PB82-199704

Biological Processes in the Treatment of Municipal Water Supplies

Rip G. Rice, et al

Public Technology, Inc.
Washington, D.C.

March 1982

U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
NTIS®

PB82-199704

EPA-600/2-82-020
January 1982

BIOLOGICAL PROCESSES IN THE TREATMENT OF MUNICIPAL WATER SUPPLIES

by

Rip G. Rice
Jacobs Engineering Group

C. Michael Robson
Purdue University

G. Wade Miller
Public Technology, Incorporated

John C. Clark
Temple, Barker & Sloane

Wolfgang Kühn
Universität Karlsruhe

Grant No. R-804385-01

Public Technology, Incorporated
Washington, D.C. 20036

Project Officer

J. Keith Carswell
Drinking Water Research Division
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

NOTICE

THIS DOCUMENT HAS BEEN REPRODUCED FROM THE BEST COPY FURNISHED US BY THE SPONSORING AGENCY. ALTHOUGH IT IS RECOGNIZED THAT CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED IN THE INTEREST OF MAKING AVAILABLE AS MUCH INFORMATION AS POSSIBLE.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-82-020	ORD Report	PB82 199704

4. TITLE AND SUBTITLE	5. REPORT DATE
"Biological Processes In The Treatment Of Municipal Water Supplies"	March 1982
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Rice, R.G., Robson, C.M., Miller, G.W., Clark, J.C. and Kuhn, W.	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Public Technology, Inc. Washington, D.C. 20036	
	11. CONTRACT/GRANT NO. R804385

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Municipal Environmental Research Laboratory - Cin., OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	
	14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer: J. Keith Carswell (513) 684-7228

16. ABSTRACT

The objective of this project was to study the use of Biologically Enhanced Granular Activated Carbon (BEGAC) technology in European water treatment plants and to determine its advantages and disadvantages for use in the United States. Seven European water works were visited in which chemical preoxidation followed by rapid media filtration then GAC adsorption was being practiced and BEGAC process details were gathered.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to public.	Unclassified	441
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

DISCLAIMER

This report has been reviewed by the Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names of commercial products constitute endorsement or recommendation for use.

FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the prevention and treatment of public drinking water supplies, and to minimize the adverse economic, social, health and aesthetic effects of pollution.

This publication is one of the products of that research; a most vital communications link between the research worker and the user community. It is a survey of biological processes used in the treatment of drinking water supplies. Particular emphasis is placed on evaluating the use of biologically enhanced granular activated carbon as it has been developed and is being practiced in certain European drinking water treatment plants today.

This study was sponsored jointly by the Industrial and Extractive Processes Division of the EPA Office of Research and Development, by the Water Supply Research Division of the Municipal Environmental Research Division and by the Office of Drinking Water in an effort to assess the performance of advanced treatment techniques for use in the production of drinking water and in the treatment of wastewaters. It is hoped that this report will be interesting and helpful to those active in these fields.

Francis T. Mayo, Director
Municipal Environmental Research Laboratory

ABSTRACT

This study resulted from a recommendation made during the course of a previous survey conducted for the U.S. Environmental Protection Agency by Public Technology, Inc. During the earlier survey, An Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies, EPA-600/2-78-147, a biological treatment technique was observed in several European drinking water treatment plants which appeared to be producing high quality drinking waters and avoiding the synthesis of halogenated organic materials during the water treatment process. This treatment technique involves the sequential application of chemical oxidation (usually by means of ozone), rapid media filtration, optional reaeration and granular activated carbon adsorption.

Because this biological treatment process seemed to have general applicability to the control of organic chemicals in drinking water, the objective of the present program was to study the use of this technology in European water treatment plants and to determine its advantages and disadvantages for use in the United States.

This biological treatment technique has been called Biological Activated Carbon, but perhaps should be more properly referred to as Biologically Enhanced Granular Activated Carbon (BEGAC). Europeans substitute the BEGAC process for prechlorination. Raw waters which contain readily biodegradable organic materials are pretreated simply by aeration or oxygenation to create high dissolved oxygen levels in the water. In the presence of high oxygen levels and readily biodegradable organic materials, aerobic biological activity is promoted in the subsequent rapid filter and GAC adsorption media. The aerobic microorganisms degrade biodegradable organics, ultimately converting them to carbon dioxide and water under optimum conditions.

If the organic materials in the raw waters are biorefractory, then chemical preoxidation may convert them into readily biodegradable materials. If not, then BEGAC will provide no advantages over granular activated carbon operating purely in its adsorption mode.

In addition to converting dissolved organic materials to carbon dioxide and water, the aerobic microorganisms also are capable of converting ammonia or ammonium ions to nitrate ions by biological nitrification mechanisms. Most of the nitrification occurs in the rapid filter medium before the GAC adsorber. Therefore, oxygenation normally is required after passage through the filtration unit.

Advantages of the BEGAC process include:

1) Extension of operating lifetimes of the GAC adsorbers before reactivation must be conducted. Swiss water treatment authorities claim a 5- to 6-fold increase in operating lifetimes. One European plant has utilized the process for over three years without requiring GAC reactivation. Newer plants are planning to operate at least two years before reactivating.

2) The process may be substituted for breakpoint chlorination to remove ammonia. This eliminates the formation of trihalomethanes and other halogenated organic compounds during the early stages of water treatment processes.

3) The Dohne plant in Mülheim (Federal Republic of Germany) converted its existing breakpoint chlorination/GAC adsorption process to BEGAC in late 1977. This involved doubling the depth of the GAC contactors and installing two-stage ozonation. Because of savings in operating labor, GAC reactivation costs and costs of chemicals, current operating costs at the Dohne plant are no higher than they were before process conversion -- and the quality of finished water is higher.

Bacteria in the GAC adsorber are present only in the large macropores, and do not interfere with the adsorption properties of the GAC for refractory organic compounds. If the raw water contains both refractory organics and readily biodegradable organics, the GAC unit can be sized to maximize biochemical conversion of organics and ammonia without allowing breakthrough of these materials. While these materials are being removed from solution biochemically, the refractory organics (i.e., halogenated organic materials) are being removed by adsorption. The GAC then is regenerated only after the refractory materials break through.

A major uncertainty exists with respect to adoption of BEGAC processes on a broad scale. This is the concern for endotoxins which may be produced when specific types of bacteria die. However, no evidences of endotoxins as yet have been found in BEGAC system effluents. All microorganisms identified to date as being present in BEGAC filter/adsorption media and their effluents are non-pathogenic soil and water bacteria, fungi and yeasts. E. coli organisms, which may be present in raw waters, cannot survive in competition with the non-pathogenic organisms present.

CONTENTS

Foreword iii
Abstract iv
Figures. ix
Tables xv
Acknowledgements xxi

1. Introduction 1
   Site visits 4
   Literature search and review. 4
2. Conclusions. 7
3. Recommendations. 12
4. Evolution of Drinking Water Treatment Processes. 15
   Early methods of treating water 15
   Combinations of physical, chemical and biological processes. 16
   Objectives of drinking water treatment. 17
   Removal of organic chemicals through biological treatment. 24
5. A Review of Biological Processes Used in Drinking Water Treatment 35
   River sand bank filtration (Üferfiltration) 35
   Slow sand filters 36
   Storage of surface waters 37
   Coarse media biological reactors. 37
   Fluidized bed nitrification 37
   Ground passage of treated water 38
   Biologically active filtration media. 38
   Biologically active granular activated carbon 39
6. Microbiological Aspects of Biological Activated Carbon 40
   General principles of biological activity 40
   Metabolism. 40
   Conditions necessary for promotion of aerobic activity. . . 44
   Stoichiometry of biochemical oxidations 46
   Studies of operational biologically enhanced GAC systems. 49
7. Granular Activated Carbon. 60
   Introduction. 60
   Granular activated carbon - basic principles. 63
   Selection of activated carbons. 66
   Operative mechanisms during drinking water treatment with GAC 67
   Applications of GAC in water treatment. 71
   Overview of European experience with GAC. 84

 Preceding page blank

8. Basic Parameters of BAC Systems. 86
Step no. 1 -- Chemical oxidation, oxygenation and aeration 86
Step no. 2 -- Inert media filtration plus biological oxidation. 90
Step no. 3 -- Reaeration/reoxygenation. 93
Step no. 4 -- GAC adsorption + biological axidation . . . 93
9. European BAC Applications And Studies. 97
Federal Republic of Germany 97
Switzerland 102
The Netherlands 102
Case histories. 105
Düsseldorf pilot plant studies and operational data.1C5
Bremen pilot plant study. 126
Mülheim. 150
Rouen-la-Chapelle. 156
10. European Microbiological Studies in Activated Carbon Filters & Adsorbers. 160
Introduction. 160
European status as of 1973. 160
Current European microbiological studies. 166
Research studies at the KIWA 166
Research studies at the University of Saarlands. . .179
Conclusions regarding microbiological aspects of BAC systems. 207
11. Estimated Costs For BAC Systems. 211
Costs for ozonation systems 211
Capital costs for ozonation systems. 212
Operating & maintenance costs of ozonation systems .217
Costs for GAC systems .220
Capital costs for GAC systems. 223
Operating & Maintenance costs of GAC systems 232
Costs for replacement GAC 240
Costs for GAC regeneration. 240
Summary of GAC treatment costs. 243
Cost savings with BAC systems 254
Conclusion. 262
12. Engineering Design Considerations For BAC Systems. 263
Introduction. 263
Parameters affecting biological growth in GAC media . . .264
Discussion of specific design parameters. 265

References 275
Bibliography 291
Appendices (Plant Descriptions)

A. Aubergenville plant (suburbs of Paris, France). 324
B. Choisy-le-Roi (Edmond Pépin plant), suburbs of Paris, France. .328
C. Düsseldorf, Federal Republic of Germany 332
D. Morsang-sur-Seine (suburbs of Paris). 341
E. The Johne plant at Mülheim, Federal Republic of Germany 366
F. Rotterdam, The Netherlands -- Kralingen water treatment plant .401

FIGURES

Number		Page
1	Examples of typical systems to be investigated	13
2	The Düsseldorf process, Düsseldorf, Federal Republic of Germany	18
3	The Lengg plant, Zürich, Switzerland	18
4	The Rouen-la-Chapelle process, Rouen, France	19
5	The Kralingen process, Rotterdam, The Netherlands	19
6	The Dohne process, Mülheim, Federal Republic of Germany	20
7	The Aubergenville process, Aubergenville, France	21
8	The Choisy-le-Roi process, Paris, France suburbs. Preozonation and detention reservoir under construction for 1980	22
9	Treatment process ultimately planned for 3 Paris suburbs plants	25
10	Suggested treatment process for raw waters containing initially non-biodegradable organic materials	29
11	Block diagram of the biological activated carbon process	33
12	Biological activated carbon system	34
13	Enzymatic oxidation of glucose (glycolysis)	42
14	The tricarboxylic acid (Krebs or citric acid) cycle	43
15	Intermediates in the β-ketoadipate pathway	45
16	Electron micrograph (4,000 x) of GAC particle showing bacterial growths	50
17	Simplified metabolic pathway used by <u>Pseudomonas putida</u> to degrade phenol	59
18	Filter/adsorber installation	62
19	Dual function filter and adsorber	62

20 Pore volume distributions of typical decolorizing activated carbons 64

21 Pore volume distributions of typical decolorizing activated carbons 65

22 Examples of chemisorption on GAC surfaces. 69

23 Process steps in the regeneration of activated carbon. 80

24 GAC regeneration system components 81

25 TOC removal upon passage of BASF activated sludge effluent through biologically enhanced (with O_2) GAC. 92

26 Schematic representation of a GAC particle, showing pore sizes and bacterial growths. 94

27 Microbiological loading of GAC -- dependence on adsorptive capacity 100

28 Behavior of microbial populations on GAC over 3 years at Wiesbaden, Federal Republic of Germany 101

29 Efficiency of removal of COD by rapid sand filter and GAC at Lengg plant, Zürich, Switzerland 103

30 Efficiency of COD removal by BAC over 3 years at Moos water works, Zürich, Switzerland. 104

31 General procedural plan for the treatment of drinking water in the bank filtration works on the lower Rhine (Düsseldorf area) . . . 109

32 Changes in Rhine river water quality parameters during passage through the Düsseldorf water treatment process 113

33 Changes in organics parameters in Düsseldorf water treatment plants 114

34 Performance of various activated carbons at Flehe test plant, Düsseldorf 116

35 Quantities of individual substances determined by temperature programmed pyrohydrolysis of GAC vs. total org. Cl loading . . . 118

36 Organics removal in Düsseldorf GAC post-adsorber by adsorption + biological activity. 120

37 Distribution profiles for organically bound chlorine and some chlorohydrocarbons in Düsseldorf GAC beds. 122

38 Distribution of organically bound chlorine in Düsseldorf GAC beds. 123

39 Organics removal with 2 types of GAC in 2 Düsseldorf treatment plants 124

40 Change in loading of 2 types of GAC with polar and non-polar organic chlorine compounds at large Düsseldorf treatment plant . 125

41 The Auf dem Werder water treatment process, Bremen, Federal Republic of Germany. 127

42 Bremen, Germany water works pilot plant. 128

43 Schematic of Bremen waterworks pilot plant GAC test units. 131

44 Comparison of chemical oxygen demand ($KMnO_4$) removal by slow sand filtration and BAC at Bremen, Federal Republic of Germany . 134

45 Variation of permanganate COD and Δ(CCD/DO) with time of year. . . 134

46 Percent decreases in colony numbers and permanganate oxygen consumption (COD) through GAC over 3+ years. 138

47 Percent reduction in colony numbers and permanganate oxygen consumption (COD) values in the Hydraffin LS-GAC filter, 1970-1971. 140

48 Variation in specific capacity for dissolved organic carbon (DOC) of a GAC filter with operating time for normal (BR) and more highly activated carbons 148

49 The Rouen-la-Chapelle process, Rouen, France 157

50 Histogram of agar plate counts, 3 days at 22°C 163

51 Bacterial numbers on GAC, granular non-activated carbon and sand, each fed with non-chlorinated tap water. 167

52 Numbers of pseudomonads and coliforms on GAC ROW 0.8 supra and on non-activated carbon ROW 0.8 during aeration at 25°C. 168

53 Numbers of bacteria and actinomycetes on GAC and GNAC; O_2 consumption with GAC and GNAC. 169

54 Colony counts in GAC, GNAC and sand filters and in their effluents over 340 days. 172

55 Colony counts in GAC, GNAC and sand. 174

56 Colony counts in effluents from GAC, GNAC and sand filters 174

57 Colony counts in Norit PKST GAC in 8 slow sand filters at Den Haag 175

58 Adsorption isotherms of 4-nitrophenol and 4-hydroxybenzoate on ROW 0.8 supra GAC, with and without bacteria 177

59 Removal of 4-nitrophenol and 4-hydroxybenzoate on passage through ROW 0.8 supra GAC. 178

60 Rate of disappearance of 4-nitrophenol and 4-hydroxybenzoate on passage through ROW 0.8 supra GAC. 179

61 Mean colony numbers at various points in the Schierstein plant, March '73-March '74. 181

62 Development of colony counts in pilot plant GAC adsorber effluents at the Schierstein plant 182

63 Development of colony counts in GAC of pilot plant adsorbers at the Schierstein plant. 183

64 Colony & cell numbers and free chlorine contents as functions of GAC adsorber length. 184

65 Oxygen and CO_2 contents of GAC effluents vs. adsorber length . . . 184

66 Organics content of GAC effluents vs. adsorber depth 185

67 Behavior of microbial populations on GAC over 3 years at Wiesbaden, Federal Republic of Germany 186

68 Microbiological loading of GAC -- dependence on adsorptive capacity 189

69 Dependence of microorganism loading of GAC with time 190

70 Dependence of microorganism loading of GAC with ion concentration. 191

71 Fluctuation of colony numbers in GAC adsorber effluents at the Schierstein plant during 1 year. 192

72 Development of microbiological activity in full scale adsorber with new GAC at the Schierstein plant. 193

73 Changes in colony numbers at each GAC step and outlet in the Schierstein plant. 194

74 Development of colony numbers in effluents of new GAC pilot plant adsorbers as a function of flow rate at the Schierstein plant. . 195

75 Development of colony numbers in new GAC charges in the Schierstein pilot plant adsorbers as a function of flow rate . . 196

76 Development of colony numbers in effluents of pilot plant adsorbers with different types of GAC at the Schierstein plant . 197

77 Bacterial adsorption on GAC. 199

78 Effect of GAC on metabolic activity of bacteria. 201

79 Effect of GAC on metabolic activity of bacteria. 203

80 Capital costs for 9- and 18-min. GAC empty bed contact times . . . 225

81 Material cost for GAC, including cost for purchase, delivery and placement. 242

82 Production cost for GAC adsorbers vs. period between reactivations. 255

83 Total production cost vs. reactivation frequency for $0.60, 0.80 & 1.00/lb GAC for 100 mgd contactor system 260

84 Cost of ozone and GAC in combination 261

85 Aubergenville water treatment plant. Process diagrams 326

86 Choisy-le-Roi water treatment plant. Process diagrams 331

87 General layout of the Morsang-sur-Seine treatment works. 342

88 Morsang-sur-Seine water treatment plant -- processes operating in 1977. 344

89 Percent reduction in levels of organic materials at Morsang. . . . 345

90 Evolution of $CHCl_3$ in Morsang waters 348

91 Process 1 performance parameters at Morsang plant. 351

92 Process 2 performance parameters at Morsang plant. 352

93 Process 3 performance parameters at Morsang plant. 353

94 Process 4 performance parameters at Morsang plant. 354

95 Analytical sampling points for the 4 water treatment processes at Morsang-sur-Seine plant, France. 355

96 Effect of ozone on GAC adsorption at Morsang plant 359

97 Breakthrough curve for the ozonated GAC adsorber without biological activity. 361

98 Cumulative plots: GAC adsorption vs. loading; with and without ozone. 362

99 Effect of biological activity on the cumulative TOC removal of a GAC adsorber 363

100 Comparison of ozonated and non-ozonated GAC adsorbers. 364

101 Comparison of actual vs. computer-predicted data for ozonized water/GAC adsorber 365

102 Schematic diagram of Dohne pilot plant process (Mülheim) 369

103 Influence of prechlorination on the effectiveness of a process consisting of flocculation, sedimentation, ozonation, filtration and GAC treatment 371

104 Performance & loading of BAC adsorbers 372

105 Process scheme for surface water treatment at the Dohne water utility in Mülheim after introduction of combined chemical and biological oxidation 380

106 Pressure filters at the Dohne (Mülheim) plant. 382

107 GAC adsorbers at Dohne plant, Mülheim, Federal Republic of Germany. 385

108 Initial performance of BAC adsorbers in the Dohne water works. . . 389

109 Kralingen (Rotterdam) plant water sources. 401

110 Process flow diagram of the Kralingen water treatment plant, Rotterdam, The Netherlands 404

111 Desorption of trihalomethanes from GAC at Kralingen plant. 410

112 Removal of detergents by Kralingen plant GAC 412

TABLES

Number		Page
1	Facilities & Organizations Visited, June, 1978	5
2	Oxygen Requirements For Conversion of Representative Organic Compounds to CO_2	47
3	Bacterial Species Found in GAC Adsorber Effluents at the Schierstein (Federal Republic of Germany) Water Treatment Plant.	52
4	Types of Fungi and Yeasts Found in GAC Adsorber Effluents at the Schierstein (Federal Republic of Germany) Water Treatment Plant.	52
5	Bacteria Isolated from GAC Adsorbers at Philadelphia, PA	54
6	Bacteria Isolated From GAC Columns and Effluents in Philadelphia	55
7	Enteric Bacteria Isolated From GAC Effluents	57
8	Adsorption Technology Milestones	61
9	GAC Adsorption of Organics	68
10	Comparison of GAC With Sand For Turbidity Removal and Service Life	73
11	Treatment of Drinking Water by GAC in Sand Filters	74
12	Comparison of GAC Filter/Adsorbers and Post-Adsorbers at Vigneux-sur-Seine Water Treatment Plant.	72
13	Partial List of European Water Treatment Plants Using GAC.	76
14	Partial List of U.S. Wastewater Treatment Plants Using GAC	79
15	The Main Components of Readily Volatile Compounds in the River Rhine at Karlsruhe	108
16	Comparisons of Organically Bound Sulfur and Chlorine in GAC Control Filters at Different Sampling Stations	108
17	Efficiency of GAC Control Filters for Measuring Dissolved Organic Substances	110

18 Chlorinated Organics Removed From GAC by Dioxane Extraction at Flehe Test Installation, Düsseldorf. 119

19 Tests With Ozone and Activated Carbon Filters (January 8 to February 2, 1970 130

20 Comparative Tests With Different Types of Activated Carbon for Purely Biological Tests. 132

21 Averages of Data Obtained During Last 9 Months of the 38-Month Study With BR Activated Carbon at Bremen, Federal Republic of Germany 136

22 Extraction of Activated Carbon Used For Different Periods. 137

23 Bacterial Data in Raw Water, GAC Filtrate and RDSFF Filtrates. . . 139

24 Comparison of Various Filtering Rates (Activated Carbon LS). . . . 141

25 Comparison of Two Activated Carbon Filters of the Same Bed Depths with Different Filtering Rates. 142

26 Comparison of Different GAC Grain Sizes (LS Activated Carbon). . . 144

27 Results of Recycling Tests at Bremen Water Works 145

28 Tests With B-12 Activated Carbon 147

29 Organo-Chlorocompounds Present After Breakpoint Chlorination . . . 150

30 Process parameters at the Dohne Waterworks (Mülheim) Before and After Change of Treatment. 152

31 Mean DOC Values After the Different Treatment Steps (Mülheim). . . 153

32 Geometric Mean Values of Bacterial Counts for the Mülheim, Germany (Dohne) Plant Using Ozone. 154

33 Performance of Biological Activated Carbon Filters. Mean Values for 6-Month Operation After a 3-Month Starting Period (Dohne Pilot Plant, Mülheim, Germany) 154

34 Rouen-la-Chapelle Plant Operational Data (1976 and 1977) 158

35 Removal of Bacteria During Caustic Soda Softening and Prechlorination at Colwick, England. 162

36 50% Reduction Time (Days) of Different Groups of Bacteria on ROW 0.8 Supra and ROW 0.8 GNAC 168

37 Percentage of Biological Removal of Organic Substances During Passage Through Granular Activated Carbon. 188

38 Microbiological Share of Oxygen Consumption and CO_2 Production During Passage Through Granular Activated Carbon 188

38A Bacterial Species Found in Effluents of Granular Activated Carbon Adsorbers at the Schierstein (FRG) Plant. 200

39 Types of Fungi and Yeasts Found in Effluents of Granular Activated Carbon Adsorbers at the Schierstein (FRG) Plant. . . . 200

40 Cost Range of Ozonation Systems (From Air) 212

41 Construction Cost: Ozone Generation Systems 213

42 Construction Cost: Concrete Ozone Contact Chambers. 213

43 Capital Costs for Drinking Water Disinfection With Ozone 214

44 Construction Costs for Small Scale Ozone Generation Systems. . . . 214

45 Construction Cost for Ozone Contact Chambers (Small Scale) 216

46 Construction Costs for Ozone Generation Systems (Large Scale). . . 218

47 Construction Costs for Ozone Contact Chambers (Large Scale). . . . 219

48 Operation and Maintenance Summary for Small Scale Ozone Generation Systems 221

49 Operation and Maintenance Summary for Large Scale Ozone Generation Systems 222

50 Conceptual Design Parameters for Package GAC Columns (7.5 min. EBCT). 224

51 Construction Costs for Package GAC Columns (7.5 min. EBCT) 226

52 Construction Costs for Concrete Gravity Carbon Contactors. 227

53 Construction Costs for Concrete Gravity GAC Contactors 228

54 Conceptual Design Parameters for Steel Gravity Flow GAC Contactors; 20 ft. GAC Depth 230

55 Construction Costs for Steel Gravity Flow GAC Contactors 231

56 Construction Costs for Steel Gravity Flow GAC Contactors 232

57 Conceptual Design Parameters for Pressure GAC Contactors 233

58 Construction Costs for Pressure GAC Contactors 234

59 Construction Costs for Pressure GAC Contactors 235

60 Construction Costs for Pressure GAC Contactors 236

61 Operation and Maintenance Summary for Package GAC Columns. 237

62 Operation and Maintenance Summary for Gravity GAC Contactors . . . 238

63 Operation and Maintenance Summary for Steel Gravity GAC Contactors 239

64 Operation and Maintenance Summary for Pressure GAC Contactors. . . 241

65 Construction Costs for Off-Site Regional GAC Regeneration -- On-Site Handling and Transportation Facilities 243

66 Operation and Maintenance Summary for Off-Site Regional GAC Regeneration -- Handling and Transportation Only 244

67 Conceptual Design Parameters for Multiple Hearth GAC Regeneration. 245

68 Construction Costs for Multiple Hearth GAC Regeneration. 246

69 Operation and Maintenance Summary for Multiple Hearth GAC Regeneration 247

70 Conceptual Design Parameters for Infrared GAC Regeneration Furnace. 245

71 Construction Costs for Infrared GAC Regeneration Furnaces. 248

72 Operation and Maintenance Cost Summary for Infrared GAC Regeneration Furnace 249

73 Conceptual Design Parameters for GAC Regeneration. 250

74 Construction Costs for GAC Regeneration -- Fluidized Bed Process . 251

75 Operation and Maintenance Cost Summary for GAC Regeneration -- Fluidized Bed Process. 252

76 Summary of Estimated Operating Costs -- Fluidized Bed GAC Regeneration System, Manchester, N.H. Water Works. 250

77 Costs of GAC Treatment (18 min EBCT), Including Regeneration . . . 253

78 Assumptions for 18 Minute EBCT GAC Adsorption. 254

79 Amortized Capital and Operating & Maintenance Costs for GAC Adsorption (18-Minute EBCT), ¢/1,000 Gallons 254

80 Comparisons Between Total Costs of Various Reclamation Process Configurations at National Institute for Water Research, Pretoria, South Africa 262

81 Effect of Preozonation (1.25 mg/l) Before Storage. 330

82 Lower Rhine River Water Treatment Data for Plants Utilizing River Bank Filtration/Ozonation/Filtration/GAC Adsorption. Averages for 1977 336

83 Plant #4. Chloro-Organic Material Data From a Single Day's Sampling in 1977 337

84 Lower River Rhine Water Treatment Data for Plants Using River Bank Filtration/$KMnO_4$/Polymer Sedimentation/Filtration/GAC. Averages for 1977. 338

85 Lower River Rhine Water Treatment Data for Plant Utilizing River Bank Filtration/GAC Adsorption. Average for 1977. 338

86 Upper Danube River Water Treatment Data for Plant Utilizing Sedimentation/Ozonation/Filtration/GAC. Average for 1977. . . . 339

87 Comparison of Processes 1, 2, 3 and 4 at Morsang-sur-Seine. Data Averaged Over 5 Months of Side-by-Side Operation. 356

88 Old Treatment Process at the Dohne Plant, Mülheim, Germany, and Median Values of Chlorinated Organics Produced During 1976 and 1977 367

89 Comparison of Treatment With & Without Breakpoint Chlorination . . 370

90 Comparison of DOC Removed During First 3 and Second 8 Months of Use of Granular Activated Carbon for 5 Activated Carbons 373

91 Removal of DOC After Treating Ozonized Water With Al^{+3} 374

92 Biological Activity in Pilot Plant GAC Columns, Jan.-Mar., 1977. . 375

93 Biological Activity in Pilot GAC Columns, June-Aug., 1977. 376

94 Biological Activity in Pilot GAC Columns. Mean Values for a 6-Month Period (Jan-June, 1977) After a 3-Month Starting Period. 377

95 Total Bacterial Counts in Biologically Active GAC Adsorbers. . . . 377

96 Biological Oxidation in Fluidized Bed Reactors 378

97 Mean DOC and UV-Extinction Values for the Different Treatment Steps at the Dohne Plant 384

98 Comparison of Old & New Plant Processes for Removal of DOC & NH_4^+. 386

99 Dohne Plant Performance Data Since Nov. 1977. DOC Data, mg/l. . . 388

100 Dohne Plant Performance Data, Jan.-June, 1978. Biological Production of Inorganic Carbon in GAC Contactors 390

101 Dohne Plant Performance Data. Comparison of DOC Removed versus Inorganic Carbon Produced in Biologically Active GAC Contactors During May - June, 1978. 391

102 Bacterial Count Data at Dohne Plant with BAC Treatment Process . . 394

103 Costs for Ozonation Systems in Mülheim, Federal Republic of Germany. 398

104 Breakdown of Costs at Dohne Plant, Mülheim, FRG. 399

105 Description of Treatment Process Units at Kralingen Plant. 405

106 Analysis of Raw and Finished Waters at Kralingen, January, 1978. . 407

107 Haloform Production in Kralingen Plant, June 1977 - March 1978 . . 408

108 Representative Colony Count Data at Kralingen Plant. 413

109 Capital Costs of Kralingen Plant 414

110 Treatment Components at the Kralingen Plant. 415

111 Annual Operating Costs of Kralingen Plant. 416

112 Annual Kralingen Water System Costs. 417

113 Rotterdam Water System Revenues, Water Deliveries and Rates. . . . 418

ACKNOWLEDGEMENTS

This report could not have been written without the cooperation of many people and organizations located in Western Europe. Developing the information necessary to this study required contacting many key individuals in Europe who are active in water and wastewater treatment, plant superintendents, engineers and chemists, research institute scientists, academic research staffs, government scientists and regulatory personnel, executives of water treatment companies, water and wastewater treatment personnel at industrial chemical manufacturing complexes and representatives of manufacturing companies supplying granular activated carbon and ozonation systems. Unfortunately, not everyone who contributed to this study can be acknowledged individually.

We are especially grateful to the following individuals:

François Fiessinger, Société Lyonnaise des Eaux et de l'Eclairage
Drs. Maurice Paré, L. Brener, J. Mignot, Capon, Picard and A. Moan, Degrémont
Daniel Versanne, Compagnie Générale des Eaux
Jacques Le Pauloüe, Trailigaz
Drs. Meijers, Kruithof, Poels and Van der Kooij, KIWA
Dr. J.J. Rook, Dr. van der Heide and Mr. Wielinga, Rotterdam Waterworks
Drs. E. de Greef and G. Piet, Rijksinstitut
Ewald Heilker and Friedrich Nolte, Dohne Waterworks, Mülheim
W. Poggenburg and Dr. C. Engels, Düsseldorf Waterworks
Prof. Dr. Heinrich Sontheimer, and Drs. F. Fuchs and M. Jekel, Engler-Bunte Institute, University of Karlsruhe
H. Engelhardt and Dr. W. Weisbrodt, BASF, Ludwigshafen
Prof. Dr. R. Schweisfurth and Drs. M. Klotz and P. Werner, University of the Saarlands
Drs. Roelke, Wirth and Otto, Lurgi, Frankfurt-am-Main
Wolfgang Kretzschmar, WABAG, Kulmbach
Drs. Eigenwann, Knüsli, Thuer and Dretscher, Ciba-Geigy, Basle
Dr. Willi Vogler, Roche, Sisseln
Messrs. M. Schalekamp, Valenta, Russell, Naves and Lucy, Zürich Wasserversorgung
Drs. J. Hoigné and Gujer, EAWAG, Dübendorf
Prof. W. Weber, University of Michigan
Dr. Paul Berger, U.S. EPA, Office of Drinking Water
Prof. Andrew Benedek, McMaster University, Canada

Throughout the study we have been appreciative of the guidance and helpful encouragement provided by Paul E. des Rosiers (Industrial & Extractive Processes Division, Office of Research & Development), Dr. Joseph A. Cotruvo (Office of Drinking Water) and J. Keith Carswell (Water Supply Research Division, Municipal Environmental Research Laboratory), our Project Officer.

SECTION 1

INTRODUCTION

The Environmental Protection Agency's Water Supply Research Laboratory in Cincinnati awarded a grant to Public Technology, Inc. in June, 1976 to conduct a state-of-the-art study of the use of ozone and chlorine dioxide technologies in municipal water treatment. The results of this study have been published as Report Number EPA-600/2-78-147 entitled, "An Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies".

The study revealed that ozonation is a technology currently being widely used for a range of purposes in at least 1,039 water treatment plants in 29 countries in 1977. As part of this study, a team of scientists and engineers visited 23 water treatment plants in France, Belgium, Germany and Switzerland in May, 1977. Twenty of these plants use ozone for one or more purposes, while chlorine dioxide is used at 14 of these plants.

During the course of this 4-week on-site survey of European water treatment facilities, the site visit team observed a biological treatment technique in use in France, the Federal Republic of Germany and Switzerland that currently is not practiced in the United States. This technique involves the deliberate promotion of aerobic biological growths on filter media (sand, anthracite) and granular activated carbon media (columns or beds) for purposes of nitrification and of removing organic chemicals. The aerobic biological activity is enhanced by an oxidation step applied prior to activated carbon treatment. Such preoxidation steps frequently involve the addition of ozone.

Evidence obtained from numerous pilot plant studies and from several full-scale operating plants in Europe supported the claim that a properly designed and operated combination of ozone and granular activated carbon unit processes enhanced organic chemicals removal and reduced the frequency of regeneration of the activated carbon media.

Several offices of the U.S. Environmental Protection Agency provided additional funding to Public Technology, Incorporated in early 1978 to study this water treatment technique further. The interest of the Environmental Protection Agency in this advanced treatment technique was stimulated by the need to learn as much as possible about methods for controlling organic chemical contaminants in drinking water.

On February 9, 1978, the EPA proposed regulations dealing with the control of organic chemical contaminants in drinking water. The proposed regulations consisted of two major sections, the first of which would set a maximum contaminant level in finished water for trihalomethanes (THMs). The THM regulations since have promulgated by EPA in November 1979. The second section of the proposed regulations would require public water supply systems that serve more than 75,000 persons and that find substantial amounts of synthetic organic chemicals (SOCs) in their raw water supplies to use granular activated carbon (GAC), or an equally effective treatment technique, to reduce the concentrations of these SOCs in their finished waters.

One of the primary concerns of public water supply systems regarding the use of GAC, in addition to the high capital cost, is the relatively high cost associated with frequent regeneration. The EPA has proposed stringent performance criteria for the GAC systems. These may be modified as a result of comments received by EPA during the public comment period. However, they were objectives against which water treatment techniques could be gauged as being cost-effective during the term of this study. The performance criteria germane to this study as proposed by EPA on February 9, 1978 are as follows:

(1) The concentration in the GAC contactor effluent of any volatile halogenated organic compounds (except for trihalomethanes) determinable by the purge-and-trap/gas chromatography method shall not exceed 0.5 μg/l;

(2) The removal of influent total organic carbon with fresh granular activated carbon shall be at least 50%, and

(3) The total organic carbon content in the GAC contactor effluent may not exceed the value obtained with fresh granular activated carbon by more than 0.5 mg/l.

Depending upon the type and quantity of synthetic organic chemicals in the raw water supply of a public water treatment system, under these proposed performance criteria, a utility might be required to regenerate its activated carbon as frequently as 4 to 8 times per year. Experiences in European water treatment plants, operating under a different set of performance criteria for organics breakthrough, have demonstrated that systems using ozonation followed by granular activated carbon adsorption can have operational lives of their GAC media as long as 2 to 3 years before regeneration is required.

Some of these experiences were reported on briefly in the earlier EPA survey report (Miller et al., 1978). Additional details were required, however, to substantiate whether biological treatment in the form of ozonation followed by GAC is a viable method of enhancing treatment effectiveness while reducing operating costs. It has been found that BAC (Biologically Active Carbon) treatment processes have been incorporated into at least two European drinking water treatment plants primarily to remove ammonia biologically (actually to convert ammonia biologically to nitrate ion). This biological process thereby replaces breakpoint chlorination and eliminates the generation of chlorinated organic materials during early stages of the water treatment processes. It was desired to learn more about the benefits of substituting the BAC process for this purpose.

Therefore, this study was undertaken to acquire information on the following specific subject areas:

- determining design criteria used for ozone/GAC systems in Europe;
- determining mechanisms by which BAC systems operate;
- determining microbiological aspects of BAC systems;
- gathering field operational and cost data on ozone/GAC systems;
- quantification of technical and cost benefits of BAC systems;
- determining changes in U.S. treatment plant designs required for retrofitting ozone/GAC systems into existing plants.

After consulting with leading European water treatment authorities during early 1978, the PTI site visit team conducted visits to selected European facilities during June, 1978. The primary questions to be answered were:

(1) Is BAC effective for removal of organic chemicals, and if so, under what conditions?

(2) Is BAC an effective replacement process for ammonia removal by breakpoint chlorination and if so, under what conditions?

(3) How and why does the BAC process achieve its effectiveness?

(4) Is a preoxidation step necessary? If so, must the preoxidant always be ozone?

(5) Can the added capital and operating costs of an ozonation or other preoxidant system be offset by the increase in operating time before the GAC must be regenerated?

(6) Is BAC safe to use for drinking water treatment, from a bacteriological point of view?

(7) What pretreatment and post-treatment steps are made necessary when BAC is incorporated into a drinking water treatment system?

(8) Does biological regeneration of the GAC truly occur, and if so, to what extent?

Answers to some of these and other questions were obtained by conducting a 3-week site visitation of:

(1) operational drinking water treatment plants employing granular activated carbon facilities designed to promote biological growth,

(2) research institutes and universities conducting studies on the BAC process,

(3) activated carbon and ozone systems manufacturers in Western Europe during June, 1978, and

(4) by reviewing the published literature on the subject.

