Readman, J.W. (1988). Institute for Marine Environmental Research, Plymouth, UK. Personal communication.

Readman, J.W., Mantoura, R.F.C., Rhead, M.M. & Brown, L. (1982). Aquatic distribution and heterotrophic degradation of polycyclic aromatic hydrocarbons (PAH) in the Tamar Estuary. Estuarine, Coastal Shelf Sci., 14, 369-389.

Readman, J.W., Mantoura, R.F.C. & Rhead, M.M. (1984a). Distribution, composition and sources of polycyclic aromatic hydrocarbons in sediments of the River Tamar catchment and estuary, U.K. In Parker, W.R. & Kinsman, D.J.J. (Eds.), Transfer Processes in Cohesive Sediment Systems, Plenum Press, New York, USA, pp. 155-170.

Readman, J.W., Mantoura, R.F.C. & Rhead, M.M. (1984b). The physico-chemical speciation of polycyclic aromatic hydrocarbons (PAH) in aquatic systems. Fresenius' Z. Anal. Chem., 319, 126-131.

Readman, J.W., Mantoura, R.F.C. & Rhead, M.M. (1987). A record of polycyclic aromatic hydrocarbon (PAH) pollution obtained from accreting sediments of the Tamar Estuary, U.K.: evidence for non-equilibrium behaviour of PAH. Sci. Total Environ., 66, 73-94.

Reichert, J., Kunte, H., Engelhardt, K. & Borneff, J. (1971). Carcinogenic substances in water and soil. XXVII. Further studies on the elimination from waste water of carcinogenic polycyclic aromatic hydrocarbons. Zentralbl. Bakteriol., Parasitenkd., Infektionskrankh. Hyg., Abt. 1: Orig., Reihe B, 155, 18-40.

Richardson, M.L. & Bowron, J.M. (1983). Catchment Quality Control, Notes on Water Research No. 32, Water Research Centre, Medmenham, UK.

Ridgway, J.W. (1985). Reuse of sewage effluent in the UK - an appraisal of health related matters. In Institution of Civil Engineers, Reuse of Sewage Effluent, Proceedings of the International Symposium, London, UK, October 30-31, 1984, Thomas Telford, London, UK, Chap. 16, pp. 249-260.

Riggin, R. & Strup, P.E. (1984). Project Summary: Screening Methods for PAH Priority Pollutants in Wastewater, Report No. EPA-600/S4-84-007, United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, USA.

Robinson, R. (1980). The Control of Pollution Act 1974. 1. Implications for river quality management. J. Inst. Water Eng. Sci., 34, 129-144.

Rossi, S.R. & Thomas, W.H. (1981). Solubility behaviour of three aromatic hydrocarbons in distilled water and natural seawater. Environ. Sci. Technol., 15, 715-716.

Rossin, A.C., Perry, R. & Lester, J.N. (1982). Removal of zeolite type A during primary sedimentation and its effect on metal removal. Water Res., 16, 1223-1232.

Rossman, L.A. (1982). Cost-effective pretreatment programs. J. Environ. Eng. Div. (Am. Soc. Civ. Eng.), 108, 665-679.

Rump, H.H. (1981). Behaviour of pollutants in municipal sewage treatment works. Forum Staedte-Hyg., 32, 77-89.

Samoilovich, L.N. & Redkin, Y.R. (1968). Contamination of the Sunzhi River with 3,4-benzpyrene from the petroleum chemical industry of Grozny. Gig. Sanit., 33, 6-9.

Santodonato, J., Howard, P. & Basu, D. (1981). Health and ecological assessment of polynuclear aromatic hydrocarbons. J. Environ. Pathol. Toxicol., 5, 1-364.

Schomburg, G., Behlau, H., Dielmann, R., Weeke, F. & Husmann, H. (1977). Sampling techniques in capillary gas chromatography. J. Chromatogr., 142, 87-102.

Schössner, V.H., Falkenberg, W. & Althaus, H. (1983). One-dimensional thin layer chromatographic separation and fluorometric quantification of polycyclic aromatic hydrocarbons in water samples. Z. Wasser Abwasser Forsch., 16, 132-135.

Schrimpff, E. (1984). Organic micropollutants' balances in watersheds of northeastern Bavaria. Fresenius' Z. Anal. Chem., 319, 147-151.

Scypinski, S. & Cline Love, L.J. (1984). Room-temperature phosphorescence of polynuclear aromatic hydrocarbons in cyclodextrins. Anal. Chem., 56, 322-327.

Searl, T.D., Robbins, W.K. & Brown, R.A. (1979). Determination of polynuclear aromatic hydrocarbons in water and wastewater by a gas chromatographic-ultraviolet spectrophotometric method. In Van Hall, C.E. (Ed.), Measurement of Organic Pollutants in Water and Wastewater, American Society for Testing and Materials Special Technical Publication 686, American Society for Testing and Materials, Philadelphia, USA, pp. 164-180.

Shiraishi, H., Pilkington, N.H., Otsuki, A. & Fuwa, K. (1985). Occurrence of chlorinated polynuclear aromatic hydrocarbons in tap water. Environ. Sci. Technol., 19, 585-590.

Shultz, D.J., Pankow, J.F., Tai, D.Y. & Stephens, D.W. (1976). Determination, storage, and preservation of low molecular weight hydrocarbon gases in aqueous solution. J. Res. U.S. Geol. Surv., 4, 247-251.

Shy, C.M. (1985). Chemical contamination of water supplies. Environ. Health Perspect., 62, 399-406.

Side, J. (1986). The European Community and dumping at sea. Mar. Pollut. Bull., 17, 290-294.

Simpson, E.A. (1978). The harmonization of the monitoring of the quality of inland fresh water. J. Inst. Water Eng. Sci., 32, 45-56.

Smith, J.H., Bomberger, D.C. Jr. & Haynes, D.L. (1980). Prediction of the volatilization rates of high-volatility chemicals from natural water bodies. Environ. Sci. Technol., 14, 1332-1337.

Smith, J.H., Mabey, W.R., Bohonos, N., Holt, B.R., Lee, S.S., Chou, T.-W., Bomberger, D.C. & Mill, T. (1978). Environmental Pathways of Selected Chemicals in Freshwater Systems. Part II: Laboratory Studies, Report No. EPA-600/7-78-074, United States Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia, USA.

Smith, R. (1969). Preliminary design of wastewater treatment systems. J. Sanit. Eng. Div., Am. Soc. Civ. Eng., 95, 117-145.

Snook, M.E. (1976). Gel filtration of methyl-substituted polynuclear aromatic hydrocarbons. Anal. Chim. Acta, 81, 423-427.

Southworth, G.R. (1979). The role of volatilization in removing polycyclic aromatic hydrocarbons from aquatic environments. Bull. Environ. Contam. Toxicol., 21, 507-514.

Southworth, G.R. & Keller, J.L. (1984). Partitioning of naphthalene, methylnaphthalenes and biphenyl between wastewater treatment sludges and water. Environ. Toxicol. Chem., 3, 575-582.

Stanbridge, H.H. (1968). Operation and performance of the Hogsmill Valley Sewage Treatment Works of the Greater London Council, 1958-1966. Water Pollut. Control (Maidstone, Engl.), 67, 21-55.

Steel, E.W. (1960). Water Supply and Sewerage, McGraw-Hill, New York, USA, 4th Edn.

Steel, J.A. (1984). Sampling to meet water quality standards. J. Inst. Water Eng. Sci., 38, 392-402.

Suess, M.J. (1972). Aqueous solutions of 3,4-benzpyrene. Water Res., 6, 981-985.

Suess, M.J. (1976). The environmental load and cycle of polycyclic aromatic hydrocarbons. Sci. Total Environ., 6, 239-250.

Suess, M.J. (Ed.) (1982). Examination of Water for Pollution Control: A Reference Handbook. Vol. 2: Physical, Chemical and Radiological Examination, Published on behalf of the World Health Organization Regional Office for Europe, Pergamon Press, Oxford, UK.

Sumption, N.R. (1987). Thames Water Authority, London, UK. Personal communication.

Susser, M. (1973). Causal Thinking in the Health Sciences: Concept and Strategies of Epidemiology, Oxford University Press, New York, USA.

Szechowycz, R.W. & Qureshi, M.M. (1973). Sedimentation in Mangla Reservoir. J. Hydraul. Div., Am. Soc. Civ. Eng., 99, 1551-1572.

Tabak, H.H., Quave, S.A., Mashni, C.I. & Barth, E.F. (1981). Biodegradability studies with organic priority pollutant compounds. J.-Water Pollut. Control Fed., 53, 1503-1518.

Taylor, M.R.G. & Denner, J.M. (1987). Sewage effluent - a water resource. J. Inst. Water Eng. Sci., 41, 40-50.

Tebbutt, T.H.Y. (1969). The performance of circular sedimentation tanks. Water Pollut. Control (Maidstone, Engl.), 68, 467-474.

Tebbutt, T.H.Y. (1979). Primary sedimentation of wastewater. J.-Water Pollut. Control Fed., 51, 2858-2867.

Tebbutt, T.H.Y. (1983). Principles of Water Quality Control, Pergamon Press, Oxford, UK, 3rd Edn.

Tebbutt, T.H.Y. & Christoulas, D.G. (1975). Performance relationships for primary sedimentation. Water Res., 9, 347-356.

Thébault, P., Cases, J.M. & Fiessinger, F. (1981). Mechanism underlying the removal of organic micropollutants during flocculation by an aluminium or iron salt. Water Res., 15, 183-189.

Thomas, W. (1981). Concentrations and total inputs of PAH, chlorinated hydrocarbons and trace metals in bulk precipitation - comparison of suburban and rural stations. Dtsch. Gewaesserkd. Mitt., 25, 120-129.

Thompson, M. (1982). Regression methods in the comparison of accuracy. Analyst (London), 107, 1169-1180.

Thompson, S. & Eglinton, G. (1978). Composition and sources of pollutant hydrocarbons in the Severn Estuary. Mar. Pollut. Bull., 9, 133-136.

Tye, R.J. (1986). Mutagens in water sources: detection and risk assessment. J. Inst. Water Eng. Sci., 40, 541-548.

Valioulis, I.A. & List, E.J. (1984a). Numerical simulation of a sedimentation basin. 1. Model development. Environ. Sci. Technol., 18, 242-247.

Valioulis, I.A. & List, E.J. (1984b). Numerical simulation of a sedimentation basin. 2. Design application. Environ. Sci. Technol., 18, 248-253.

Vanoni, V.A. (Ed.) (1975). Sedimentation Engineering, ASCE Manuals and Reports on Engineering Practice No. 54, American Society of Civil Engineers, New York, USA.

Vo-Dinh, T., Gammage, R.B., Hawthorne, A.R. & Thorngate, J.H. (1978). Synchronous spectroscopy for analysis of polynuclear aromatic compounds. Environ. Sci. Technol., 12, 1297-1302.

Voice, T.C. & Weber, W.J. Jr. (1983). Sorption of hydrophobic compounds by sediments, soils and suspended solids - I. Theory and background. Water Res., 17, 1433-1441.

Voice, T.C. & Weber, W.J. Jr. (1985). Sorbent concentration effects in liquid/solid partitioning. Environ. Sci. Technol., 19, 789-796.

Voice, T.C., Rice, C.P. & Weber, W.J. Jr. (1983). Effect of solids concentration on the sorptive partitioning of hydrophobic pollutants in aquatic systems. Environ. Sci. Technol., 17, 513-518.

Wahlberg, E.J. & Keinath, T.M. (1988). Development of settling flux curves using SVI. J.-Water Pollut. Control Fed., 60, 2095-2100.

Walters, R.W. & Luthy, R.G. (1982). Model for predicting adsorption of PAH from aqueous systems. In Cooke, M., Dennis, A.J. & Fisher, G.L. (Eds.), Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry, Sixth International Symposium, Battelle Press, Columbus, Ohio, USA, pp. 873-883.

Walters, R.W. & Luthy, R.G. (1984a). Equilibrium adsorption of polycyclic aromatic hydrocarbons from water onto activated carbon. Environ. Sci. Technol., 18, 395-403.

Walters, R.W. & Luthy, R.G. (1984b). Liquid/suspended solid phase partitioning of polycyclic aromatic hydrocarbons in coal coking wastewaters. Water Res., 18, 795-809.

Walther, W., Teichgräber, B., Schäfer, W. & Dähne, M. (1986). Polycyclic aromatic and chlorinated hydrocarbons in soil zones and ditches in agricultural areas. GWF, Gas- Wasserfach: Wasser/Abwasser, 127, 184-190.

Water Research Centre (1976). Emission Standards in Relation to Water Quality Objectives, Water Research Centre Technical Report TR 17, Water Research Centre, Medmenham, UK.

Water Resources Board (1973). Water Resources in England and Wales, Her Majesty's Stationery Office, London, UK.

Weast, R.C. (Ed.) (1987). CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, Florida, USA, 68th Edn.

Weber, W.J. Jr., Voice, T.C., Pirbazari, M., Hunt, G.E. & Ulanoff, D.M. (1983). Sorption of hydrophobic compounds by sediments, soils and suspended solids - II. Sorbent evaluation studies. Water Res., 17, 1443-1452.

Weil-Malherbe, H. (1946). The solubilization of polycyclic aromatic hydrocarbons by purines. Biochem. J., 40, 351-363.

White, J.B. & Allos, M.R. (1976). Experiments on wastewater sedimentation. J.-Water Pollut. Control Fed., 48, 1741-1752.

Whitehouse, B. (1985). The effects of dissolved organic matter on the aqueous partitioning of polynuclear aromatic hydrocarbons. Estuarine, Coastal Shelf Sci., 20, 393-402.

Whitehouse, B.G. (1984). The effects of temperature and salinity on the aqueous solubility of polynuclear aromatic hydrocarbons. Mar. Chem., 14, 319-332.

Wijayaratne, R.D. & Means, J.C. (1984). Sorption of polycyclic aromatic hydrocarbons by natural estuarine colloids. Mar. Environ. Res., 11, 77-89.

Wilkins, J.R. III, Reiches, N.A. & Krusé, C.W. (1979). Organic chemical contaminants in drinking water and cancer. Am. J. Epidemiol., 100, 420-448.

Wilson, J.T., McNabb, J.F., Cochran, J.W., Wang, T.H., Tomson, M.B. & Bedient, P.B. (1985). Influence of microbial adaptation on the fate of organic pollutants in ground water. Environ. Toxicol. Chem., 4, 721-726.

Wise, S.A., Bonnett, W.J., Guenther, F.R. & May, W.E. (1981). A relationship between reversed-phase C_{18} liquid chromatographic retention and the shape of polycyclic aromatic hydrocarbons. J. Chromatogr. Sci., 19, 457-465.

Witte, H., Langenohl, T. & Offenbächer, G. (1988). Investigation of the entry of organic pollutants into soils and plants through the use of sewage sludge in agriculture. Part A: Organic pollutant load in sewage sludge. Korresp. Abwasser, 35, 440-448.

World Health Organization (1970). European Standards for Drinking Water, World Health Organization, Geneva, Switzerland, 2nd Edn.

World Health Organization (1971). International Standards for Drinking Water, World Health Organization, Geneva, Switzerland, 3rd Edn.

World Health Organization (1983). IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Vol. 32: Polynuclear Aromatic Compounds, Part 1: Chemical, Environmental and Experimental Data, World Health Organization International Agency for Research on Cancer, Lyon, France.

World Health Organization (1984). Guidelines for Drinking-Water Quality, Vols. 1 & 2, World Health Organization, Geneva, Switzerland.

Wszolek, P.C. & Wachs, T. (1982). Occurrence of polycyclic aromatic hydrocarbons in municipal sewage sludge ashes. Arch. Environ. Contam. Toxicol., 11, 69-72.

Xue-Zhong, L. (1985). Action exerted on reaction turbines by sand flow. Water Power Dam Constr., 37, 26-27.

Young, D.D. (1985). Reuse via rivers for potable supply. In Institution of Civil Engineers, Reuse of Sewage Effluent, Proceedings of the International Symposium, London, UK, October 30-31, 1984, Thomas Telford, London, UK, Chap. 1, pp. 11-22.

Zadelis, D. & Simmons, M.S. (1983). Effects of particulates on the photodecomposition of polynuclear aromatic hydrocarbons in aquatic systems. In Cooke, M. & Dennis, A.J. (Eds.), Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement, Seventh International Symposium, Battelle Press, Columbus, Ohio, USA, pp. 1279-1290.

Zafiriou, O.C., Joussot-Dubien, J., Zepp, R.G. & Zika, R.G. (1984). Photochemistry of natural waters. Environ. Sci. Technol., 18, 358A-371A.

Zanoni, A.E. & Blomquist, M.W. (1975). Column settling tests for flocculent suspensions. J. Environ. Eng. Div. (Am. Soc. Civ. Eng.), 101, 309-318.

Zepp, R.G. & Schlotzhauer, P.F. (1979). Photoreactivity of selected aromatic hydrocarbons in water. In Jones, P.W. & Leber, P. (Eds.), Polynuclear Aromatic Hydrocarbons: Third International Symposium on Chemistry and Biology - Carcinogenesis and Mutagenesis, Ann Arbor Press, Ann Arbor, Michigan, USA, pp. 141-158.

Zepp, R.G., Schlotzhauer, P.F., Simmons, M.S., Miller, G.C., Baughman, G.L. & Wolfe, N.L. (1984). Dynamics of pollutant photoreactions in the hydrosphere. Fresenius' Z. Anal. Chem., 319, 119-125.

APPENDIX 1

TABLE 69
Accuracy and Precision
of the Daily GC-MS Calibration Procedure
for PAH Determination by Selected Ion Monitoring

PAH	Concentration ($\mu g\ l^{-1}$) and RSD (%, in parentheses) for determination of 1.00 $\mu g\ l^{-1}$ calibration standard as test sample				
	Day 1[a]	Day 2[a]	Day 3[a]	Day 4[a]	Mean[b]
AY	1.013 (8.6)	0.932 (2.7)	0.914 (3.2)	0.945 (2.0)	0.951±0.031 (6.1)
AE	1.030 (8.7)	0.988 (3.2)	0.956 (3.3)	0.963 (2.1)	0.984±0.029 (5.5)
F	1.005 (11.3)	0.930 (1.4)	0.882 (3.9)	0.932 (2.1)	0.937±0.038 (7.6)
PA	1.003 (7.3)	0.881 (1.4)	0.839 (4.2)	0.853 (2.0)	0.894±0.041 (8.6)
A	1.037 (7.7)	1.043 (2.1)	1.030 (3.3)	1.021 (8.5)	1.033±0.030 (5.4)
FL	1.045 (10.6)	0.902 (2.6)	0.867 (4.3)	1.084 (1.8)	0.975±0.058 (11.2)
P	1.018 (9.1)	0.937 (3.2)	0.929 (3.6)	1.031 (2.9)	0.979±0.036 (6.9)
BaA	1.054 (3.7)	1.072 (1.6)	1.069 (4.1)	1.092 (4.1)	1.072±0.019 (3.4)
CH	1.012 (4.6)	0.939 (1.6)	0.922 (1.7)	0.929 (1.7)	0.951±0.024 (4.6)
BkF	1.008 (3.7)	1.051 (1.6)	1.063 (4.9)	1.083 (2.9)	1.051±0.023 (4.1)
BaP	0.881 (6.7)	1.174 (5.8)	1.229 (6.3)	1.169 (3.9)	1.113±0.081 (13.6)
IP	0.978 (3.9)	1.103 (3.1)	1.084 (11.7)	1.069 (8.7)	1.058±0.047 (8.4)
BghiP	0.975 (5.6)	1.027 (3.0)	1.051 (4.5)	1.030 (3.1)	1.021±0.025 (4.7)
DBahA	0.959 (3.4)	0.998 (3.2)	1.036 (7.3)	1.057 (3.0)	1.013±0.031 (5.7)

[a] Mean for four replicate determinations.
[b] Mean concentration with 95% confidence limits, and total RSD, for all 16 determinations.