However, the scope of this study could not be confined to ozone/GAC treatment systems alone. Early in the study, it became apparent that Europeans employ many biological processes in the treatment of drinking water, and that biological activated carbon was simply a more advanced treatment system, which was based on earlier operating experiences with other biological processes applied to the treatment of drinking water supplies. Therefore, the scope of this study was extended to include discussion of other European biological drinking water treatment methods. Because of the complexity of the problems of organic chemicals removal however, our primary emphasis remained on ozone and granular activated carbon systems.

SITE VISITS

A complete listing of European facilities visited by the survey team is shown in Table 1. Pertinent findings from each plant visited are discussed in Section 9 and a thorough account of the plants visited is included in the Appendices.

Several industrial wastewater treatment facilities also were visited, primarily to learn if the BAC process was being applied to wastewaters, and if so, to what extent. If BAC was not being applied to the treatment of industrial wastewaters, why not and did the process hold any potential for industrial wastewaters in the United States? The potentials of biological activated carbon processes applied to industrial wastewaters are reported in a separate document which has been submitted for review to the EPA Industrial & Extractive Processes Division, Office of Environmental Engineering and Technology, Office of Research & Development (P.E. des Rosiers, Project Officer).

LITERATURE SEARCH AND REVIEW

A substantial number of papers were obtained from persons and institutions visited during the June, 1978 survey. In addition, two technical conferences, one dealing with Oxidation Techniques in Water Treatment, held in Karlsruhe, Federal Republic of Germany during September, 1978, and the other on Adsorption From the Aqueous Phase, part of the 176th Annual Meeting of the American Chemical Society held in Miami Beach, Florida, also in September, 1978, contributed several meaningful and timely papers. A search

TABLE 1. FACILITIES & ORGANIZATICNS VISITED, JUNE, 1978

Organization	Type	Location
la Chapelle Plant	Municipal Owned, Privately Operated Waterworks	Rouen, France
Morsang-sur-Seine	Privately Owned & Operated Waterworks	Villabé, France
Degrémont	Equipment Supplier	Reuil Malmaison, France
KIWA (Keuringsinstitut voor Waterleidingsbedrijven) (Testing & Research Inst. of The Netherlands Water Supply)	Research Institute	Rijswijk, The Netherlands
Rijksinstituut voor Drink-watervoorziening (National Institute for Water Supply)	Government Water Laboratory	Voorburg, The Netherlands
Kralingen Plant	Municipal Waterworks	Rotterdam, The Netherlands
KIWA/Rijksinstituut Water Reuse Facility	Pilot Plant Test Unit	Dordrecht, The Netherlands
Dohne Water Treatment Plant	Municipal Waterworks	Mülheim, Federal Republic of Germany
Holthausen Plant	Municipal Waterworks	Düsseldorf, Federal Republic of Germany
Flehe Plant	Municipal Waterworks	Düsseldorf, Federal Republic of Germany
Engler-Bunte Institut der Universität Karlsruhe	Research Inst.-University	Karlsruhe, Federal Republic of Germany
University of Saarlands	University	Homburg/Saar, Federal Republic of Germany
The Lurgi Group	Carbon Supplier	Frankfurt, Federal Republic of Germany
Hardhof Plant	Municipal Waterworks	Zürich, Switzerland
EAWAG (Eidgenössische Anstalt für Wasserversorgung Abwasserreinigung und Gewässerschutz (Swiss Federal Inst. for Water Resources & Water Pollution Control	Government Research Laboratory	Dübendorf, Switzerland

of the published literature yielded a significant number of papers by Weber, Packham, Rook, Eberhardt, Sontheimer, Benedek and others which are applicable to the subject. Results of this literature review are interwoven throughout this report.

SECTION 2

CONCLUSIONS

1) It is universally accepted that the provision of drinking water free from pathogenic microorganisms is the primary responsibility of a drinking water producer. Water supply utilities of the United States, in achieving this goal, have sought to preclude the growth of all types of microorganisms within the water treatment system. In other countries, many water utilities intentionally incorporate biological processes into their water treatment systems to reduce the levels of dissolved organics and still maintain strict pathogen-free qualities of the finished waters.

2) The treatment of drinking water by the application of biological processes is not new. Biological activity is one of the processes in the slow sand filter, which was a key treatment step of early water treatment facilities, but which is generally considered obsolete in contemporary U.S. practice. However, biological treatment, in many forms, is an important process in many European drinking water treatment systems. Examples of biological treatment of drinking water include the following:

- river sand bank filtration
- surface water storage
- gravity clarification
- coarse media biological reactors
- fluidized bed nitrification
- biologically active filter media
- biologically enhanced granular activated carbon (BAC)
- ground passage of treated water

3) The incorporation of biological treatment steps into water treatment processes offers the following prospective benefits in water treatment:

- reduction of the level of dissolved organic materials
- lower oxidant (chlorine, chlorine dioxide or ozone) demand
- reduced operational costs
- reduced bacterial regrowths in distribution systems.

4) Biologically enhanced granular activated carbon (BAC) can be defined as the sequential unit processes consisting of:

(a) oxygenation by aeration, oxygen injection or chemical oxidation,
(b) sand, anthracite or multi-media filtration,

(c) optional reoxygenation and
(d) granular activated carbon (GAC) adsorption.

This combination of processes, chemical oxidation, adsorption and biochemical oxidation is capable of removing ammonia and some (but not all) soluble organic substances from drinking water.

5) Dissolved organic materials in drinking water can be classified into four generalized categories as follows:

(a) biodegradable, adsorbable by GAC
(b) biodegradable, non-adsorbable by GAC
(c) non-biodegradable, adsorbable by GAC
(d) non-biodegradable, non-adsorbable by GAC

Although these are simplified generalities stated for the purpose of discussing treatment of dilute water streams, they provide a framework for postulating mechanisms by which biological activated carbon probably functions. Weber (1978b) points out that,

> "Bacteria, unless specifically controlled, will grow on virtually any surface, particularly those of fine grained media. The objective of biological treatment schemes to take advantage of this phenomenon should be to provide optimum conditions for growth".

6) Both the filtration media and GAC provide supports for the biomass which utilizes soluble organics and ammonia as substrates. The application of strong oxidants, such as ozone, to a raw water stream being treated can change the chemical nature of the dissolved organic materials. Strong oxidants can convert some (but not all) non-biodegradable materials into biodegradable materials. Biochemical decomposition of organic nutrients adsorbed by the high surface area in granular activated carbon appears to restore a portion of the sites to again become available for adsorption. Thus, one objective of preoxidation is to couple adsorption with biological degradation.

7) The porous structure of GAC presents an ideal medium for proliferation of attached biological growth (fixed film biological growth). Both biomass and substrate are retained by the large surface area of the GAC. A relatively low food/microorganism ratio can be maintained to be able to remove relatively low levels of dissolved organic materials.

8) Bacteria become attached to GAC media only on the outer surface and in the larger macropores near the outer surface which are sufficiently large to house them. As a result, only 1 to 2% of the total surface area available for adsorption of dissolved organics is utilized by the bacteria, and this amount of bacterial growth is not sufficient to interfere with normal adsorption processes.

9) Bacterial growths build up rapidly in granular activated carbon media. Those species which consume mainly carbonaceous organic materials attain their maximum concentrations within 24 to 48 hours after virgin or reactivated carbon is placed in service. Nitrogen-converting bacteria take longer to build up to their equilibrium concentrations (30 to 90 days), but low levels of ammonia are converted to nitrate within a few days of fresh or reactivated GAC being placed into service.

10) Operational water treatment plants utilizing biological activated carbon processes demonstrate that regeneration cycles of GAC adsorbers can be extended significantly if a large proportion of the soluble organics entering the GAC system are biodegradable and if essential conditions, such as minimum dissolved oxygen levels, are maintained. While no single BAC system design is as yet universally accepted, sufficient data exist from a number of plants, to enable the design engineer to commence to establish design criteria for BAC systems. It is clear that, under certain conditions, a design can be prepared to take advantage of extended GAC operational life by enhanced biological activity on both the filter media and on the GAC.

11) Several microbiological studies have demonstrated that the predominant microorganisms in the GAC media and in the water leaving the BAC system are typical, non-pathogenic, soil and water bacteria. It has been shown that pathogenic bacteria entering a properly designed and operated BAC system cannot compete with the predominant microorganisms present, and therefore the pathogenic species die off. Further study is required to confirm the absence of harmful endotoxins. It has been demonstrated that only low dosages of post-disinfectant are necessary to achieve the prerequisite levels of bacteriological quality of the treated water being discharged to the water distribution system.

12) Any decision to install GAC should not be made solely on the benefits which can be gained from BAC. Rather, the decision to utilize GAC to remove specific organic materials should be made first. Cnce the decision to install GAC has been taken, then careful consideration should be given to extending the operational lifetime and improving the overall organic removal process performance of the GAC by enhancing biological activity in this medium.

13) Reactivation criteria for BAC should be the same as those for GAC, and should be based upon the particular dissolved organic materials present in the raw water.

14) BAC will not provide any significant advantages over GAC when the dissolved organics to be removed are non-biodegradable and cannot be made biodegradable even by chemical oxidation with ozone. Exemplary materials of this type include many of the halogenated organic compounds produced upon prechlorination of raw waters.

15) BAC systems have replaced breakpoint chlorination processes in several new and older European drinking water treatment plants. This process change has provided the advantage of not producing halogenated organic materials

during the early stages of the drinking water treatment process (which, once synthesized, then are difficult to remove). In addition, replacement of prechlorination with BAC systems also has produced higher quality finished waters, with respect to dissolved organics, ammonia, lower turbidity levels and lowered post-disinfectant (chlorine, chlorine dioxide or ozone) demands.

16) Chemical preoxidation with ozone applied before sand, anthracite or dual media filtration units followed by GAC (BAC) adsorption in European water treatment plants has resulted in extending the times between backwashing in each medium by a factor of about 2.

17) One older European plant replaced breakpoint chlorination with BAC in 1977 at no increase in annual operating costs, including allowances for annualized capital costs.

18) In retrofitting BAC systems into existing drinking water treatment plants as post-adsorbers (after sand or other media filtration), provision should be made to incorporate air scouring into the backwash cycles of both the filtration and granular activated carbon media.

19) Biodegradable organic materials generally are polar and less tightly held by granular activated carbon upon adsorption. Non-biodegradable organics tend to be non-polar also, for example, many of the halogenated organic compounds produced upon prechlorination. Some of these non-polar, non-biodegradable organic materials can be adsorbed to a higher degree and be held more tightly by GAC. Because of these differences, some halogenated organic compounds are able to displace less strongly adsorbed, polar organic materials from GAC surfaces by the process of desorption. As a result, even though a biologically enhanced GAC adsorber may be operating at biological equilibrium and appears to be saturated with respect to adsorption of biodegradable organic materials, it still can be capable of adsorbing non-polar, non-biodegradable organics which may be present. In such instances, reactivation should be carried out only when the non-polar, non-biodegradable materials begin to break through the GAC medium.

20) A suggested screening test can be conducted to determine if a specific raw water supply will be benefitted by biologically enhancing GAC. The amount of biodegradation which can occur in the raw water can be determined, say by use of a Warburg respirometer. Next, another sample of the raw water can be ozonized with low utilized ozone dosages (1 to 10 mg/l), and the amount of biodegradable material now present is compared with that of the non-ozonized raw water. If oxidation of the organic materials present with ozone does not increase the rate of biological activity (the amount of biodegradable materials present), then it can be concluded that BAC will not show any advantages over GAC for that water supply. On the other hand, if the amount of biodegradable organic material present is increased by low level ozonation, then biological enhancement of GAC should provide performance advantages. The extent of such improvements must be determined for each raw water supply in order to assess whether these process improvements will justify the increased costs for chemical preoxidation, preoxygenation or preaeration.

21) For a hypothetical 50 mgd drinking water treatment which has installed GAC columns having empty bed contact times of 9 minutes and which must be reactivated every two months, it has been shown that if preoxidation with 2 mg/l of applied ozone dosage will extend the GAC reactivation time to six months, the costs associated with installing this amount of ozonation equipment are balanced by the savings in GAC regeneration costs. Further extension of the GAC reactivation time (to two and three years as currently occurs in some European drinking water treatment plants using BAC processes) will provide additional operating cost savings.

SECTION 3

RECOMMENDATIONS

1. Investigate the applicability of various biological water treatment processes for treatment of drinking water. This would include the use of granular activated carbon, but also other adsorptive or inert media. Such studies should be conducted on systems not using initial breakpoint chlorination and, ideally, on systems using no prechlorination at all. Examples of typical treatment systems to be tested are given in Figure 1.

2. Confirm the non-pathogenic nature of bacteria in biologically active GAC media and in the effluents from such media.

3. Identify the endotoxins produced by these microorganisms and determine their toxicological significance.

4. Conduct studies to confirm the nature of the operative mechanisms occurring with BAC, i.e., adsorption/desorption versus apparent biological regeneration.

5. Obtain more detailed operating information at selected European plants, including the Rouen, Dohne, Düsseldorf, Rotterdam and Schierstein plants. Such information would include characteristics of influent and BAC media effluents with respect to TOC, COD, DOC, UV absorption, TOCl, ammonia, etc. Determine the specific parameters used at each operating plant to ascertain when the BAC must be reactivated.

6. Determine the operational costs and treatment consequences of doing away with prechlorination in drinking water treatment plants. For example, modification of filter bottoms to allow air scouring and the necessity for more frequent backwashing. Operate prototype U.S. plants in both modes (chlorination versus preoxidation by other means) over a (minimum) one year cycle.

7. Screen a variety of raw water sources to determine the applicability of biological treatment processes. Categorize raw waters according to the biodegradability of their organic components before and after preoxidation.

8. Evaluate European water treatment operating practices with particular emphasis on GAC used without preoxidation.

9. Demonstrate biological processes for nitrification of ammonia as possible replacements for breakpoint chlorination.

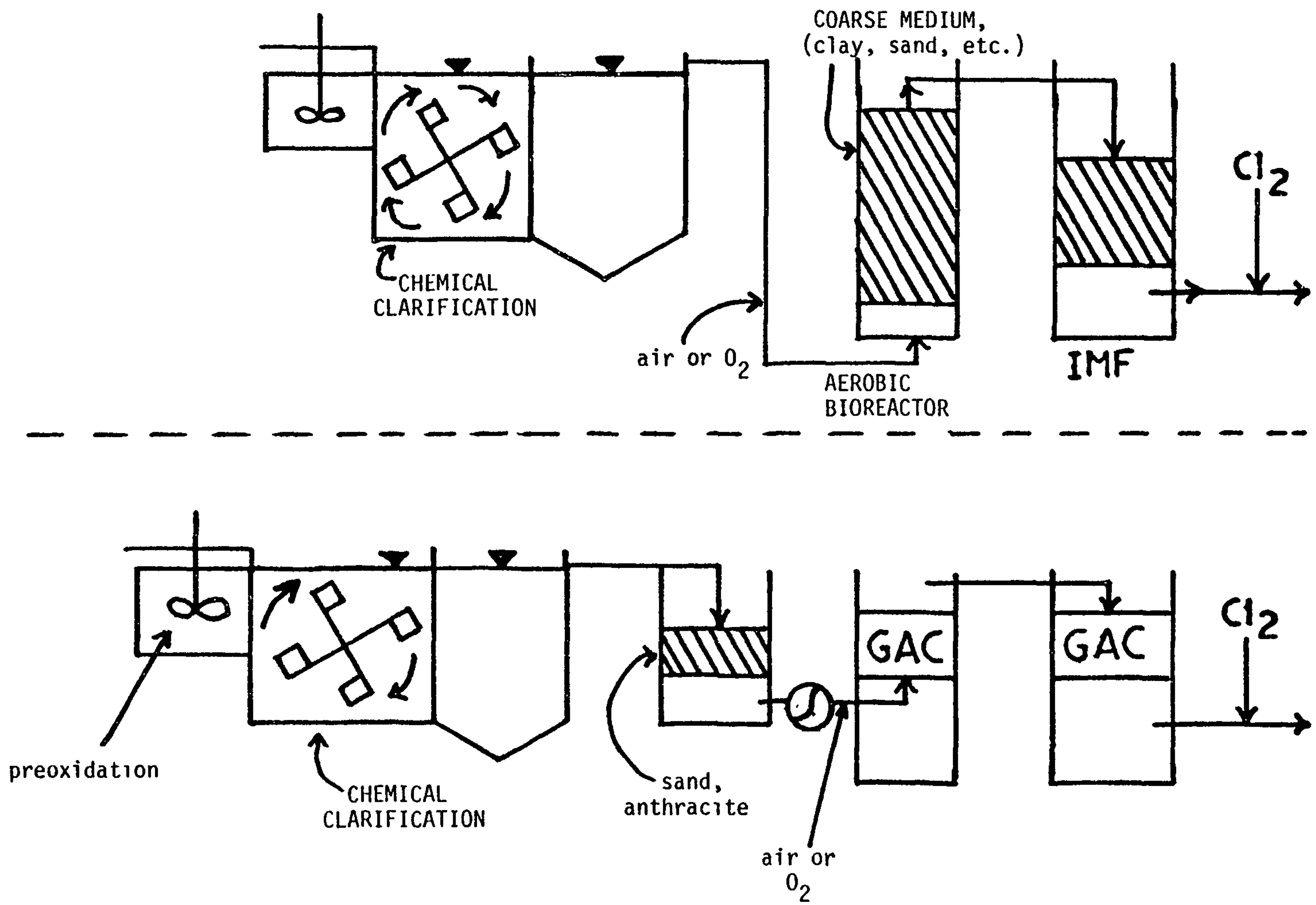


Figure 1. Examples of typical systems to be investigated

10. Study use of oxidants other than ozone for the preoxidation step. Candidate oxidants other than ozone include H_2O_2, $KMnO_4$, UV (plus air or oxygen), ClO_2 (free of excess chlorine) and $ClNH_2$ (free of excess chlorine).

11. Study parameters affecting bacterial breakthrough in biologically enhanced GAC adsorbers, such as has been reported in studies conducted at the Schierstein, Federal Republic of Germany drinking water treatment plant after three years of use. It is possible that a bacterial monitoring parameter should be considered for BAC systems.

SECTION 4

EVOLUTION OF DRINKING WATER TREATMENT PROCESSES

EARLY METHODS OF TREATING WATER

The treatment of water for potable purposes has been conducted in a variety of manners during the history of mankind. Early practitioners believed that filtration of seawater through sand would purify it sufficiently for drinking. Others prescribed the settling of water in copper containers. Still other methods called for exposure of water to sunlight and, interestingly, filtration through charcoal (Baker, 1949).

Throughout the centuries, however, techniques used for purifying drinking water began to evolve a common treatment theme. The initial methods used were physical in nature -- first sedimentation and later various filtration methods. Coagulation by chemical addition was used in ancient Egypt, China and India, but was not practiced widely until the first third of the 19th century. Alum and other chemicals for coagulation were first used in the United States around 1885 and became accepted practice in the early 1900s.

Likewise, the use of certain types of chemicals for disinfection has been practiced for a long time. Early attempts at disinfecting were by boiling. Chlorine was first used in the United States in 1908 in a large scale water works at the Boonton Reservoir of the Jersey City, New Jersey Water Works.

The use of bacterial action for purifying water is not considered in the classic U.S. texts on water treatment, although it is common knowledge that bacteria present in surface waters are the key actors in purifying those waters naturally through stabilization or decomposition of organic materials.

Infiltration of polluted surface waters through a soil mantle constitutes an efficient combination of biological and physical treatment processes which results in purified groundwaters. Infiltration occurs in two phases: first, infiltration through the air-saturated (aerobic) zone, then through an air-deficient (anaerobic) zone. Organics removal occurs mainly in the unsaturated zone.

The upper layers of soil constitute effective biological filters. Evidence indicates that microbial action for purposes of stabilizing organic materials does not usually exceed 3 meters of soil depth. This is because most types of bacteria cannot survive in the highly competitive environment (Hutchinson & Ridgeway, 1977). In the saturated zone, pollutant removal is limited to adsorption. Some microorganisms may be present, but are carried passively by the flow. Horizontal microbiological penetration through soils can be as much as 30 meters (Romero, 1970).

Biological treatment of wastewater, either through the classical trickling filter method or by the more recent activated sludge process, has been practiced successfully for more than half a century. The so-called "trickling filter" process was developed in England and was first installed there in 1893. In this process, biological processes are promoted on the surface of the very coarse media which also provide a small degree of filtration.

The activated sludge process also was developed in England (1914) and was so named because it involved the production of an activated mass of microorganisms capable of aerobically stabilizing a waste stream (Metcalf & Eddy, Inc., 1972). The trickling filter process, also developed in England, is a combination of physical (filtration) and biological processes. The first trickling filter was installed and operated in England in 1893.

Several other methods of purifying drinking water have been applied with varying degrees of success over the past century. Physical methods (such as microstraining) are used successfully in England and the Federal Republic of Germany. Ozone, although rarely used in the U.S.A., is now used in at least 1,039 drinking water treatment plants throughout the world, as of 1977 (Miller et al., 1978). Many other oxidants also are used; these include chlorine dioxide, chlorine and potassium permanganate.

COMBINATIONS OF PHYSICAL, CHEMICAL AND BIOLOGICAL PROCESSES

Twentieth century processes for treating water for potable purposes have changed appreciably in some respects, but not in others. The methods that have evolved over the years are either physical, chemical or biological in nature. As noted, early methods were mainly physical in nature. Chemical methods came to be practiced much later on. Today, faced with ever increasing population growth, man-made pollution and rising costs of service delivery, biological treatment processes coupled with physical and chemical methods are being restudied and employed because of their efficiencies and their relatively low costs.

In describing water treatment developments in Europe, Rook (1976) noted that "national differences have led to a number of (treatment) schools: the English school practices purely biological treatment; the French school adheres to flocculation, often induced by pulsation, with ozone used as a disinfectant and color oxidant; many German water engineers swear by the wholesomeness of groundwater, to such an extent that in some instances fully chemically treated river water is used for artificial replenishment of groundwater".

This report will focus on biological water treatment processes, primarily on those occurring in granular activated carbon contactors or adsorbers enhanced by a preoxidation step. Before introducing the concept of treating drinking water biologically, it will be useful to review the purposes for treating drinking water.

OBJECTIVES OF DRINKING WATER TREATMENT

The ultimate objective of water treatment is to provide a palatable, safe supply of water to the public at minimum cost. Water must be treated in many cases because (1) groundwater supplies may contain high levels of dissolved solids, minerals or undesireable contaminants or (2) surface waters have become polluted by urban and agricultural runoff, industrial discharges and/or municipal wastewater treatment plant discharges. Specific objectives of water treatment are to reduce levels of turbidity to acceptable levels and to ensure removal of chemical, microbiological and viral contaminants. These objectives are attained by subjecting the raw water to a series of unit treatment processes.

Various combinations of physical, chemical and biological treatment processes have been developed and are practiced widely in Europe. To illustrate some of these treatment process combinations, several simplified process flow diagrams of processes being practiced during 1978 at selected European drinking water treatment plants are presented in Figures 2 through 8.

Each of these plant processes represents a different approach to drinking water treatment and includes at least one biological treatment step. The specific process chosen depends upon (1) local conditions, (2) the raw water source, (3) plant resources available, (4) local philosophy of water treatment and (5) standards for finished water quality in the respective countries. Yet each process is made up of a combination of physical, chemical and biological steps. The physical and chemical unit processes are readily recognized, but the biological process steps require identification.

River sand bank filtration at the Düsseldorf, Federal Republic of Germany, plants removes 60 to 75% of the TOC and some ammonia during ground passage, which requires about three weeks. (River sand bank filtration is required at all German plants using the lower Rhine as a raw water source.) Most of this removal occurs biologically. Additional biology in the granular activated carbon columns contributes to organics removal and ammonia conversion.

In the la Chapelle plant at Rouen, France, most of the conversion of ammonia occurs in the 100 cm deep sand filters placed after preozonation. Most of the biological degradation of dissolved organic chemicals takes place in the 75 cm deep granular activated carbon beds. That these organic materials are biodegradable at Rouen is evidenced by the lack of need to reactivate the GAC after nearly three years of use.

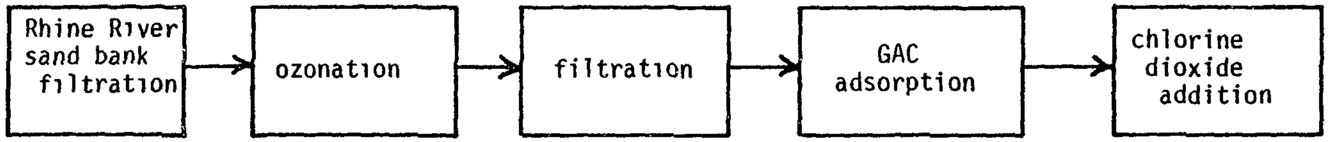


Figure 2. The Düsseldorf Process, Düsseldorf, Federal Republic of Germany

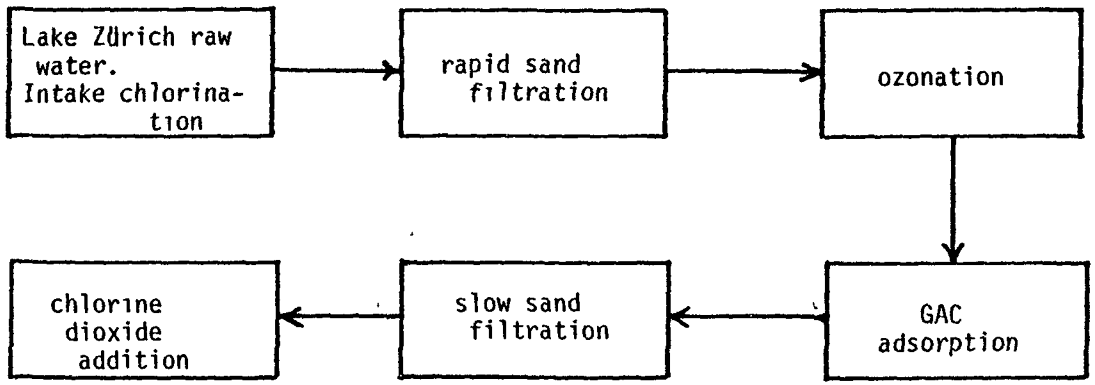


Figure 3. The Lengg Plant, Zürich, Switzerland

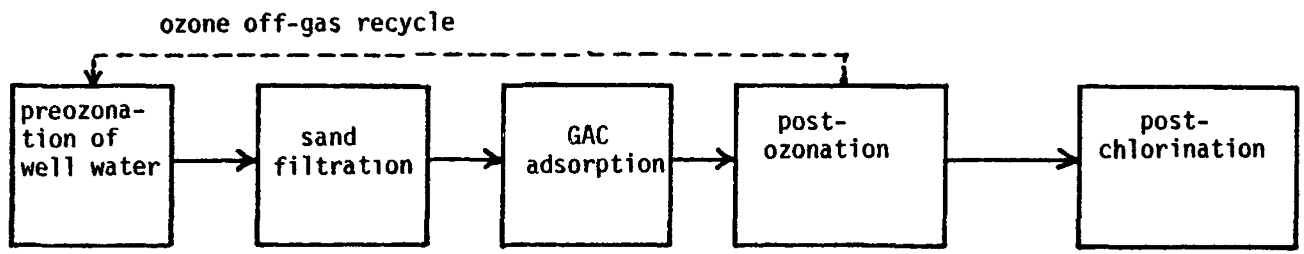


Figure 4. The Rouen-la-Chapelle Process, Rouen, France

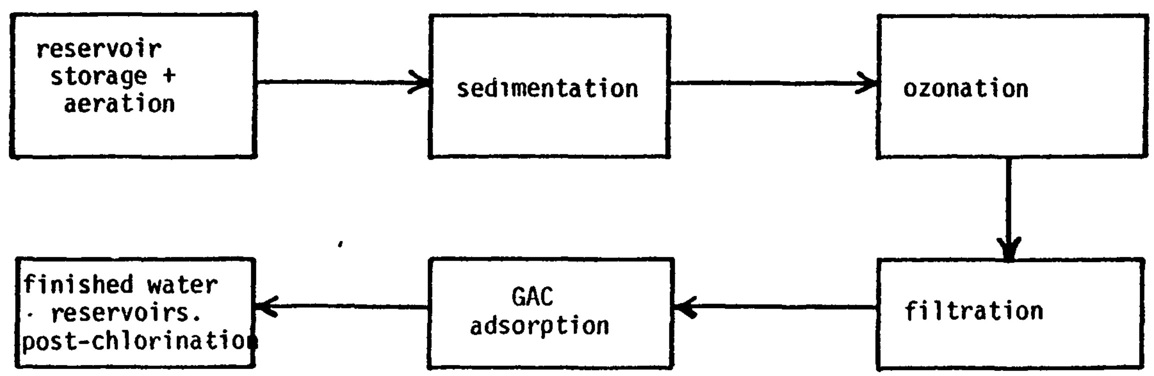


Figure 5. The Kralingen Process, Rotterdam, The Netherlands

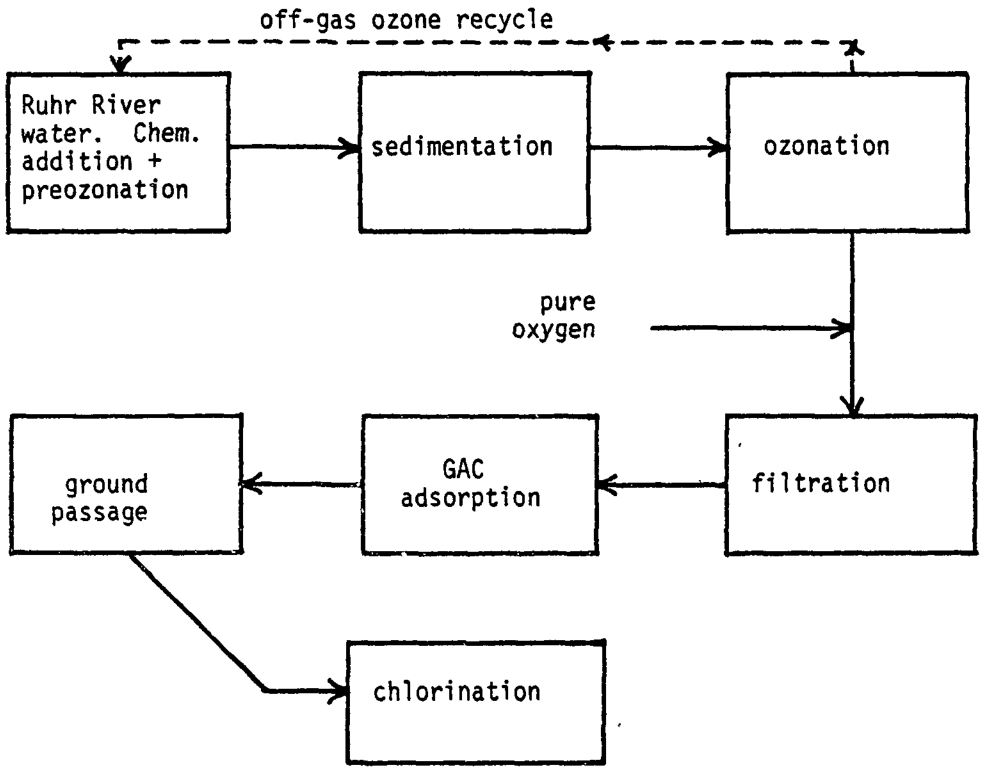


Figure 6. The Bohne Process, Mülheim, Federal Republic of Germany

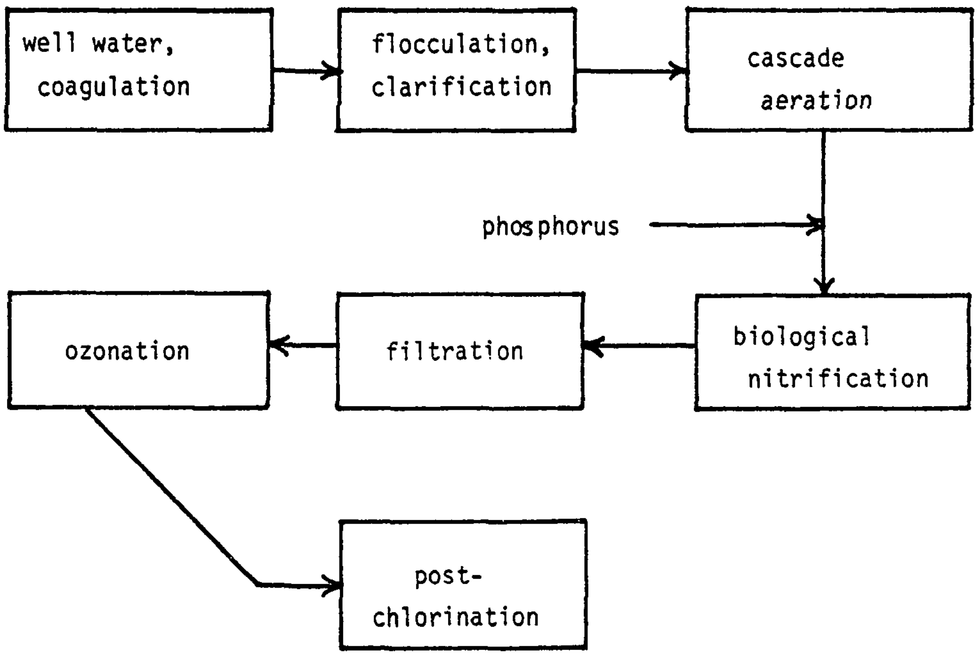


Figure 7. The Aubergenville Process, Aubergenville, France.

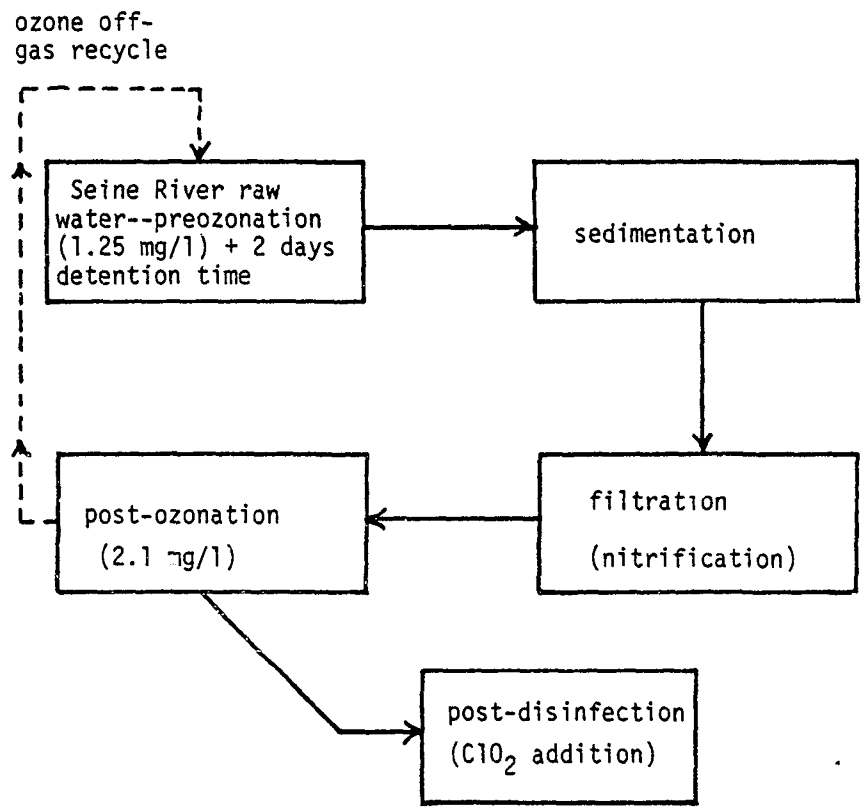


Figure 8. The Choisy-le-Roi Process, Paris, France suburbs. Preozonation and detention reservoir under construction for 1980.

At the Dohne plant in Mülheim, Federal Republic of Germany, most of the ammonia conversion occurs in the sand filters, after ozonation and after addition of pure oxygen. Biological degradation of organics then occurs in the GAC columns. The 4 meter deep GAC adsorbers have not required reactivation during the first year of use, and plant management does not plan to reactivate the GAC there for at least two years of use. This decision is based upon results of a detailed pilot plant study using the BAC process.

Before entering the Kralingen plant in Rotterdam, The Netherlands, biological activity in the raw water is promoted by aeration of one of the two raw water storage reservoirs during an average retention time of 3 months. Aeration also prevents stratification in this reservoir. During this time, levels of ammonia and TOC are lowered as a result of nitrification and biodegradation, respectively. Additional biological activity is present in the sand filters and GAC contactors of the plant itself.

In the Lengg plant in Zürich, Switzerland, some biological degradation is known to take place both in the granular activated carbon adsorbers and in the following slow sand filters. However, the raw water supply from the Lake of Zürich is of very high quality (less than 2 mg/l TOC), and the resulting nutrient accumulation in the GAC and sand media is insufficient to sustain high levels of bacterial proliferation.

At the Aubergenville plant, located downstream of Paris on the Seine River, well water is treated by chemical clarification, cascade aeration, phosphorus addition, biological nitrification, ozonation and post-chlorination. This specific process sequence has been used since 1969, although the biological nitrification step was used when the plant was constructed in 1961.

Finally, recent pilot plant studies at the Choisy-le-Roi plant on the Seine River in the Paris, France suburbs has been conducted on ozonation of raw Seine River water, followed by chemical addition and two day detention before introduction into the treatment plant itself (Gerval, 1978, 1979). This new technique has replaced breakpoint chlorination followed by dechlorination by sodium bisulfite. This modified process has produced significant savings because of biological action and is being added to the full-scale plant treatment process (Schulhof, 1980). Biological nitrification now occurs in the rapid sand filters.