APPENDIX 2

Finalised Method for Determination of PAH in Municipal Waste Waters, and Procedure Performance Characteristics (Table 70)

Method

1. Glassware

Borosilicate glassware is utilised throughout and is cleaned by soaking in a solution (5% V/V) of 'Decon 90' detergent (BDH Ltd., UK) for a minimum of 6 h. Subsequently, thorough rinsing with tap water with final rinsing (three times) with glass-distilled deionised water is performed, followed by oven-drying at 110°C. Polytetrafluoroethylene (PTFE) centrifuge bottles and chromatography column taps, and volumetric glassware are similarly cleaned, but oven-dried at 60°C.

2. Solvents

Cyclohexane, n-hexane and acetone are of 'Distol' grade (Fisons Ltd., UK). n-Octane is of general purpose reagent grade (BDH Ltd., UK) and is purified by simple distillation in glass.

3. Standard Solutions

Individual stock solutions of approximately 1 mg ml^{-1} are prepared in acetone from standard compounds AY, AE, F, BghiP and DBahA (Aldrich Ltd., UK), PA, A, CH and BaP (R.N. Emanual Ltd., UK), FL, P and BaA (British Carbonisation Research Association, UK) and BkF and IP (Phase Separations Ltd., UK), each of at least 95% purity by mass. A stock solution of deuterated anthracene (A-d_{10}) (Aldrich Ltd., UK), of approximately 1 mg ml^{-1}, is prepared in octane for the provision of an internal standard for GC-MS determination. From the stock solutions three calibration standards are prepared in octane, each one a mixed (i.e. composite) standard solution containing all PAH, at (individual component) concentrations of 2.50, 10.0 and 20.0 μg ml^{-1} and containing A-d_{10} dosed to the equivalent of 10.0 μg ml^{-1}. Stock and standard solutions are made up in 10 ml volumetric flasks, Teflon-sealed, stored at ambient temperature in the dark, and replaced after six months.

4. Sample Collection and Preservation

Samples, collected in borosilicate glass or tin-plate vessels, are preserved immediately by the addition of formaldehyde solution (1% V/V) of analytical reagent quality (Fisons Ltd., UK), and stored at ambient temperature in the dark for a maximum of eight weeks. Unpreserved samples are extracted within 24 h of collection.

5. Sample Extraction

A 1.00 l sample of raw sewage or primary effluent is extracted with 150 ml of cyclohexane in a 1.5 l separating funnel by a laboratory disperser (Model X1920, Scientific Instrument Co. Ltd., UK) for *ca.* 5 min at 50% full revolutions. After separation of the phases, the aqueous layer is run off and retained, and the organic layer transferred to a 200 ml capacity PTFE centrifuge bottle. Centrifugation (Laboratory Centrifuge, Gallenkamp Ltd., UK) at 2000 rev min^{-1} (*ca.* 5000 *g*) for 20 min yields a clear organic phase which is pipetted into a 250 ml round-bottomed flask. The remaining aqueous phase with solids is returned, with 3 x 1 ml washings (glass-distilled deionised water), to the separating funnel together with the original aqueous portion, and extracted as above with a further 100 ml of solvent. The extracts are combined and reduced to *ca.* 2 ml under reduced pressure at 28°C by means of a rotary evaporator (Rotavapor-R, Büchi A.G., Switzerland).

A sample of primary sludge is extracted in the same manner except that a sample volume of 50.0 ml is extracted directly in a centrifuge bottle, with centrifugation following immediately.

6. Sample Cleanup

Aluminium oxide (Merck 90 active, neutral, particle size 0.063-0.200 mm / 70-230 mesh ASTM, BDH Ltd., UK) is activated at approximately 400°C for *ca.* 6 h in a porcelain dish, and subsequently deactivated to 5.0% (±0.5%) (W/W glass-distilled deionised water), 24 h prior to dry-packing

with tapping of 5.0 g in a 140 mm x 12 mm i.d. glass chromatographic column. Application of sample extract to column, together with 3 x 1 ml washings (cyclohexane), is followed by elution with cyclohexane placed in a 100 ml reservoir. The first ca. 30 ml of eluate is collected in a 50 ml measuring cylinder and thence transferred to a 50 ml round-bottomed flask with 3 x 1 ml washings (cyclohexane). The eluate is evaporated just to dryness under reduced pressure and the residue immediately re-dissolved in ca. 3 ml of hexane.

The residue is applied, with 3 x 2 ml washings (hexane), to an identical column containing 5.0 g of silica gel (Merck 40, particle size 0.063-0.200 mm / 70-230 mesh ASTM, BDH Ltd., UK) activated in the same manner as aluminium oxide but deactivated to 1.0% (±0.1%) (W/W glass-distilled deionised water), 24 h prior to dry-packing with tapping. Eluent is hexane placed in a 250 ml reservoir. The first 24 ml of eluate is discarded, and the subsequent 190 ml collected in a 250 ml measuring cylinder, the operation performed at a constant ambient temperature of 15°C (±2°C) to ensure repeatability of the PAH fraction elution volume. Precautionary measures to shield the column from light are unnecessary. The PAH fraction is transferred to a 250 ml round-bottomed flask with 3 x 1 ml washings (hexane), reduced to ca. 2 ml under reduced pressure, transferred to a 5 ml round-bottomed flask with washings, and subsequently evaporated just to dryness and the residue immediately re-dissolved in 0.200 ml of octane.

For the purpose of an internal standard for GC-MS determination, A-d_{10} is dosed, from stock solution, to the treated sample to the equivalent of 10.0 µg ml^{-1}.

7. Sample Determination

A gas chromatograph (Carlo Erba Fractovap 4200, Erba Science Ltd., UK) is interfaced to a double-focussing mass spectrometer (JEOL JMS-D300, with JMA-2000H data processing system, JEOL Ltd., Japan). A fused-silica capillary column 25 m x 0.20 mm i.d., wall-coated, film thickness 0.11 µm, with SE-34 liquid phase (Hewlett-Packard Ltd., UK), is inserted directly into the ion source, with helium as

carrier gas. The GC oven temperature programme is as follows: 100°C for 2 min, 10°C min^{-1} to 300°C, held for 23 min, giving an analysis turn-round time of 53 min. Injector temperature is 280°C. Portions of 2.00 µl of treated sample and calibration standards are injected using a 10 µl syringe (Hamilton 800 Series, Phase Separations Ltd., UK) into a 'Grob-type' split-splitless injector using the 'splitless hot-needle' injection technique (Grob & Grob, 1974; Grob & Grob, 1978). The septum purge gas flow rate from the injector is set at 5.0 ml min^{-1} and the bottom split valve, opened 45 s after injection, is set at 50 ml min^{-1}. The selected ion monitoring (SIM) mode of operation of the MS under electron impact (EI) ionisation is employed, the molecular ion of each PAH (with m/z value equal to that of the molecular weight of the PAH) monitored as the characteristic ion. The following ions are thus monitored: m/z 152, 154, 166, 178, 188, 202, 228, 252, 276 and 278 (188 being that of the internal standard, A-d_{10}). The MS instrument settings are: ionising voltage 70 eV, ionising current 300 µA, ion source temperature 260°C, scan range 40-500 µm, mass sweep range 1.50 amu, ion dwell time 0.1 s, resolution 800, electron multiplier 1.50 kV, and GC-MS interface temperature 320°C.

Integrated peak area of the characteristic ion of the determinand is measured, with 'analytical response constant' defined as the ratio of peak area of characteristic ion of determinand divided by peak area of characteristic ion of internal standard. Calibration employing the three calibration standards of concentration 2.50, 10.0 and 20.0 µg ml^{-1} (equivalent to 0.500, 2.00 and 4.00 µg l^{-1} respectively in samples of 1.00 l and final treated samples of 0.200 ml) is performed daily, with single determinations of calibration standards and treated sample. The calibration curve through the three datum points for each PAH is constructed by linear regression analysis (unweighted).

TABLE 70
Procedure Performance Characteristics

1. Substances determined	Acenaphthylene (AY), acenaphthene (AE), fluorene (F), phenanthrene (PA), anthracene (A), fluoranthene (FL), pyrene (P), benz[a]anthracene (BaA), chrysene (CH), benzofluoranthenes (benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BjF) and benzo[k]fluoranthene (BkF)) as BkF, benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), benzo[ghi]perylene (BghiP) and dibenz[a,h]anthracene (DBahA).
2. Type of sample	Raw sewage (1.00 l), primary effluent (1.00 l) and raw primary sludge (50.0 ml) from municipal waste water treatment works.
3. Basis of method	Sample is extracted with cyclohexane and subjected to a two-step column chromatographic cleanup employing aluminium oxide and silica gel, with final determination by GC-MS (SIM).
4. Range of application[a]	Up to 4.0 µg l^{-1} for each PAH.
5. Detection limit[a]	AY 0.01, AE 0.01, F 0.01, PA 0.01, A 0.01, FL 0.02, P 0.02, BaA 0.05, CH 0.05, BkF 0.05, BaP 0.05, IP 0.05, BghiP 0.05 and DBahA 0.05 µg l^{-1} approx.
6. Quantification limit[a]	AY 0.02, AE 0.02, F 0.02, PA 0.02, A 0.02, FL 0.05, P 0.05, BaA 0.10, CH 0.10, BkF 0.10, BaP 0.10, IP 0.10, BghiP 0.10 and DBahA 0.10 µg l^{-1}.
7. Calibration function[a]	Linear from quantification limit to 4.0 µg l^{-1} for each PAH.
8. Interferences	None.
9. Time required for analysis	Total analytical and single operator times are identical: two and four days for one and eight samples respectively.
10. Sensitivity[a]	Approximate analytical response (peak area, dimensionless) for 0.500 µg l^{-1}: AY 19.1, AE 9.6, F 9.5, PA 14.7, A 8.2, FL 6.8, P 4.1, BaA 1.1, CH 2.3, BkF 1.2, BaP 1.0, IP 0.9, BghiP 0.8 and DBahA 0.8.