In the detention tank before entering the plant, ammonia and TOC levels are lowered biologically. After subsequent processing, the post-ozonation step now requires about half the ozone dosage that was required without preozonation. Overall, the total amount of ozone now used in pre- and post-ozonation at Choisy has been reduced by 25% to 33%. Furthermore, the product water now contains less TOC and the chlorine dioxide post-disinfectant demand also is lowered.

This recent process modification at the Choisy-le-Roi plant was based on everal years of successful operation at the East Moscow, Russia water treatment plant, constructed by the French Compagnie Générale des Eaux (Schulhof, 1979).

A more recent program to upgrade the three large water treatment plants in the Paris suburbs has been presented by Schulhof (1980). At each plant, plans have been made and construction has been initiated to install triple-stage ozonation and biologically enhanced sand filters and GAC adsorbers. Raw river water will be treated with low levels of ozone (less than 1 mg/l) and the ozonized water allowed to stand in storage 2 to 3 days, during which time some settling and biological degradation will occur.

A second ozonation (0.5 to 0.8 mg/l dosage) will follow, then chemical treatment (aluminum polychloride, powdered activated carbon), flocculation/-sedimentation, then sand filtration. Most of the nitrification of ammonia will occur in these sand filters. The third stage of ozonation will be next, for disinfection, followed by GAC adsorption. Finally, chlorination (0.2 to 0.3 mg/l residual) will be provided prior to distribution. A schematic diagram of this treatment process is shown in Figure 9. Notice that chlorine is added only after the maximum amount of dissolved organics have been removed. This treatment approach will minimize the amount of chlorinated organics which will form in the treated water.

REMOVAL OF ORGANIC CHEMICALS THROUGH BIOLOGICAL TREATMENT

Introduction

From the time when municipal water supplies first became a reality for mankind until the early 1900s when chlorine was first used as a water disinfectant, primary emphasis has been placed on finding treatment methods to prevent outbreaks of diseases such as cholera, dysentery and typhoid fever, all of which are waterborne diseases. Chlorination, along with improved methods of filtration, sedimentation and coagulation, served to reduce the risk of transmission of these diseases by bacteria present in the finished water supplies to the point that the problem today is almost non-existent in the U.S.A. and other developed countries.

During the 1970s, however, a new problem has been presented to water treatment scientists and practitioners. This is the problem of potentially hazardous organic chemicals in finished drinking water supplies. Some of the more than 700 organic chemicals identified to date in raw or treated water supplies are known or suspected carcinogens to animals or humans. The precise threshold levels at which they may be carcinogenic to humans currently are unknown. In order to reduce the potential risk to the general populace and to protect the public health, the water supply industry must address itself to this new problem. The U.S. Environmental Protection Agency has been studying treatment techniques for removal of these types of organic chemicals for several years.

The majority of these potentially harmful organic chemicals are a result of industrialization. More than 4,000,000 different organic chemicals are now in existence, more than double the number which existed only a decade ago. They find their way into raw water supplies in numerous ways --

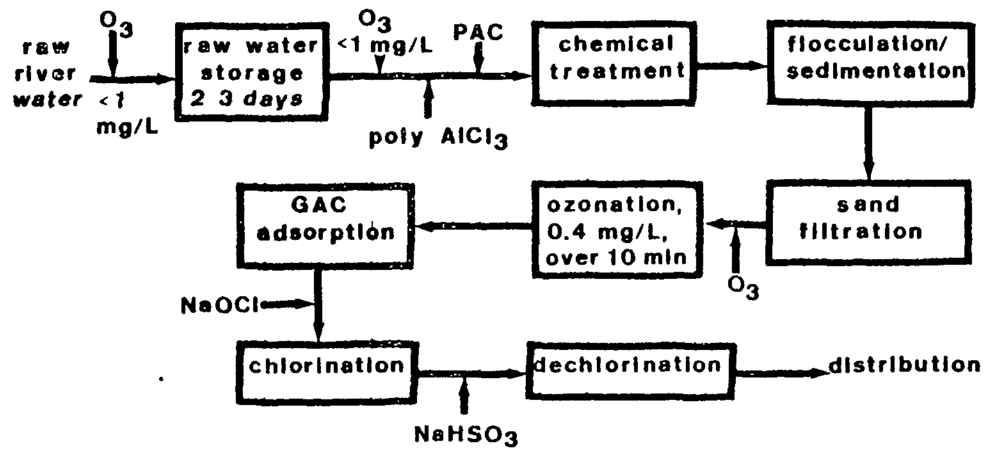


Figure 9. Treatment process ultimately planned for 3 Paris suburbs plants.

(Schulhof, 1980)

through industrial discharges, urban and agricultural runoff and by accidental spills during transportation from one part of the country to another.

The so-called "conventional" water treatment process that has served the U.S. water treatment industry in such good stead for several decades now is being recognized as inadequate for removal of most of these man-made organic chemicals. Many European countries, with no strongly unified continent-wide control legislation to protect surface water supplies from industrial contamination, have been forced to investigate and put into practice what to United States specialists are viewed as advanced drinking water treatment techniques. Many of these techniques are quite expensive, especially in first-time capital cost. As a result, the Europeans have sought to offset the expenses associated with the use of ozonation, granular activated carbon and other high cost techniques by exploiting biological treatment processes. Such processes sometimes are viewed in the U.S.A. as involving risks of biological contamination of the processed waters. Nevertheless, they are being utilized on full-scale in many European drinking water treatment plants, where they offer substantial treatment benefits. When properly designed and controlled, biological processes, as they are being practiced in European water treatment plants appear to entail few, if any, public health risks. The remainder of this report will be devoted to discussion of the use of these biological water treatment processes.

Contrasting Water Treatment Philosophies - USA & Western Europe

European water treatment philosophies and practices are somewhat different from those in the U.S.A. The Europeans appear to adopt more of a systems approach to water treatment. This means that they determine the raw water quality, define the qualities and characteristics that the finished water should possess and then design a new treatment plant or upgrade an existing plant process to achieve that quality goal.

In the United States, an inordinate amount of emphasis and faith has been placed on a "conventional" treatment and, until recent years, there has been little concern as to the chemical qualities of finished drinking waters. American water treatment practitioners traditionally have been more concerned with bacteriological quality of drinking water than with chemical quality, and they have used the amount of chlorine necessary to ensure (presumably) achievement of that bacteriological quality without concern for the chemical quality side effects that decision entailed.

Europeans cannot understand the American obsession for using large amounts of chlorine nor why Americans eschew the use of biological processing steps in drinking water treatment. On the other hand, American water treatment officials believe that European systems are too costly and they are concerned about the deliberate promotion of bacterial growths as part(s) of the water treatment process.

The major differences in approaches to water treatment appear to be two in number:

(1) The Europeans, especially the Dutch and Germans, do not like to add chemicals to water, preferring physical and biological methods, unless chemical use is absolutely necessary;

(2) The Europeans are not concerned with "a few bacteria" in the water (as long as they are non-pathogenic in nature), believing that chemical safety is more important than protection against non-pathogenic bacteria.

According to Prof. Dr. Heinrich Sontheimer of the Engler-Bunte Institute of the University of Karlsruhe, Federal Republic of Germany, American and European water treatment practices were quite similar until a few years ago when it was discovered that breakpoint chlorination causes potentially harmful halogenated organic compounds to be produced. As a result, the Germans began to study treatment techniques that could replace breakpoint chlorination. One of the techniques studied, and which now is being used on full scale, involves a biological treatment step, which can occur on the surface of sand filters, on the surfaces of anthracite or hydroanthracite media and on the surface and in the macropores of granular activated carbon adsorbers.

Prof. Sontheimer cautions that biological processes should be taken to completion in the water treatment plant (i.e., all of the biodegradable materials should be allowed to biodegrade in the water treatment plant filters and adsorbers), otherwise biogrowths can occur in the distribution systems, unless larger than desired amounts of residual disinfectants (chlorine, chlorine dioxide or chloramines) are applied. Thus, biological activated carbon and other biological treatment steps were tried initially because the Germans were studying the use of biological treatment processes to substitute for chemical addition, specifically prechlorination.

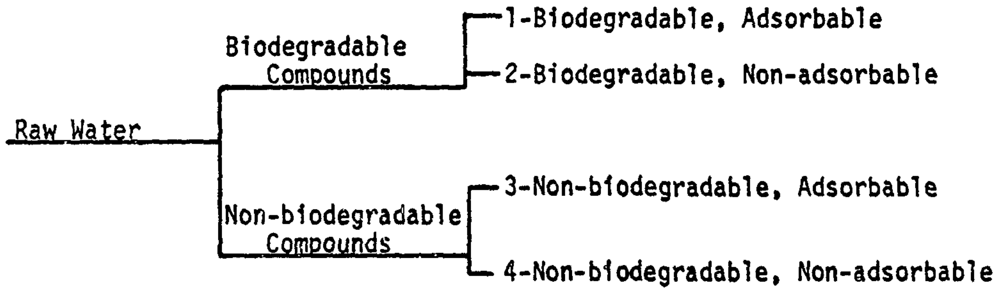
It should not be inferred from the above discussion that European technology has been far in advance over that of the United States regarding the use of biological processes in water treatment. References to current European drinking water literature (Water Research Center, 1977) indicate that there is no widespread consideration of biological processes as being commonly used continent-wide. However, "ammonia removal using biological practices is practiced on a limited scale in France, Germany and the United Kingdom" (Water Research Center, 1977). It would appear, therefore, that should the United States water treatment industry seriously consider the use of biological treatment processes in drinking water treatment, we would not be far behind the European level of knowledge on the subject.

Treating A Dilute Water Stream

The use of microorganisms, particularly bacteria, to treat water can require adaptation of some of the techniques utilized in wastewater treatment. Raw water supplies normally are far purer than is the average treated wastewater. Therefore, the pollutants present in raw drinking water normally will be present in far more dilute concentrations than those present in wastewaters. However, the same basic mechanisms apply to biological oxidations conducted in either medium, including nitrification and denitrification. Basic sanitary engineering textbooks (Metcalf & Eddy, 1972; Water Pollution Control Federation, 1977) include discussions of biological processes which may be used as reference materials as long as the reader remembers the vast difference in quality between raw drinking water and raw wastewaters.

Secondary treated municipal wastewater effluents in the United States normally contain 10 to 30 mg/l of BOD_5 and a similar concentration of suspended solids. Tertiary treatment can reduce these concentrations to less than 10 mg/l. Raw water supplies, even when obtained from polluted surface water sources, usually contain a lesser concentration of biodegradable organic substances than do secondary treated wastewaters. Thus, when one attempts to apply biological wastewater treatment process theories to drinking water treatment, the relatively low concentration of dissolved organics must be taken into account, as well as a relative level of biodegradability.

Consider a dilute water or wastewater stream containing 10 mg/l or less of total organic carbon (TOC). The organic portion of this water stream can be divided, theoretically, into four fractions as follows:



If a substantial portion of the raw water stream consists of organics which fall into Fractions 1 or 2, the potential exists for biodegradation to occur, either in a sand, anthracite or hydroanthracite filter, or in a granular activated carbon adsorber, without necessarily requiring preoxidation.

The biological oxidation potential of the raw water constituents, particularly those of the type of Fraction 3, may be increased further by subjecting the water stream to preoxidation. By oxidizing the components of Fraction 3 with ozone, for example, high molecular weight organic molecules that normally are not readily biodegradable can be converted into smaller, lower molecular weight organic molecules which now contain more oxygen than did the original organic materials and which are now more readily biodegraded.

In a water treatment process such as that shown in simplified form in Figure 10, the use of ozone followed by filtration then granular activated carbon adsorption should be effective if biodegradable components of the types comprising Fractions 1 and 2 are relatively low in concentration and the types comprising Fraction 3 are high in concentration. Using the same reasoning, if the stream to be treated consists mainly of biodegradable organic compounds, neither ozonation nor granular activated carbon may be

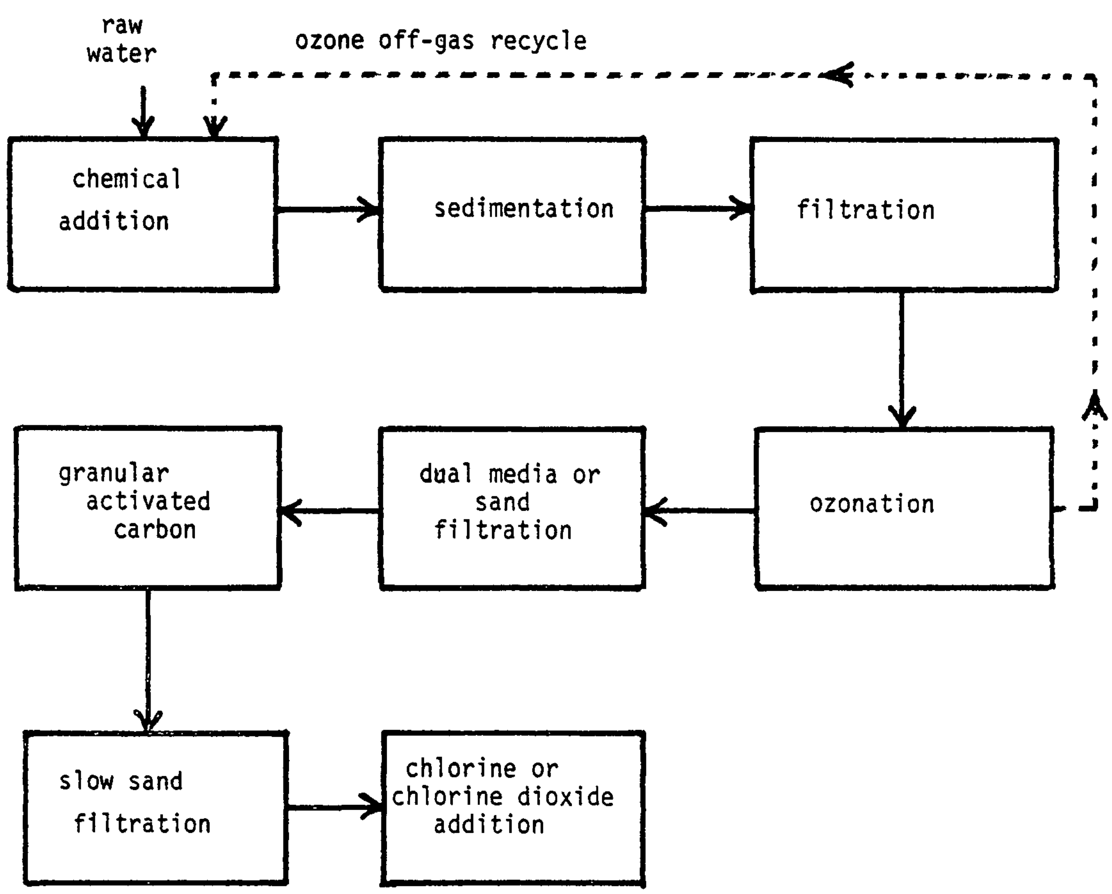


Figure 10. Suggested treatment process for raw waters containing initially non-biodegradable organic materials.

required. Slow sand filtration alone may remove a substantial portion of Fraction 1 and Fraction 2 materials biologically.

According to Sontheimer (1978), two general conditions must exist in order for significant biological activity to occur in granular activated carbon media. First, the dissolved organic materials present must be adsorbable by the carbon; second, they must be of such a molecular nature that they can be biodegraded at or near the activated carbon surface.

There are substances that fall into neither of these categories, and these will pass through carbon adsorbers and other biologically active media without being adsorbed and without being biodegraded (Fraction 4).

One should be cognizant of the fact that segregation of the organic components of a dilute stream into these four fractions is merely a convenient way of developing a useful hypothesis of the biological and adsorptive removal of organic chemicals from solution. A number of caveatemptors should be mentioned, however, in order to alert the reader to potential pitfalls that may be encountered during actual drinking water treatment practice:

(1) In general, the more biodegradable an organic compound is, the less adsorbable (by GAC) it is. This is due to its increased polarity as a result of containing more oxygen atoms. On the other hand, the less polar an organic compound is (the more non-polar the compound) the more adsorbable (by GAC) it will be. The converse also is true: the more polar a compound is, the less readily adsorbed by GAC the compound will be.

    Thus, when ozone oxidizes the readily adsorbed, non-polar organic compounds, this will result in more polar, more biodegradable, but less easily adsorbable compounds being formed.

(2) According to several prominent European water treatment scientists who have studied the use of ozone for many years, ozonation should be followed by either coagulation/filtration or an adsorption step. In quantities normally used in treating drinking water (1 to 5 mg/l), ozone will rarely oxidize organic materials completely to carbon dioxide and water. Reduction in concentrations of TOC due to ozonation alone is very modest in Maas River water (Rook, 1972).

    Therefore, one of the primary disadvantages of chemical oxidation techniques for organics removal is that oxidation often results merely in chemical changes in the chemical structures of organic compounds present, but it does not, in general, result in their total removal. Non-biodegradable organics may be converted to biodegradable compounds. This results in a lower COD concentration, but in a commensurate increase in BOD_5. Therefore, a biological or adsorption step becomes necessary to effect BOD_5 removal (Gauntlett & Packham, 1973a, 1973b).

(3) When biological action is promoted in carbon adsorbers by preoxidation, chlorine should not be used in breakpoint quantities as a predisinfecting or preoxidizing agent. The use of chlorine results in some strains of bacteria being destroyed and promotes competition among surviving types. There is also evidence to show that bacterial concentrations are much higher in solutions leaving activated carbon columns than in the influent solutions, even when high levels of chlorine are applied (Hutchinson & Ridgeway, 1977). In addition, the surviving bacteria now are so resistant to chlorine that they may persist throughout the distribution system.

(4) Sontheimer (1978) notes that the biological treatment step should be carried to completion, i.e., all of the biodegradable material should be completely converted to CO_2 and water. Otherwise, biodegradable organic materials will remain that could continue to provide food for bacteria in the distribution system.

(5) One of the concerns regarding the use of a biological treatment step, for example, granular activated carbon preceeded by ozonation, is that bacteria will slough off the carbon column and be present in the column filtrates. However, frequent backwashing, properly sizing the depth of the activated carbon and controlling bacterial growth rate kinetics appear to be adequate mechanisms for prevention of bacterial "slough off". With regard to this latter condition, Characklis (1973) states that the growth rate of slime-forming bacteria becomes limited when the attaching surface becomes completely covered with a single layer of cells. At this point the rate of increase in mass of organisms shifts from logarithmic to linear.

GAC Adsorption Preceeded By Ozonation As An Organics Removal Technique

After years of research, the U.S. Environmental Protection Agency's Water Supply Research Laboratory in Cincinnati has concluded that granular activated carbon adsorption is the most effective technique currently available for broad range removal of organic chemicals from drinking water (Symons, 1978). The primary concern regarding GAC is its high cost, both in terms of capital costs and the recurring cost of frequent regeneration of the carbon. Research conducted at the Düsseldorf, Federal Republic of Germany, city waterworks has shown that organics removal, when ozonation is applied prior to GAC filters, is greater than the amount of removal that could be attributed to that of GAC and ozonation acting independently (Hopf, 1960). Thus it was concluded that a synergistic effect must exist. After further investigation at Düsseldorf, Bremen and Mülheim in subsequent years, it has been concluded that additional organics removal is the result of biological activity in the carbon columns.

In European pilot studies and in drinking water treatment plants it has been shown by many workers (Scheidtmann, 1975; Schalekamp, 1975; Van Lier et al., 1975; Sontheimer, 1975; Eberhardt, 1975; Van der Kooij, 1975; Kühn, Sontheimer & Kurz, 1978; Gomella & Versanne, 1977; Sontheimer et al., 1978) that preozonation followed by activated carbon adsorption results in:

- Increased capacity of the carbon to remove organics (by a factor of about 10),
- Increased operating life of the carbon columns before having to be regenerated (up to 3 years), especially if the GAC can be kept free of halogenated organics,
- Biological oxidation of ammonia in inert media and GAC columns, which occurs simultaneously with removal of dissolved organics,
- Use of less ozone or less GAC for removing a given amount of organics than using either process alone (BAC can be cost-effective over ozonation or GAC in removing Dissolved Organic Carbon - DOC).

Independent studies on physical/chemical treated sewage at the Cleveland Regional Sewer District (Guirguis et al., 1976a,b,c,d; 1978) and in Israel (Wachs et al., 1977), have confirmed these advantages with respect to removing organic materials.

The terminology, Biological Activated Carbon has been applied by Rice et al. (1977, 1978) and Miller et al. (1978) to the combination of treatment processes consisting of (1) ozonation followed by (2) filtration through an inert medium, such as sand or anthracite, followed by (3) adsorption in Granular Activated Carbon columns or beds. However, chemical oxidants other than ozone, and sometimes simply aeration, can be used in step (1). A reoxygenation step may be desirable before passage of the water through GAC, in order to maintain high levels of dissolved oxygen. This is because biological activity in the inert medium also results in conversion of dissolved organic carbon to CO_2 and of ammonia to nitrate, and the DO content of the inlet water is lowered correspondingly. Figure 11 shows a schematic of the BAC subsystem. Figure 12 expands upon the subsystem shown in Figure 11.

Granular activated carbon and the preceding inert filter media (sand, anthracite, etc.) are made biologically active by the deliberate introduction of sufficient dissolved oxygen (DO) to aqueous streams just before they are passed through the filter media or GAC columns or beds. As long as the influent water contains sufficient DO to maintain aerobicity of the bacteria and sufficient dissolved organic carbon to provide food, the aerobic bacteria will thrive in this environment. Eberhardt (1975) has likened bacterial activity in such an ideal environment to a "herd of cows grazing in a luscious meadow".

In Section 9 the available information on the performances, mechanisms of action and technological benefits are discussed. Costs aspects are discussed in Section 11 and in Section 12, design considerations are discussed which must be considered when installing biological treatment processes, as practiced in Europe, into United States water treatment plants.

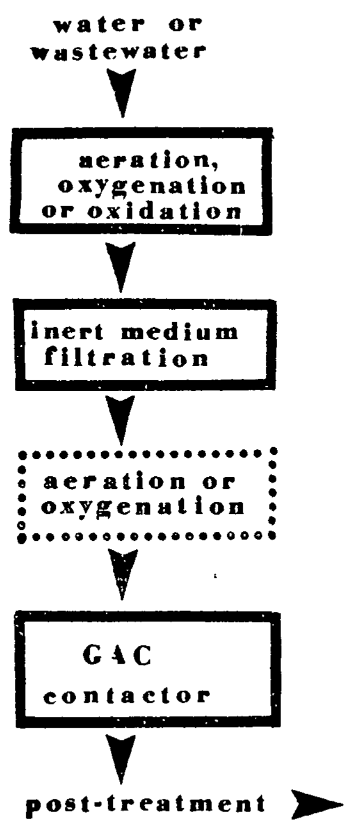


Figure 11. Block diagram of the Biological Activated Carbon process.

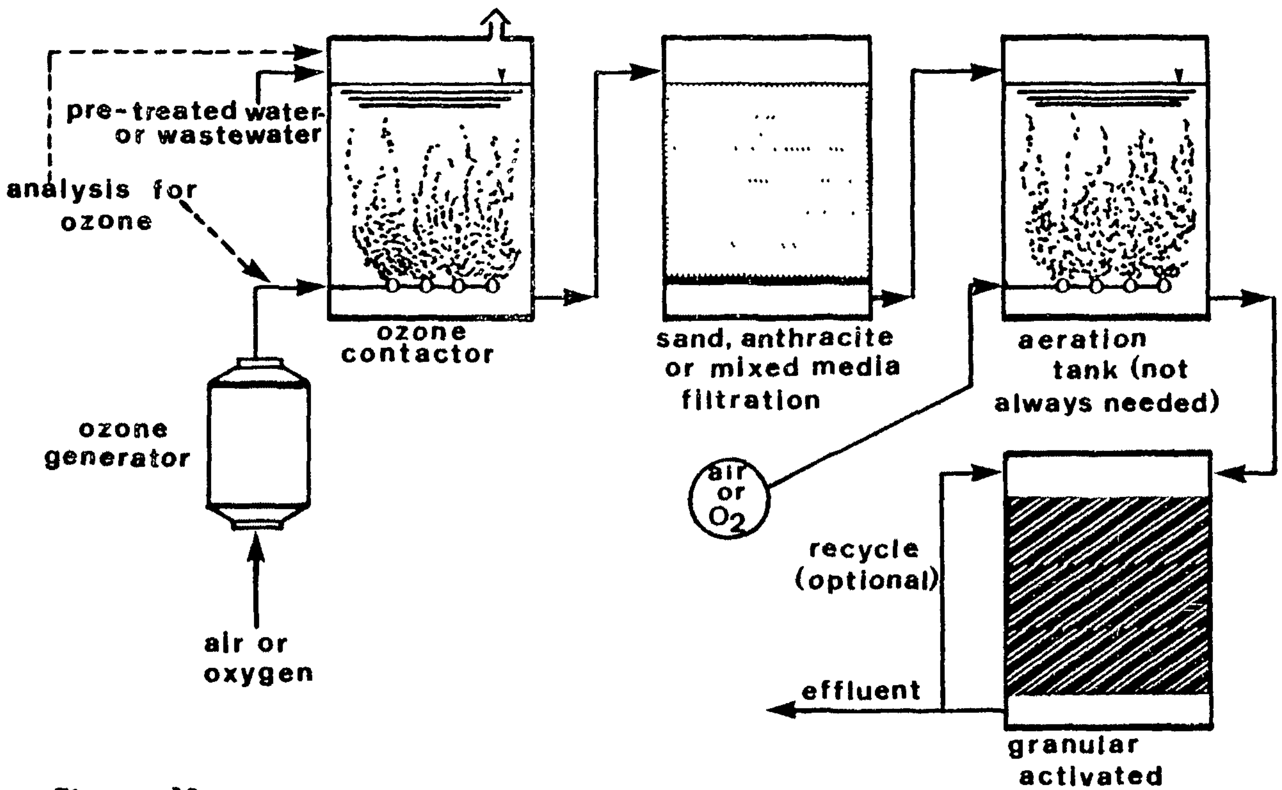


Figure 12. Biological activated carbon system.

SECTION 5

A REVIEW OF BIOLOGICAL PROCESSES USED IN DRINKING WATER TREATMENT

For purposes of this report, biological processes for treating drinking water can be divided into two categories: (1) those that occur naturally when only a medium of growth and proper nutrients are provided: and (2) those that are stimulated or enhanced by a chemical oxidation step. It should be recognized that generally the same biological processes occur in processes listed in both categories, and that the pretreatment techniques involving chemical oxidation merely change the nature of the substrates utilized by the bacteria. This section provides a review of the traditional, well-known natural processes and previews the newer processes that are commanding more attention currently.

RIVER SAND BANK FILTRATION (UFERFILTRATION)

Along the lower Rhine River, in the region around Düsseldorf, Feceral Republic of Germany, the river banks are comprised of diluvial gravel and sand sediments. Advantage is taken of these deposits by utilizing them as natural filtration media. All water works located in this region and on the Rhine take water not from the Rhine directly, but from 10 to 30 m deep, vertical or horizontal, wells situated 50 to 250 meters from the river itself (Poggenburg, 1975).

About two-thirds of the water taken from these wells is Rhine water which has passed into the wells over an average period of three weeks. The balance is groundwater which flows from the land to the Rhine.

During the three week time of passage from the Rhine to the wells, about 60 to 70% of the organic materials present in the river water is removed by means of biological processes. Those organics removed are the easily biodegraded materials originally present in the river water. The more biorefractory organic compounds, such as halogenated organics, pass through the river sand bank filters unaffected, and enter the treatment plant.

The combined bank filtrate and groundwater in the wells is clear and almost always bacteriologically acceptable (Poggenburg, 1975). In addition to removing the easily biodegradable organic materials originally present in the Rhine River, the river sand bank filters reduce some of the nitrate ion present to nitrite and ammonia (Hopf, 1970b). Also, iron and manganese are extracted from the sand and are present in the raw water entering the treatment plant. All of these contaminants then are treated in the plant by other techniques.

Further details on the processes occurring during river sand bank filtration can be found in the description of the Düsseldorf water treatment process in Appendix C of this report and in recent articles by Kussmaul (1979), Piet (1979), Piet & Zoeteman (1980) and Sontheimer (1980).

SLOW SAND FILTERS

Although all treatment processes may have some effect on the microbiological quality of water, only certain of these processes are biological in nature. A classical biological action in water treatment occurs in slow sand filters. Removal of impurities by slow sand filtration is effected by a combination of different processes. The most important of these are mechanical straining, sedimentation and some adsorption, chemical and biological activity. Through chemical and biological oxidation, ammonia is converted to nitrate and soluble ferrous and manganous compounds compounds are oxidized into insoluble ferric and manganic compounds.

The magnitude of the bacterial activities necessary to effect these biological changes are most pronounced in the upper part of the filters, but biological activity continues to a depth of 0.4 to 0.7 meter. Several types of predatory organisms thrive in this upper layer of the filter bed. However, in the lower part of the bed, the level of concentration of the organic matter has been reduced to the point that few bacteria are able to survive. Similar conditions arise in granular activated media.

Depending upon whether the slow sand filter is constructed open or closed, a significant reduction in concentration of organic matter can occur. This is brought about by the presence of a thin, shiny matting on top of the sand, which consists of threadlike algae and numerous other forms of aquatic life.

When water is filtered at a slow rate through fine sand, a biologically active filter mat forms in the top few centimeters of the sand. This mat, termed a "schmutzdecke", removes suspended matter, bacteria and modifies the character of the water biochemically. There is evidence that the ability of slow sand filters to remove microorganisms is due to microbial competition and predation of protozoa and invertebrates (Hutchinson & Ridgeway, 1977).

According to Huisman (1978), the most important purifying action of a slow sand filter is the removal of bacteria, including _E. coli_, and pathogens when they are present in the raw water. The total bacterial count may be reduced by a factor of 1,000 to 10,000 and the _E. coli_ count by a factor of 100 to 1,000.

According to Rook (1974), for many lake waters and some impounded surface waters in which the contents of biorefractory organics remain low, slow sand filtration is the best technical means of providing a single step, efficient reduction in levels of pathogenic and coliform organisms and producing biooxidation of ammonia and biodegradable organic matter.

Recently Schmidt (1978) has described the removal of micropollutants (dissolved organic compounds) in slow sand filters.

STORAGE OF SURFACE WATERS

Although principally used for reasons other than storage, many valuable chemical and biological changes in the characteristics of the raw water can occur when surface waters are stored. Specific changes include reduction in the concentrations of organic materials, reduction in bacterial levels in general and in virus, pathogenic bacteria and fecal organism levels in particular. Mechanisms by which these actions occur include ultraviolet radiation, natural flocculation and sedimentation, competition for available nutrients, production of biocidal waste products by various microorganisms, and predation by protozoa and possible parisitic bacteria of the genus Bdellovibrio (Fry & Staples, 1976; Hutchinson & Ridgeway, 1977).

British research scientists have reported biological sedimentation methods for removal of ammonia, which can occur during reservoir storage. This is achieved by controlling the water flow closely in horizontal and upflow tanks and thereby holding a biofloc seeded on river silt, sand or alum floc in suspension. The ammonia can be removed if a large enough surface area of biologically active floc is maintained (Milliner et al., 1972).

COARSE MEDIA BIOLOGICAL REACTORS

Coarse media reactors have been applied successfully in drinking water treatment plants for biological conversion of ammonia-nitrogen to nitrate-nitrogen and have the potential for biological denitrification. A survey of European water treatment practice (Water Research Center, 1977) states that biological conversion of ammonia is practiced on groundwaters in France at Croissy, Aubergenville and Villeneuve.

The 7,000 cubic meter per hour (44 mgd) Aubergenville water treatment plant which supplies water to the suburbs of Paris, France has included a biological nitrification process since 1961 (Blue, 1979). Water drawn from wells in the vicinity of the Seine River contains ammonia levels of approximately 3 mg/l. Treatment includes chemical clarification, cascade aeration, nitrification, filtration, ozonation and post-chlorination. Ammonia concentrations are reduced from 3 mg/l as the water enters the nitrification reactor to a level of 0.1 to 0.2 mg/l leaving the reactor. This level is further reduced to only trace quantities after sand filtration. A dosage of 0.1 to 0.2 mg/l of phosphorus (as P_2O_5) is added to the water before it passes upward through the 2.5 meter (8.2 feet) deep bed. Supplemental air is provided by blowers on a cycle of 2 munites on and 6 minutes off. The reactor medium is 0.15 cm to 0.5 cm pozzolanic (volcanic stone) material. Further information on the Aubergenville plant is provided in the Appendix.

FLUIDIZED BED NITRIFICATION

A fluidized bed bioreactor for intensified nitrification of ammonia has been developed at the Water Research Centre in the United Kingdom (Jekel, 1978a). This bioreactor uses fine sand grains as a support medium for the nitrifying bacteria. Several investigators have reported the feasibility of carrying the reaction to completion by denitrifying the nitrate ion to nitrogen gas in an aerobic phase of biological sedimentation. This can be achieved by the addition of methanol. Rook (1972) notes that this same type of reactor can be used for biological denitrification of river water. It has been demonstrated that fluidization of river solids and attached bacteria can reduce nitrate ions to nitrogen effectively in feed waters made anaerobic by dosing with ammonia and subsequently dosing with methanol.

GROUND PASSAGE OF TREATED WATER

This technique sometimes is used for further biochemical polishing of treated waters. The Dohne plant at Mülheim, Federal Republic of Germany subjects treated water to ground passage with a retention time of 12 to 50 hours. Prior to installation of the new BAC process at Dohne, dissolved organic chlorine (DOCl) concentrations were lowered from 151 µg/l to 92 µg/l during ground passage. In addition, total bacteria plate count numbers were lowered from 3,700 counts/ml in the GAC effluents to 27 counts/ml after ground passage. DOC levels were lowered on the average from 3.4 mg/l before ground passage to 2.0 mg/l after ground passage during 1975 and 1976 (Sontheimer, *et al*., 1978).

When ground passage was first incorporated at the Dohne treatment plant, it was a necessary part of the treatment process, providing a desired degree of polishing. Since installing the new BAC process, however, Dohne's plant management is using ground passage only as a convenient method of treated water storage. At the two other plants in Mülheim which were installing the BAC process in 1978, there will be no need for ground passage because of the higher quality of water produced (Heilker, 1978).

BIOLOGICALLY ACTIVE FILTRATION MEDIA

Biological activity is known to occur in filtration media such as anthracite, hydroanthracite and granular activated carbon. Anthracite and hydroanthracite are used in dual media filters placed before GAC adsorbers in water treatment processing.

Anthracite frequently is used as an upper layer in a dual media filter. The lower layer can be a sand filter having grain sizes of 0.5 to 2.0 mm. In between, there can be a layer of coarser anthracite to form a graded dual medium anthracite prefiltration unit which prevents blinding of the sand filter. Anthracite also has a lower specific gravity than sand, so that after backwashing, this coarser medium will settle on top of the sand filter.

Anthracite also is used as an upper layer in post-filtration activated carbon adsorbers of the pressurized, down-flow type, found in the Düsseldorf, Federal Republic of Germany, plants. While its purpose in these plants is to provide a medium for filtering insoluble ferric and manganic compounds, anthracite also can provide a medium for bacterial growth.

Although no specific applications of this type have been noted in European drinking water treatment plants, European water research scientists have shown that both anthracite and hydroanthracite can support bacterial growth. The primary difference between anthracite and granular activated carbon, with respect to supporting bacterial growth, is that anthracite behaves similarly to a trickling filter medium, whereas activated carbon can accumulate nutrients through adsorption of organic molecules into macro-, meso- and micropores.

BIOLOGICALLY ACTIVE GRANULAR ACTIVATED CARBON

Bacterial growths in granular activated carbon contactors have been reported by many investigators. These growths can occur under either anaerobic or aerobic conditions, provided that sufficient substrate is available and provided that toxic inhibitors are absent (Presecan, 1978). In fact, addition of toxic inhibitors, such as chlorine, heavy metals, silver or heat in the form of steam can prevent biological growths from occurring. Until recently, these biological growths, especially in wastewater treatment applications, have been viewed as nuisances, causing fouling, increased head losses and production of hydrogen sulfide when the activated carbon adsorbers were operated under anaerobic conditions.

In recent years, water and wastewater research scientists have begun to recognize the beneficial effects of biological growths in granular activated carbon adsorbers. Studies by Weber & Ying (1977), Guirguis _et al_. (1978) and Argo (1978) in wastewater treatment applications in the U.S.A. and by Jekel (1977, 1978), Sontheimer _et al_. (1978) and by Schweisfurth and his coworkers in the Federal Republic of Germany (Klotz, Werner & Schweisfurth, 1975; Werner, Klotz & Schweisfurth, 1978) have demonstrated that biological action can contribute significantly to enhancing treated water quality and reducing the frequency of granular activated carbon regeneration.

These effects can best be achieved by (1) using water streams containing a substantial portion of biodegradable organic materials or substances which can be converted into biodegradable materials by preoxidation, (2) elimination of chlorination as an initial treatment step (i.e., breakpoint chlorination) and (3) use of empty bed contact times (EBCT) of more than 10 minutes.

SECTION 6

MICROBIOLOGICAL ASPECTS OF BIOLOGICAL ACTIVATED CARBON

In this section those fundamental principles of biological activity which are considered most germane to understanding the various phenomena which are believed to occur in operating BAC systems will be discussed. These biological processes take place during passage of the aqueous solution through GAC in conjunction with the physical processes of adsorption/desorption. Both the biological and adsorption processes can be strongly affected by the prior treatment step of chemical oxidation.

In addition, microbiological data will be discussed which have been obtained from operating pilot plant or full scale plant BAC media.

GENERAL PRINCIPLES OF BIOLOGICAL ACTIVITY

Background for this discussion has been taken from Clark, Viessman & Hammer (1971), Rafelson, Brinkley & Hayashi (1971) and Moat, 1979).

Several factors affect the growth and proliferation of aerobic microorganisms, the most important of which include temperature, pH, availability of nutrients, oxygen supply, the presence of toxins and type of substrate. Psychrophilic (cold-loving) bacteria grow best at temperatures slightly above freezing (4°C to 10°C). Thermophilic (heat-loving) bacteria function best at an optimum temperature range of 50°C to 55°C. Mesophilic (moderation-loving) bacteria grow best in a temperature range of 20°C to 40°C.

Most biological treatment systems operate best in a neutral pH environment. For example, the optimum pH range for operation of activated sludge systems is between pH 6.5 and 8.5. At pH 9.0 and above, microbial activity is inhibited. Below pH 6.5, fungi are favored over bacteria in the competition for food.

Bacterial toxins commonly present in water and wastewater include certain heavy metals, such as copper, mercury, lead, zinc, cadmium, chromium; polychlorinated organic materials and systemic poisons, such as cyanides.

METABOLISM (Rafelson _et al._, 1971)

Heterotrophic bacteria (those which use organic compounds as an energy and carbon source) include the aerobes, anaerobes and facultative bacteria (which use free oxygen, when available, but can also respire and multiply in its absence). In heterotrophic metabolism, organic matter is the substrate (food). However, the majority of organic molecules present in wastewater are in the form of large (high molecular weight) molecules which cannot penetrate bacterial cell membranes and be assimilated. In order to metabolize high molecular weight substances, the bacteria must be capable of hydrolyzing these large molecules into diffusible fractions for assimilation into their cells. Bacteria perform this function by generating oxidation-reduction enzymes, which are organic catalysts which aid in performing biochemical reactions at temperatures and chemical conditions compatible with biological life. Co-enzyme components of the enzyme systems determine what chemical reactions will occur.

The primary product of aerobic metabolism is energy, according to equation 1:

$$\text{Organics} + \text{oxygen} \xrightarrow{\text{bacteria}} CO_2 + H_2O + \text{energy} \qquad \text{eq. 1}$$

Microorganisms use the energy thus generated to process organic matter to create new cells. During heterotrophic metabolism of wastewater organics, and for a given population of microorganisms, the maximum rate of removal of organic matter occurs during periods of maximum biological growth. Conversely, the lowest rate of removal of organic matter occurs when microbiological growth ceases. In aerobic metabolism, assuming an abundance of dissolved oxygen, biologically available carbon is the limiting factor. The supply of substrate is rapidly exhausted through respiration of CO_2 and synthesis into new cells. An aerobic process results in complete metabolism and synthesis of the substrate into a large quantity of biological growth.

If the dissolved oxygen supply becomes depleted during metabolism, anaerobes will develop. On the other hand, if the dissolved organic supply becomes depleted, then the viable aerobic microorganisms will compete for the small amount of substrate still in solution. The rate of metabolism thus decreases at an increasing rate, resulting in a rapid decrease in the number of viable microorganisms. Starvation then occurs, such that the rate of microbiological deaths exceeds the rate of cell production. The total mass of microbial protoplasm decreases as the cells utilize their own protoplasm as an energy source. Under these circumstances, microbial activity is termed endogenous. Cells become old, die and lyse (rupture), releasing nutrients back into solution. Cell lysis decreases both the number and the mass of microorganisms. Consequently, it is not possible to convert all organic carbonaceous material present to CO_2 by means of biological processes.

<u>Chemical Reactions Involved With Metabolism</u>

Metabolism involves a large number of individual biochemical reactions, which can be grouped into the categories of the tricarboxylic acid cycle, lipid metabolism, carbohydrate metabolism, amino acid metabolism, or any permutation of these. It is the nature of metabolism that there is no beginning or end of these multiple processes. All of the reactions are occurring at the same time, in a very carefully controlled and coordinated manner. For the purposes of this and subsequent discussions of metabolic reactions occurring during BAC processing, we shall consider only some of the reactions which are known to occur with carbohydrates and tricarboxylic acids.

Glycolysis--

The term glycolysis usually is restricted to the series of enzymatic reactions involved in the biological transformation of either glucose or glycogen to lactic acid. This series of reactions is also known as the Embden-Meyerhof pathway. A simplified summation of the reactions which occur and the structures of organic intermediates and products involved which are pertinent to discussion of pretreatment by chemical oxidation (given in Section 8) is given in Figure 13. One mole of glucose (a 6-carbon molecule) is converted to two moles of trioses (3-carbon molecules) by a series of 4 enzyme-catalyzed reactions, which then are converted into two moles of pyruvic acid by a series of 5 additional enzymatic reactions. Pyruvic acid can be converted, reversibly, into lactic acid by reduction or to acetaldehyde by continued enzymatic oxidation. Under aerobic metabolic conditions, pyruvic acid is not reduced to lactic acid, but is further oxidized to CO_2 and water through the tricarboxylic acid cycle (see next section).

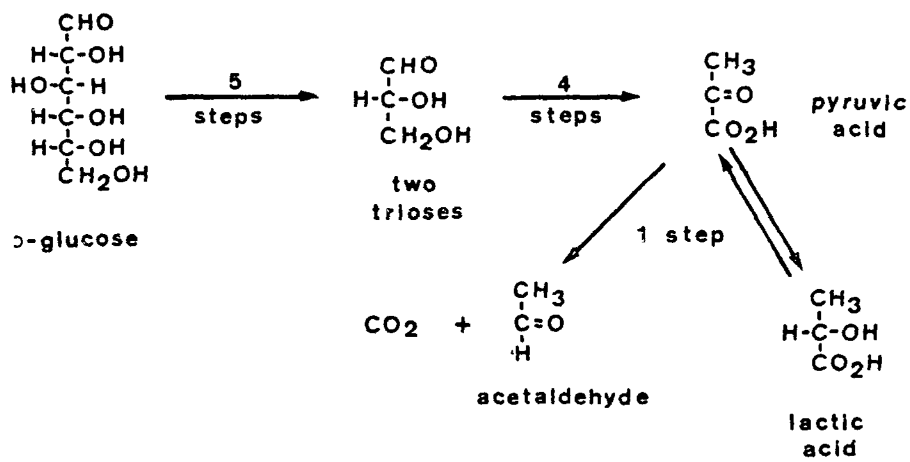


Figure 13. Enzymatic oxidation of glucose (glycolysis).

(Rafelson, Binkley & Hayashi, 1971).

Tricarboxylic Acid Cycle (Krebs Cycle; Citric Acid Cycle)--

This cycle includes the reactions which occur during glycolysis, but also involves reactions of other organic acids, specifically oxalacetic, malic, fumaric, succinic, citric, aconitic, isocitric, oxalosuccinic and α-ketoglutaric. Figure 14 shows a simplified representation for the relationships between these compounds during the tricarboxylic acid cycle. The structures of these organic acids become of greater significance when it is realized that many of these same acids are produced when many of the organic pollutants present in water and wastewater are ozonized. This point will be discussed in greater detail in Section 8 of this report.

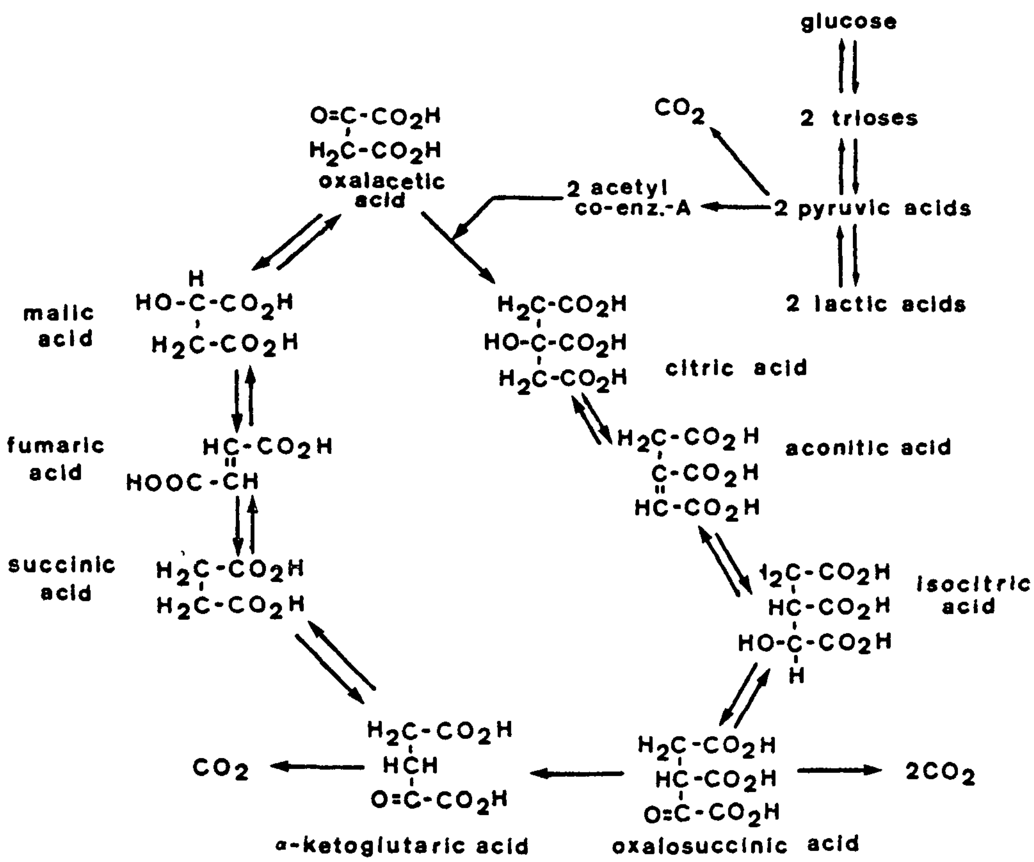


Figure 14 The tricarboxylic acid (Krebs or citric acid) cycle. (Rafelson, Binkley & Hayashi, 1971).

The β-Ketoadipate Pathway--

Figure 15 shows the structures of chemical intermediates which are formed then oxidized further during the degradation of benzoic and p-hydroxybenzoic acids by reaction sequences catalyzed by a variety of enzymes to produce succinic acid. Once formed by these mechanisms, succinic acid can be further oxidized according to the Krebs cycle. Many of the chemical intermediates produced during the β-ketoadipate cycle also have been identified during chemical oxidation of aromatic compounds (see Section 8).

CONDITIONS NECESSARY FOR PROMOTION OF AEROBIC ACTIVITY

In the balance of this Section, only the promotion of aerobic biological growth will be considered, because BAC processing, as currently practiced, involves aerobic microorganisms. In order to maximize the aerobic bioactivities required, it is necessary to first maintain a minimum level of dissolved oxygen (DO) in the aqueous medium being treated. The total amount of DO considered minimal to convert the maximum amount of dissolved organic carbon (DOC) to CO_2 will be a function of the concentration of biologically oxidizable materials present. Raw waters being processed into drinking water contain relatively small amounts of DOC and ammonia, thus the maintenance of 3 to 6 mg/l of DO, sufficient to guarantee aerobic conditions, can be accomplished by addition of relatively small amounts of oxygen or air. On the other hand, industrial wastewaters usually contain much higher concentrations of organic substrate materials. Therefore, the amount of oxygen required to maintain an aerobic biomass will be considerably higher.

Solubility of Air and Oxygen in Water

Air contains only 21% oxygen, most of the balance being nitrogen. As a consequence, when water is saturated with air, the maximum concentration of dissolved oxygen which can be attained is on the order of 6 to 9 mg/l, depending upon the temperature. The solubility of oxygen and nitrogen in water increases as the water temperature decreases, so that the maximum solubility of each of these gases occurs near 0°C.

On the other hand, when water is saturated with nominally pure oxygen rather than air, the maximum concentration of dissolved oxygen which can be attained rises to 40 mg/l (at 20° to 25°C) and to 69 mg/l (at 0°C). Therefore, use of pure oxygen will allow 7 to 8 times the DO level to be attained in aqueous systems than will the use of air. This point is of significance when the initial loading of biodegradable material is high.

The point is also significant when considering the rates of aerobic microbiological reactions, which depend upon the DO concentrations. The faster the rate of microbial oxidation in an operating BAC system, the lower will be the detention time required for the aqueous medium to be in contact with the microbial species performing the oxidations. Thus, the higher the rate of biological oxidation, the smaller can be the biological reactor and/or the faster can be the flow rate of water or wastewater to be put through the specific treatment system being employed.

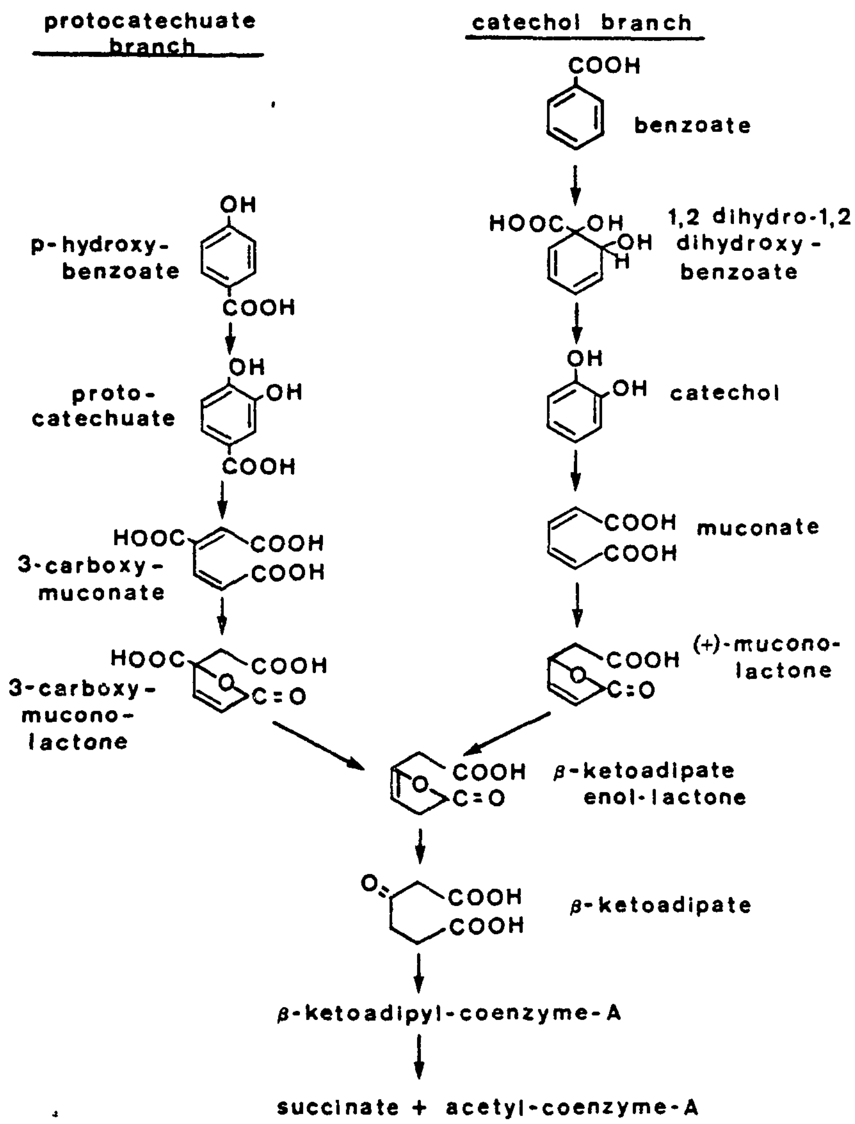


Figure 15. Intermediates in the β-ketoadipate pathway. (Moat, 1979)

STOICHIOMETRY OF BIOCHEMICAL OXIDATIONS

Dissolved Organic Carbon

Organic compounds have basic carbon-carbon backbone chains. Those organic materials which contain only carbon and hydrogen atoms are called "hydrocarbons". Examples include methane, butane, benzene, gasoline, kerosene and phenanthrene. When the organic molecule also contains oxygen atoms, in addition to simply carbon and hydrogen, the material is called generically a "carbohydrate". Examples include alcohols, acids, aldehydes, ketones, phenols and sugars. In a sense, one can consider carbohydrates as partially oxidized hydrocarbons, on the way to being oxidized completely to CO_2 and water.

One can generalize the chemistry involved in the total oxidation of hydrocarbons as follows:

$$C_xH_y + (x + 0.25y)O_2 \longrightarrow xCO_2 + 0.5yH_2O \qquad \text{eq. 2}$$

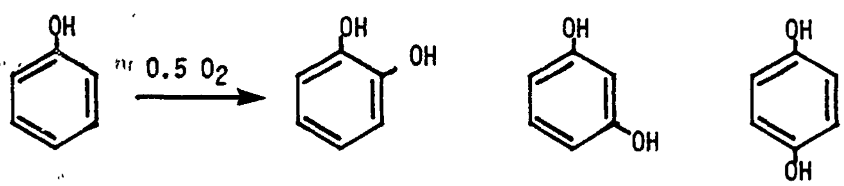
The amount of oxygen theoretically required (x + 0.25y) for complete oxidation of all dissolved organic carbon to carbon dioxide and for converting all hydrogen to water will depend upon the relative amounts of these two elements which are present initially. If adequate oxygen is present for the reaction to proceed to completion, the products can be as shown by equation 2. If insufficient oxygen is available however, only partially oxidized intermediate organic products, will be obtained. In addition, once the dissolved oxygen supply has been depleted, the predominant microbial species may become anaerobes, which can draw their required oxygen from the partially oxidized intermediates (carbohydrates) and regenerate reduced organic ccm-pounds as end products, such as in the reversible conversion of pyruvic acid to lactic acid.

The amount of oxygen required for complete conversion of an organic material to CO_2 and H_2O also depends upon the composition and the degree of oxidation of the starting material. For example, Table 2 shows the amount of oxygen required to attain 100% oxidation to CO_2 and H_2O starting with the 2-carbon-containing hydrocarbons ethane (C_2H_6), ethylene (C_2H_4) and acetylene (C_2H_2), the 2-carbon-containing carbohydrates ethanol (CH_3CH_2OH), acetaldehyde (CH_3CHO), acetic acid (CH_3COOH), oxalic acid (HOOC-COOH) and the 6-carbon-containing compound phenol (C_6H_5OH). The two-carbon compound containing the most hydrogen (ethane) requires the most oxygen, in the 2-carbon-containing series. On the other hand, oxalic acid, which contains four atoms of oxygen and only two hydrogen atoms, requires the smallest amount of additional oxygen to carry the oxidation to completion.

TABLE 2. OXYGEN REQUIREMENTS FOR CONVERSION OF REPRESENTATIVE ORGANIC COMPOUNDS TO CO_2

$CH_3{-}CH_3 + 3.5\ O_2 \longrightarrow 2CO_2 + 3H_2O$
$CH_2{=}CH_2 + 3\ O_2 \longrightarrow 2CO_2 + 2H_2O$
$CH{\equiv}CH + 2.5\ O_2 \longrightarrow 2CO_2 + H_2O$
$CH_3CH_2OH + 3\ O_2 \longrightarrow 2CO_2 + 3H_2O$
$CH_3CHO + 2.5\ O_2 \longrightarrow 2CO_2 + 2H_2O$
$CH_3CO_2H + 2\ O_2 \longrightarrow 2CO_2 + 2H_2O$
$HO_2C{-}CO_2H + 0.5\ O_2 \longrightarrow 2CO_2 + H_2O$
$C_6H_5OH + 7\ O_2 \longrightarrow 6CO_2 + 3H_2O$

For comparison, the corresponding oxygen requirement of the six-carbon compound, phenol (C_6H_5OH) to go to completion is 7 moles of oxygen per mole of phenol. If only 0.5 mole of oxygen is available, the maximum oxidation which phenol can undergo would be to a dihydroxyaromatic compound, either catechol, resorcinol or hydroquinone:



phenol catechol resorcinol hydroquinone

eq. 3

When organic materials contain nitrogen or sulfur, even more oxygen may be required to convert these elements to their fully oxidized states. For example, amine groups ($-NH_2$) will require 1.5 equivalents of oxygen per equivalent of amine-nitrogen to produce a nitro group, and 2 equivalents of oxygen to produce an equivalent of nitrate ion. Sulfur-containing compounds can require 2 equivalents of DO per equivalent of sulfur atom to produce one equivalent of sulfate ion, depending upon its degree of oxidation in the original organic compound.

From these considerations, it is clear that in order to operate BAC processes at maximum efficiency, sufficient oxygen should be employed to convert the maximum amount of dissolved organic carbonaceous material into CO_2 and water. It must be remembered, however, that biological processes cannot remove 100% of the dissolved organic carbonaceous material. This is because microbial processes inevitably involve cell lysis and release of bacterial cell contents to solution.

Nitrification

Autotrophic bacteria use CO_2 as a carbon source and oxidize inorganic compounds for energy. Autotrophs of greatest significance in sanitary engineering are the nitrifying, sulfur and iron bacteria. Free ammonia and/or ammonium ions react with oxygen biochemically in the presence of nitrifying organisms to produce nitrite ions and, ultimately, nitrate ions:

$$NH_3 + O_2 \xrightarrow{\text{Nitrosomonas}} NO_2^- + \text{energy} \qquad \text{eq. 4}$$

$$NO_2^- + O_2 \xrightarrow{\text{Nitrobacter}} NO_3^- + \text{energy} \qquad \text{eq. 5}$$

overall:

$$NH_3 + O_2 \longrightarrow NO_3^- + [H_2O,\ H^+ \text{ or } (OH)^-] + \text{energy} \qquad \text{eq. 6}$$

The actual stoichiometry involved will depend upon the pH of the medium. On the alkaline side of pH 7, ammoniacal hydrogen will be converted to hydroxyl ions, some of which will not proceed to water molecules. On the acid side of pH 7, some hydrogen atoms will be converted to hydrogen ions, which will not continue to react further to become water.

Gomella & Versanne (1977) have stated that one equivalent of ammoniacal nitrogen should require 4.57 equivalents of oxygen to produce one equivalent of nitrate ion. On the other hand, these authors found during full-scale drinking water treatment plant studies at the Rouen-la-Chapelle plant in France, that only 3.2 equivalents of oxygen actually were required to eliminate ammoniacal ammonia from the raw water. It is possible that the nitrification is incomplete at Rouen (see Section 9) and that some nitrite is present after GAC treatment along with nitrate. This would explain the lower-than-theoretical amount of oxygen apparently required at Rouen.

On the other hand, Jekel (1978) considers the stoichiometry of nitrification which occurs at the Dohne plant in Mülheim, Federal Republic of Germany, to require 3.56 equivalents of oxygen per equivalent of ammonium-nitrogen, according to the following equation:

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O \qquad \text{eq. 7}$$

From the above considerations, it is clear that for maximum conversion of dissolved organic compounds into CO_2 and water and for the maximum amount of nitrification to occur, a considerable amount of DO can be required. This amount depends upon the components of the original organic material present originally. In most cases, however, the equivalent amount of oxygen necessary is some multiple (3 to 10) of the equivalents of ammonia-nitrogen and dissolved organic carbon and hydrogen present originally. The presence of other oxygen-demanding elements, such as sulfur, can increase the requisite amount of DO even further.

There is one more important point to consider with nitrifying bacteria. In the presence of large quantities of heterotrophic microorganisms, the growth and proliferation of nitrifiers is suppressed. Therefore, when treating industrial wastewaters containing high levels of readily biodegradable pollutants, nitrification may not be observed. On the other hand, in treating raw drinking waters (which contain much lower levels of DOC), the density of heterotrophic microorganisms will be much lower. Therefore, nitrifiers will have a better environment in which to proliferate and function.

STUDIES OF OPERATIONAL BIOLOGICALLY ENHANCED GAC SYSTEMS

Van der Kooij (1975) investigated the presence and behavior of bacteria on granular activated carbon filters treating drinking waters. Tests were conducted on three experimental filters: GAC, granular non-activated carbon and sand. Each filter was fed with tap water at 13° to 17°C and 3.5 m/hr (3 minutes contact time) flow-through rates over a 10 month period (side-by-side experiments). Bacterial counts were made at regular intervals by the colony count technique on diluted agar (0.35 g/l beef extract, 0.65 g/l peptone, 10 g/l agar) after incubation 10 days at 25°C. The number of bacteria on the GAC was found to be 2 to 3 times the number found on inert media (van der Kooij, 1978).

From these experiments, van der Kooij (1975) calculated the average surface area occupied by a single bacterial cell on activated carbon to be 40 square microns when the colony count was 10^8/cu cm. Since the surface area of the activated carbon used for these tests was much greater than 40 sq cm/cu cm, it was concluded that the density of bacteria on the carbon surface was very low. This was confirmed by electron microscopy. It was also concluded that normal adsorption processes of organic solutes on activated carbon were not hindered by the presence of the bacteria on the carbon, using a dilute substrate solution such as drinking water.

In support of this work of van der Kooij, it has been shown by Weber, Pirbazari & Melson (1978) in the USA that individual bacteria are small enough to be able to fit into the macropores (50 to 100 microns in size) of the GAC, where they are protected from shear forces. On the other hand, bacteria are too large (1 to 16 microns) to fit into the GAC micropores, some of which are less than 0.05 micron in diameter. Since the micropores make up about 99% of the available carbon surface area, the fact that bacteria occupy only 1% of the total GAC surface area is consistent with this ratio.

Figure 16 is a 4,000 times magnification scanning electron micrograph of a GAC particle taken from a GAC column operating at the Philadelphia Torresdale drinking water treatment pilot plant, and shows a typical bacterial population (Cairo et al., 1979). Microorganisms are found to be scattered over the carbon surface, with heavier concentrations in the areas of the macropores. Bacteria were not observed to form a uniform biofilm over the entire surface area of the GAC particle, as has been hypothesized by some investigators. Few higher forms of life, such as protozoa, were observed on the GAC particle surface. Although such an advanced ecosystem was observed in wastewater GAC systems by Weber, Pirbazari & Melson (1978), lower concen-

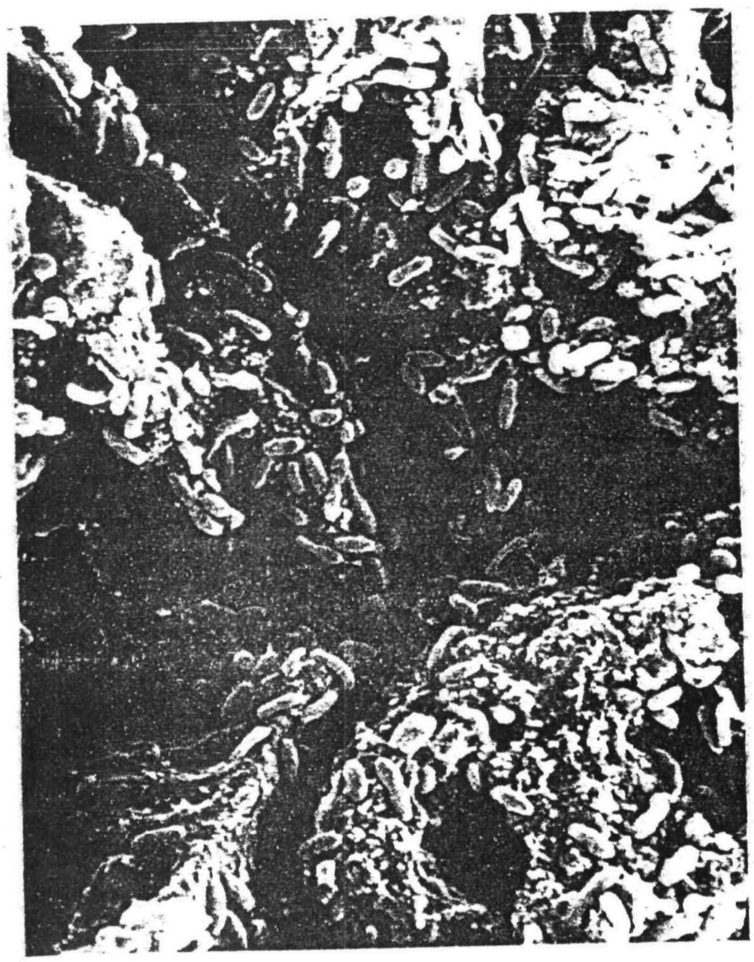


Figure 16. Electron micrograph (4,000 x) of GAC particle showing bacterial growths.

(Cairo, McElhaney & Suffet, 1979)

There is one more important point to consider with nitrifying bacteria. In the presence of large quantities of heterotrophic microorganisms, the growth and proliferation of nitrifiers is suppressed. Therefore, when treating industrial wastewaters containing high levels of readily biodegradable pollutants, nitrification may not be observed. On the other hand, in treating raw drinking waters (which contain much lower levels of DCC), the density of heterotrophic microorganisms will be much lower. Therefore, nitrifiers will have a better environment in which to proliferate and function.

STUDIES OF OPERATIONAL BIOLOGICALLY ENHANCED GAC SYSTEMS

Van der Kooij (1975) investigated the presence and behavior of bacteria on granular activated carbon filters treating drinking waters. Tests were conducted on three experimental filters: GAC, granular non-activated carbon and sand. Each filter was fed with tap water at 13° to 17°C and 3.5 m/hr (3 minutes contact time) flow-through rates over a 10 month period (side-by-side experiments). Bacterial counts were made at regular intervals by the colony count technique on diluted agar (0.35 g/l beef extract, 0.65 g/l peptone, 10 g/l agar) after incubation 10 days at 25°C. The number of bacteria on the GAC was found to be 2 to 3 times the number found on inert media (van der Kooij, 1978).

From these experiments, van der Kooij (1975) calculated the average surface area occupied by a single bacterial cell on activated carbon to be 40 square microns when the colony count was 10^8/cu cm. Since the surface area of the activated carbon used for these tests was much greater than 40 sq cm/cu cm, it was concluded that the density of bacteria on the carbon surface was very low. This was confirmed by electron microscopy. It was also concluded that normal adsorption processes of organic solutes on activated carbon were not hindered by the presence of the bacteria on the carbon, using a dilute substrate solution such as drinking water.

In support of this work of van der Kooij, it has been shown by Weber, Pirbazari & Melson (1978) in the USA that individual bacteria are small enough to be able to fit into the macropores (50 to 100 microns in size) of the GAC, where they are protected from shear forces. On the other hand, bacteria are too large (1 to 16 microns) to fit into the GAC micropores, some of which are less than 0.05 micron in diameter. Since the micropores make up about 99% of the available carbon surface area, the fact that bacteria occupy only 1% of the total GAC surface area is consistent with this ratio.

Figure 16 is a 4,000 times magnification scanning electron micrograph of a GAC particle taken from a GAC column operating at the Philadelphia Torresdale drinking water treatment pilot plant, and shows a typical bacterial population (Cairo et al., 1979). Microorganisms are found to be scattered over the carbon surface, with heavier concentrations in the areas of the macropores. Bacteria were not observed to form a uniform biofilm over the entire surface area of the GAC particle, as has been hypothesized by some investigators. Few higher forms of life, such as protozoa, were observed cn the GAC particle surface. Although such an advanced ecosystem was observed in wastewater GAC systems by Weber, Pirbazari & Melson (1978), lower concen-

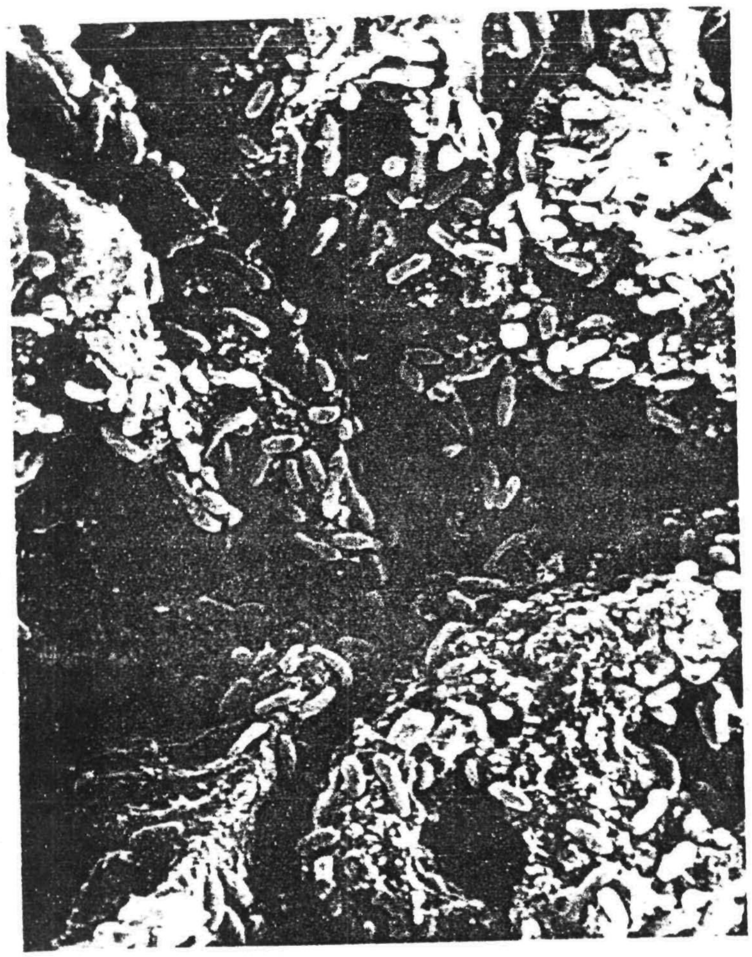


Figure 16. Electron micrograph (4,000 x) of GAC particle showing bacterial growths.

(Cairo, McElhaney & Suffet, 1979)

trations of nutrients in the potable water GAC system are considered by Cairo et al. (1979) to be responsible for the limited biological colonization on the GAC particles.

On the other hand, soluble organic compounds generally are small enough to be able to fit inside and be adsorbed by the GAC micropores. Therefore, since the adsorption of organics occurs mostly where the bacteria are not present, it would be predicted that bacterial presence will not interfere with the normal GAC adsorption processes, unless the number of bacteria become so high so as to physically encapsulate the carbon particles, thereby preventing the diffusion of soluble organics to the micropores (Weber & Van Vliet, 1978). However, such excessive bacterial growth is dependent upon the amount of soluble, biodegradable organics (food) present, and raw drinking water supplies simply do not contain this much DOC. Even physical-chemical treated sewage containing as much as 25 mg/l of BOD_5 does not cause biological blinding of the BAC columns (Guirguis et al., 1978), provided that backwashing is conducted in the proper manner and at proper intervals.

Section 9 includes a discussion of research studies of Eberhardt, Madsen & Sontheimer (1974) conducted at the Bremen (Federal Republic of Germany) water treatment plant which showed that GAC which had a higher fraction of macropores (2%) than did normal GAC (1%) removed higher amounts of DOC (about 50% as opposed to 20 to 25%) after attaining biological equilibrium. Macropores are capable of housing bacteria, therefore the improved removal of DOC was explained by the higher fraction of macropore area available to house more bacteria. These results suggest that if GAC can be prepared with even higher macropore contents, even higher DOC removals might be attainable with BAC systems.

However, Tzesos & Benedek (1980) compared the performance of two types of GAC (Filtrasorb 400 and Special A) treating phenol and operated under biologically enhanced, fluidized bed conditions. After establishing biological equilibrium, the TOC concentration in the effluents from the 2 GAC columns was about the same. Thus it was concluded that Special A GAC (which has a surface area about 10% of that of Filtrasorb 400, produced by transitional pores near 70 Å in size) adsorbs similarly to Filtrasorb 400, once corrections for surface area differences are made. This appears to indicate no special benefit of larger pores. Hence, Tzesos & Benedek (1980) also concluded that the biologically generated residual organic molecules (from microbial metabolism of phenol) are likely to be smaller than 70 Å in molecular size.

Studies by Werner, Klotz & Schweisfurth (1978) have been conducted on biologically active GAC columns used for more than three years at the Schierstein water treatment plant at Wiesbaden, Federal Republic of Germany. Microbiological species listed in Tables 3 and 4 have been extracted and identified from these GAC materials. All of the species identified to date are non-pathogenic in nature, and are found naturally occurring in soils and waters.

TABLE 3. BACTERIAL SPECIES FOUND IN GAC ADSORBER EFFLUENTS AT THE SCHIERSTEIN (FEDERAL REPUBLIC OF GERMANY) WATER TREATMENT PLANT

Psuedomonas alcaligenes	Chromobacterium violaceum
Pseudomonas cepacia	Neisseria sicca
Pseudomonas facilis	Acinetobacter calcoaceticum
Pseudomonas fluorescens	Micrococcus luteus
Pseudomonas lemoignei	Staphylococcus saprophyticus
Pseudomonas mendocina	Bacillus cereus
Pseudomonas ruhlandii	Bacillus circulans
Pseudomonas stutzeri	Bacillus licheniformis
Pseudomonas spec.	Bacillus megaterium
Gluconobacter oxidans	Bacillus pumulis
Azomonas agilis	Bacillus thuringensis
Azomonas insignis	Corynebacterium spec.
Azomonas macrocytogenes	Micromonospora spec.