/Continued overleaf

TABLE 70/Continued

11. Sampling	Samples are collected in borosilicate glass or tin-plate vessels, and stored in the dark at ambient temperature. Samples unextracted within 24 h may be preserved for up to 56 d with the addition of formaldehyde solution (1% V/V).
12. Accuracy: efficiency	AY 69%, AE 79%, F 83%, PA 87%, A 83%, FL 75%, P 84%, BaA 75%, CH 87%, BkF 69%, BaP 91%, IP 89%, BghiP 127% and DBahA 79%. Parameter independent of determinand concentration and sample type.

13. Precision: error

	Random error	Systematic error	Total error
AY	C (± 7.0%)	x 0.854 (±16.2%)	$C_{corr.}$ (±17.6%)
AE	C (± 2.8%)	x 0.893 (±12.6%)	$C_{corr.}$ (±12.9%)
F	C (± 3.0%)	x 0.732 (±13.0%)	$C_{corr.}$ (±13.3%)
PA	C (± 2.4%)	x 0.709 (±10.3%)	$C_{corr.}$ (±10.6%)
A	C (± 4.4%)	x 0.852 (±13.0%)	$C_{corr.}$ (±13.7%)
FL	C (± 3.0%)	x 0.597 (± 9.9%)	$C_{corr.}$ (±10.3%)
P	C (± 2.9%)	x 0.623 (±12.9%)	$C_{corr.}$ (±13.2%)
BaA	C (± 6.6%)	x 0.382 (±12.7%)	$C_{corr.}$ (±14.3%)
CH	C (± 3.5%)	x 0.529 (±16.4%)	$C_{corr.}$ (±16.8%)
BkF	C (± 4.5%)	x 0.410 (±17.6%)	$C_{corr.}$ (±18.2%)
BaP	C (± 8.9%)	x 0.377 (±14.3%)	$C_{corr.}$ (±16.8%)
IP	C (±10.1%)	x 0.492 (±18.8%)	$C_{corr.}$ (±21.3%)
BghiP	C (± 8.1%)	x 0.551 (±13.0%)	$C_{corr.}$ (±15.3%)
DBahA	C (± 6.3%)	x 0.498 (±18.0%)	$C_{corr.}$ (±19.1%)

Confidence limits (95%) for analytical result C ($\mu g\ l^{-1}$), with systematic error factors shown inversed for computation of corrected result $C_{corr.}$ (= C x factor). Random and systematic errors independent of determinand concentration and sample type.

14. Bias	Positive and relative: see under 'systematic error' in Subsection 13. A treated sample matrix effect associated with the measurement stage and of special importance for high molecular weight determinands. Bias factors should be re-determined for particular GC-MS system employed by a method of standard additions (Section 3.1.1.11.1).

[a] For samples of 1.00 l and treated samples of 0.200 ml.

APPENDIX 3

TABLE 71
Mean Influent, Mean Effluent and Sludge Concentration of SS, NVSS, VSS, Total and Soluble COD Obtained at Each Hydraulic and SS Loading of the Primary Sedimentation Pilot Plant

Hydraulic loading	SS loading[a]	Sample type[b]	Concentration (mg l^{-1})[c]				
			SS[a]	NVSS	VSS	COD_{tot}	COD_{sol}
0.5 DWF	SS_0	I	437	88	349	690	144
		E	130	51	79	330	145
		S	2600	560	2040	3500	400
	SS_1	I	565	120	445	749	140
		E	146	57	89	325	134
		S	3720	680	3040	3850	320
	SS_2	I	781	159	622	957	147
		E	166	59	107	348	136
		S	5220	940	4280	5950	820
	SS_3	I	981	194	787	1500	191
		E	227	72	155	497	205
		S	9040	1660	7380	12900	960
1.0 DWF	SS_0	I	322	60	262	503	132
		E	134	31	103	251	128
		S	3060	660	2400	4900	490
	SS_1	I	479	80	399	776	142
		E	158	34	124	284	138
		S	5960	960	5000	11000	670
	SS_2	I	677	204	473	881	141
		E	242	127	115	349	96
		S	4800	1200	3600	7700	1150
	SS_3	I	858	229	629	1140	190
		E	304	160	144	475	124
		S	8900	1650	7250	15800	1800
3.0 DWF	SS_0	I	408	92	316	611	134
		E	215	57	158	449	122
		S	3940	800	3140	5900	780
	SS_1	I	792	157	635	892	162
		E	245	61	184	552	139
		S	9340	1940	7400	9300	600
	SS_2	I	822	153	669	922	170
		E	267	74	193	530	151
		S	9980	2120	7860	17700	940
	SS_3	I	944	171	773	1320	193
		E	332	70	262	702	167
		S	6660	1000	5660	9200	580

/Continued overleaf

TABLE 71/Continued

Hydraulic loading	SS loading[a]	Sample type[b]	Concentration (mg l^{-1})[c] SS[a]	NVSS	VSS	COD_{tot}	COD_{sol}
5.0 DWF	SS_0	I	442	104	338	935	126
		E	196	66	130	394	95
		S	4550	940	3610	5800	430
	SS_1	I	464	129	335	724	163
		E	208	94	114	434	136
		S	5280	1300	3980	5400	309
	SS_2	I	651	167	484	982	151
		E	263	119	144	518	94
		S	7450	1600	5850	9550	370
	SS_3	I	767	149	618	1100	197
		E	258	67	191	579	158
		S	7240	1160	6080	12300	290

[a] SS loading equivalent to mean influent SS concentration at particular hydraulic loading. Mean SS_0 = 402, SS_1 = 575, SS_2 = 733, SS_3 = 888 mg l^{-1}.
[b] I = influent, E = effluent, S = sludge.
[c] Each a mean of ten composite samples, each constituted from six grab samples; sludge a single grab sample only.

APPENDIX 4

TABLE 72
Primary Sedimentation Data for Hogsmill Valley Water Pollution Control Works Over Period of Pilot Plant Experimentation Programme[a]

Experiment no.	Flow rate[b] (l s^{-1})	SS			COD_{tot}		
		I[c] (mg l^{-1})	E[d] (mg l^{-1})	R[e] (%)	I[c] (mg l^{-1})	E[d] (mg l^{-1})	R[e] (%)
1 and 2	628	302	90	70.2	527	288	45.4
	614	346	90	74.0	540	272	49.6
3 and 4	804[f]	362	136	62.4	554	300	45.8
	741[g]	362	128	64.6	547	280	48.8
5 and 6	770	382	118	69.1	680	292	57.1
7 and 8	709	490	104	78.8	767	264	65.6
9 and 10	695	328	103	68.6	547	272	50.3
11 and 12	782	348	96	72.4	580	292	49.7
13 and 14	733	450	124	72.4	774	344	55.6
	662	610	84	86.2	994	268	73.0
	643	368	94	74.5	860	312	63.7
15 and 16	840	390	130	66.7	514	252	51.0
	655	360	102	71.7	547	264	51.7
	652	346	120	65.3	634	272	57.1

[a] Daily means for whole works.
[b] Inclusive of returned flows.
[c] I = influent, inclusive of returned flows.
[d] E = effluent.
[e] R = removal.
[f] Storm sewage to river 23 l s^{-1}.
[g] Storm sewage to river 144 l s^{-1}.

APPENDIX 5

Raw Data for PAH
Obtained During the Primary Sedimentation Pilot Plant
Experimentation Programme
(Table 73-88)

TABLE 73
Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 0.5 DWF and a Mean SS Loading of 437 mg l^{-1} (SS_0)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.0441	0.0921	0.0453	0.0884	0.0502	0.0640
	E	0.0907	0.0613	0.104	0.0880	0.0876	0.0863
	S	0.304					
AE	I	1.39	3.45	1.48	2.31	1.16	1.96
	E	2.31	1.35	2.71	1.48	1.62	1.89
	S	10.5					
F	I	1.14	2.37	1.34	1.70	1.08	1.53
	E	1.43	0.944	1.58	1.19	1.05	1.24
	S	9.24					
PA	I	1.03	1.96	1.32	1.46	1.35	1.42
	E	0.924	0.668	0.879	0.921	0.690	0.816
	S	9.48					
A	I	0.152	0.386	0.277	0.508	0.427	0.350
	E	0.216	0.149	0.250	0.236	0.184	0.207
	S	3.60					
FL	I	0.448	0.705	0.524	0.649	0.612	0.588
	E	0.263	0.189	0.254	0.293	0.238	0.247
	S	4.28					
P	I	0.771	0.899	0.645	0.964	0.923	0.840
	E	0.329	0.244	0.307	0.329	0.290	0.300
	S	7.12					
BaA	I	0.200	0.321	0.230	0.522	0.389	0.332
	E	0.0811	0.0515	0.101	0.0539	0.0516	0.0678
	S	2.51					
CH	I	0.340	0.387	0.246	0.366	0.349	0.338
	E	0.139	0.0986	0.107	0.122	0.111	0.116
	S	2.64					
BkF	I	0.419	0.516	0.368	0.780	0.607	0.538
	E	0.154	0.115	0.142	0.133	0.108	0.130
	S	4.64					
BaP	I	0.226	0.340	0.212	0.444	0.381	0.321
	E	0.115	0.0780	0.0568	0.0751	0.0794	0.0809
	S	3.12					
IP	I	0.107	0.145	0.119	0.234	0.188	0.159
	E	0.0578	0.0440	0.0373	0.0579	0.0447	0.0483
	S	1.46					
BghiP	I	0.139	0.190	0.136	0.330	0.235	0.206
	E	0.0912	0.0681	0.0641	0.0846	0.0702	0.0756
	S	1.82					
DBahA	I	0.0452	0.0558	0.0438	0.0883	0.0608	0.0588
	E	0.0296	0.0122	0.0206	0.0274	0.0255	0.0231
	S	0.512					

[a] I = influent, E = effluent, S = sludge.
[b] Each a composite of 12 grab samples; sludge a single grab sample only.