Source: Werner, Klotz & Schweisfurth, 1978

TABLE 4. TYPES OF FUNGI AND YEASTS FOUND IN GAC ADSORBER EFFLUENTS AT THE SCHIERSTEIN (FEDERAL REPUBLIC OF GERMANY) WATER TREATMENT PLANT

Filamentous fungi	Phialophora hoffmannii
	Phialophora mutabilis
	Taphrina spec.
Yeasts	Rhodotorula minuta var. texensis
	Cryptococcus uniguttulatus
	Candida guillermondii var. guillermondii
	Hansenula anomala var. anomala

Source: Werner, Klotz & Schweisfurth, 1978

Bacteria listed in Table 5 are those which have been isolated and identified from the GAC pilot plant columns or from their effluents operating at Philadelphia's Torresdale drinking water treatment plant during initial studies by Cairo, McElhaney & Suffet (1979). The API system and other biochemical tests for enterobacteriaceae and other gram-negative bacteria were used. The most predominant bacteria that were isolated and identified belonged to the genus Pseudomonas. Members of the genus Bacillus also were found in large numbers. Bacteria that were identified in this study were predominantly soil or water saprophytic chemo-organotrophs and have no known pathogenic significance to man. However, some species of Flavobacterium, Pseudomonas and Alcaligenes are known to be opportunistic pathogens, chlorine resistant, or suppressors of total coliform.

Table 6 (McElhaney et al., 1980) lists results of further bacterial studies conducted by the Philadelphia scientists. One objective of this later study was to determine the effects of varying linear flow velocity of water being treated through GAC columns on the distribution of microbial species in GAC media and in their effluents. Two GAC columns were studied, one operated at 55.6 ml/min and the second at 166.7 ml/min. Both columns were designed so as to have empty bed contact times of 9 minutes. In the column treated at the slower flow rate, the predominant bacteria in the initial stages of the microbial community were Pseudomonas cepacia and two species of Acinetobacter. As the community became more established, the Acinetobacter group was replaced by Bacillus brevis, however Pseudomonas cepacia remained stable throughout the study.

In the column operated at the faster flow rate, the microbial community was dominated from the beginning by members of the genus Flavobacterium and Ps. cepacia. As the community developed, a member of the family Actinomycetes also became established. Other, less common, bacteria also appeared and there was a shift in the composition of the communities with depth of GAC column.

Although the species composition was different in both columns, the composition of bacteria in the effluents of both columns was similar, being composed of Flavobacterium and Bacillus brevis throughout the 70 day study, with Ps. cepacia and Actinomycetes developing during the last 20 and 30 days, respectively. There was no difference found in the bacterial densities either on the GAC or in the effluents. In addition, there was no difference in TOC removal at the 2 different flow rates studied.

Even though high levels of microbiological species exist in the biologically active GAC media and even though high levels can pass into the GAC effluents, only small amounts of chlorine or chlorine dioxide are used in European drinking water treatment plants following BAC treatment to provide satisfactory disinfection. Maximum dosage levels of 0.3 to 0.6 mg/l of chlorine are prescribed by German drinking water laws (Sontheimer, 1977). At the French Rouen water treatment plant, 0.5 to 0.6 mg/l of chlorine follows post-ozonation, which, itself follows BAC passage (Gomella & Versanne, 1977).

TABLE 5. BACTERIA ISOLATED FROM GAC ADSORBERS AT PHILADELPHIA, PA

Identification	API Code	Comment
Ps. putida	2 200 004 41	acceptable
	2 201 004 41	acceptable
Ps. fluorescens	2 005 006	excellent
Ps. maltophilia	1 000 000 41	acceptable
	1 202 000 51	very good
Ps. pseudoalcaligenes	0 000 004 50	best fit
Pseudomonas spp. other	2 000 004 50	good likelihood but low selectivity
Pseudomonas spp. other	0 000 004 50	good likelihood but low selectivity
Pseudomonas spp other	0 000 0C4 51	good likelihood but low selectivity
Pseudomonas spp other	0 002 004 41	good likelihood but low selectivity
Pseudomonas spp other	0 002 004 40	good likelihood but low selectivity
Pseudomonas spp other	0 001 004 50	good likelihood but low selectivity
Pseudomonas spp other	2 200 004 51	good likelihood but low selectivity
Achromobacter spp	1 010 004 41	best fit
Alcaligenes odorans	0 001 004 50	best fit
Alcaligenes spp	0 000 004 40	best fit
Flavobacterium odoratum	0 002 004 01	best fit
CDC IV E	0 010 004 01	best fit
CDC II F	0 202 004 00	best fit
	0 242 004 00	excellent

Source: Cairo *et al.*, 1979

TABLE 6. BACTERIA ISOLATED FROM GAC COLUMNS AND EFFLUENTS IN PHILADELPHIA

Identification	Relative Abundance
Ps. cepacia	common
Ps. acidovorans	common
Ps. paucimobilis	occasional
Ps. pituda	common
Acinetobacter - 3 species	common
Azotobacter	common
Actinomycetes - 2 species	common
Flavobacterium - 3 species	common
Cytophaga	rare
II B	common
Alcaligenes odorans	common
Alcaligenes denitrificans	occasional
Alcaligenes SP. other	common
Bacillus brevis	common

Source: McElhaney *et al.*, 1980

It is significant that BAC processing never is the final step in European drinking water treatment plants. A small amount (0.3 to 0.6 mg/l) of chlorine or chlorine dioxide always is added to disinfect the GAC effluents and to maintain an adequate residual in the distribution system.

McElhaney & McKeon (1978) reported on studies of the biology in GAC media at the Torresdale Filter Plant of the City of Philadelphia. Column influents (after passage through sand filters) had an average pH of 8.6 and a free chlorine concentration of 2 mg/l. There was no preoxidation (other than prechlorination) or preaeration of column influent waters. Bacterial levels in the GAC column effluents increased to 10^3 to 10^4 bacteria/ml within the first month of continuous use, then decreased and remained at slightly lower levels for the balance of the study. Bacterial levels in the GAC effluents at all times were significantly higher than those of the sand filter effluents. The most predominant species of bacteria identified belonged to the genus *Pseudomonas*. The following bacteria were isolated and identified in addition to those isolated and identified by Werner, Klotz & Schweisfurth, (1979): Ps. pituda, Ps. maltophila, Achromobacter sp., Alcaligenes odorans, Alcaligenes sp. and Flavobacterium odoratum, CDC IV E and CDC II F.

Latoszek & Benedek (1979) isolated and identified bacterial species present in biologically active GAC columns used for treating coagulated, settled and sand-filtered domestic wastewater. Extensive growths of bacteria, up to 10^9 viable cells/g of wet drained GAC, were detected. The majority of isolates were classified as belonging to the genus Pseudomonas and to the Flavobacterium cytophaga group. A high percentage of the bacteria exhibited denitrifying ability. These authors concluded that the microbial life in activated carbon adsorbers used to treat wastewaters appears to be similar in nature and numbers to that found in activated sludge mixed liquor.

Brewer & Carmichael (1979) also studied and characterized microbial populations of GAC adsorber systems used to treat drinking water following ozonation. GAC samples were taken from two 6-foot deep columns operated at the U.S. Environmental Protection Agency laboratories in Cincinnati, Ohio, which were treating Ohio River water. One column received ozonated water during the six week study, and the second column received untreated water. In most cases, only about 10% of the bacteria present in the influent was recovered in the effluents. Counts in the effluents ranged from 1.10×10^2 to 1.30×10^3, with a mean of 4.4×10^2 colony-forming units (CFU)/ml. Fungi did not appear in the effluents until the third week, after which approximately 80% of the fungi was recovered in the effluents.

Counts of enteric bacteria in the influents ranged from 50 to 1,000 CFU/mL, but only about 25% was recovered in the effluents. Coliform bacteria in effluents were detected only during the first week of sampling, the number of colonies being similar to those present in the influents. No fecal coliforms were detected in the ozonated waters. Pseusomonads were detected in all influent samples, but only in one effluent sample. Table 7 shows the results of bacterial characterization of gram-negative populations determined by Brewer & Carmichael (1979). Enterobacter agglomerans was the most prevalent bacterium isolated (54.3% of the total isolates). Species of the genus Proteus also were prominent (P. mirabilis, 29% and P. vulgaris, 5%). No enteric pathogens were isolated, and E. coli represented only 2.6% of all isolates. These investigators noted a shift in population, however, during the first 3 weeks of the study. Initially, Proteus was the significant genus isolated, but Enterobacter dominated all plates during the last 3 weeks.

Brewer & Carmichael (1979) also estimated the potential endotoxin concentrations present in the GAC column effluents by correlating with enteric bacterial populations using the Limulus lysate method of Evans, Schillinger & Stuart (1978). Endotoxin concentrations averaged 0.011 and 0.006 mg/l in the effluents from the ozonated and untreated samples, respectively. These averages represent 28% and 13% of endotoxin recovery in the effluent from each water sample, respectively. These authors cautioned that these data indicate the retention of endotoxins by the GAC adsorbers, and that subsequent release of such material into water passing through the adsorbers might produce endotoxin levels sufficiently high to cause illness in human beings.

TABLE 7. ENTERIC BACTERIA ISOLATED FROM GAC EFFLUENTS

Organism Isolated	Percentage of Total Isolated
Enterobacter agglomerans	54.3%
Enterobacter cloacae	0.9
Proteus mirabilis	29.0
Proteus vulgaris	5.2
Escherichia coli	2.6
Citrobacter freundii	1.7
Serretia liquifaciens	1.7
Unknown	4.4
(Brewer & Carmichael, 1979)	

On the other hand, Wolf, Camp & Hawkins (1979) studied the pyrogenic activity of GAC-filtered water supplies and wastewaters treated by advanced waste treatment techniques, including GAC containing aerobic microbial activity. One of the main public health concerns about biological growth in GAC adsorbers, particularly for preparing potable water supplies, is the potential for generating unwanted microorganisms and/or their toxic by-products. Among the toxic by-products to be aware of are the gram-negative endotoxins, which are lipopolysaccharides which are all thought to cause a pyrogenic response (fever) when injected into animals. The rabbit is used in the standard United States Pharmacopeia (USP) pyrogen test, but man reportedly can be 1CO-fold more sensitive to endotoxins than is the rabbit.

Major conclusions drawn by Wolf et al. (1979) are as follows:

(1) The numbers of bacteria found to be present in GAC effluent waters from water treatment plants in which the GAC had been operated as long as 110 months were "very few and certainly would constitute no public health concern as long as a disinfection process is subsequently applied".

(2) All four disinfection processes employed subsequent to GAC treatment (ultraviolet, chlorination, high pH and ozonation) appeared to decrease endotoxin content.

(3) Free endotoxin appears to be not adsorbed by GAC. Bound endotoxin appears to be removed via a filtration mechanism. Hence, total endotoxin is removed during passage through GAC only by the amount of bound endotoxin filtered out.

(4) Using 2 GAC columns in series with a filtered, nitrified activated sludge effluent, the first column removed 20% of the COD and total, bound and free endotoxins by 64%, 77% and 41%, respectively. Additional removals in COD, total and bound endotoxins of 35%, 20% and 42%, respectively, were observed in the second GAC column (which had a longer empty bed contact time -- 45 minutes versus 30 minutes), but free endotoxin content increased by 12%.

(5) Pyrogenicity (in rabbits) was demonstrated for advanced wastewater treatment (AWT) effluents but not for GAC-processed drinking waters. Although endotoxin levels generally were lower for drinking waters, many samples possessed higher endotoxin activity than some of the AWT samples which resulted in pyrogenic responses. This suggests some basic differences in water quality, which must be studied further.

Finally, Scott et al. (1975) have pointed out that the biological degradation of phenolic-type compounds has been studied extensively. Various types of Pseudomonas bacteria (which have been identified in biologically operating GAC media) appear to be best adapted for degradation of phenol. An example of such a metabolic degradation pathway was determined for Pseudomonas pituda by Sala-Trepot, Murray & Williams (1972), and is reproduced in Figure 17. Notice that this pathway involves initial addition of oxygen to the aromatic ring, producing catechol, after which ring rupture occurs, followed by further oxidative degradation to produce acetaldehyde and pyruvic acid. These are three of the same products which have been identified as oxidation products isolated upon ozone oxidation of phenol (Rice & Miller, 1977).

Heilker (1979) has presented a detailed description of the BAC process which has been operating on full scale at the Dohne drinking water treatment plant at Mülheim, Federal Republic of Germany. Discussion of this plant and the process employed is presented in Section 9 and in Appendix E. One observation made during the summer of 1978 will be pointed out here. When the process first was installed, it was found that backwashing frequency of the rapid sand and GAC media could be decreased to periods greater than every 7 days. During the summer of 1978 "a population explosion of nematodes" was observed in both of these media. Because the reproduction cycle of these nematodes is 3 to 4 days, simply increasing the backwashing frequency to 3 days has eliminated this problem.

On the basis of studies conducted to date, McElhaney et al. (1980) conclude that when GAC adsorbers are first installed or when virgin or regenerated GAC is first utilized, microbial populations initially increase exponentially for the first 2 to 3 weeks, then enter a phase of negative growth acceleration where populations level off and finally develop into a pseudo-steady state. Populations in the top levels of the GAC column reached approximately 10^8 bacteria/g of wet GAC in the pseudo-steady state. This growth curve is similar to the sigmoidal type of growth curve which is typical of most species during their initial stages of growth, except for the absence of an observed initial lag phase.

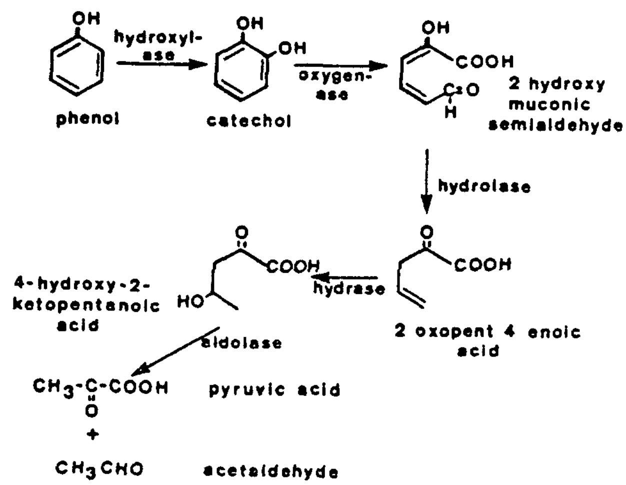


Figure 17 Simplified metabolic pathway used by Psuedomonas putida to degrade phenol

(Sala Trepot, Murray & Williams, 1972)

The predictability of microbial growth curves in a GAC system is important when evaluating the effect of environmental factors, such as linear velocity, on that growth. McElhaney et al. (1980) and Klotz et al. (1976) showed that bacterial densities decreased with increasing depth in the GAC column, which might be attributed to a decrease in food supply. McElhaney et al. (1980) showed that TOC levels in the GAC also decrease with increasing depth. TOC levels are a good indicator of the microbial food supply because carbon is the major source of energy for all of the bacteria identified in their study.

With these few fundamental principles regarding microbiological and biochemical oxidations in hand, we can now address the basic parameters of BAC systems (see Section 8) so as to combine the best features of three treatment processes (chemical oxidation, GAC adsorption and biological oxidation). Successful design of BAC systems appears to provide treatment systems which can be more efficient in removing organic pollutants than either of the three processes taken individually. In addition, savings in the operational costs of GAC adsorption systems can be effected, under certain conditions, by incorporating chemical preoxidation of the water or wastewater to be treated and by promoting aerobic microbial activity in the filter and GAC adsorption media.

SECTION 7

GRANULAR ACTIVATED CARBON

INTRODUCTION

Granular activated carbon (GAC) has a long history of successful applications in the purification of liquids and gases. This section will address the applications of granular activated carbon to the treatment of drinking water. Mechanisms of pollutant removal from water by GAC treatment, historical GAC applications and modern GAC applications in European drinking water treatment plants will be discussed.

The first application of GAC for drinking water treatment was described by Batchelor (1977) to have occurred in 1910 at Reading, England, where drinking water was superchlorinated to oxidize organic materials and then was dechlorinated by passage through activated carbon. Subsequent applications of GAC to municipal water treatment were at Hamm, Germany in 1929 and at Bay City, Michigan in 1930 (Hasler, 1974). Economic analyses, however, indicated that powdered activated carbon (PAC) was more cost-effective at the dosages normally found necessary at that time. The first municipal application of PAC was at the Hackensack Water Company at New Milford, New Jersey (Kornegay, 1978). Subsequently, more than 1,000 water treatment plants have adopted the use of powdered activated carbon for taste and odor control.

Deteriorating raw water quality caused ever-increasing dosages of PAC and this renewed interest in the use of granular activated carbon for taste and odor control. An organization which has made major investments in the application of GAC for this purpose commencing at Hopewell, Virginia in 1961 is the American Water Works Service Company (Blanck, 1978).

Ten filters of the Nitro, West Virginia water treatment plant were converted to GAC in 1965 and were operated successfully until 1973, at which time the plant was abandoned in favor of a new facility using a different, higher quality raw water supply which did not require the use of GAC. A multiple hearth furnace was used at the original Nitro plant for GAC regeneration. The Nitro plant was the subject of considerable study during its operational life (Woodward, et al., 1964; Dostal et al., 1965; Flentje & Hager, 1964).

Based on successful applications at the Hopewell and Nitro water treatment plants, the American Water Works Service Company has converted sand filters to filter/adsorbers by replacing a portion of the sand filter media with GAC at other of the company-owned water treatment plants (Blanck, 1978). They currently have 20 plants operating in this mode (Moser, 1978). This type of installation is illustrated by Figure 18. Overall, there are more than 60 municipal water treatment plants in the United States currently using GAC, primarily in the sand replacement mode (Froelich, 1978). Table 8 summarizes important milestones attained with carbon adsorption technology.

TABLE 8. ADSORPTION TECHNOLOGY MILESTONES

Year	
1550 B.C.	Early recorded use of charcoal
1811 A.D.	Bone char used for sugar processing
1828	First char regeneration instituted
1852	First granular charcoal filter, Elizabeth, N.J.
1889	Hershoff multiple hearth furnace introduced
1906	First commercial production of activated carbon (Eponite, Europe)
1910	First application of GAC in drinking water treatment (Reading, England)
1913	First commercial production of activated carbon in the U.S.
1928	First use of powdered activated carbon for taste and odor control (Chicago meat packers)
1929	First GAC filter installed (Hamm, Germany)
1930	First municipal use of powdered activated carbon for taste and odor control (Hackensack Water Company)
1961	GAC filters installed at Hopewell, VA water treatment plant
1965	First advanced wastewater treatment plant incorporating GAC (South Lake Tahoe, California)
1978	First fluidized bed GAC regeneration furnace installed in the U.S.

Source: Kornegay, 1978

Granular activated carbon pressure post-adsorbers were installed in a number of water works in the lower Rhine River area of the Federal Republic of Germany in the 1950s and early 1960s. These units incorporated both pressure filtration and pressure adsorption in a single vertical steel vessel, as illustrated in Figure 19. The upper compartment utilizes an inert medium for the removal of turbidity as well as oxidized iron and manganese compounds. The lower compartment utilizes GAC as a post-adsorption medium. The pressure units were installed originally for taste and odor removal as well as dechlorination, but now serve as biological reactors and adsorbers due to the elimination of prechlorination and addition of a preozonation step ahead of filtration.

Pressurized post-adsorber GAC units have been in operation in the Foxcote Treatment Works of the Bucks Water Board of England since 1960. GAC was installed at this plant for taste and odor control.

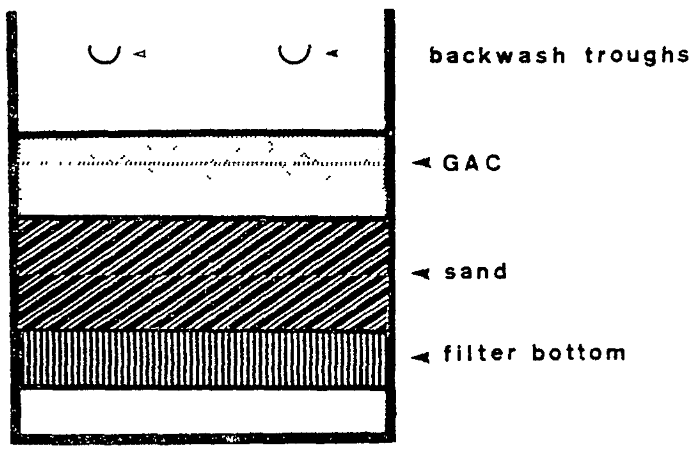


Figure 18. Filter/adsorber installation.

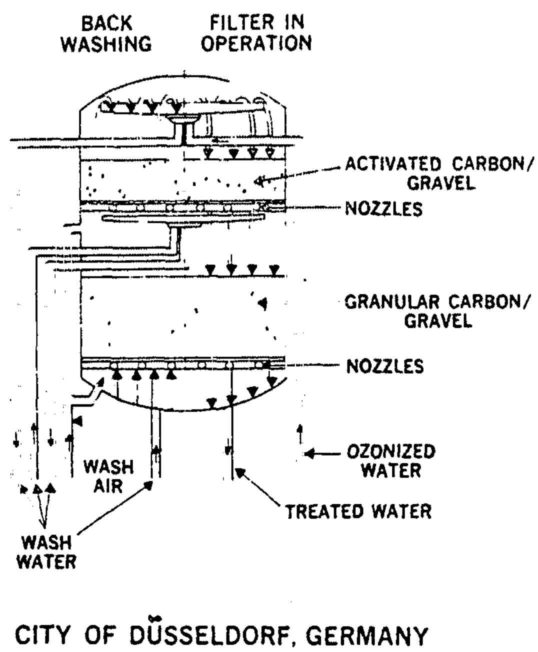


Figure 19. Dual function filter and adsorber.

(Source: Hagar & Fulker, 1968)

GRANULAR ACTIVATED CARBON

Charcoal long has been applied for the purification of liquids such as drinking water. The "activation" of charcoal during manufacture or treatment to enhance its adsorptive power has broadened its applications in the purification of liquids and gases. Activated carbon is manufactured from a number of carbonaceous materials which include the following:

Bituminous coal
Coconut shells
Lignite
Wood
Pulp mill residues

Activation is carried out by treatment of the carbon to achieve a high degree of porosity and an associated high surface area. The high surface area renders activated carbon an excellent adsorbent for a wide range of substances from both liquid and gaseous phases. Activation of carbon is accomplished by one of two processes, gas activation and chemical activation.

Manufacture of activated carbon by gas activation is essentially a two-step process, carbonization and activation. Carbonization usually is achieved by burning of the carbonaceous raw material in the absence of oxygen, a process known as pyrolysis. The carbonized intermediate product is activated by being brought into contact with steam or carbon dioxide to form the necessary porous structure.

Manufacture of activated carbon by chemical activation is a process in which uncarbonized carbonaceous materials are mixed with chemicals which are capable of dehydrating and oxidizing. The chemically treated material then is heated to create the necessary pore structure. The activating agents, such as zinc chloride, phosphoric acid, sulfuric acid, etc., are washed out and recovered.

In conventional practice, activated carbon is used as an adsorbent. Its capacity for adsorption is governed by:

(a) the adsorbent surface area actually available to the adsorbate molecules and

(b) the affinity of the adsorbate molecules for the available adsorbent surface areas.

The following information is important, therefore, when evaluating activated carbon as an adsorbent for contaminants present in a liquid phase:

a. Surface area
b. *Pore volume distribution*
c. Chemical nature of the activated carbon surface area
d. Chemical structure of the adsorbate molecule(s)

Activated carbons in common use have total surface areas (sum of the outside surface area plus available internal surface area inside the pores) ranging from 450 to 1,500 square meters per gram. The total surface area normally is determined by the Brunauer, Emmett & Teller (BET) method, in which the total volume of nitrogen gas adsorbed at liquid nitrogen temperature (minus 195°C) is measured at various pressures. The plot of volume of adsorbed nitrogen versus pressure at constant temperature is called an adsorption isotherm, and this enables calculation of the volume (and hence the surface area) of a layer of nitrogen one molecule thick. However, the molecules encountered in liquid phase operations usually are much larger than the nitrogen molecule. As a result, the actual area available for adsorption normally will be considerably less than the total surface area as measured by the BET method.

Another measure of activated carbon capacity is pore size distribution within the carbon particles. One method for measuring pore size distribution is by using a range of adsorbate molecules of varying size as molecular probes (Calgon Corporation literature, undated). Adsorbate probes include mercury, nitrogen and water. Edwards (1979) points out that pore volume distributions may be a function of both raw material (Figure 20) and activation conditions (Figure 21).

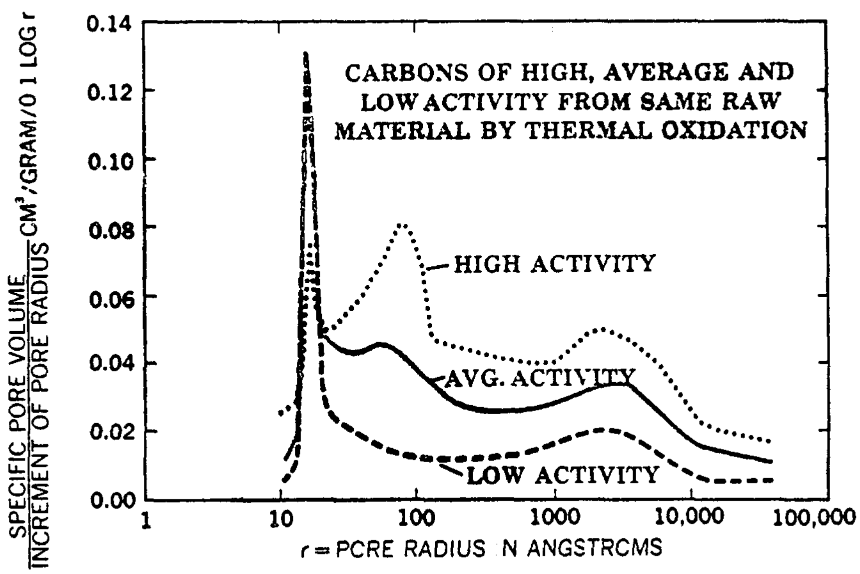


Figure 20. Pore volume distributions of typical decolorizing activated carbons.

(Edwards, 1979)

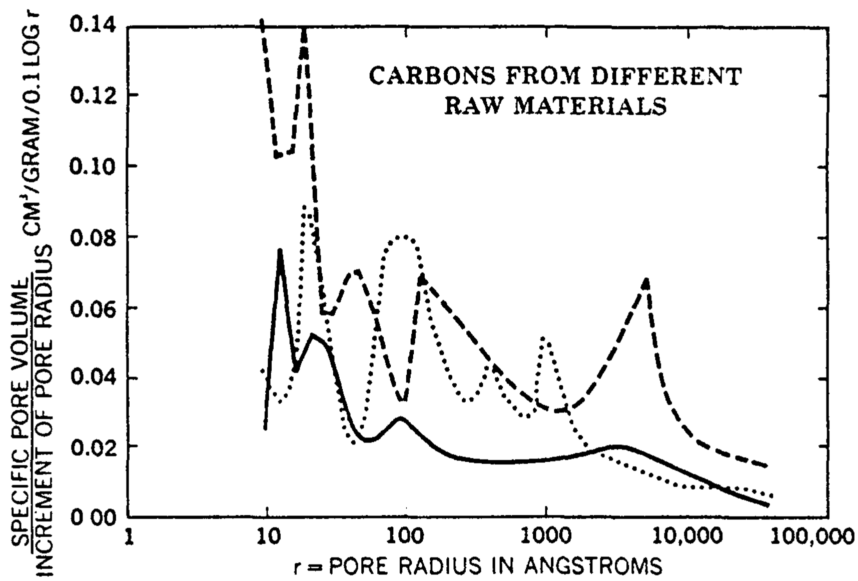


Figure 21. Pore volume distributions of typical decolorizing activated carbons.

(Edwards, 1979)

The nomenclature used in designating pore volume size ranges is not universal. United States practice appears to refer to pore sizes larger than 1,000 angstroms (Å) diameter as "macropores" and pore sizes from 10 to 1,000 Å in diameter as "micropores" (Weber, 1972; Calgon Corporation literature, undated). Reference to European literature, however, indicates that such categories are by no means universal. Juntgen (1975) uses the following classification: macropores $\geq$ 500 Å diameter, mesopores $\leq$ 500 to 20 Å in diameter, micropores < 20 to 8 Å diameter and submicropores < 8 Å in diameter. A Lurgi publication (1976) uses the following definitions: macropores $\geq$ 200 Å diameter, transitional pores $\leq$ 200 Å and > 20 Å diameter, micropores $\leq$ 20 Å diameter. This point is emphasized to ensure care in transposing European experiences to the United States. Pore size distribution is particularly important in considering the use of biological activated carbon (BAC), discussed in Section 8.

The nature of the carbon surface is important in determining the capacity of activated carbons for a specific adsorbate molecule. Greater knowledge is developing in this area as the use of activated carbon for water treatment increases. The necessity of removing trace quantities of toxic organic compounds demonstrates that need.

The nature of the adsorbate affects the efficiency of adsorption. Some adsorbates are strongly adsorbed while others are weakly adsorbed. Liquid streams containing a number of chemical compounds further confuse the issue because of the chemisorption phenomenon, which is discussed in a following subsection.

SELECTION OF ACTIVATED CARBONS

Selection of the type of activated carbon to be used depends upon a number of factors. Powdered activated carbon (PAC) is used predominately for routine applications in the United States mainly on the basis of economics (AWWA, 1971). The use of both PAC and GAC is growing in the European countries (Water Research Center, 1977) for the following reasons:

"(a) It is more economic to use a granular carbon bed if large doses (72O mg/l) of powdered carbon are normally required, and

(b) a granular carbon filter is held to be more effective in the removal of micropollutants." (Micropollutants are generally understood to be those soluble materials which cannot be removed by simple filtration.)

The remainder of this discussion will be limited to GAC since the evaluation of Biological Activated Carbon (BAC) for drinking water purposes has been limited to this form of activated carbon. Primary properties to be considered in GAC selection include the following:

Capacity
Hardness
Permeability
Solubility

The capacity of GAC used for a specific water treatment objective can be determined by pilot plant evaluations. Standardized equipment and procedures are available, but some insight is required to determine periods of study and the number of studies required for a specific water source. The effects of biological activity and desorption further complicate the situation.

The hardness of the GAC is a factor in determining the amount of carbon loss and associated cost of makeup GAC per each adsorption-regeneration cycle. Other factors which influence GAC losses during use are handling and burnoff losses during the reactivation process. It is not clear which of these factors is of greatest significance, but since losses can range from 3.5 to 10% or more, they are of obvious importance.

Permeability of the activated carbon is of obvious importance in terms of head loss in downflow contactors and of bed expansion in upflow units. Permeability is a function both of particle size and gradation. The smallest particle size of GAC normally would be expected to be specified so as to maximize the available total surface area. This intent would be tempered by the available hydraulic head or the sensitivity to plugging due to biological activity in the contactor. Solubility of adsorbate in water is of significance also, since the more polar the molecule is, the greater is its solubility in water and the less readily removed from water it is by activated carbon adsorption. Surface characteristics (outer surface and inner pore surfaces) also affect adsorption of water soluble molecules, and these characteristics depend upon the raw material used to produce the carbon, the activation process and the solutes to be removed from aqueous solution.

OPERATIVE MECHANISMS DURING DRINKING WATER TREATMENT WITH GAC

Successful use of granular activated carbon in the treatment of drinking water results from a number of mechanisms and processes, including adsorption, filtration and biological activity. These factors are discussed in the following subsections.

Adsorption

This is the most commonly recognized function of GAC. It consists of removal of solutes from solution and their concentration on the surfaces (external and internal) of the adsorbent. The three types of adsorption are (Weber, 1974):

(1) exchange adsorption (electrical attraction of the solute to the adsorbent)

(2) physical or ideal attraction (involving weak van der Waals forces)

(3) Chemisorption or chemical adsorption (chemical reaction of the adsorbate with the carbon surface).

In water treatment by means of GAC, the primary mechanisms are physical adsorption (which is reversible) and chemisorption, which is generally considered to be irreversible.

Physical adsorption is a function of a number of factors, including the following (Edwards, 1979):

(1) solubility of the adsorbate (pollutant)

(2) affinity of adsorbate for the adsorbent (GAC) surface

(3) properties of the adsorbent (GAC).

An adsorbate of low solubility in water will be more adsorbable by GAC and vice-versa. Chemical compounds vary in their affinity for GAC surfaces due to a number of factors, including the presence in the adsorbate molecules of specific functional groups as well as the molecular shapes and structures of the molecules themselves. Table 9 lists a number of organic compounds and their relative adsorbabilities onto GAC. Additional information on the adsorption of organic chemical compounds by GAC is provided in Section 8. The primary desired GAC properties for use in water treatment are high available surface area and pore size distribution, which were described in an earlier subsection.

Chemisorption involves chemical reactions of the solute with the GAC surface. This can occur, for example, by carbonyl or hydroxyl groups (present on the activated carbon surface) condensing with amine, hydroxyl or activated hydrogen groups in the adsorbate to form very strong covalent bonds, as indicated in Figure 22. Restoration of the GAC surface with respect to chemisorbed solutes results in the physical destruction of the carbon surface involved in the chemical reaction. Because the amount of chemisorption involved with removal of organic pollutants generally is very small compared with physical adsorption, chemisorption will not be discussed further in this section.

TABLE 9. GAC ADSORPTION OF ORGANICS

Strongly Adsorbed	Weakly Adsorbed
• Aromatic Solvents: benzene, toluene, nitrobenzenes, etc.	• alcohols
• Chlorinated Aromatics: PCBs, chlorobenzene, chloronaphthalene	• low molecular weight ketones, acids & aldehydes
• Phenol & Chlorophenols	• sugars and starches
• Polynuclear Aromatics: acenaphthene, benzopyrenes, etc.	• very high molecular weight or colloidal organics
• Pesticides & Herbicides: DDT, Aldrin, Chlordane, BHCs, Heptachlor, etc.	• low molecular weight aliphatics
• Chlorinated Non-Aromatics: CCl_4, chloroalkylethers, heaxchlorobutadiene, etc.	
• High Molecular Weight Hydrocarbons: dyes, gasoline, amines, humic acids	

A major concern with physical adsorption is competitive adsorption between two or more solutes present in the solution being purified. A weakly adsorbed pollutant will be displaced from the activated carbon surface by a more strongly adsorbed pollutant. The displaced, weakly adsorbed material then will be readsorbed further down in the activated carbon medium. This repeated adsorption, desorption and readsorption seqeuence is known as "the chromatographic effect".

Desorption of an adsorbed pollutant also may occur if the concentration of the pollutant in the liquid feed to the GAC medium becomes significantly lower and the adsorbed pollutant is not strongly adsorbed. This behavior is of particular concern when removal of certain toxic organic compounds, such as chloroform, is required.

Each adsorbable dissolved organic compound is held on the GAC surface or in its pores usually by physical forces, the strengths of which depend upon a number of factors related to the molecular structure and polarity of the adsorbed molecule. If the GAC is loaded with a weakly adsorbed compound and the influent solution now is spiked with a second dissolved organic compound which is more strongly adsorbed than the first, then the first compound will be displaced, or desorbed, from the surface and/or the pores by the second, which now becomes the adsorbed solute. For example, phenol is readily adsorbed by GAC, but is readily desorbed by p-chlorophenol.

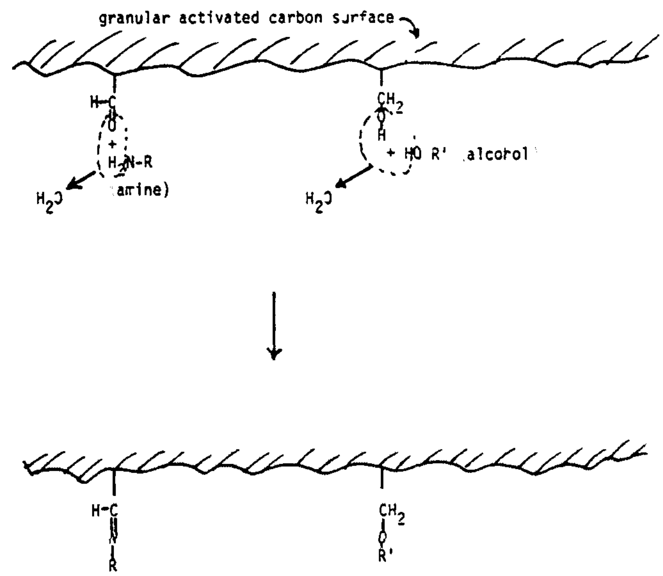


Figure 22. Examples of chemisorption on GAC surfaces.

If the volume of influent solution is adjusted so that phenol is adsorbed only in the initial few centimeters of the GAC column and then a dilute solution of p-chlorophenol is passed through the column, desorption of the phenol will occur. In the next lower section of the GAC, which has not yet been exposed to p-chlorophenol, the phenol desorbed from the higher levels will be readsorbed. When more p-chlorophenol reaches the second layer of GAC containing adsorbed phenol, desorption again occurs. This process of phenol adsorption, followed by desorption, continues until finally, phenol is removed completely from the GAC and is eluted into the GAC effluent.

This chromatographic effect has been noted recently at the Kralingen plant in Rotterdam, The Netherlands, with respect to adsorption of chloroform by GAC (Rook, 1978). The Kralingen plant began operating a process including ozonation, sand filtration and granular activated carbon adsorption in early 1977. Raw water is taken from two reservoirs located 20 kilometers away from the plant and through which water flows in series to the plant. One of these reservoirs is aerated to control algae, but this practice also promotes aerobic biodegradation of organics and nitrification of ammonia during the three months average residence time of the water in these reservoirs.

During summer, biological growth occurs in the 20 km long raw water transport pipe from the reservoir to the Kralingen plant, and low level prechlorination (0.5 to 2.0 mg/l dosage -- called "transport chlorination") then is employed to eliminate this growth. Use of prechlorination produces chloroform and other trihalomethanes, which are not removed during the subsequent coagulation, flocculation, sedimentation or ozonation processing steps, but are adsorbed by the granular activated carbon.