TABLE 74

Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 0.5 DWF and a Mean SS Loading of 565 mg l^{-1} (SS_1)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.107	0.123	0.116	0.127	0.131	0.121
	E	0.0413	0.0443	0.117	0.0569	0.0588	0.0637
	S	0.508					
AE	I	2.28	3.43	2.74	3.15	2.91	2.90
	E	1.00	1.42	3.06	1.66	1.48	1.72
	S	22.6					
F	I	1.55	2.19	1.82	2.04	2.25	1.97
	E	0.717	0.873	1.88	0.953	0.861	1.06
	S	18.4					
PA	I	2.21	2.02	1.97	2.04	1.85	2.02
	E	0.861	0.701	1.24	0.800	0.745	0.869
	S	21.7					
A	I	0.392	0.365	0.350	0.361	0.304	0.354
	E	0.170	0.168	0.347	0.160	0.160	0.201
	S	4.40					
FL	I	1.89	1.04	0.770	0.847	0.707	1.05
	E	0.591	0.332	0.478	0.334	0.262	0.399
	S	9.72					
P	I	2.41	1.34	1.06	1.15	0.797	1.35
	E	0.643	0.402	0.578	0.405	0.334	0.472
	S	8.92					
BaA	I	1.34	0.633	0.395	0.472	0.201	0.608
	E	0.292	0.144	0.228	0.149	0.130	0.189
	S	2.26					
CH	I	1.05	0.540	0.303	0.394	0.383	0.534
	E	0.285	0.170	0.216	0.162	0.122	0.191
	S	3.70					
BkF	I	1.76	0.768	0.367	0.531	0.425	0.770
	E	0.529	0.238	0.310	0.204	0.146	0.285
	S	5.00					
BaP	I	1.09	0.522	0.193	0.303	0.188	0.459
	E	0.300	0.152	0.197	0.171	0.0727	0.167
	S	2.13					
IP	I	0.386	0.165	0.0807	0.137	0.111	0.176
	E	0.160	0.0741	0.102	0.0686	0.0435	0.0896
	S	1.29					
BghiP	I	0.479	0.254	0.125	0.184	0.161	0.241
	E	0.204	0.0970	0.130	0.0883	0.0630	0.116
	S	2.08					
DBahA	I	0.122	0.0705	0.0381	0.0432	0.0667	0.0681
	E	0.0617	0.0276	0.0355	0.0321	0.0205	0.0355
	S	0.544					

[a] I = influent, E = effluent, S = sludge.

[b] Each a composite of 12 grab samples; sludge a single grab sample only.

TABLE 75
Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 0.5 DWF and a Mean SS Loading of 781 mg l^{-1} (SS_2)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.138	0.160	0.137	0.156	0.0800	0.134
	E	0.0495	0.0555	0.131	0.0516	0.0661	0.0707
	S	0.616					
AE	I	3.80	9.63	4.39	4.13	2.87	4.96
	E	2.51	1.85	3.22	1.30	2.21	2.22
	S	28.9					
F	I	2.55	6.14	2.64	3.70	2.47	3.50
	E	1.60	1.19	1.88	0.812	1.29	1.35
	S	24.4					
PA	I	2.79	5.79	2.13	3.48	2.22	3.28
	E	1.35	1.21	1.43	0.820	0.918	1.15
	S	21.6					
A	I	0.710	1.61	0.590	0.446	0.395	0.750
	E	0.374	0.252	0.296	0.138	0.194	0.251
	S	3.74					
FL	I	2.09	3.03	0.802	1.41	0.909	1.65
	E	0.854	0.694	0.510	0.349	0.329	0.547
	S	10.8					
P	I	2.77	3.99	1.07	1.43	0.927	2.04
	E	0.988	0.882	0.611	0.421	0.430	0.666
	S	10.4					
BaA	I	1.50	2.19	0.362	0.486	0.219	0.951
	E	0.400	0.397	0.195	0.185	0.144	0.264
	S	3.04					
CH	I	1.08	1.35	0.328	0.555	0.534	0.769
	E	0.440	0.333	0.260	0.189	0.188	0.282
	S	5.44					
BkF	I	1.72	2.01	0.400	0.624	0.666	1.08
	E	0.771	0.616	0.328	0.243	0.218	0.435
	S	7.20					
BaP	I	1.07	1.46	0.241	0.235	0.306	0.662
	E	0.499	0.411	0.204	0.158	0.114	0.277
	S	3.21					
IP	I	0.376	0.401	0.0802	0.164	0.192	0.243
	E	0.211	0.174	0.102	0.0833	0.0634	0.127
	S	2.12					
BghiP	I	0.453	0.543	0.104	0.241	0.286	0.325
	E	0.282	0.211	0.139	0.113	0.0892	0.167
	S	2.83					
DBahA	I	0.117	0.143	0.0305	0.0828	0.0705	0.0888
	E	0.0785	0.0645	0.0503	0.0252	0.0190	0.0475
	S	0.664					

[a] I = influent, E = effluent, S = sludge.
[b] Each a composite of 12 grab samples; sludge a single grab sample only.

TABLE 76
Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 0.5 DWF and a Mean SS Loading of 981 mg l^{-1} (SS_3)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.0750	0.136	0.0891	0.109	0.0980	0.101
	E	0.0933	0.0811	0.100	0.0638	0.0726	0.0822
	S	0.612					
AE	I	4.64	7.15	4.89	4.39	4.09	5.03
	E	2.77	2.63	3.27	1.70	1.78	2.43
	S	43.6					
F	I	3.23	4.78	3.47	3.69	3.21	3.68
	E	2.00	1.70	2.07	1.24	2.02	1.81
	S	35.0					
PA	I	2.83	4.09	2.95	3.87	3.03	3.35
	E	1.44	1.19	1.39	1.15	1.96	1.43
	S	33.2					
A	I	0.618	0.876	0.633	1.25	1.09	0.893
	E	0.356	0.257	0.360	0.267	0.680	0.384
	S	14.4					
FL	I	1.18	1.59	1.15	2.06	1.37	1.47
	E	0.465	0.397	0.447	0.432	0.647	0.478
	S	16.2					
P	I	1.60	1.90	1.40	3.05	2.23	2.04
	E	0.606	0.493	0.550	0.536	0.756	0.588
	S	26.0					
BaA	I	0.668	0.858	0.609	1.65	1.07	0.971
	E	0.165	0.128	0.191	0.207	0.255	0.189
	S	13.3					
CH	I	0.628	0.960	0.567	1.12	0.782	0.811
	E	0.243	0.200	0.220	0.204	0.226	0.219
	S	9.16					
BkF	I	0.968	1.15	0.951	2.59	1.65	1.46
	E	0.314	0.266	0.288	0.302	0.322	0.298
	S	18.2					
BaP	I	0.687	0.809	0.657	1.72	0.990	0.973
	E	0.209	0.167	0.200	0.227	0.229	0.206
	S	12.8					
IP	I	0.247	0.319	0.288	0.893	0.501	0.450
	E	0.124	0.0813	0.0907	0.103	0.0903	0.0979
	S	5.16					
BghiP	I	0.349	0.383	0.349	1.19	0.672	0.589
	E	0.166	0.123	0.123	0.136	0.146	0.139
	S	7.04					
DBahA	I	0.0879	0.130	0.114	0.362	0.191	0.177
	E	0.0523	0.0260	0.0211	0.0464	0.0384	0.0368
	S	1.82					

[a] I = influent, E = effluent, S = sludge.
[b] Each a composite of 12 grab samples; sludge a single grab sample only.

TABLE 77
Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 1.0 DWF and a Mean SS Loading of 322 mg l^{-1} (SS_0)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.0772	0.0350	0.0518	0.0755	0.0696	0.0618
	E	0.0557	0.0739	0.0405	0.0465	0.0811	0.0595
	S	0.181					
AE	I	2.39	1.11	1.64	2.70	3.07	2.18
	E	1.26	1.44	0.659	1.24	2.79	1.48
	S	17.3					
F	I	1.90	1.10	1.22	2.21	2.35	1.76
	E	0.869	0.877	0.481	1.01	1.96	1.04
	S	14.6					
PA	I	1.40	0.977	1.01	1.73	1.91	1.41
	E	0.795	0.711	0.422	1.04	1.38	0.870
	S	13.4					
A	I	0.214	0.120	0.181	0.331	0.346	0.238
	E	0.189	0.167	0.0724	0.165	0.238	0.166
	S	2.20					
FL	I	0.530	0.360	0.434	0.626	0.547	0.499
	E	0.314	0.231	0.148	0.335	0.417	0.289
	S	5.80					
P	I	0.542	0.477	0.561	0.672	0.639	0.578
	E	0.447	0.300	0.186	0.359	0.425	0.343
	S	7.20					
BaA	I	0.190	0.163	0.206	0.348	0.201	0.221
	E	0.0862	0.0809	0.0590	0.0897	0.137	0.0906
	S	3.66					
CH	I	0.245	0.255	0.299	0.298	0.308	0.281
	E	0.187	0.106	0.110	0.215	0.233	0.170
	S	3.08					
BkF	I	0.333	0.367	0.534	0.577	0.465	0.455
	E	0.234	0.167	0.136	0.246	0.278	0.212
	S	5.92					
BaP	I	0.411	0.401	0.526	0.599	0.532	0.494
	E	0.255	0.177	0.240	0.292	0.303	0.253
	S	6.48					
IP	I	0.128	0.153	0.266	0.234	0.199	0.196
	E	0.0811	0.0430	0.0562	0.0920	0.121	0.0787
	S	1.97					
BghiP	I	0.196	0.305	0.414	0.277	0.219	0.282
	E	0.216	0.0896	0.0777	0.178	0.177	0.148
	S	2.68					
DBahA	I	ND[c]	ND	ND	ND	ND	-----
	E	ND	ND	ND	ND	ND	-----
	S	ND					

[a] I = influent, E = effluent, S = sludge.
[b] Each a composite of 12 grab samples; sludge a single grab sample only.
[c] ND = non-detectable.

TABLE 78
Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 1.0 DWF and a Mean SS Loading of 479 mg l^{-1} (SS_1)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.0579	0.0341	0.0359	0.125	0.0969	0.0700
	E	0.0727	0.0433	0.0617	0.0399	0.113	0.0661
	S	0.210					
AE	I	2.50	1.21	1.28	2.32	5.13	2.49
	E	1.50	1.08	0.976	1.23	2.57	1.47
	S	20.6					
F	I	2.18	1.18	1.17	2.00	3.61	2.03
	E	1.22	0.759	0.754	0.966	1.98	1.14
	S	17.4					
PA	I	1.87	1.32	1.23	1.92	2.73	1.81
	E	1.13	0.741	0.605	0.900	1.45	0.965
	S	16.8					
A	I	0.337	0.186	0.234	0.365	0.420	0.308
	E	0.292	0.180	0.118	0.142	0.288	0.204
	S	3.24					
FL	I	0.798	0.554	0.558	0.744	0.873	0.705
	E	0.467	0.266	0.232	0.315	0.442	0.344
	S	7.84					
P	I	0.844	0.657	0.711	0.864	1.06	0.827
	E	0.596	0.350	0.244	0.323	0.465	0.396
	S	9.92					
BaA	I	0.365	0.318	0.378	0.383	0.394	0.368
	E	0.145	0.103	0.0696	0.0817	0.196	0.119
	S	5.68					
CH	I	0.383	0.283	0.264	0.437	0.521	0.378
	E	0.313	0.148	0.133	0.170	0.227	0.198
	S	4.32					
BkF	I	0.597	0.485	0.498	0.666	0.894	0.628
	E	0.457	0.177	0.189	0.169	0.327	0.264
	S	8.16					
BaP	I	0.737	0.549	0.619	0.751	0.890	0.709
	E	0.632	0.280	0.348	0.209	0.334	0.361
	S	8.76					
IP	I	0.270	0.153	0.218	0.263	0.300	0.241
	E	0.304	0.0754	0.0848	0.0607	0.0998	0.125
	S	2.12					
BghiP	I	0.427	0.266	0.297	0.383	0.394	0.353
	E	0.625	0.140	0.195	0.128	0.177	0.253
	S	3.44					
DBahA	I	ND[c]	ND	ND	ND	ND	-----
	E	ND	ND	ND	ND	ND	-----
	S	ND					

[a] I = influent, E = effluent, S = sludge.
[b] Each a composite of 12 grab samples; sludge a single grab sample only.
[c] ND = non-detectable.

TABLE 79
Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 1.0 DWF and a Mean SS Loading of 677 mg l^{-1} (SS_2)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.182	0.0915	0.0959	0.0981	0.112	0.116
	E	0.110	0.0678	0.0734	0.0589	0.0790	0.0778
	S	0.836					
AE	I	4.31	2.11	1.58	2.65	2.78	2.69
	E	2.32	1.43	1.11	1.12	1.50	1.50
	S	24.5					
F	I	2.86	1.96	1.20	2.11	2.29	2.08
	E	1.79	1.07	0.908	0.907	1.33	1.20
	S	18.9					
PA	I	2.50	1.98	1.29	2.38	2.63	2.16
	E	1.48	0.985	0.928	1.00	1.64	1.21
	S	22.4					
A	I	0.682	0.404	0.306	0.591	0.606	0.518
	E	0.323	0.281	0.133	0.258	0.527	0.304
	S	5.72					
FL	I	1.20	0.985	0.669	1.42	1.52	1.16
	E	0.646	0.405	0.426	0.578	0.753	0.562
	S	14.7					
P	I	1.65	1.42	1.06	1.85	2.04	1.60
	E	0.853	0.603	0.580	0.755	0.921	0.742
	S	18.5					
BaA	I	0.992	0.759	0.494	1.05	1.25	0.909
	E	0.371	0.252	0.228	0.382	0.388	0.324
	S	11.6					
CH	I	0.704	0.573	0.506	0.881	0.831	0.699
	E	0.384	0.253	0.272	0.359	0.356	0.325
	S	8.64					
BkF	I	1.22	0.952	0.905	1.66	1.47	1.24
	E	0.575	0.345	0.372	0.580	0.560	0.486
	S	16.5					
BaP	I	0.980	0.705	0.692	1.45	1.19	1.00
	E	0.463	0.302	0.270	0.461	0.425	0.384
	S	14.0					
IP	I	0.319	0.212	0.227	0.457	0.448	0.333
	E	0.162	0.104	0.109	0.182	0.155	0.142
	S	4.60					
BghiP	I	0.403	0.275	0.302	0.609	0.620	0.442
	E	0.218	0.168	0.159	0.268	0.209	0.204
	S	5.64					
DBahA	I	0.119	0.0781	0.0866	0.163	0.183	0.126
	E	0.0617	0.0450	0.0402	0.0664	0.0583	0.0543
	S	1.57					

[a] I = influent, E = effluent, S = sludge.
[b] Each a composite of 12 grab samples; sludge a single grab sample only.

TABLE 80

Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 1.0 DWF and a Mean SS Loading of 858 mg l^{-1} (SS_3)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.188	0.0964	0.101	0.103	0.136	0.125
	E	0.106	0.0658	0.0747	0.0742	0.0761	0.0794
	S	1.34					
AE	I	4.02	2.32	1.94	2.90	4.47	3.13
	E	2.50	1.53	1.18	1.75	1.72	1.74
	S	41.6					
F	I	3.19	1.80	1.36	2.62	3.64	2.52
	E	1.86	1.06	0.877	1.30	1.31	1.28
	S	30.0					
PA	I	2.83	1.76	1.36	3.03	4.38	2.67
	E	1.69	1.09	0.826	1.33	1.33	1.25
	S	32.4					
A	I	0.636	0.460	0.385	0.661	1.02	0.632
	E	0.413	0.247	0.189	0.350	0.335	0.307
	S	8.20					
FL	I	1.33	1.00	0.744	1.75	2.88	1.54
	E	0.727	0.538	0.391	0.717	0.648	0.604
	S	20.7					
P	I	1.85	1.38	1.15	2.24	3.72	2.07
	E	1.03	0.749	0.590	0.946	0.846	0.832
	S	26.4					
BaA	I	1.01	0.754	0.588	1.20	2.60	1.23
	E	0.459	0.340	0.251	0.432	0.371	0.371
	S	15.3					
CH	I	0.757	0.595	0.496	0.921	1.64	0.882
	E	0.459	0.327	0.246	0.423	0.396	0.370
	S	11.5					
BkF	I	1.34	1.07	0.889	1.74	2.78	1.56
	E	0.644	0.503	0.368	0.665	0.600	0.556
	S	22.1					
BaP	I	1.08	0.760	0.737	1.56	2.57	1.34
	E	0.536	0.422	0.290	0.519	0.409	0.435
	S	19.6					
IP	I	0.317	0.260	0.230	0.536	0.752	0.419
	E	0.176	0.141	0.100	0.194	0.153	0.153
	S	5.84					
BghiP	I	0.398	0.309	0.319	0.684	0.885	0.519
	E	0.245	0.204	0.149	0.275	0.224	0.219
	S	7.56					
DBahA	I	0.124	0.0937	0.0708	0.208	0.313	0.162
	E	0.0713	0.0526	0.0446	0.0625	0.0521	0.0566
	S	2.40					

[a] I = influent, E = effluent, S = sludge.

[b] Each a composite of 12 grab samples; sludge a single grab sample only.

TABLE 81
Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 3.0 DWF and a Mean SS Loading of 408 mg l^{-1} (SS_0)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.106	0.119	0.148	0.153	0.164	0.138
	E	0.0690	0.107	0.137	0.124	0.128	0.113
	S	0.532					
AE	I	2.44	2.86	5.24	3.45	3.43	3.48
	E	1.14	2.45	3.33	3.02	2.77	2.54
	S	11.6					
F	I	1.61	2.04	2.94	2.92	2.16	2.33
	E	0.734	1.46	2.05	1.85	1.71	1.56
	S	11.4					
PA	I	1.44	1.76	2.00	2.41	1.94	1.91
	E	0.701	1.10	1.48	1.34	1.37	1.20
	S	11.8					
A	I	0.427	0.498	0.570	0.522	0.492	0.502
	E	0.199	0.325	0.404	0.355	0.429	0.342
	S	2.71					
FL	I	0.639	0.762	0.725	1.18	0.770	0.815
	E	0.307	0.435	0.479	0.575	0.546	0.468
	S	6.08					
P	I	0.794	0.954	0.899	1.45	0.897	0.999
	E	0.385	0.507	0.575	0.734	0.654	0.571
	S	7.32					
BaA	I	0.272	0.436	0.368	0.565	0.376	0.403
	E	0.137	0.197	0.230	0.296	0.248	0.222
	S	4.00					
CH	I	0.349	0.367	0.377	0.669	0.331	0.419
	E	0.158	0.183	0.218	0.305	0.237	0.220
	S	2.97					
BkF	I	0.509	0.577	0.586	0.968	0.461	0.620
	E	0.210	0.258	0.314	0.436	0.310	0.306
	S	5.56					
BaP	I	0.367	0.498	0.419	0.685	0.352	0.464
	E	0.153	0.197	0.192	0.319	0.233	0.219
	S	4.60					
IP	I	0.150	0.203	0.176	0.261	0.145	0.187
	E	0.0666	0.0782	0.0968	0.127	0.0911	0.0919
	S	1.94					
BghiP	I	0.218	0.259	0.226	0.387	0.192	0.256
	E	0.0902	0.112	0.144	0.174	0.134	0.131
	S	2.41					
DBahA	I	0.0632	0.0759	0.0660	0.103	0.0442	0.0705
	E	0.0285	0.0305	0.0393	0.0458	0.0385	0.0365
	S	0.768					

[a] I = influent, E = effluent, S = sludge.
[b] Each a composite of 12 grab samples; sludge a single grab sample only.