On the other hand, chloroform appears rapidly in the effluents of the Kralingen plant biologically active GAC columns, and its concentration in the effluent approaches that in the influent after about 10,000 to 12,000 bed volumes of water have been passed through, indicating that the GAC is not very efficient for the adsorption of chloroform.

When prechlorination is halted, however, chloroform continues to be found in the GAC column effluents, and its concentration decreases continually during the next few months. No "transport chlorination" is necessary during winter months at Kralingen, yet chloroform continues to be eluted from the GAC, probably by desorption caused by more strongly adsorbed organic compounds.

Filtration

Water filtration incorporates both physical and chemical processes for the removal of suspended and colloidal materials from water. While sand and crushed anthracite coal currently are the most commonly used media, experience has shown that GAC can serve as a substitute filter medium. The physical characteristics of GAC, when used as a filter medium, would lead to the definition of GAC filtration as deep bed filtration or depth filtration. Weber (1972) described depth filtration as a combination of a number of mechanisms, including first a transport mechanism which brings a solute particle from the bulk of the liquid within the void space close to the surface of the filtration medium. Secondly, an attachment mechanism retains the solute particle as it contacts the filter medium or a previously retained particle. Both surface and depth filtration mechanisms are thought to occur in deep bed filters, but it is expected that deep bed mechanisms would predominate in GAC filtration, similar to those in anthracite coal media.

Biological Activity

In granular activated carbon adsorbers, biological activity is a well recognized phenomenon. Evidence of the benefits of biological activity is manifested by operational full scale GAC systems in water and wastewater treatment applications which achieve removals of organic carbon in excess of those which could be predicted by adsorption alone.

GAC provides an excellent surface for biomass attachment and a favorable environment for growth of organisms (Weber & Ying, 1977). The biomass may be aerobic, anoxic or even anaerobic, depending upon the concentrations of biodegradable soluble organic materials present and the oxygen resources of the liquid stream entering the GAC bed. Operational practice with GAC in U.S.A. wastewater treatment applications normally has been to attempt to inhibit biological activity, as it frequently results in the formation of hydrogen sulfide odor problems. In contrast, a number of European water treatment facilities make efforts to enhance biological activity in GAC post-adsorbers by providing supplemental oxygenation.

Weber & Ying (1977) point out that bacteria will grow on any fine media surface. The rough GAC surface provides many good places for attachment, while the adsorption capability of the medium is unimpaired. The activity of the biomass will be enhanced by moderate rates of air scour, but the biomass itself will not be removed without vigorous air and water backwashing. The adsorptive capacity of the GAC is believed by Weber & Ying to concentrate organic substances on the surface of the carbon, thereby providing a more concentrated substrate for the biomass and enhancing biological growth and substrate removal. However, this hypothesis currently is in dispute (Benedek et al., 1979, 1980).

APPLICATIONS OF GAC IN WATER TREATMENT

There are a number of operational examples of the various GAC mechanisms and processes discussed previously. Therefore, those considering the application of GAC can base their decisions on data and experiences of full scale operational facilities in both the drinking water and wastewater treatment fields.

For the purpose of this discussion, operational GAC facilities are divided into three categories, which are:

Filter/adsorbers
Post-adsorbers
Biological reactors

Filter/adsorbers combine the function of both filters and adsorbers as they are not preceeded in the process by a filtration step. On the other hand, the post-adsorber unit is preceeded by a filter for the removal of particulates. The major function of the post-adsorber is to adsorb organic materials, in contrast to the dual function of the filter/adsorber.

Both filter/adsorbers and post-adsorbers can function as biological reactors in that the GAC media serve to retain the biomass. The filter/-adsorber and post-adsorber can continue to serve as biological adsorbers even after the GAC adsorption capacity appears to be exhausted.

Filter/Adsorber Applications of GAC

The use of coal as the upper layer of dual media filtration units is common practice in modern water treatment. Replacing the upper portion of a sand filter with coal provides greater solids storage capacity, longer filter runs, lower backwash rates and shorter backwash runs. GAC can and has been used in place of coal in filters where it serves as filter medium, adsorbent, and for dechlorination within its capacity limit. Even after exhaustion of its adsorption capacity, the GAC continues to serve as an effective filtration medium. Table 10 compares sand versus GAC as filter media in terms of turbidity removal and length of filter runs. Table 11 provides information on GAC in sand filters for removal of THMs and TOC.

Blanck (1979a) describes design criteria successfully used in conversion of existing sand filters to dual media units. The upper 18 to 30 inches of existing sand filters was removed and replaced with 12 x 40 mesh GAC. The dual media (GAC and sand) filters were operated at a rate of 2.0 to 3.0 gal/min/sq ft. Operating backwash rate was 10.5 gal/min/sq ft. The GAC/sand filters served a dual purpose, both to remove taste and odor as well as to filter out particulate matter.

Richard (1973) described French experiences at the Vigneux-sur-Seine water treatment plant near Paris. Filter/adsorbers were compared with post-adsorbers on a plant scale operation. While a major part of the test was intended to compare different granular activated carbons, several conclusions can be drawn, including the practical operating conditions which are summarized in Table 12:

TABLE 12. COMPARISON OF GAC FILTER/ADSORBERS AND POST-ADSORBERS AT VIGNEUX-SUR-SEINE WATER TREATMENT PLANT

Parameter	Units	Sand Filter	GAC Filter/-Adsorber	GAC Post-Adsorber
Bed Depth	m	0.8	0.8	2.5
Filtration Rate	$m^3/m^2/hr$	5.0	5.0	13.6
Empty Bed Contact Time	minutes	---	9.6	9.6
Backwash				
Air Scour	$m^3/m^2/hr$	55	55	55
Water Wash	$m^3/m^2/hr$	20	20	*

* varied, depending upon type of GAC used

Source: Richard, 1973

(1) No special operational difficulties were encountered using GAC in either mode of operation.

(2) The cost of GAC was less than that of PAC to maintain a similar water quality.

TABLE 10. COMPARISON OF GAC WITH SAND FOR TURBIDITY REMOVAL AND SERVICE LIFE

Site	Turbidity (JTU) Influent	Turbidity (JTU) Effluent Sand	Turbidity (JTU) Effluent GAC	Bed Depth (feet) Sand	Bed Depth (feet) GAC	Flow Rate (gpm/sq ft)	Service Life (hours) Sand	Service Life (hours) GAC
Pennsylvania	±2.1+0.9*	±0.18+0.05 anthracite	±0.2-0.06	2.0 anthracite	FS-300 4.0	2.0	32	65
Canada	±9.1+5.0*	±0.33+0.03	±0.35-0.08	3.5	FS-300 2.5	3.6	±14+2	±23+3
Pennsylvania	±4.9+1.1*	±0.48+0.16	+0.45-0.19	2.5	FS-400 2.5	1.4	ND***	53
Pennsylvania	±13+7.2**	ND***	±0.38-0.18	2.0	FS-400 2.0	2.0-3.0	ND***	ND***
Wisconsin	±1.5-0.75**	±0.38+0.14	±0.36-0.12	3.0	FS-400 2.9	1.8	±73+	±62+10

* after pretreatment ** raw water data (no treatment) *** operators noted no difference

Source: Froelich, 1978

TABLE 11. TREATMENT OF DRINKING WATER BY GAC IN SAND FILTERS

Plant Location	Contact Time (minutes)	THM -- Time To Reach			TOC -- Time To Reach	
		20% Breakthrough	100% Breakthrough	0.5 mg/l Over Initial	50% Breakthrough	0.5 mg/l Over 50%
California	10	--	--	4 wks	12 wks	12 wks
West Virginia	7.5	6 wks	18 wks	6 wks	3 wks	10 wks
Canada	8.5	4 wks	14 wks	2 wks	8 wks	12 wks
Pennsylvania	11.0	2 wks	10 wks	2 wks	6 wks	7 wks
Pennsylvania	7.5	2 wks	14 wks	4 wks	4 wks	8 wks

Source: Froelich, 1978

(3) Use of GAC as the post-adsorber resulted in better water quality than when used as a filter/adsorber.

(4) Backwash cycles in the filter/adsorber would be dependent on headloss or some other operational parameter. It was found that better effluent quality resulted from use of the GAC as a post-adsorber with backwashing once per week.

Post-Adsorber Applications of GAC

The use of GAC as a "post-adsorber" (after a filtration step) has been practiced frequently in the United States (Hager & Flentje, 1965; Hager & Fulker, 1968). However, the majority of experience with this mode of operation in drinking water treatment currently exists in Europe. Table 13 provides a partial listing of European plants using granular activated carbon. Of these, it is known that water treatment plants of the Federal Republic of Germany on the lower Rhine River (Düsseldorf, Duisburg and Wuppertal) placed GAC post-adsorber pressure units in operation in the late 1950s and early 1960s. The Foxcote Treatment Works of the Bucks Water Board (England) has operated GAC units after rapid gravity sand filtration since 1960 (Ford, 1973). At the Foxcote plant, filtrate is pumped to 2.44 meter high and 2.4 meter diameter steel pressure vessels with 0.91 meter of GAC providing a contact time of 323 seconds.

Several water treatment facilities are operated by the Goleta Water District of California, in which pressure GAC post-adsorbers are used following diatomaceous earth filtration (Hager & Fulker, 1968; Lawrence, 1968). Several continuous backwash GAC adsorbers also are in operation in the New England area.

Much can be learned regarding GAC post-adsorber design and operation from U.S. municipal wastewater treatment facilities incorporating this mode of treatment (Culp, 1980). A number of wastewater treatment systems are in operation or are under construction. Most of these facilities include on-site GAC reactivation systems. Table 14 provides a partial listing of U.S. wastewater treatment plants which incorporate GAC adsorption. Guidance on the design of GAC systems is available from an EPA Design Manual (U.S. EPA, 1973) as well as from technical articles (Culp, 1980; Carnes, 1979). Technical representatives of GAC material suppliers also are good sources of design information.

Biological Reactors

The intentional enhancement of biological activity in GAC filter/-adsorbers and post-adsorbers is not common practice in United States water or wastewater treatment plants, although it is practiced in a number of European water treatment facilities. The phenomenon of biological activated carbon (BAC) is described in detail in Sections 8 and 9. It is recognized that GAC will continue to serve as a biomass retention medium long after the exhaustion of its adsorption capacity.

TABLE 13. PARTIAL LIST OF EUROPEAN WATER TREATMENT PLANTS USING GAC

Location	Plant	Type of GAC Contactor	Plant Capacity cu m/day	Preozonation
BELGIUM				
Wourren	de Blankaart	beds	43,200	yes
FEDERAL REPUBLIC OF GERMANY				
Albstadt	--	--	18,000	yes
Cologne	--	--	--	yes
Cologne	--	--	--	---
Duisburg	Wittlaer III	columns	72,000	yes
Düren	--	--	36,000	yes
Düsseldorf	Holthausen	columns (MH)	192,000	yes
Düsseldorf	Flehe	columns	88,000	yes
Düsseldorf	Am Staad	columns	119,000	yes
Frankfurt	--	--	--	---
Friedrichshafen	--	--	30,000	yes
Koblenz	--	--	--	---
Königswinter	--	--	4,800	yes
Langenau	--	beds	198,700	yes
Leverkusen	--	--	--	---
Mainz	--	--	--	---
Mülheim	Dohne	columns	48,000	yes
Schwabisch Hall	--	--	--	---
Siegburg	--	--	70,000	yes
Solingen	--	--	2,000	no

TABLE 13 (CONTINUED)

Location	Plant	Type of GAC Contactor	Plant Capacity cu m/day	Preozonation
Stolberg	Stolberger	--	30,000	no
Stuttgart	Berg	columns	90,000	no
Süsel	--	--	30,000	yes
Vallendar	Vallena	--	30,000	yes
Wiesbaden	Schierstein	columns	24,400	no
Wuppertal	Benrath	columns (FB)	150,000	yes
FRANCE				
Dunkirk	Mouelle	beds	50,000	---
Nancy	--	--	--	---
Paris	Morsang-sur-Seine	beds	150,000	---
Paris	Vigneux-sur-Seine	beds	36,000	yes
Paris	Viry Chantillon	beds	120,000	no
Rouen	la Chapelle	beds	50,000	yes
ITALY				
Turin	River Po	beds	86,400	no
NETHERLANDS				
Amsterdam	--	--	82,200	---
Rotterdam	Kralingen	columns	210,000	yes
The Hague	--	--	--	---
SWITZERLAND				
Arbon	--	--	30,000	yes
Biel	--	--	36,000	yes

TABLE 13 (CONTINUED)

Location	Plant	Type of GAC Contactor	Plant Capacity cu m/day	Preozonation
Kreuzlingen	--	beds	32,400	yes
St. Gallen	Riet	--	60,000	yes
Zürich	Lengg	beds (FB)	250,000	yes
Zürich	Moos	beds	---	yes
SWEDEN				
Göteborg	Alelyckan	beds (MH)	---	no
Göteborg	Lackareback	beds	---	no
UNITED KINGDOM				
Church Milne	--	(MH)	---	no
Foxcote	--	columns	9,100	no

NOTES: (MH) = on-site Multiple Hearth GAC regeneration facilities
(FB) = on-site Fluidized Bed GAC regeneration facilities

Regeneration Methods and European Costs

Granular activated carbon loses its adsorptive capacity as the surface area of GAC becomes covered with adsorbed molecules of pollutants. This adsorbed material must be removed if the activated carbon surfaces are to be reused. GAC regeneration is the process of reactivation or removal of the adsorbed materials from the activated carbon surfaces.

There are many means for regeneration of GAC, including steam, chemicals, desorption, and even biological activity. However, for water and wastewater treatment applications, thermal regeneration using high temperatures and oxidizing atmospheres is the most commonly utilized method. Thermal regeneration is similar to the original activation process and consists of three phases: drying, pyrolysis and regeneration. Figure 23 illustrates the three process steps, while Figure 24 provides a diagram of the steps involved in on-site activated carbon regeneration.

TABLE 14. PARTIAL LIST OF U.S. WASTEWATER TREATMENT PLANTS USING GAC

Plant Location	Type of Contactor	Operational Status Sept. 1980	mgd Plant Flow	Type Of Treatment
Upper Occoquon, VA	U, P/S	I.O.	15	tertiary
Tahoe Truckee, CA	D, P/S	I.O.	5	tertiary
S. Lake Tahoe, NV	D, P/S	I.O.	7.5	tertiary
Orange County, CA	D, P/S	I.O.	15	tertiary
Rocky River, OH	D, P/S	O.S.	10	P/C
Fitchburg, MA	D, P/S	I.O.	15.3	P/C
Piscataway, MD	D, P/S	O.S.	5	tertiary
Derry Township, PA	U, G/C	I.O.	5	P/C
Vallejo, CA	U, P/S	I.O.	13	tertiary
N. Tonawanda, NY	U, G/C	I.C.	14	P/C
Ocean Beach, NY	U, G/C	I.O.	0.7	P/C
Alexandria, VA	U, G/C	I.C.	54	tertiary
Tra, TX	U, G/C	I.C.	100	tertiary
Garland, TX	U/D, G/C	I.C.	30	P/C
Niagara Falls, NY	D, G/C	I.C.	48	P/C
Arlington, VA	D, G/C	I.C.	30	tertiary
Fairfax County, VA	D, G/C	I.C.	36	tertiary
Pomona, CA	D, G/C	I.O.	10	dechlorination
Cortland, NY	D, P/S	I.C.	10	P/C
Leroy, NY	D, P/S	I.O.	1	P/C
Cedar Creek, NY	D, P/S	I.C.	5.5	tertiary
Colorado Springs, CO	D, P/S	I.O.	3	P/C
Clvld (Westerly), OH	D, P/S	I.C.	50	P/C
Rosemount, MN	D, P/S	I.O.	0.6	P/C
Waterville Vly, NH	D, P/S	I.O.	0.5	P/C & de-Cl_2
St. Charles, MO	D, G/C	I.O.	5.5	tertiary
Sylvan Beach, NY	U, G/C	I.C.	2	P/C
Aquia, VA	U, G/C	I.C.	3	P/C
Seneca Creek, MD	U, G/C	I.O.	5	dechlorination
Horsepen Branch, MD	U, G/C	I.O.	1	dechlorination
Lower Anacostia, MD	U, G/C	O.S.	2	dechlorination
Santa Clara, CA	U, P/S	--	4	tertiary
Ely, MN	D, P/S	O.S.	0.6	P/C
Damascus, MD	U, G/C	I.O.	0.75	dechlorination

Abbreviations: P/S = pressurized steel contactors
G/C = gravity concrete contactors
U = upflow contactor
D = downflow contactor
I.O. = believed to be In Operation
O.S. = believed to be Out of Service
I.C. = believed to be In Construction
P/C = Physical/Chemical treatment
tertiary = following conventional secordary treatment
dechlorination = functions primarily as a dechlorination unit

drying

$$\text{CARBON} \bullet \text{ADSORBATE} + H_2O \xrightarrow[300^\circ F]{\text{heat}} \text{CARBON} \bullet \text{ADSORBATE} + H_2O\uparrow$$

pyrolysis

$$\text{CARBON} \bullet \text{ADSORBATE} \xrightarrow[900^\circ\ 1400^\circ F]{\text{heat}} \text{CARBON} \bullet C' + \text{VOLATILIZED ADSORBATE}\uparrow$$

regeneration

$$\text{CARBON} \bullet C' + H_2O \xrightarrow[1500^\circ\ 1800^\circ F]{\text{heat}} \text{CARBON} + C'O\uparrow + H_2\uparrow$$

Figure 23. Process steps in the regeneration of granular carbon.

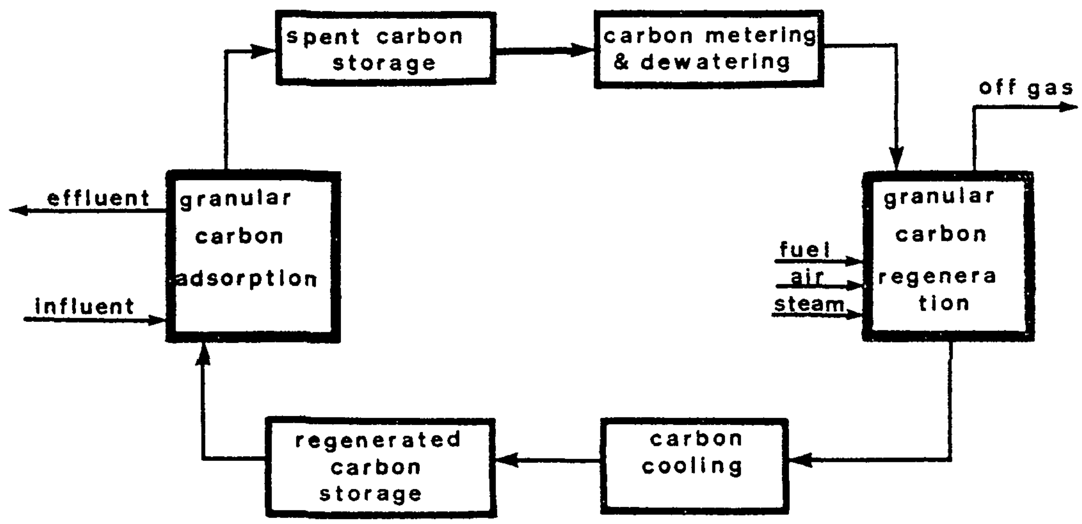


Figure 24. GAC regeneration system components.

The four basic types of GAC regeneration furnace are as follows:

(a) multiple hearth
(b) rotary kiln
(c) fluidized bed
(d) electric moving belt

Each of these units has its individual advantages and disadvantages, with multiple hearth units being the most commonly used in the United States.

In 1978, the PTI site visitation team inspected the Lurgi, six metric ton per day, fluidized bed GAC regeneration facility at Düsseldorf, Federal Republic of Germany. Further information on this installation is provided in the Düsseldorf plant description of Appendix C. A WABAG designed and constructed fluidized bed GAC regeneration furnace is in operation at the Wuppertal, Benrath, Federal Republic of Germany water treatment plant. A Norit fluidized bed furnace is used to regenerate GAC at the Zürich, Switzerland, Lengg water treatment plant. Multiple hearth regeneration furnaces are known to be in operation at the Alelyckan water treatment plant of Göteborg, Sweden and at the Church Milne Treatment Works, Nottingham, England.

The prices charged for granular activated carbon in Europe generally are higher (65¢ to 80¢/lb) than those charged in the United States (58¢/lb, average in 1978). Several figures were obtained during the site visits which verified this fact and each will be discussed below. Prior to describing these details, several general points will be made about the basis for such a comparison.

There are three general factors which account for much of the price difference. The first is that since GAC is such an energy-intensive product to manufacture, its price reflects the higher energy costs which prevail in Europe. Wholesale prices for petroleum fuel in Europe were as much as twice those in the United States during 1978, and fuel is estimated roughly to account for 10 to 20% of the total production cost of GAC in the United States.

The second factor is the higher cost of labor in France, Germany, Switzerland and The Netherlands, due to high social and welfare taxes. Many of these payments are taxed directly to the employer, often as a percentage of payroll costs.

Conversations with utility managers revealed a third factor which may influence prices, namely a desire to buy from carbon suppliers doing business primarily in the purchaser's home country. These national loyalties may reduce competitive pressures, since each of these countries has very few activated carbon manufacturers.

The prices of carbon which were quoted during the 1978 site visits are not manufacturers' list prices, but rather the actual costs paid by utilities and frequently were based upon competitive bidding. Utility representatives interviewed agreed that list prices have little bearing on actual cost and hence are not useful for cost reviews. They also pointed out that actual costs paid frequently reflect many influences which relate only to that single purchase. For instance, the size of the purchase has an obvious influence on cost per unit volume. Also, some bidders may quote prices below normal profit margins when the initial purchase is expected to lead to future, higher margin, sales. Some contracts also may call for regeneration services, which is another way for the supplier of activated carbon to recover from a reduced initial price. These regeneration contracts may contain restrictions, however, that require the seller to guarantee high adsorption efficiency after regeneration, and these limits may boost prices charged. Finally, bid prices may be somewhat higher when the seller expects to be in an advantageous position due to the national loyalties of the buyer.

The result of all these factors is that one should recognize that any or all of these influences may be present in the prices discussed below. Hence, some may be above and others below what would be considered an accurate market price.

In France, the Société Lyonnaise des Eaux et de l'Eclairage (SLEE) operates several water treatment plants using GAC. Several purchases of GAC had been made in months immediately prior to June, 1978. The first of these was based on a full set of competitive bids, with the terms including a guarantee of the effectiveness upon reactivation. The accepted price was 6.9 French francs per kilogram, or approximately 68 cents/pound, based on the prevailing exchange rate (in mid-1978) of just under 5 francs per dollar. A separate purchase of additional GAC for the Vigneux-sur-Seine plant was quoted at 2,800 French francs/cubic meter, or about 65¢/lb, based on the average density of that type of GAC.

In The Netherlands, the City of Rotterdam installed GAC in their new Kralingen plant in 1977. The carbon has been leased for two years from the manufacturer on a basis which includes reactivation services. Although no purchase price was set, the utility manager mentioned a likely cost of 1,3C0 Dutch guilders per cubic meter if a flat sales price had been set. Using the same assumptions as above, this figure converts to 67¢(U.S.)/lb, using the exchange rate prevailing in mid-1978 of 2 Dutch guilders per U.S. dollar.

Treatment plants at Mülheim and Düsseldorf, Federal Republic of Germany both purchase carbon directly for their own use. At Düsseldorf, only a general cost figure was provided, with the comment that some purchases have been made below this price of 3,500 Deutsch marks (DM) per ton, or approximately 80 cents/pound based on the then prevailing exchange rate (mid-1978) of just under 2 DM/dollar. The Mülheim plant presented a purchase price (which did not include reactivation guarantees) of 1,400 DM/cubic meter, or 75¢/lb upon converting in the same fashion.

In summary, GAC prices quoted in Europe ranged from about 65 to 80 cents per pound from five separate sources. Although prices in the United States can be as high, given certain conditions of purchase, a recent study has shown estimated U.S. average prices in 1978 to be 58 cents per pound (Temple, Barker & Sloane, 1978). With this figure as a base, carbon prices in Europe range from about 20% to 50% higher than in the United States.

The regeneration of granular activated carbon used in drinking water treatment plants in Europe, as previously noted, is carried out on-site in a few cases, but generally involves returning the GAC to the manufacturer for reactivation. Most of the plants which were visited during 1978 relied upon outside reactivation services. The costs of this service, however, are difficult to estimate since the financial arrangements for the service often are indirect.

Although the Kralingen plant in Rotterdam purchases this reactivation service from the GAC manufacturer, these costs are included in a two-year activated carbon lease which has complicated terms. The Dohne plant in Mülheim (Federal Republic of Germany) also was unable to break out these costs explicitly. The Société Lyonnaise des Eaux et de l'Eclairage (France) uses a general figure of about 40% of the cost of virgin carbon. This estimate was confirmed by a recent negotiation for reactivation service, including removal from the plant, transportation, reactivation and return. The price of 2.9 French francs per kilogram, approximately 29¢/lb, is equivalent to 42% of the purchase price of this activated carbon.

Several of those plants currently sending GAC out for reactivation were examining the possibility of purchasing their own regeneration furnaces. Such a decision involves examining the relative costs of on-site and off-site regeneration. Although none of the results of these studies were made available to the site visitation team in June, 1978, they will provide much additional data in the future, if and when released.

The fluid bed regeneration furnace operating on-site in Düsseldorf (Federal Republic of Germany) has been the study of previous research reports published in the United States (Symons et al., 1978; Miller et al., 1978) and in Germany (Poggenburg, 1975). The furnace has a capacity of about 6 metric tons/day and operates in a two-stage fashion. Carbon losses averaged 8 to 9% per reactivation cycle during the first year of operation, with about 4 to 5% of this loss taking place in the furnace itself, and the balance occurring during movement of GAC from the adsorption beds to the furnace and return. At Düsseldorf, the spent GAC from each of the three city water treatment plants is piped by aqueous slurry to the single reactivation facility installed at the centrally located Holthausen water treatment plant.

Although the actual capital and operating costs of this furnace have not been disclosed as yet, an estimate was made by the utility director that the total reactivation cost is somewhat less than 30% of the original price of the virgin GAC. Based on the figure of 80¢/lb noted above as being somewhat high, the total cost of regeneration in this unit would be about 20¢/lb. However, this is based on several uncertain assumptions, which thus make the 20¢ figure itself uncertain.

CVERVIEW OF EUROPEAN EXPERIENCE WITH GAC

Observations made by the 1978 site visitation team were intended primarily to address the subject of BAC. However, certain insights into GAC applications in specific European countries were obtained. Just as treatment philosophies vary from country to country, so do the applications of GAC. In any case, generalizations into national or continental philosophies must be viewed cautiously.

French applications of GAC include the replacement of sand in filters at plants such as Vigneux-sur-Seine and Viry-Chantillon (Richard, 1978) and its application as gravity post-adsorbers such as at Morsang-sur-Seine and the Rouen-la-Chapelle plants. GAC currently is used for taste and odor control, but the BAC process is being practiced full-scale at Rouen-la-Chapelle and studied on pilot plant scale at Morsang-sur-Seine. GAC is regenerated off-site at these plants. After 3 years of service at Rouen, one of the GAC beds was reactivated, simply to determine what plant operating techniques would be affected and to determine the properties of the reactivated material (Schulhof, 1980a).

The single Netherlands plant visited (Kralingen plant at Rotterdam) uses a steel pressure GAC post-adsorber after gravity filtration. Despite the relatively large capacity of the treatment plant, off-site activated carbon regeneration is practiced, perhaps due to the presence of a commercial regeneration facility in close proximity to the Kralingen plant. A survey of European water treatment practice (Water Research Center, 1977) states that GAC is applied in The Netherlands to remove the micropollutants which give rise to taste and odor problems, toxic materials and to remove as much of the TOC as possible.

GAC adsorbers in the Federal Republic of Germany were observed to be of the pressurized post-adsorber type. Many of those used in the treatment plants of the lower Rhine River are incorporated into a unique, two-level unit which incorporates filtration in an upper level and adsorption in a lower level (Figure 19). Other facilities incorporate post-adsorber designs more familiar to United States practice, as illustrated in the plant description of the Dohne (Mülheim) plant in Appendix E. The previously referenced survey of European water treatment practice (Water Research Center, 1977) describes GAC practice in the Federal Republic of Germany as follows:

> "Activated carbon is extensively used in the treatment of surface water, primarily for the removal of organics and taste and odor. Activated carbon is used only in the granular form, mostly in pressure filters operated at approximately two atmospheres and with a bed depth of two meters. At present, regeneration is carried out by the manufacturers; however, in the immediate future, some treatment plants will carry out regeneration on-site using fluidized bed techniques. Some of these regeneration plants are already under construction.
>
> Karlsruhe University operates a monitoring service for treatment works experiencing difficulties with activated carbon filters. Their work has included identification of organic groups in water and development of TCC measurement apparatus and techniques."

Some GAC installations appear to utilize reinforced concrete, gravity post-adsorbers. Due to the high quality of Swiss raw water sources, the application of GAC appears to be more of insurance against chemical spills rather than an everyday need for specific contaminant removal.

SECTION 8

BASIC PARAMETERS OF BAC SYSTEMS

The four component steps of BAC processing [(1) chemical oxidation, oxygenation, aeration, (2) inert media filtration, (3) GAC adsorption and (4) biological oxidation] will be discussed in this section. It is important that each individual step be taken only to the point at which the processing can be passed along to the next stage, in order to assure maximum cost-effectiveness.

STEP NO. 1 -- CHEMICAL OXIDATION, OXYGENATION AND AERATION

Chemical Oxidation

Chemical oxidation reactions of organic materials rarely proceed at constant rates. If the first oxidation product is more oxidatively stable than was the starting material, the oxidation reaction rate will tend to slow down as the starting material becomes depleted. This is because chemical reaction rates usually are concentration-dependent. In the early stages, when the readily oxidized starting material is present at its highest concentration, the oxidation rate will be at its fastest. However, as the starting material reacts to produce a more oxidation-resistant material, its concentration is lowered, and the overall rate of oxidation will decrease.

The concentration of chemical oxidant frequently is important in such reactions, but less so than is the concentration of the oxidizable organic starting material. Nevertheless, when the initial chemical oxidation rate slows down, because of lower concentration of starting material, it is a natural thought to try to increase the overall oxidation rate by addition of more oxidant. In some cases this may be effective, but not if the kinetics of the pertinent oxidation reactions are slow. In such cases, the addition of excessive quantities of oxidant will only increase costs relative to that for the initial stage of chemical oxidation.

A primary objective of chemical oxidation, as the first step in BAC processing, is to convert as much biorefractory dissolved organic material as possible to biodegradable material using as little oxidant as possible. However, examination of Figures 13, 14 and 15 (which show structures of chemical intermediates formed during enzymatic oxidation of several types of organic compounds) indicates a possible secondary role of chemical oxidation. The biochemical pathways by which these compounds are oxidized involve the presence of many biologically generated enzymes, and a progression of biological oxidation steps to produce smaller compounds. Even if some of the starting organic compounds present in the water/wastewater to be treated by

BAC processing already may be biodegradable, chemical oxidation may result in effectively skipping several enzymatic steps in the biological oxidation process. It is known (Rice & Miller, 1977) that chemical oxidation of many organic compounds with ozone or chlorine dioxide produces the same oxidized organic compounds that are produced upon biological oxidation.

In considering chemical oxidation as the first step of BAC processing, one should keep in mind the following key points:

1) The relative ease of chemical oxidation of the starting material,

2) The relative ease of chemical oxidition of intermediate oxidation products,

3) The stability of the "end products" to further chemical oxidation,

4) The cost-effectiveness of additional oxidant necessary after the initial oxidation reaction has slowed,

5) The cost-effectiveness of increasing detention time in the presence of excess oxidant after the initial oxidation reaction has slowed.

Point No. 3 is of sufficient interest to warrant more detailed explanation. Gould & Weber (1976) have shown that when phenol is ozonized, many intermediate organic oxidation products are produced (including catechol, an intermediate in the β-ketoadipate pathway of bacterial oxidation -- Figure 15) and that oxalic acid (HOOC-CCOH) is a relatively stable end product. In addition, Gilbert (1977) has shown that the rate of oxidation of water solutions of oxalic acid with ozone is very slow, as measured by the rate of generation of CO_2. On the other hand, when small amounts of hydrogen peroxide, H_2O_2, were added to the solution, then the rate of conversion of oxalic acid to CO_2 upon ozonation increased rapidly.

Thus it is possible to chemically oxidize some organic materials to end products which are quite stable, and therefore, to be unable to convert them completely to CO_2 and water by continued chemical oxidation. Fortunately, however, these stable end oxidation products usually contain more oxygen than did the original organic materials. This means that they are more likely to be rapidly biodegradable compared with the starting organic materials before chemical oxidation.

On the other hand, some biorefractory organics will require relatively high dosages of ozone to increase their biodegradability. For example, Gilbert (1978) reported on ozone oxidation of dilute aqueous solutions of aniline, benzenesulfonic acid, 4-chloro-o-cresol and 2-nitro-p-cresol. He showed that utilized ozone dosages of 3 to 6 g/g of DOC originally present were required to increase the biodegradability of the oxidized products significantly over those of the starting materials. In addition, aniline itself was shown to be more biodegradable than were its initial oxidation products.

The significance of the preceeding discussion is that if chemical oxidation is incorporated into the BAC process as the initial step, it will be beneficial to determine what specific organic compounds are present in the water to be treated. This knowledge will allow use of only the minimum amount of the appropriate chemical oxidant as is necessary to convert the starting organic material(s) to oxidation products which are now more biodegradable (and in most cases, less GAC adsorbable) than they were before oxidation. Chemical oxidation should not be coupled with BAC processing when the objective of oxidation is to convert the organic material to CO_2 and water in a single step. The lower the amount of chemical oxidant which must be employed to attain this initial objective, the lower will be the chemical cost of the overall BAC process.

Chemical oxidants which have been employed in this initial BAC processing step include ozone, potassium permanganate, chlorine and chlorine dioxide (Rice et al., 1979a; 1979b). It is likely that other strong oxidants, such as hydrogen peroxide, also can be employed, with the degree of success dependent upon the relative costs and oxidation powers of each oxidant involved and the specific organic materials to be oxidized.

Kappe (1978) conducted a study of pretreatment methods for the Hagerstown, Maryland sewage treatment plant. The Hagerstown plant effluent includes wastes from 130 industrial firms classified into more than 25 different product categories. Some of the industrial wastewater components exert high immediate and ultimate oxygen demands that either could not be satisfied by the treatment plant, or were otherwise detrimental to the biological processes of the treatment system. Pretreatment methods tested at Hagerstown were intended to assist the plant to satisfy the oxygen demands by providing initial oxidation. The methods used were: diffused aeration (with and without the addition of waste activated sludge), addition of sodium nitrate, chlorination (at dosages of 12, 24, 30 and 60 mg/l) and potassium permanganate (at dosages of 0.53, 1.1, 2.1 and 4.2 mg/l). Preaeration and prechlorination (at the lowest level of applied chlorine) proved to be effective pretreatment methods, increasing the BOD_5 removal efficiency of the plant under dry weather conditions from less than 70% to above than 90%. However, $KMnO_4$ at the low levels used did not increase biodegradability of the Hagerstown sewage.

In other recently reported studies, Coco et al. (1979) evaluated ozonation as a pretreatment for biorefractory industrial petrochemical wastewaters from halogenated hydrocarbon, isocyanate, acetylene and styrene manufacturing industries. Complete oxidation of the biorefractory components of these wastewaters with ozone proved to be uneconomical. However, ozonation was shown to be effective for pretreatment of wastewaters from the manufacture of toluene diisocyanate, ethylene glycol, styrene monomer and ethylene dichloride. Batch biooxidation studies showed that ozonation improved the biotreatability of these industrial wastewaters.

It should be noted that potassium permanganate has the disadvantage of producing insoluble manganous hydroxide sludges, which must be removed from the system. Chlorine and, in some instances, chlorine dioxide can produce chlorinated organic materials, which normally are less biodegradable than are non-chlorinated organic materials. In addition, chlorinated organics may not be removed efficiently by subsequent GAC adsorption. Even if they are adsorbed by GAC later in the process, the fact that they are not as rapidly biodegraded means that eventually they can saturate the GAC and require regeneration of the GAC at that time. Studies by Rook at the Rotterdam (The Netherlands) Water Works (Private Communication, 1978) have shown that chloroform can be adsorbed by GAC, but is slowly eluted from the column (before saturation and breakthrough) when chloroform-free water is passed through the GAC media. This behavior has been confirmed by McElhaney et al. (1980) during studies at Philadelphia's Torresdale drinking water treatment plant. Thus, chemical oxidation via chlorination actually can add to subsequent BAC processing costs by causing early breakthrough of halogenated organics.

In general, ozone, hydrogen peroxide, chlorine and chlorine dioxide will produce only small quantities of insoluble by-products by the process known as microflocculation (see discussion of Step No. 2, below). In addition, neither ozone nor H_2O_2 are yet known to produce biorefractory organic oxidation products, and, as of the present state of knowledge, must be considered to be the preferred chemical oxidants. It is also likely that chlorine dioxide (in the absence of free chlorine) can be a preferred oxidant for many organic contaminants; however, chlorinated organics are produced under certain conditions (Rice & Miller, 1977). As will be presented later in this report, most of the BAC studies reported to date have involved ozonation or aeration; very little research has been done with peroxide.