TABLE 82
Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 3.0 DWF and a Mean SS Loading of 792 mg l^{-1} (SS_1)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.114	0.136	0.227	0.140	0.152	0.154
	E	0.102	0.128	0.242	0.233	0.162	0.173
	S	1.34					
AE	I	3.25	5.65	4.94	5.25	3.77	4.57
	E	1.64	2.49	4.17	4.42	4.12	3.37
	S	47.6					
F	I	2.13	3.65	4.01	3.65	3.29	3.35
	E	1.25	1.71	3.32	2.81	2.69	2.36
	S	36.8					
PA	I	1.99	2.99	4.27	3.61	3.67	3.31
	E	1.08	1.37	2.57	2.32	2.16	1.90
	S	39.6					
A	I	0.381	0.523	0.833	0.777	0.666	0.636
	E	0.244	0.375	0.494	0.530	0.524	0.433
	S	9.84					
FL	I	0.937	1.17	2.44	2.51	2.38	1.89
	E	0.368	0.481	1.12	1.34	1.11	0.884
	S	26.0					
P	I	1.18	1.40	2.84	2.75	2.63	2.16
	E	0.443	0.594	1.29	1.48	1.25	1.01
	S	29.5					
BaA	I	0.549	0.544	1.39	1.54	1.40	1.08
	E	0.204	0.231	0.644	0.796	0.500	0.475
	S	15.5					
CH	I	0.528	0.582	1.60	1.69	1.32	1.14
	E	0.176	0.227	0.558	0.751	0.627	0.468
	S	15.5					
BkF	I	0.847	0.901	2.54	3.03	2.33	1.93
	E	0.278	0.358	1.07	1.51	1.00	0.843
	S	27.2					
BaP	I	0.621	0.606	2.02	2.47	1.65	1.47
	E	0.237	0.308	0.874	1.32	0.683	0.684
	S	22.2					
IP	I	0.235	0.249	0.654	0.879	0.579	0.519
	E	0.110	0.113	0.299	0.469	0.298	0.258
	S	7.24					
BghiP	I	0.353	0.403	0.978	1.18	0.786	0.740
	E	0.167	0.186	0.408	0.665	0.441	0.373
	S	10.4					
DBahA	I	0.0962	0.0840	0.251	0.301	0.211	0.189
	E	0.0404	0.0401	0.0998	0.174	0.112	0.0933
	S	2.56					

[a] I = influent, E = effluent, S = sludge.
[b] Each a composite of 12 grab samples; sludge a single grab sample only.

TABLE 83

Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 3.0 DWF and a Mean SS Loading of 822 mg l^{-1} (SS_2)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.0863	0.105	0.244	0.171	0.136	0.148
	E	0.129	0.150	0.240	0.281	0.0958	0.179
	S	1.52					
AE	I	3.04	4.31	6.84	6.10	4.36	4.93
	E	1.75	2.76	4.59	5.11	2.76	3.39
	S	59.6					
F	I	1.97	3.17	5.02	4.27	3.59	3.60
	E	1.21	1.87	3.19	3.52	1.82	2.32
	S	44.0					
PA	I	1.89	2.95	4.47	4.10	4.01	3.48
	E	1.04	1.52	2.54	2.77	1.51	1.88
	S	47.2					
A	I	0.408	0.656	1.07	0.999	0.882	0.803
	E	0.270	0.460	0.556	0.596	0.310	0.438
	S	10.2					
FL	I	0.833	1.11	2.59	2.76	2.48	1.95
	E	0.361	0.525	1.02	1.56	0.735	0.840
	S	30.2					
P	I	0.986	1.44	3.11	3.09	2.88	2.30
	E	0.452	0.660	1.27	1.83	0.792	1.00
	S	33.2					
BaA	I	0.398	0.486	1.67	1.72	1.50	1.15
	E	0.201	0.277	0.578	0.794	0.361	0.442
	S	17.1					
CH	I	0.447	0.600	1.62	1.75	1.38	1.16
	E	0.167	0.232	0.509	0.977	0.404	0.458
	S	17.2					
BkF	I	0.691	0.810	2.77	3.17	2.27	1.94
	E	0.289	0.376	0.991	1.71	0.648	0.803
	S	30.2					
BaP	I	0.496	0.549	2.36	2.51	1.79	1.54
	E	0.245	0.308	0.778	1.19	0.420	0.588
	S	25.4					
IP	I	0.210	0.229	0.746	0.871	0.663	0.544
	E	0.0866	0.120	0.324	0.543	0.220	0.259
	S	8.24					
BghiP	I	0.276	0.376	1.05	1.23	0.836	0.754
	E	0.146	0.180	0.440	0.705	0.281	0.350
	S	11.4					
DBahA	I	0.0819	0.0840	0.270	0.298	0.227	0.192
	E	0.0304	0.0701	0.210	0.197	0.0698	0.115
	S	2.77					

[a] I = influent, E = effluent, S = sludge.

[b] Each a composite of 12 grab samples; sludge a single grab sample only.

TABLE 84

Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 3.0 DWF and a Mean SS Loading of 944 mg l^{-1} (SS_3)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.197	0.223	0.225	0.218	0.259	0.224
	E	0.108	0.148	0.163	0.150	0.159	0.146
	S	0.744					
AE	I	5.50	6.82	7.47	6.12	6.12	6.41
	E	1.99	3.76	4.63	3.74	4.17	3.66
	S	24.5					
F	I	3.57	4.19	4.66	4.40	4.38	4.24
	E	1.50	2.28	2.68	2.29	2.67	2.28
	S	20.8					
PA	I	3.06	3.70	3.67	4.16	4.10	3.74
	E	1.35	1.80	2.01	1.80	2.11	1.81
	S	20.5					
A	I	0.826	1.00	1.04	0.937	1.03	0.967
	E	0.325	0.541	0.632	0.557	0.576	0.526
	S	5.16					
FL	I	1.36	1.57	1.58	2.07	1.78	1.67
	E	0.574	0.730	0.782	0.776	0.815	0.735
	S	10.1					
P	I	1.73	2.13	1.96	2.53	2.10	2.09
	E	0.724	0.940	1.01	1.01	1.03	0.943
	S	13.1					
BaA	I	0.700	0.945	0.923	1.30	1.07	0.988
	E	0.306	0.388	0.398	0.380	0.458	0.386
	S	6.76					
CH	I	0.712	0.843	0.773	0.969	0.773	0.814
	E	0.262	0.333	0.380	0.411	0.362	0.350
	S	5.16					
BkF	I	1.05	1.29	1.29	1.61	1.25	1.30
	E	0.425	0.486	0.521	0.619	0.539	0.518
	S	9.08					
BaP	I	0.802	1.03	1.05	1.31	1.03	1.04
	E	0.299	0.380	0.432	0.425	0.415	0.390
	S	8.48					
IP	I	0.279	0.374	0.397	0.456	0.396	0.380
	E	0.117	0.145	0.154	0.167	0.153	0.147
	S	2.70					
BghiP	I	0.375	0.504	0.477	0.595	0.485	0.487
	E	0.157	0.191	0.205	0.236	0.207	0.199
	S	3.76					
DBahA	I	0.108	0.133	0.147	0.165	0.139	0.138
	E	0.0482	0.0548	0.0548	0.0702	0.0536	0.0563
	S	1.02					

[a] I = influent, E = effluent, S = sludge.

[b] Each a composite of 12 grab samples; sludge a single grab sample only.

TABLE 85

Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 5.0 DWF and a Mean SS Loading of 442 mg l^{-1} (SS_0)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.205	0.673	0.254	0.320	0.273	0.345
	E	0.346	0.134	0.176	0.309	0.328	0.259
	S	1.29					
AE	I	3.96	14.7	6.48	7.96	5.74	7.77
	E	8.52	5.38	4.12	6.27	5.66	5.99
	S	38.8					
F	I	2.59	6.14	3.76	4.09	2.99	3.91
	E	5.42	3.35	2.44	3.33	3.11	3.53
	S	25.0					
PA	I	1.98	3.66	2.97	2.13	1.53	2.45
	E	2.74	2.00	1.82	1.85	1.67	2.02
	S	19.8					
A	I	0.478	1.07	0.852	0.585	0.492	0.695
	E	0.611	0.452	0.522	0.449	0.359	0.479
	S	5.16					
FL	I	0.805	1.17	0.916	0.653	0.552	0.819
	E	0.624	0.629	0.596	0.521	0.474	0.569
	S	7.76					
P	I	0.944	1.42	1.07	0.852	0.722	1.00
	E	0.672	0.799	0.761	0.614	0.571	0.683
	S	9.64					
BaA	I	0.409	0.668	0.492	0.291	0.256	0.423
	E	0.162	0.306	0.322	0.216	0.163	0.234
	S	4.52					
CH	I	0.446	0.636	0.379	0.379	0.317	0.431
	E	0.283	0.359	0.279	0.234	0.226	0.276
	S	4.60					
BkF	I	0.712	1.05	0.525	0.532	0.466	0.657
	E	0.368	0.511	0.386	0.328	0.298	0.378
	S	7.96					
BaP	I	0.576	0.838	0.417	0.362	0.331	0.505
	E	0.230	0.394	0.319	0.243	0.223	0.282
	S	6.12					
IP	I	0.232	0.322	0.154	0.169	0.159	0.207
	E	0.139	0.159	0.135	0.105	0.144	0.136
	S	2.52					
BghiP	I	0.344	0.412	0.193	0.223	0.224	0.279
	E	0.198	0.296	0.155	0.163	0.198	0.202
	S	3.15					
DBahA	I	0.110	0.128	0.0434	0.0684	0.0690	0.0838
	E	0.0688	0.0608	0.0497	0.0395	0.0760	0.0590
	S	1.00					

[a] I = influent, E = effluent, S = sludge.