One major benefit of using ozone as the chemical oxidant is that the DO content of the aqueous medium becomes elevated concurrently as the ozone is added. When ozone is generated in air, a gaseous mixture containing 1% to 2% of ozone in 99% to 98% of air is produced. When ozone is generated from oxygen, a gaseous mixture containing 2% to 4% of ozone in 96% to 98% of oxygen is produced. Thus, during ozonation, considerable amounts of oxygen are passed through the aqueous solution, thereby elevating the DO content prior to inert media filtration.

With solutions containing organic materials which are resistant to ozone oxidation (PCBs, pentachlorophenol, heptachlorepoxide, etc.), it may be possible to couple ultraviolet radiation with ozonation to oxidize these refractory compounds. Ozone/UV combinations have been shown to increase the rate of oxidative destruction of such compounds (Prengle & Mauk, 1978; Arisman et al., 1979). Chloroform, which does not react with ozone to form soluble chloride ion in aqueous solutions, has been shown to form chloride ion when subjected to simultaneous ozone and ultraviolet radiation treatment (Prengle & Mauk, 1978).

Oxygenation, Aeration

Chemical oxidation is not always required during step 1. If the organic materials present already are biodegradable and are non-biorefractory, then an oxidant will not be mandatory. In such cases, the first step can be merely a preaeration or preoxygenation so as to provide the required quantity of DO to allow the subsequent biochemical conversions to occur to the desired degree(s). Aeration conditions are employed in several drinking water treatment plants in the Federal Republic of Germany. Preaeration of the partially treated raw water is effected before passage through slow sand filters and/or through GAC. On the other hand, wastewaters which contain large quantities of BOD_5, for example, should be pretreated biologically before considering BAC treatment for removal of the more biorefractory components. Otherwise large amounts of DO will be required during BAC processing, causing large quantities of sludge to be produced. In turn, these will require more frequent backwashing of the inert and GAC media.

STEP NO. 2 -- INERT MEDIA FILTRATION PLUS BIOLOGICAL OXIDATION

One practical reason for this intermediate filtration step is simply to protect the GAC media from becoming fouled with insoluble materials, which would require more frequent backwashing of the GAC column or bed. One major source of these insoluble materials is the "microflocculation" which occurs as a result of chemical oxidation of the soluble micropollutants.

The terminology "micropollutant" has evolved from European drinking water treatment practice to describe small amounts of soluble polluting components which cannot be removed easily from raw water supplies by the normal processes of flocculation, coagulation, sedimentation and filtration. When these micropollutants are chemically oxidized, they become more polar in nature, due to the introduction of oxygen into their structures. In turn, the increased polarity allows them to hydrogen bond to other organic molecules which contain labile hydrogen atoms, thus increasing the effective molecular weight of the organic molecules. If this molecular weight increase becomes sufficiently high, water solubility will decrease. In addition, if polyvalent cations (such as magnesium, calcium, iron, aluminum, etc.) are present, these cations can react with the oxidized micropollutants, causing them to coagulate and precipitate.

The combination of all these secondary effects, which occur after chemical oxidation, is termed microflocculation, or flocculation of the micropollutants. In many European drinking water treatment plants, the ozonation step is followed by sand or anthracite filtration in order to remove the increased turbidity produced upon ozonation. An excellent discussion of the phenomena involved in microflocculation has been presented by Maier (1979).

In addition to being water insoluble, many of the materials present in the microflocculant are biodegradable, because of the introduction of oxygen into their chemical structures. As a result, there can be an increase in biological activity in the solid media through which these materials are filtered. Therefore, if inert media filtration follows chemical oxidation, the insoluble flocculated micropollutants will be physically removed from solution and a significant portion of the biological activity which results can be caused to occur in the inert media employed.

In European drinking water treatment plants which are utilizing BAC processes, it has been found that when the raw waters contain ammonia, most of the nitrification (about 80%) occurs in the inert media which precede GAC adsorption (Rice, 1979a; 1979b). Therefore, the GAC medium is allowed to perform its primary tasks, first as an adsorber of soluble organic materials, and second as a biologically active medium in which at least a portion of the adsorbed organic material is biologically degraded to CO_2 and water and in which some adsorption sites are regenerated.

In sewage treatment, two fluidized sand bed processes have been described in which biological treatment is conducted. It is claimed that both processes save considerable space over classical biological treatment processes.

Jeris et al. (1977) describe the Hy-Flo process in which sand beds are fluidized with water and the medium is maintained aerobic by addition of pure oxygen. Three pilot plant studies using the Hy-Flo process were reported by Jeris et al. (1977) in Nassau County, New York. These ranged in size from 40,000 gal/day for denitrification to 80,000 gal/day for reduction in levels of carbonaceous BOD_5 and nitrification. Complete BOD_5 and ammonia removal was obtained in a fraction of one hour of treatment and in less than 5% of the space required to obtain comparable removals by either the activated sludge or trickling filter processes. The empty bed contact time of the sand beds was 6 minutes. However, optimum contaminant removals were obtained when a recycle ratio (recycle flow/primary effluent flow) of 1.5 was employed. This corresponded to an actual empty bed contact time of 15 minutes.

A second fluidized sand bed process, the Oxitron system (Anonymous, 1979), also uses pure oxygen and partial recycle. A pilot plant study was conducted on wastewater from a corn wet-milling plant in Iowa and 95% BOD_5 removals were attained. Estimated total energy required (for oxygen regeneration, feed and recycle stream pumping and biomass separation) for treatment of a 3,000 mg/l BOD_5 influent at 1 mgd was 544 hp. It is claimed that a comparable air-activated sludge system would require 650 hp for powering aerators and sludge recycle pumps.

The BASF plant at Ludwigshafen, Federal Republic of Germany has been operating an activated sludge plant for treating wastewaters from more than 300 separate organic chemicals manufacturing processes along with sewage from several nearby cities. Effluent from this treatment plant currently is discharged to the Rhine River. The daily BOD_5 load is 150 to 350 tons/day (average 260 to 270) and the effluent normally contains 10 to 13 tons/day (95% BOD_5 removal) and 50 tons/day of total organic carbon (TOC).

The BOD_5 contained in the BASF effluent is of no concern to German authorities, since it will continue to be degraded biologically in the Rhine River. However, there is concern for the COD which is discharged, since it could contaminate raw drinking water supplies further downstream.

BASF is conducting pilot plant scale tests which involve recirculating the effluent from their large activated sludge treatment plant through GAC adsorbers (downflow) with continuous aeration or oxygenation. Sontheimer (1979b) reported that this pilot plant test system has been operating continuously for 18 months and has been removing over 90% of the TOC (Figure 25) present in the activated sludge plant effluent.

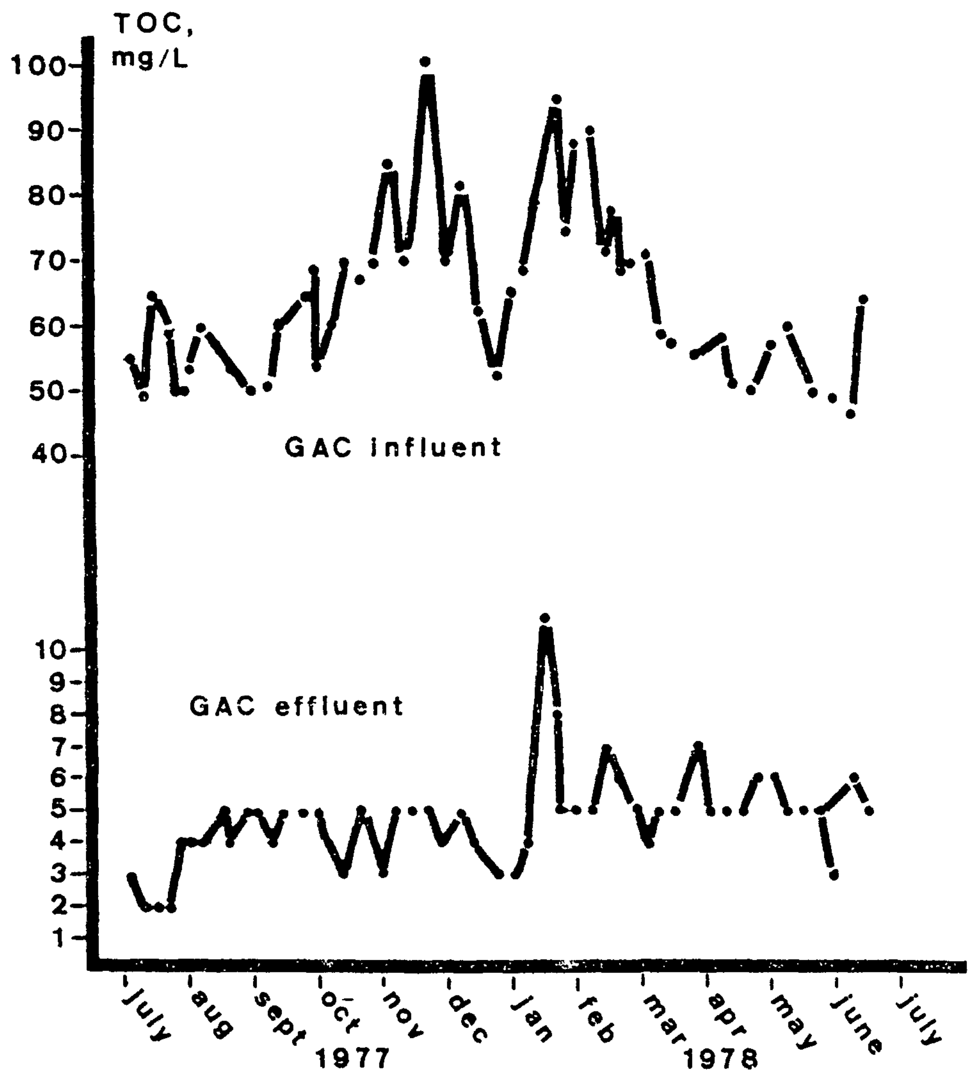


Figure 25. TOC removal upon passage of BASF activated sludge effluent through biologically enhanced (with O_2) GAC.

(Sontheimer, 1979)

Finally, if ozonized wastewater is passed directly into GAC media without intermediate filtration, there is the possibility of residual dissolved ozone being present. This will be destroyed by reacting with the GAC, but, consequently, will oxidize some of the carbon. The net result will be a slow loss of GAC. This effect has been noted at Water Factory 21, in Orange County, California, where ozonized secondary effluent has been passed directly into GAC columns. After a number of months of such operation, the GAC particles have been found to be much smaller than their initial size (Argo, 1979, Private Communication).

STEP NO. 3 -- REAERATION/REOXYGENATION

Because the biological activity which occurs in the inert medium utilizes oxygen (recall that nitrification alone requires 3 to 4.5 equivalents of DO per equivalent of ammonia-N to produce nitrate), the aqueous solution which passes through the inert medium can become depleted in DO. If this occurs, then inert medium filtration should be followed by a reaeration or reoxygenation step. The choice between reaeration or reoxygenation will depend upon the amount of oxygen which will be required to satisfy the biological demands of dissolved organic materials during subsequent passage through GAC.

STEP NO. 4 -- GAC ADSORPTION + BIOLOGICAL OXIDATION

Following chemical oxidation, inert media filtration and reoxygenation, the aqueous medium now is ready for passage through GAC, during which adsorbable organic materials present will be adsorbed. In addition, other slowly biodegradable organic materials, which were not completely degraded during passage through the inert filtration medium, will continue to be biologically oxidized as the aqueous solution passes through the GAC medium. This can occur because GAC media operating in biologically enhanced modes contain bacterial colonies on the outer surface layers and in the large macropores. The macropores normally represent only about 1% of the total pore surface area available in GAC, but these are the only pore openings large enough to physically house bacteria. On the other hand the micropores, which make up about 99% of the total GAC pore volume, are too small to accomodate bacteria. Figure 26 schematically shows the relationship between micropores, macropores and bacteria.

GAC macropores are the large openings through which a dissolved organic molecule must pass on its way into the smaller micropores, where it is adsorbed. Thus the dissolved organic molecules are exposed to bacterial action as they pass by on their way into the micropores. If and when the adsorbed organic molecule is later desorbed from the micropores and diffuses back out into the main solution stream, it must pass the bacterial colonies located in the macropores once again.

Bacteria can secrete enzymes which are much smaller in size than are the bacteria themselves. Enzymes are molecular in size, and some may be small enough to find their way into the micropores of the GAC. In the presence of sufficient dissolved oxygen, these enzymes can cause partial oxidation of some of the organic molecules adsorbed in the micropores, changing their adsorption characteristics and causing them to desorb. As they are desorbed, they pass out of the GAC micropores and past the bacteria located in the macropores, where they can be further biodegraded.

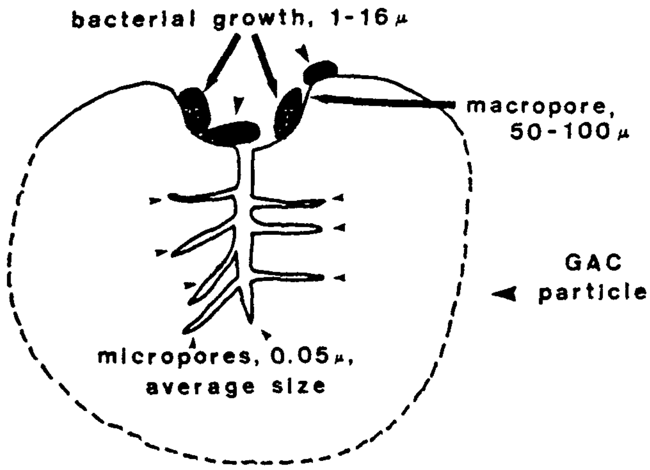


Figure 26. Schematic representation of a GAC particle, showing pore sizes and bacterial growths.

Enzymes are not the only cause of desorption of adsorbed molecules, however. Other organic chemicals which are more tightly bound by GAC than are the originally adsorbed molecules can be present in the water/wastewater being treated. As an example, chlorinated organic molecules are more strongly adsorbed (and also are less biodegradable) than are materials such as phenols. Thus GAC can be saturated with phenols and, at the same time, the biological activity present can be degrading adsorbed phenols into CO_2 and water. If the concentration of phenol in the water passing through the GAC, the DO, the size of the GAC column or bed and the detention time of the aqueous medium (the empty bed contact time) all are properly chosen, then the system can attain an equilibrium status. At this point, the rate of biochemical oxidation of adsorbed phenol will be equal to the rate of adsorption/desorption of phenol, and the net effect will be that the system is in balance. Under ideal circumstances, all phenol contained in the original solution will be removed, either by adsorption or by biological oxidation, and the effluent will contain no phenol.

If a chlorinated organic material, say chloroform, is introduced into this balanced system, the balance will be upset. Chloroform will desorb some of the phenol and itself be adsorbed. However, the rate of biochemical oxidation of chloroform is very much slower than is that of phenol. The result will be that the empty bed contact time now will be much too short for attainment of a chloroform equilibrium such as was obtained with phenol.

In addition, adsorbed phenol will be desorbed at a rate faster than the bacteria can decompose it, and thus non-degraded phenol will be present in the BAC effluent.

As a result, the loading of adsorbed chloroform will increase until one of two conditions prevails. If the GAC becomes saturated with chloroform and devoid of phenol, the GAC must be removed from the adsorber and be thermally reactivated. Alternatively, the concentration of adsorbed chloroform can reach a point that even though saturation does not occur, desorption (or leakage) of chloroform still begins to occur. In either event, chloroform now appears in the GAC effluent in unacceptable quantities, and the GAC must be reactivated.

It is clear, therefore, that if a dynamic equilibrium can be established whereby the rate of adsorption of organic impurities and biochemical oxidation of desorbing organic impurities become equal, the biologically enhanced GAC system will continue to remove biodegradable organic impurities from solution without the need to thermally reactivate the GAC. It will only be necessary to maintain a necessary level of DO and to backwash the inert media filters and the GAC adsorption medium periodically to continue the process. When such an equilibrium has been established, the ability of the GAC to adsorb sudden surges of non-biodegradable organic compounds (which are less polar and, therefore, are more strongly adsorbed by GAC) is still available.

One should not assume from the preceeding discussion that effluents from GAC columns operating under optimized adsorption and biological conditions will be entirely free of dissolved organic carbon. During early stages of GAC use, when the activated carbon acts purely as an adsorber, all adsorbable dissolved organic carbonaceous material can be removed from solution. However, as biological activity develops over a period of several weeks, the DOC content of the GAC effluents has been shown to increase. At equilibrium, the amount of DOC "apparently removed" from the influent ranges from 20% to 50%. We emphasize "apparently removed" because the composition of the organics in the effluent currently is unknown. Since the influent organics have been exposed to biological activity, at least some of the organics now present are likely to be products of biochemical oxidation and/or decomposition products of the organics originally fed to the GAC media. There is also a high probability of by-products of bacterial metabolic processes being present. Finally, high bacterial colony counts always are present in GAC effluents, once the biological activity has built up in the media. These will be measured as DOC or TOC by normal analytical techniques.

It is also important to recognize that microorganisms require different lengths of time in which to adapt to the particular soluble organic materials present in the waters being treated. The term "readily biodegradable" actually applies only when the microorganisms adapt quickly to their substrates. This can take a short time (less than 24 hours), as in the case of glucose, or significantly longer (several weeks), as in the case of p-nitroaniline (Benedek et al., 1979).

Stephenson et al. (1980) determined that the effect of ozonation on biodegradation of organic materials has not yet been studied in a thorough scientific manner and, therefore, undertook an investigation with this purpose in mind. In the first report in this series, ozonation of two river waters and solutions of o- and p-nitroaniline was followed by respirometric biodegradation studies. Oxygen uptake and organic uptake during biodegradation were found to be improved by ozonation, except in the case of p-nitroaniline, oxidation products of which became less biodegradable. These investigators concluded that intermediates were formed upon ozonation which either inhibited biological activity or to which the inoculum was unable to acclimate over the period of study (3 weeks).

Stephenson et al. (1980) also defined a new parameter which indicates the fraction of dissolved organic material made biodegradable by ozonation. This parameter, f, is defined as:

$$f = [\Delta COD_o - (X)\Delta TOC_o]/COD_o \qquad \text{eq. 8}$$

where
f = fraction of COD partially oxidized
COD = COD concentration after ozonation
ΔCOD_o = change in COD concentration due to ozonation
ΔTOC_o = change in TOC concentration due to ozonation
X = oxygen equivalent required to oxidize organic molecules to CO_2 and water

The value of X was calculated (Stephenson, 1979) to be 2.62 for the two river waters and 3.33 for nitroaniline solutions.

Finally, Stephenson et al. (1980) found that TOC removal from solution by a combined ozonation-biodegradation process ranged from 10% to 70%, depending upon the specific ozone dosage applied and the water source studied, and that an ozone dosage of 2 mg/l was the most cost-effective for the waters studied.

In the second part of the above study, Benedek et al. (1980) studied the effect upon GAC adsorption of river water organics after ozonation, either followed directly by GAC adsorption or followed by biodegradation, then GAC adsorption. Prior to biodegradation, a 2 mg/l ozone dosage increased the GAC adsorptivity, but at higher ozone dosages GAC adsorptivity decreased. However, following ozonation and biodegradation, GAC adsorption of the remaining organics was increased. These authors concluded that pretreatment (coagulation, flocculation, filtration) can remove about 35% of the TOC in river water, ozonation removes very little TOC (at a 2 mg/l dosage), biodegradation removes another 15% and adsorption at a GAC dosage of 160 mg/L removes an additional 38% of the TOC.

SECTION 9

EUROPEAN BAC APPLICATIONS AND STUDIES

FEDERAL REPUBLIC OF GERMANY

Introduction of granular activated carbon into European drinking water treatment practices occurred before World War II, its initial applications being for dechlorination and for taste and odor control (Hopf, 196C). When surface waters undergo high levels of prechlorination, considerable amounts of residual chlorine and chlorinated organics are produced in the water (Sontheimer et al., 1978). European water treatment objectives are to process surface waters to the same quality as that of natural groundwater (which does not have to be treated in many cases). Therefore, prechlorinated waters have to be dechlorinated before they are treated further or distributed (Sontheimer, 1977a).

Düsseldorf

The City of Düsseldorf originally installed ozone for oxidation of iron and manganese in its sand bank filtered Rhine River raw water in the mid-1960s (Miller et al., 1978; Hopf, 1960). Today, ozonation is followed by 20 to 30 minutes retention in a holding tank, then by filtration through an inert medium, then granular activated carbon, then treatment with a small quantity (up to 0.3 mg/l) of chlorine dioxide for residual. During storage of the ozonized raw water at Düsseldorf, oxidized iron and manganese ions are allowed to flocculate and settle. In addition, excess ozone (and small amounts of permanganate formed by ozonation of manganese ions) continue to oxidize dissolved organics. This holding time is not practiced at all European plants employing preozonation followed by filtration.

The Rhine River in the Düsseldorf area contains considerable amounts of chlorinated organic materials which are not removed during river sand bank filtration. These halogenated organics also are more resistant to oxidation by ozone than are non-halogenated organics, and thus are less likely to be converted into readily biodegradable materials. In addition, halogenated organics are more tightly adsorbed by the GAC (Kühn & Fuchs, 1975; Kölle, Sontheimer & Steiglitz, 1975).

Combining the stronger adsorptivity of halogenated organics onto granular activated carbon with their lesser reactivity upon ozonation and their lower biodegradability, simply means that breakthrough of halogenated organics can occur more rapidly than does breakthrough of non-halogenated organic compounds from GAC columns, even though the GAC columns may contain optimal biological activity. Thus, German water works along the Rhine in the Düsseldorf area monitor their carbon column capacities for Total Organic Chlorine (TOCl) (by the method of Kühn & Sontheimer, 1973a,b; Kühn, 1974; Kühn & Sontheimer, 1974), as well as for DOC (by the method of Wölfel & Sontheimer, 1974) and UV absorption. Carbon columns at three Düsseldorf plants along the Rhine (Flehe, Am Staad, Holthausen) are backwashed every 4 to 6 weeks and are regenerated every 5 to 6 months when the adsorbed TOCl on the GAC itself reaches the lower 25% of the carbon beds or if soluble TOCl appears in the carbon column effluent before adsorbed TOCl reaches the lower 25% of the carbon bed (Miller et al., 1978; Poggenburg, 1977, 1978).

When Düsseldorf activated carbons are regenerated, however, only some 80% of the carbon charge is taken out of the columns. This leaves a portion of biologically active carbon in the column so that the level of bioactivity will not drop significantly when fresh or regenerated carbon is added. With fresh carbon columns, about 15 days of operation usually are required for biological activity to build up to an effective "steady state", particularly for ammonia removal (Poggenburg, 1977).

It is likely that the following processes are occurring simultaneously in the granular activated carbon beds at Düsseldorf:

1) Non-adsorbable, biodegradable organic materials are being converted biologically into CO_2 and water as they pass through the bed (as they would be degraded biologically in a slow sand filter),

2) Adsorbable, biodegradable organic materials are being adsorbed and may be degraded biologically. Breakthrough of these materials and those of 1) above is not observed because the GAC column sizes and flow rates of water being processed are designed so that the rate of overall biodegradation is at least equal to the rate of loading of the GAC columns from the ozonized waters.

3) Adsorbable, non-biodegradable compounds (such as those making up Total Organic Chlorine, TOCl), are being adsorbed by the GAC but not being biodegraded at any appreciable rate,

4) Non-adsorbable, non-biodegradable organic materials are passing through the GAC unaffected and

5) Some of the adsorbable, non-biodegradable materials may be desorbed if more strongly adsorbed but still non-biodegradable compounds enter the GAC bed. In such cases, those materials so desorbed from the early portion of the GAC column can be readsorbed in lower portions of the GAC medium.

Thus, in terms of EPA's THM regulations and proposed SOC regulations, Düsseldorf plants are using GAC to:

1) remove THM precursors (by partial oxidation during ozonation, followed by filtration through biologically active "inert" media, then adsorption onto GAC and/or biological degradation),

2) remove chlorinated synthetic organic chemicals (by adsorption) and

3) remove those unidentified, adsorbable non-biodegradable SOCs which are more strongly adsorbed by the GAC and whose breakthrough would occur only after TOCl breakthrough.

Over the years which followed installation of "the Düsseldorf Process, it was noted that more dissolved organic carbon was being removed than could be expected on the basis of the simple summation of the known effects of ozonation and of GAC adsorptive treatment. When it was also discovered that ammonia levels were much lower after GAC treatment than before, the aerobic biological activity within the activated carbon columns was recognized as being beneficial and was examined in closer detail. An extensive, 3-year pilot plant testing program was conducted on biologically enhanced granular activated carbon at the Auf-dem-Werder water treatment works in Bremen, Federal Republic of Germany by Eberhardt, Madsen & Sontheimer (1974), which will be described in some detail later in this section.

Wiesbaden

Klotz, Werner & Schweisfurth (1975) reported on a continuing study of the microbiology in granular activated carbon filters at the Schierstein water treatment plant in Wiesbaden. At this plant, Rhine River water is aerated, settled, chlorinated to the breakpoint, flocculated, filtered through sand, then granular activated carbon, then sent to ground infiltration. There is no preozonation of the activated carbon column.

Studies of the performances of and bacterial activities in activated carbon columns at Wiesbaden over a period of 3 years have shown that seasonal influences are only slight. There is a tendency for decreased microbial activity in winter, as indicated by lower oxygen consumption and carbon dioxide production values. However, changes in raw water quality also were shown to cause substantial changes in the colony numbers (total count of living and dead bacteria) present in the GAC columns.

Adsorption isotherms were determined for bacteria loaded on the carbon. At high colony numbers (above 10^{10}/ml) the system tended to saturation. At 10^7 to 10^8/ml, up to 90% of the bacteria were adsorbed onto the carbon (Figure 27, upper). After 20 to 30 hours of operation, adsorption and desorption were nearing the steady state (Figure 27, lower) of about 10^8 colonies/g of carbon. Electron scan microscopic analysis of granular activated carbons treated differently showed that the bacteria are never present in greater than a single bacterial layer. Thus the total carbon surface area is only fractionally utilized (about 1%) by the adsorbed bacteria, leaving 99% of the total surface (pore) area of the carbon free for adsorption of dissolved organic materials. This confirms the work of Van Der Kooij (1975) in The Netherlands.

Figure 28 shows the numbers of bacterial colonies present in the Wiesbaden raw water, in the sand filtrate and in the GAC filtrate for the nearly 4 year period of early 1972 through 1975. Bacterial levels in the inlet and after the sand filter remained essentially the same throughout

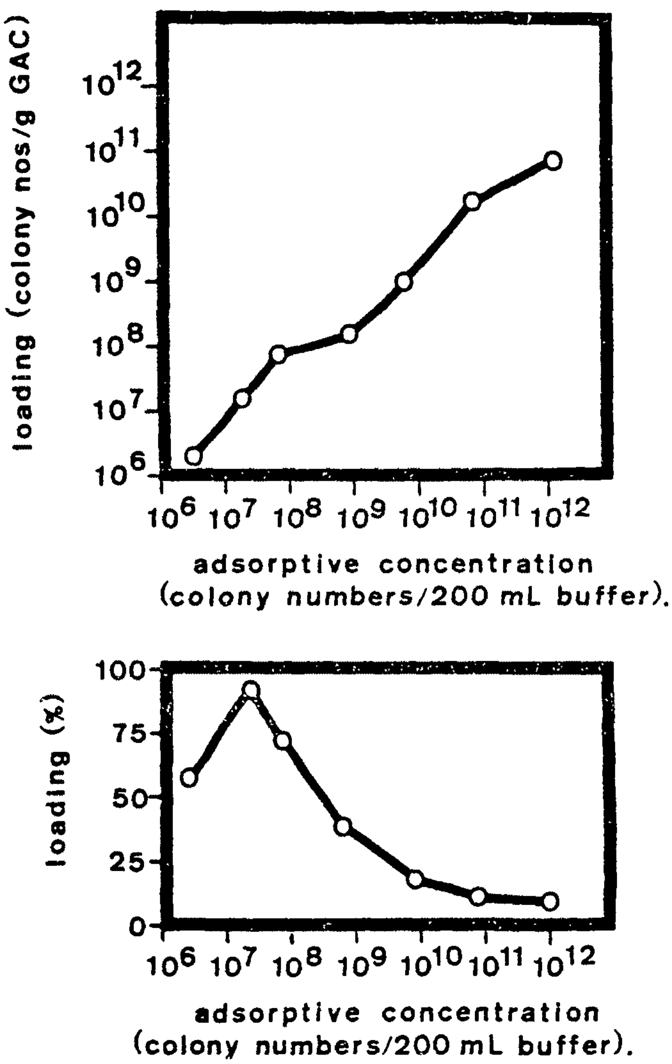


Figure 27. *Microbiological loading of GAC -- dependence on adsorptive capacity.*

(Klotz, Werner & Schweisfurth, 1975)

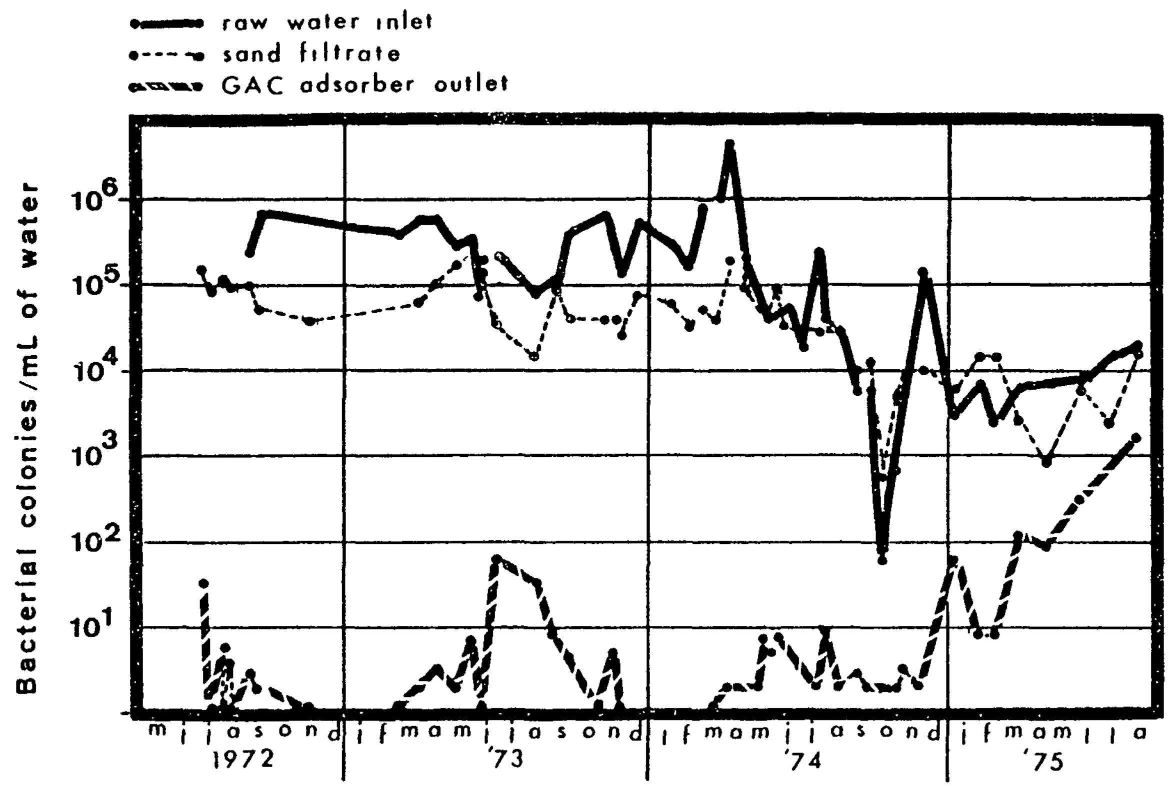


Figure 28. Behavior of microbial populations on GAC over 3 years at Wiesbaden, F.R. Germany.

(Klotz, Werner & Schweisfurth, 1975)

this period. On the other hand, levels of bacterial colonies in the BAC filtrates were usually less than 100/ml for nearly three years, after which the levels increased rapidly to approach those of the plant inlet. This is an indication that, at least under the Wiesbaden plant operating conditions and for this raw water, bacterial breakthrough of the BAC occurs after about 3 years of operation. Bacterial breakthrough was not related to other effluent parameters, such as TOC, COD, TOCl, etc., and may indicate that satisfactory BAC operation may only be effective for this length of time (3 years) before regeneration would be required regardless of other parameters being monitored.

SWITZERLAND

Activated carbon was installed at Zürich initially to protect against oil spillage, later for protection against phenol spills, and for dechlorination (Schalekamp, 1975). Zürich's Lengg and Moos plants take raw water from the Lake of Zürich, which contains very low concentrations of chlorinated organics and is otherwise a very clean raw water. There is no need for breakpoint chlorination because of very low ammonia content, but a small dose of chlorine (1 mg/l maximum) is added at the intake to prevent growth of mussels. Granular activated carbon insures dechlorination of this amount of chlorine. Before activated carbon filtration, however, the water is ozonized at dosages of 1 to 1.5 mg/l.

In plant studies (Schalekamp, 1975), at the end of 7 months both the top and bottom layers of the carbon beds showed equal loadings of organics, as measured by UV absorption and COD analyses, thus indicating the need for regeneration. However, regeneration of this carbon was not required because the continued efficiency of removal of dissolved organic carbon from the aqueous medium by this carbon remained nearly the same as that of the new carbon (Figure 29). This behavior was attributed by Schalekamp to biological activity within the carbon bed.

At the Zürich Moos plant, the slow sand filter was covered with a 5 cm layer of granular activated carbon. The efficiency of COD removal from the aqueous solution remained essentially constant over the three year period (about 2.8 mg/l residual COD in the filtrate), (Figure 30). This performance, again attributed to bacterial degradation of the adsorbed organics, was obtained without reactivation of the carbon, although twice weekly backwashes were required.

THE NETHERLANDS

Van Lier et al. (1975) describe experiences with granular activated carbon filters in pilot plant studies at Amsterdam. Three carbon pilot units were studied side by side, using 2 meter column heights and 8 cu m/sq m/hr flow rates for 3 months. The water was treated by iron coagulation, rapid sand filtration, chlorination, then:

Process #1: Ozonation, rapid sand filtration, granular activated carbon, slow sand filtration,

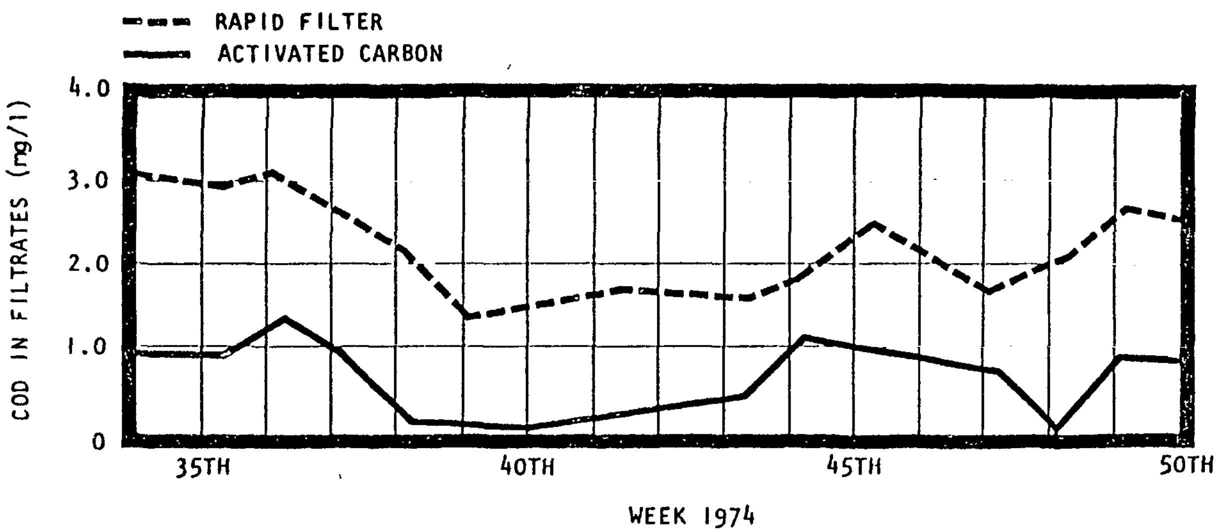


Figure 29. Efficiency of removal of COD by rapid sand filter and GAC at Lengg plant, Zürich, Switzerland.