[b] Each a composite of 12 grab samples; sludge a single grab sample only.

TABLE 86
Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 5.0 DWF and a Mean SS Loading of 464 mg l^{-1} (SS_1)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.0839	0.124	0.180	0.136	0.162	0.137
	E	0.0844	0.0861	0.118	0.102	0.151	0.108
	S	0.980					
AE	I	1.50	2.59	3.44	2.88	4.13	2.91
	E	1.24	1.68	2.19	2.10	4.02	2.25
	S	21.3					
F	I	1.11	1.99	2.69	1.99	3.55	2.27
	E	1.02	1.23	1.73	1.45	3.09	1.70
	S	19.3					
PA	I	1.30	2.12	2.48	1.52	2.27	1.94
	E	0.950	1.09	1.70	1.09	1.78	1.32
	S	21.1					
A	I	0.349	0.487	0.603	0.432	0.490	0.472
	E	0.219	0.262	0.349	0.283	0.427	0.308
	S	5.20					
FL	I	0.572	1.00	1.06	0.741	0.736	0.822
	E	0.371	0.454	0.624	0.388	0.526	0.473
	S	11.2					
P	I	0.743	1.28	1.22	1.04	0.866	1.03
	E	0.449	0.538	0.725	0.512	0.590	0.563
	S	15.2					
BaA	I	0.344	0.583	0.609	0.499	0.385	0.484
	E	0.138	0.183	0.319	0.187	0.239	0.213
	S	8.96					
CH	I	0.305	0.588	0.526	0.466	0.405	0.458
	E	0.191	0.200	0.337	0.194	0.319	0.248
	S	6.60					
BkF	I	0.476	0.914	0.782	0.761	0.668	0.720
	E	0.275	0.250	0.463	0.278	0.473	0.348
	S	13.6					
BaP	I	0.332	0.668	0.607	0.553	0.412	0.514
	E	0.178	0.193	0.301	0.204	0.393	0.254
	S	9.76					
IP	I	0.138	0.259	0.256	0.223	0.198	0.215
	E	0.0845	0.0853	0.141	0.0883	0.107	0.101
	S	4.16					
BghiP	I	0.207	0.360	0.342	0.305	0.281	0.299
	E	0.132	0.150	0.219	0.137	0.212	0.170
	S	5.00					
DBahA	I	0.0445	0.0986	0.108	0.0848	0.0720	0.0816
	E	0.0308	0.0283	0.0638	0.0331	0.0529	0.0418
	S	1.29					

[a] I = influent, E = effluent, S = sludge.
[b] Each a composite of 12 grab samples; sludge a single grab sample only.

TABLE 87
Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 5.0 DWF and a Mean SS Loading of 651 mg l^{-1} (SS_2)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.298	0.589	0.414	0.338	0.185	0.365
	E	0.341	0.221	0.295	0.379	0.164	0.280
	S	2.52					
AE	I	5.79	13.0	9.48	8.75	4.27	8.26
	E	8.10	4.62	6.44	7.52	3.54	6.04
	S	70.4					
F	I	3.14	6.09	5.41	5.16	3.00	4.56
	E	5.06	2.80	3.11	3.57	2.23	3.35
	S	45.6					
PA	I	2.32	4.22	3.51	2.82	2.07	2.99
	E	2.74	1.84	1.99	2.05	1.51	2.03
	S	36.6					
A	I	0.706	1.16	0.920	0.864	0.573	0.845
	E	0.568	0.475	0.542	0.512	0.408	0.501
	S	9.48					
FL	I	1.11	1.61	1.17	1.13	0.954	1.19
	E	0.657	0.614	0.678	0.661	0.522	0.626
	S	16.7					
P	I	1.47	2.07	1.46	1.51	1.37	1.58
	E	0.790	0.855	0.904	0.811	0.689	0.810
	S	21.1					
BaA	I	0.733	1.03	0.518	0.621	0.672	0.715
	E	0.268	0.425	0.361	0.247	0.271	0.314
	S	10.1					
CH	I	0.607	0.836	0.589	0.615	0.571	0.644
	E	0.336	0.354	0.362	0.362	0.275	0.338
	S	9.16					
BkF	I	1.09	1.34	0.836	0.989	0.979	1.05
	E	0.467	0.536	0.541	0.501	0.390	0.487
	S	17.0					
BaP	I	0.933	1.07	0.559	0.707	0.679	0.790
	E	0.336	0.423	0.407	0.349	0.317	0.366
	S	11.8					
IP	I	0.0342	0.397	0.257	0.259	0.242	0.238
	E	0.146	0.165	0.182	0.162	0.130	0.157
	S	4.92					
BghiP	I	0.429	0.486	0.344	0.319	0.326	0.381
	E	0.206	0.239	0.250	0.211	0.180	0.217
	S	5.72					
DBahA	I	0.111	0.147	0.102	0.0862	0.0904	0.107
	E	0.0522	0.0549	0.0676	0.0717	0.0480	0.0589
	S	1.63					

[a] I = influent, E = effluent, S = sludge.
[b] Each a composite of 12 grab samples; sludge a single grab sample only.

TABLE 88

Influent, Effluent and Sludge Concentration of PAH in Samples from the Primary Sedimentation Pilot Plant Operated at a Hydraulic Loading of 5.0 DWF and a Mean SS Loading of 767 mg l^{-1} (SS_3)

PAH	Sample type[a]	Concentration (µg l^{-1}) in sample[b] 1	2	3	4	5	Mean
AY	I	0.113	0.162	0.206	0.171	0.201	0.171
	E	0.0788	0.107	0.149	0.111	0.178	0.124
	S	1.13					
AE	I	2.17	3.36	5.55	4.93	6.40	4.48
	E	1.36	1.99	2.71	2.55	3.74	2.47
	S	31.6					
F	I	1.73	2.41	3.82	3.56	4.49	3.20
	E	1.17	1.59	2.26	1.78	2.49	1.86
	S	26.6					
PA	I	1.95	2.51	3.66	3.07	3.43	2.92
	E	1.15	1.46	2.04	1.49	1.76	1.58
	S	28.5					
A	I	0.458	0.574	1.02	0.839	0.927	0.764
	E	0.254	0.304	0.398	0.319	0.454	0.346
	S	8.24					
FL	I	0.908	1.11	1.67	1.50	1.50	1.34
	E	0.475	0.602	0.705	0.527	0.600	0.582
	S	17.4					
P	I	1.08	1.42	1.96	2.12	1.92	1.70
	E	0.546	0.724	0.859	0.738	0.778	0.729
	S	22.1					
BaA	I	0.514	0.664	0.991	1.02	0.927	0.823
	E	0.195	0.278	0.343	0.249	0.330	0.279
	S	12.6					
CH	I	0.455	0.623	0.876	0.933	0.865	0.750
	E	0.242	0.273	0.369	0.299	0.316	0.300
	S	9.56					
BkF	I	0.685	0.965	1.37	1.46	1.38	1.17
	E	0.393	0.429	0.495	0.421	0.454	0.438
	S	21.5					
BaP	I	0.469	0.690	1.03	1.16	1.04	0.878
	E	0.222	0.295	0.376	0.305	0.280	0.296
	S	16.5					
IP	I	0.176	0.252	0.381	0.406	0.438	0.331
	E	0.113	0.117	0.173	0.121	0.152	0.135
	S	6.36					
BghiP	I	0.273	0.363	0.492	0.544	0.533	0.441
	E	0.174	0.221	0.237	0.154	0.191	0.195
	S	8.64					
DBahA	I	0.0682	0.0808	0.122	0.134	0.139	0.109
	E	0.0418	0.0468	0.0770	0.0462	0.0545	0.0533
	S	2.03					

[a] I = influent, E = effluent, S = sludge.

[b] Each a composite of 12 grab samples; sludge a single grab sample only.

APPENDIX 6

TABLE 89
Linear Regression Function, Arcsin Transformed, for Removal Efficiency of PAH on Removal Efficiency of SS Achieved During Primary Sedimentation

PAH	Regression function[a]
AY	$R = 0.194\ R_{SS} + 13.8$
AE	$R = 0.689\ R_{SS} - 1.5$
F	$R = 0.924\ R_{SS} - 12.3$
PA	$R = 1.08\ R_{SS} - 16.7$
A	$R = 0.864\ R_{SS} - 5.9$
FL	$R = 0.997\ R_{SS} - 7.0$
P	$R = 1.07\ R_{SS} - 10.3$
BaA	$R = 1.03\ R_{SS} - 2.6$
CH	$R = 0.957\ R_{SS} - 3.7$
BkF	$R = 0.763\ R_{SS} + 9.4$
BaP	$R = 0.704\ R_{SS} + 12.6$
IP	$R = 0.500\ R_{SS} + 20.6$
BghiP	$R = 0.660\ R_{SS} + 9.8$
DBahA	$R = 0.555\ R_{SS} + 16.2$

[a] Where R = removal efficiency (degrees) of PAH
R_{SS} = removal efficiency (degrees) of SS.
Range of application of functions: surface loading rate 6.10-61.0 $m^3\ m^{-2}\ d^{-1}$; SS loading ca. 300-1000 mg l^{-1}; hydraulic retention time 0.46-4.58 h.