(Schalekamp, 1975)

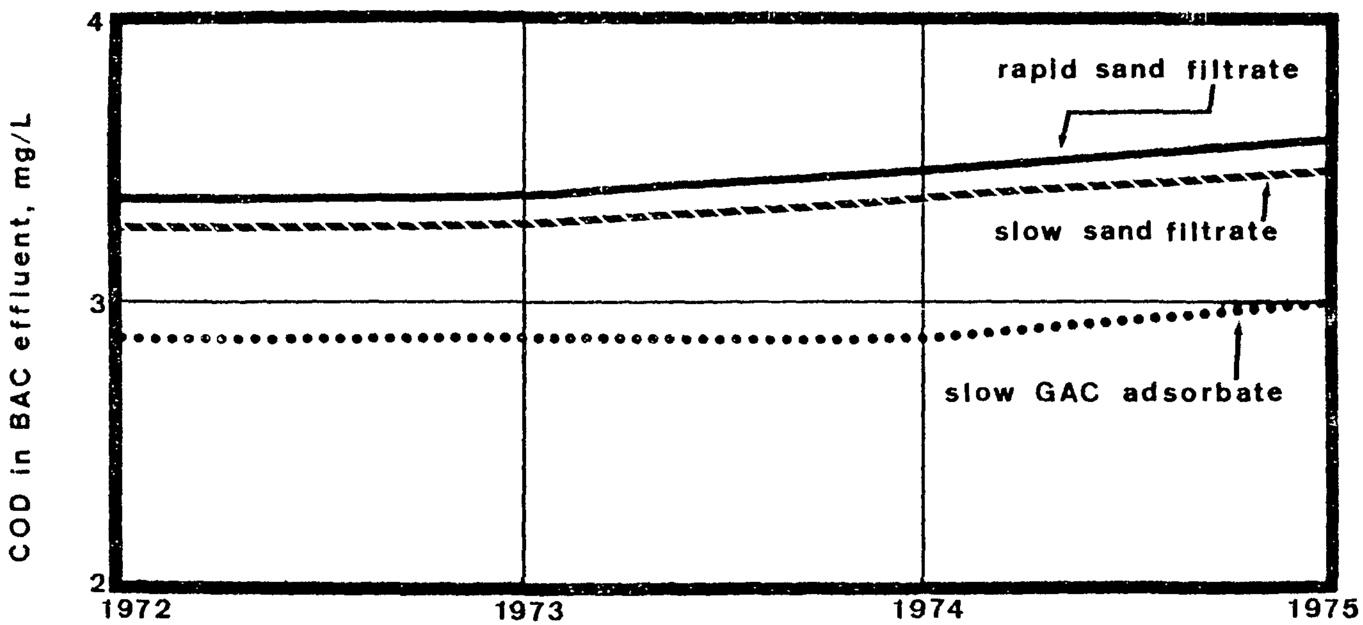


Figure 30. Efficiency of COD removal by BAC over 3 years at Moos water works, Zürich, Switzerland.

(Schalekamp, 1975)

Process #2: Rapid sand filtration, slow sand filtration,

Process #3: Granular activated carbon, slow sand filtration.

These researchers concluded that:

1) Ozonation increases bacterial counts considerably after rapid and slow sand filtration,

2) Water treated by Process #1 (with ozone) produces water with better color, UV absorption and $KMnO_4$ consumption values (a measure of the amount of oxidizable organic matarials present) than waters treated by Processes #2 or #3 without ozone,

3) Slow sand filtration in all three systems reduces bacterial counts, color and $KMnO_4$ consumption values,

4) Water qualities by Processes #2 and #3 are about the same, but the frequency of backwashing of the slow sand filters is more frequent in these processes, which do not include ozonation,

5) Service time of the granular activated carbon column with prior ozone treatment of the water was much longer (300 days) than those without ozone (175 days) as measured by UV absorption of the filtrates. Longer service times were observed for BAC columns which had optimum contact times of 20 to 30 minutes (empty bed).

6) For the same applied DOC, the amount of DOC removed by the activated carbon in summer was much greater than in the winter. This was explained on the basis of increased biological activity in the carbon columns at the higher summer temperatures. Oxygen consumption in the winter was found to be 0.006 g/hr/kg of carbon and 0.024 to 0.030 g/hr/kg of carbon in summer.

CASE HISTORIES

In this sub-section several case histories of pilot plant and full scale plant studies of biological activated carbon processes will be discussed in some detail. These are studies conducted at:

(1) Düsseldorf, Federal Republic of Germany - pilot plant study and operational data
(2) Bremen, Federal Republic of Germany - pilot plant study
(3) Mülheim, Federal Republic of Germany - pilot plant study and operational data at the Dohne plant
(4) Rouen, France - operational data

Düsseldorf, Federal Republic of Germany - Pilot Plant Studies And Operational Data

The City of Düsseldorf began using ozonation for taste and odor control in 1954 (Hopf, 1970b). At that time, only 0.7 to 1.0 mg/l of ozone dosage, along with 7 to 10 mg/l of permanganate, controlled the problems satisfactorily. Over the years, however, the quality of the Rhine River water worsened, such that ozone dosages of 1.5 to 2.5 mg/l of ozone were required, and sometimes as much as 4 mg/l. Installation of additional ozone generation capacity was possible, but this would have been uneconomical since the high production rate would have been used only infrequently (Hopf, 1970b).

As a result, experiments with activated carbon were conducted to overcome taste and odor problems. In one section of Düsseldorf, only 1.0 to 1.5 mg/l of activated carbon placed after ozonation was found to be sufficient to control the taste and odor problems. This is only 1/10th of the amount of activated carbon that was necessary without the ozone treatment (estimated at 30 to 40 mg/l). The average operational lifetime of the carbon filters for taste and odor removal was 15 months. This time could be lengthened if several filters or filter groups could be operated in periodic stages (Hopf, 1970b).

Although the river sand bank filtered Rhine River raw water which had been treated with ozone was, for all practical purposes, free of bacteria, the activated carbon filters which follow at Düsseldorf not only are not sterile, but contain a significant amount of biological activity which was recognized as being beneficial shortly after activated carbon was installed.

Ammonia (which is not attacked by ozone) is one of the substances present in the river sand bank filtrate which is transformed biologically and is entirely removed during passage through the carbon media. Even in freshly filled carbon filters at Düsseldorf, biological conversion of ammonia to nitrate begins after just a few days (Hopf, 1970b). The dissolved oxygen content of the effluents from the activated carbon filters is 7 to 8 mg/l.

Water leaving the Düsseldorf activated carbon filters is very low in bacteria content, even though the GAC media are biologically active. However, the filtering velocity at Düsseldorf is unusally high (35 cu m/sq m/hr), which means that the total 3 m depth (originally installed bed depth) is passed by the water in less than 2 minutes (Hopf, 1970b). This rapid filtration rate at Düsseldorf is unique, in that all three Düsseldorf water treatment plants (Am Staad, Flehe and Holthausen) operate "on demand", because there is very little reservoir storage capacity available (Miller et al., 1978). Thus, all three plants are designed to produce water at peak demand rates. As a result, high rates of flow sometimes are employed at these plants.

Poggenburg et al. (1974) reported results of some of the many studies conducted at one or more of the three water treatment plants in Düsseldorf, all processing river sand bank filtered River Rhine water. Studies reported in this article included pilot plant tests and data obtained from the full scale plant operations. A detailed pilot plant study comparing various types of granular activated carbons was conducted for the removal of various types of organic chemicals.

Raw Water Quality at Düsseldorf--

In the lower Rhine region of the Federal Republic of Germany, the raw water of the River Rhine contains many organic pollutants, including a significant fraction of chlorinated organics. Over the years, the level of organic pollution in the Rhine has increased considerably. For example, Fuchs & Kühn (1975) reported that in 1962 it was possible to extract samples of loaded powdered activated carbon (loaded by shaking 40 l of water 30 minutes with 20 g of powdered activated carbon) with ether and to obtain about 2 mg of orgànic extract per liter of ether (Holluta, 1959, 1960). In comparison, in 1975 and using dimethylformamide (DMF) as the extractant, about 8 mg of organic materials was extracted per liter of DMF used. This higher amount of organic extract not only is due to an increased amount of pollution of the River Rhine, but also to nearly quantitative desorption by the DMF as opposed to ether, as well as a higher capacity of the more modern activated carbon during the 30 minutes of loading. Nevertheless, most of the increased organic material extracted is due to increased levels of pollution in the Rhine water (Fuchs & Kühn, 1975).

Analysis of ether extracts of loaded activated carbons made in 1964 showed the presence of a polar, biodegradable fraction along with a non-polar fraction which comprised about 20% of the total organics extracted (Holluta, 1964). Fuchs & Kühn (1975) state:

> "Similar fractions of polar and non-polar materials are found today. However, whereas formerly the most important of the non-polar materials were mineral oil hydrocarbons, today analysis shows that the extensive group of lipophilic, frequently toxic, organochloro- compounds are much more important."

For example, Fuchs & Kühn (1975) reported some of the then unpublished work of Stieglitz at the University of Karlsruhe on readily isolated and identified volatile compounds from the Rhine River near Karlsruhe by adsorption on granular activated carbon, then extraction first with dioxane (to remove the non-polar compounds, generally less than 10% of the total organics adsorbed), then with DMF. Some of the compounds obtained are listed in Table 15, many of which are halogenated organics.

Comparison of the quality of River Rhine water at Basel, Switzerland (the upper Rhine) and at Duisburg, 30 km north of Düsseldorf, FRG (the lower Rhine) in terms of organic sulfur and organochlorine compounds which are adsorbed by activated carbon, is given in Table 16. In Table 17 are listed some data obtained at various places along the Rhine and the amounts of polar and non-polar organic substances adsorbed by GAC.

The Düsseldorf Water Treatment Process--

At all three Düsseldorf City water treatment plants (Am Staad, Flehe, Holthausen), as well as at almost all water works on the lower Rhine River in that region of the Federal Republic of Germany, the general water treatment procedure consists of five basic unit operations, as shown in Figure 31 (Poggenburg, et al., 1974).

TABLE 15. THE MAIN COMPONENTS OF READILY VOLATILE COMPOUNDS IN THE RIVER RHINE AT KARLSRUHE

Compound	B.P., °C	Compound	B.P., °C
cyclohexane	80	dichlorobenzene	179
trichloroethylene	87	isobutylbenzene	170
toluene	110	hexachloroethane	185 (subl.)
tetrachloroethylene	121	tetrachlorobutadiene	188
monochlorobenzene	132	pentachlorobutadiene	---
xylene	142	trichlorobenzene	213
tetrachloroethane	147	hexachlorobutadiene	215
bromobenzene	156	dodecane	215
cumene	163	tetradecane	252
mesitylene	159	pentadecane	270
isocumene	159		

Source: Fuchs & Kühn (1975)

TABLE 16. COMPARISON OF ORGANICALLY BOUND SULFUR AND CHLORINE IN GAC CONTRCL FILTERS AT DIFFERENT SAMPLING STATIONS

sampling station	adsorbed organic substances mg/cu m	sulfur %	chlorine %	organic bound sulfur mg/cu m	organic bound chlorine mg/cu m
Rhine @ Basel	2,900	1.5	2.3	44	67
Rhine @ Duisburg	6,500	5.1	2.3	332	150

Source: Fuchs & Kühn (1975)

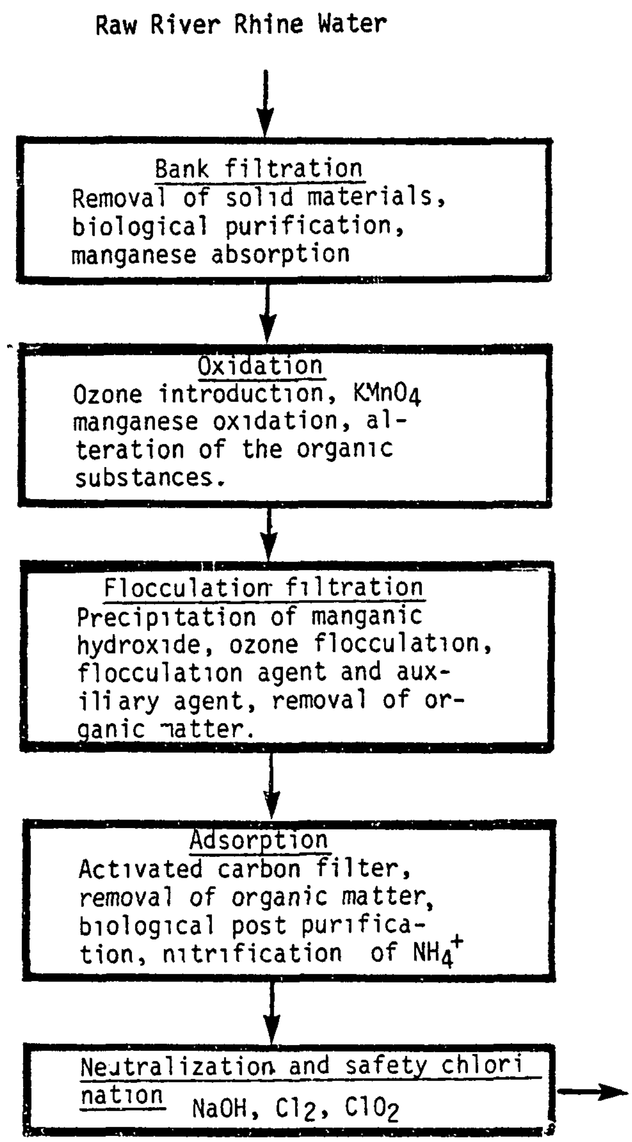


Figure 31. General procedural plan for the treatment of drinking water in the bank filtration works on the lower Rhine (Düsseldorf area)

Source: Poggenburg, et al., 1974

TABLE 17. EFFICIENCY OF GAC CONTROL FILTERS FOR MEASURING DISSOLVED ORGANIC SUBSTANCES

sampling station	organic substances (from DOC) mg/l	adsorbed organic substances mg/l	non-polar organic substances mg/l
Upper Rhine @ Basel	5.6	2.9	0.36
Lower Rhine @ Duisburg	12.0	6.5	1.19
bank filtrate (Düssel-dorf-Benrath), Lower Rhine	5.0	4.4	0.87
bank filtrate (Hamborn) Lower Rhine	6.0	5.3	0.66

Source: Fuchs & Kühn (1975)

Step #1 -- River Sand Bank Filtration--This is a technique whereby the raw Rhine River water is allowed to undergo some biological treatment in the ground before entering the treatment plant itself. Wells have been dug into the sand banks of the Rhine about 50 to 100 meters from the shore. Water is pumped from these wells into the plant for further treatment. About two-thirds of this well water has passed from the Rhine through the river sand banks during an average period of three weeks (Miller et al., 1978). The balance is much cleaner groundwater which flows to the Rhine.

During the three week time of passage from the Rhine to the wells, about 60 to 7C% of the organic materials present in the river water is removed from the water biologically. Those organics removed are the easily biodegraded materials originally present. The more biorefractory organic compounds, such as halogenated organics, pass through the river sand bank filters unaffected, and enter the treatment plant.

In addition to removing the easily biodegraded organic materials originally present in the River Rhine, the river sand bank filters reduce some of the nitrate ion present to nitrite and ammonia (Hopf, 197Cb). Also, manganese and iron are extracted from the sand banks and are present in the water entering the treatment plant.

Step #2 -- Oxidation--Upon entering the plant, the river sand bank filtered water is subjected to ozonation (1 to 3 mg/l dosage). Several benefits are observed during this step. First, ferrous ions are oxidized to ferric ions, which hydrolyze and precipitate. Manganous ions are oxidized to their manganic and permanganate states. In the manganic state, the insoluble manganic hydroxide is formed, which is easily filtered out of solution. Manganese in the permanganate state is quite water soluble, imparting a pink color to the water.

Finally, some oxidation of the dissolved organic materials also occurs. Some of the organics are partially oxidized completely to CO_2 and water. This can be deduced from the lower pH after ozonation. However, most of the organics which react with ozone are only partially oxygenated. This increases their ability to be biodegraded, however. On the other hand, there are still other organic materials present which do not react with ozone, and these (non-readily-biodegradable) materials pass through the oxidation stage unaffected.

Step #3 -- Flocculation and filtration--The ozonized water is passed into a holding tank where it remains about 30 minutes. During this time ferric and manganic hydroxides precipitate, some of the oxidized organic materials flocculate (assisted by the coagulating ferric and manganic hydroxides) and permanganate and residual ozone continue to oxidize more dissolved organic materials. As permanganate performs this oxidation function, it is reduced to the manganic state, at which it precipitates as the insoluble hydroxide or as manganese dioxide. As ozone continues to oxidize organics, it reverts back to oxygen. Those organic materials which are oxidized during this holding stage become oxygenated and more easily biodegraded.

Following the 30 minute holding time, the treated water is passed into a two-stage pressure filter. The first stage is a 1.5 m depth of granular carbon which has not been activated. The original filter material was 1 meter deep granular activated carbon (0.5 to 2.5 mm grain size), but this had several undesireable drawbacks (Poggenburg, 1975). First, the GAC was "inadequate as a filter material and for the biological conversion of ammonia to nitrate". A considerable fraction of the suspended matter passed through the upper layer to the second GAC layer, the function of which is to remove organic materials by adsorption.

On the other hand, the use of 1.5 m of non-activated carbon for filtration has produced the following benefits (Poggenburg, 1975):

- there are now no noticeable amounts of filterable materials in the GAC adsorbers when the combined unit is operated at "reasonable" filtration rates,
- degradation of ammonia occurs in the non-activated carbon bed, rather than in the GAC adsorbers,
- "due to the good filtration obtained in the upper layer of non-activated carbon, the adsorption process is necessarily improved in the GAC lower section".

Most of the filterable substances are retained in the first 0.5 meter of the non-activated carbon layer, but a bed depth of 1.5 meters is employed to remove the finer particles and attain a turbidity of 0.1 to 0.2 turbidity units.

Step #4 -- GAC Adsorption--A mixture of the activated carbons LS Supra and F-300 are used (Poggenburg, 1975) in the second layer of the pressure filters. The granule size of these carbons is 0.5 to 2.5 mm (mean diameter

1.4 to 1.6 mm) and the density is about 40% higher than the activated carbons used earlier. The layer heights of GAC in this second section of the pressure filters were increased from 2 meters to 2.5 meters and the operating velocity was reduced by about 50% (Poggenburg, 1975).

The adsorption layers in the Düsseldorf GAC adsorbers are changed twice each year (Poggenburg, 1975), now that the carbon is used to remove synthetic organics. Previously (when used only for taste & odor control), they were changed once per year. According to the process control procedures in use in 1975 (determination of the total organic components by UV absorption at 250 nm) the adsorption capacity of the GAC for organics (measured by this UV technique) was only 20% after a throughput of between 400,000 cu m and 600,000 cu m of water per adsorber containing 40 cu m of GAC. The adsorption capacity of new or freshly reactivated GAC for UV absorbing organics generally lies between 70 and 80% at this point in the process at Düsseldorf (Poggenburg, 1975). Taking as a basis this degree of loading and a mean operating velocity of 12 m/hr, the GAC would have to be reactivated or replaced in each adsorber 4 to 5 times each year if adsorption were the only organics removal mechanism occurring in the GAC adsorbers. The fact that regeneration was not required 4 to 5 times per year, as predicted, but rather only once per year, is attributed to biological removal of UV-absorbing organic materials in the GAC adsorbers.

Step #5 -- pH Adjustment and safety chlorination--Because of the formation of CO_2 (from biodegradation of organic materials in the pressure filters/adsorbers), NaOH is added, followed by a maximum dosage of 0.3 mg/l of a mixture of chlorine and chlorine dioxide. This mixture is produced by adding excess chlorine gas to a solution of sodium chlorite. The amount of chlorine added in excess is such as to produce two moles of free chlorine (as hypochlorite) for each mole of chlorine dioxide produced (Miller et al., 1978). This low dosage of mixed disinfectant is sufficient to guarantee water of acceptable bacteriological quality in the Düsseldorf distribution systems.

Düsseldorf Process Performance--

Figure 32 shows the pertinent water quality parameters measured at Düsseldorf and how they change at each stage of treatment. Figure 33 shows the percent removal of organic substances, as measured by DOC, COD and UV absorption analyses at the various process stages.

Taking the organics content of the raw Rhine River water as 100%, almost 60 to 65% is removed during river sand bank filtration. Ozonation then lowers DOC and COD values an additional 3 to 5%, but lowers UV absorption values about 18%. This fact, coupled with only a slight simultaneous lowering of DOC and COD, shows that UV-absorbing organic materials are changed structurally, but are not all converted to CO_2 and water upon ozonation. Rather, they are converted to other organic materials which still are measureable by DOC and COD analyses.

Finally, GAC adsorption lowers the organics content by an addition 8 to 10%. Overall, the Düsseldorf treatment process lowers the DOC and COD 70 to 80% and UV-absorbing organics over 85% (from the Rhine River initial values).

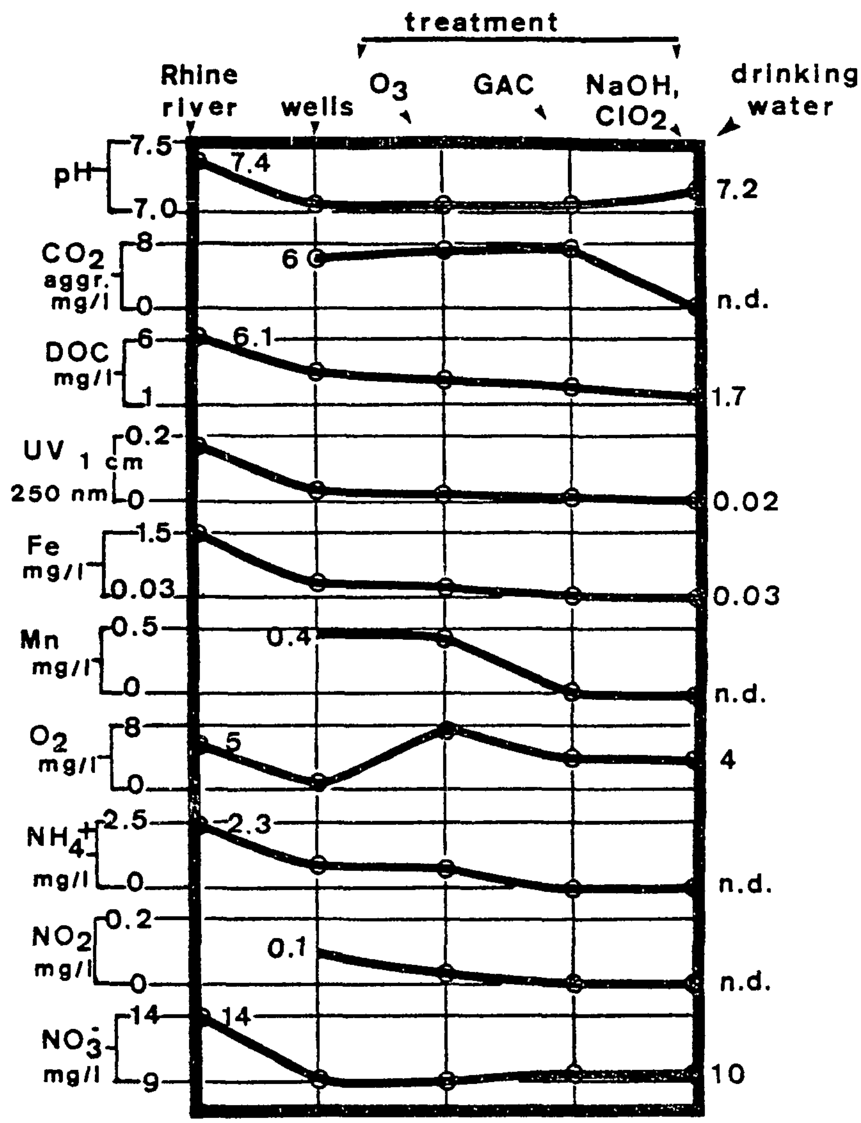


Figure 32. Changes in Rhine river water quality parameters during passage through the Düsseldorf water treatment process.

(Poggenburg, 1975)

However, starting with river sand bank filtered water entering the plant, the combination of ozone and GAC adsorption steps lowers COD and DOC values only an additional 10 to 15% and UV-absorbing organics values about 25% additionally.

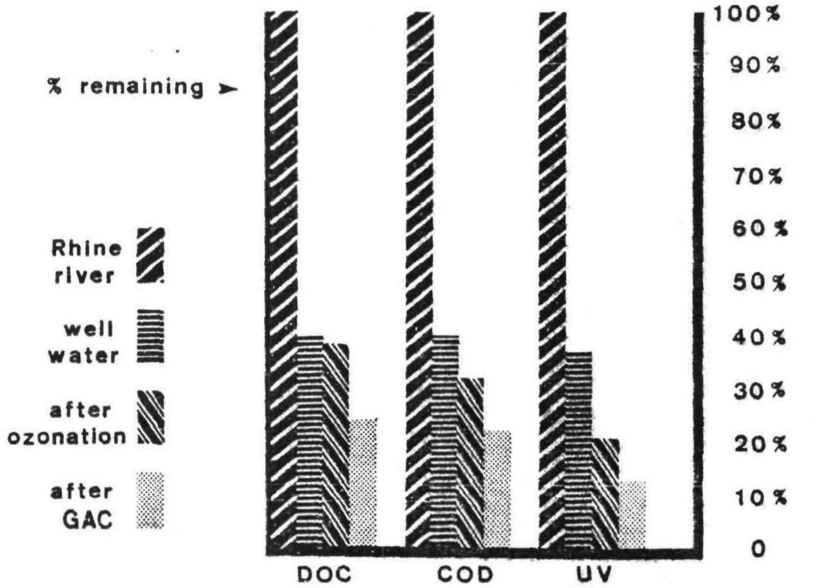


Figure 33. Changes in organics parameters in Düsseldorf water treatment plants.

(Poggenburg, 1975)

Pilot Plant Studies at Düsseldorf For Removing Chlorinated Organics and Determining Benefits of Biological Activity in GAC Adsorbers

An experimental pilot plant installation was constructed at the Flehe plant which consisted of ten plexiglass columns which could be operated in parallel (individually) or in series (one after the other). Each column was about 20 meters in diameter and held a charge of granular activated carbon sufficient to provide a 1 meter bed depth.

In the first series of tests, eight different types of GAC were compared with each other, then the four best performing carbons were selected for more detailed studies. Many of these studies were conducted with the four types of GAC operating side by side in the pilot plant test facilities. Under such conditions, two or three of the test columns were connected in series. This allowed measurements to be made at various GAC total bed depths.

Granular activated carbons (labelled Types F, L, N and B) were treated with 50,000 cu m of water (13.2 million gallons) per cu m of GAC present in the columns, presumably at a flow velocity equivalent to that at which the dual media pressure filters/adsorbers of the large scale plant operated. At various levels of throughput [about 12,000, 25,000 and 50,000 cu m (3.17, 6.61 and 13.2 million gallons, respectively)/cu m of GAC passed through during the test], GAC samples were removed from the columns and three values were determined:

(1) The Total Organic Substances (TOS) removed from the water (determined by continuous measurement of UV absorption and occasional parallel determination of the concentration of dissolved organic carbon (DOC)

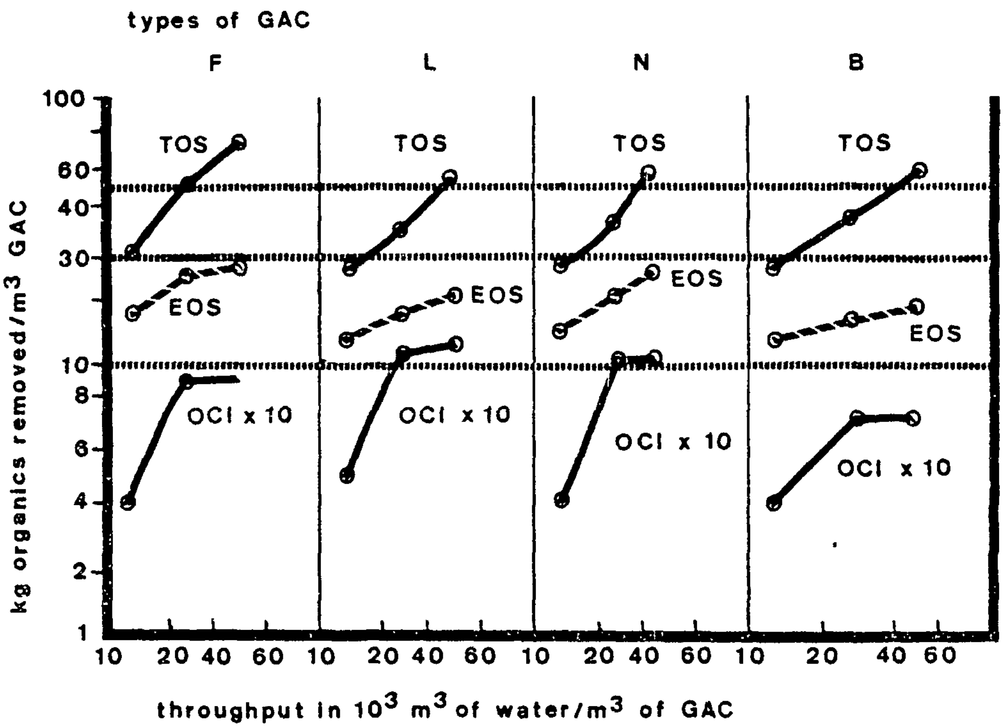
(2) The organic substances which could be extracted from the GAC with dimethylformamide (Extractable Organic Substances = EOS) and

(3) Adsorbed organochlorine compounds, as chlorine (OrgCl).

Pertinent data concerning these studies are plotted on log-log scale in Figure 34. It can be seen that all three curves have similar shapes with all four granular activated carbons. It is also clear that considerably more total organic substances (TOS) were removed from the water during passage through the pilot plant test adsorbers than were recovered by extraction of GAC samples with DMF (EOS). The DMF extraction procedure has been shown (Maier, 1971; Sontheimer & Maier, 1973) to extract organic substances adsorbed by granular activated carbon nearly quantitatively from the carbon. Therefore, the differences between the total organic substances removed during passage through the GAC adsorbers and the amount of organic substances extracted from the GAC after various amounts of water throughput is that amount of organic materials which were decomposed biologically during passage through the biologically active filters/adsorbers. This amount of organics removed biologically was 2 to 3 times that which was extracted by DMF after 50,000 cu m of water (13.2 million gallons) had been passed through each cu m of GAC, and each type of granular activated carbon gave somewhat different results.

It can also be seen from Figure 34 that after approximately 25,000 cu m of water (6.6 million gallons) had been passed through each cubic meter of GAC, essentially no additional increase in adsorption of chlorinated organic substances occurred.. It is also apparent that those activated carbons which adsorbed the highest amounts of organochloro compounds (Types L and N) removed less total organic substances than did types F and B. The maximum amount of organochloro materials adsorbed by GAC type L was about 12 kg/cu m of GAC after 25,000 cu m of water (6.6 million gallons) had been passed through 1 cubic meter of GAC. At the same time, Type L GAC removed about 50 kg of TOS/cu m of GAC, about 22 kg/cu m of which was recovered by DMF extraction, leaving about 28 kg/cu m of GAC which was destroyed biologically.

These pilot plant data obtained at Düsseldorf are particularly significant, since they provide a practical limit of organochloro materials which can be adsorbed by a given volume of granular activated carbon. It was pointed out earlier in this section that the Düsseldorf full-scale plant GAC



TOS = total org. substances adsorbed and removed from water
EOS = organic substances extractable with DMF
OCl = organic chlorine compounds adsorbed, as Cl

Figure 34. Performance of various activated carbons at Flehe test plant, Düsseldorf.

(Poggenburg *et al.*, 1974)

adsorbers contain a mixture of LS Supra and F-300 carbons. This is presumably because one has a higher capacity for chlorinated organics while the other has a higher capacity for Total Organic Substances.

Extensive studies then were conducted on samples of GAC which had been in use for a period of 6 months using the programmed temperature pyrohydrolysis method of Kühn & Sontheimer (1973a). In this procedure, the sample is subjected to preliminary drying at 40°C, then is burned at approximately 800°C in an oxygen-water carrier gas which is swept through the furnace. The temperature is sufficiently high to decompose the organic materials and produce chloride ion (hydrogen chloride) from the chlorine present, which then is adsorbed in water and this is titrated or is determined with an ion-selective electrode. This gives a measure of the amount of chlorine originally present in the organic compound. Since chloride ion also is adsorbed from water by the GAC, this must be determined separately. The loaded activated carbon is exchanged with 0.1N sodium nitrate and the chloride removed is determined titrimetrically. The amount of chloride ion originally adsorbed by the GAC is subtracted from the total chloride ion determined by the pyrohydrolysis procedure. This difference gives the amount of chlorine bound as chlorinated organic materials (Engler-Bunte Institute, 1977).

In addition, Kölle (1974) identified several individual chlorinated organic compounds by dioxane extraction of the loaded activated carbons, followed by chromatographic analysis of the extracts.

Figure 35 summarizes the results which were obtained using the programmed temperature pyrohydrolysis analyses of the activated carbon adsorbers connected in series and filled with various types of activated carbon. The total amount of chlorine found (in g/kg of activated carbon) in each type of GAC is shown as the upper limit. This number then is divided according to the temperature at which the individual portions of the total amount either volatilize or are decomposed. The hatched portions of Figure 35 indicate the relative amount of total chlorinated organic material that Kölle (1974) was able to identify as individual chlorinated organic compounds, which ranged from 7 to 35%.

Kölle (1974) was able to identify ten different substances in the dioxane extracts of carefully dried GAC samples. These dioxane-extracted chloroorganics are the non-polar compounds adsorbed. Pertinent data are listed in Table 18. For each individual substance and for each type of GAC, the amount removed from the water is given as the mg of material per cu m of water which must be removed from the water in order to obtain the measured carbon loading. From consideration of these data, carbon L appears to be greatly superior to carbons F and N.

Poggenburg et al. (1974) also caution that even though small scale studies with GAC can give consistent data, past experience at Düsseldorf has shown that large scale tests still must be made in the operating water treatment plant. This is because of variations in the performance of different batches of granular activated carbon, even though they may be of the same type, and variations in wetability, abrasion resistance, amount of turbidity removed, backwash capacities and regeneration conditions.

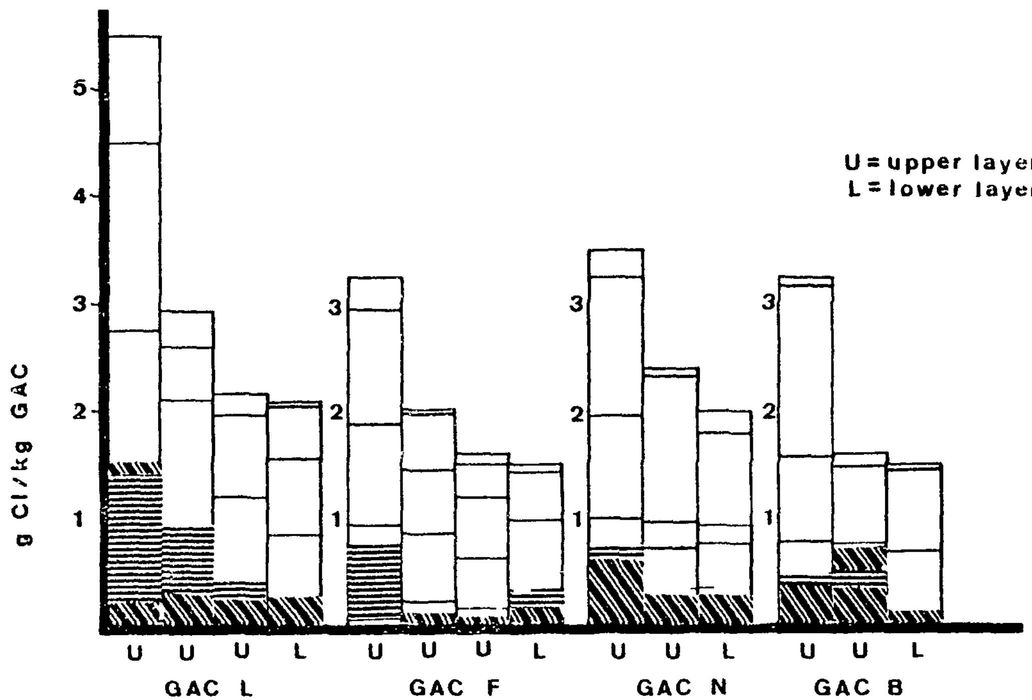


Figure 35 Quantities of individual substances determined by temperature *programmed pyrohydrolysis of GAC vs total org. Cl loading.*

(Poggenburg et al., 1974)

TABLE 18. CHLORINATED ORGANICS REMOVED FROM GAC BY DIOXANE EXTRACTION AT FLEHE TEST INSTALLATION, DUSSELDORF*

compound	quantity removed from the water by GAC of the type: F mg/cu m	L mg/cu m	H mg/cu m
chloroform	0.05	0.23	0.09
1,2-dichloroethane	0.16	0.52	0.21
1,2-dichloropropane	0.36	3.C6	0.54
trichloroethylene	0.34	0.88	0.48
tetrachloroethylene	0.46	0.82	0.46
bis-(2-chloroisopropyl) ether	4.52	8.81	3.88
o-dichlorobenzene	0.13	0.27	0.13
hexachlorobutadiene	0.74	1.79	0.75
hexachlorocyclohexane	0.11	0.18	0.14
tris-(2-chloroethyl) phosphate	0.83	1.21	1.08
sum of the above chlorinated compds.	7.7	17.8	7.8
stated in mg/cu m of water	3.9	9.6	4.0
total chloroorganics removed	∿26	∿4C	∿23
total organic substances	1,450	1,150	1,325
therefore extractable	853	646	651

* GAC height = 3 m; filtration velocity = 15 m/hr; 78 to 86 cu m water per kg GAC

Source: Poggenburg *et al*. (1974)

Comparison of performances of various activated carbons in actual practice also is made more difficult by the fact that after a period of 3 to 4 weeks, biological processes occur at significant rates in the large scale GAC media. Figure 36 shows some typical organic loadings per kg of GAC obtained from one of Düsseldorf's plant adsorbers charged with 16,800 kg of Type F activated carbon and operated over a period of 250 days. The middle curve shows the cumulative total organic loading if the carbon had been acting solely as an adsorber (data obtained by measuring adsorption isotherms). However, the upper curve shows the cumulative amount of organic materials actually removed from the water. By adsorption only the cumulative amount of organic materials removed from water after 250 days of use would have been about 1,800 kg. However, the total weight of organics removed by the GAC was about 2,900 kg. The difference of 1,100 kg was the amount of organic materials removed from the water biologically.

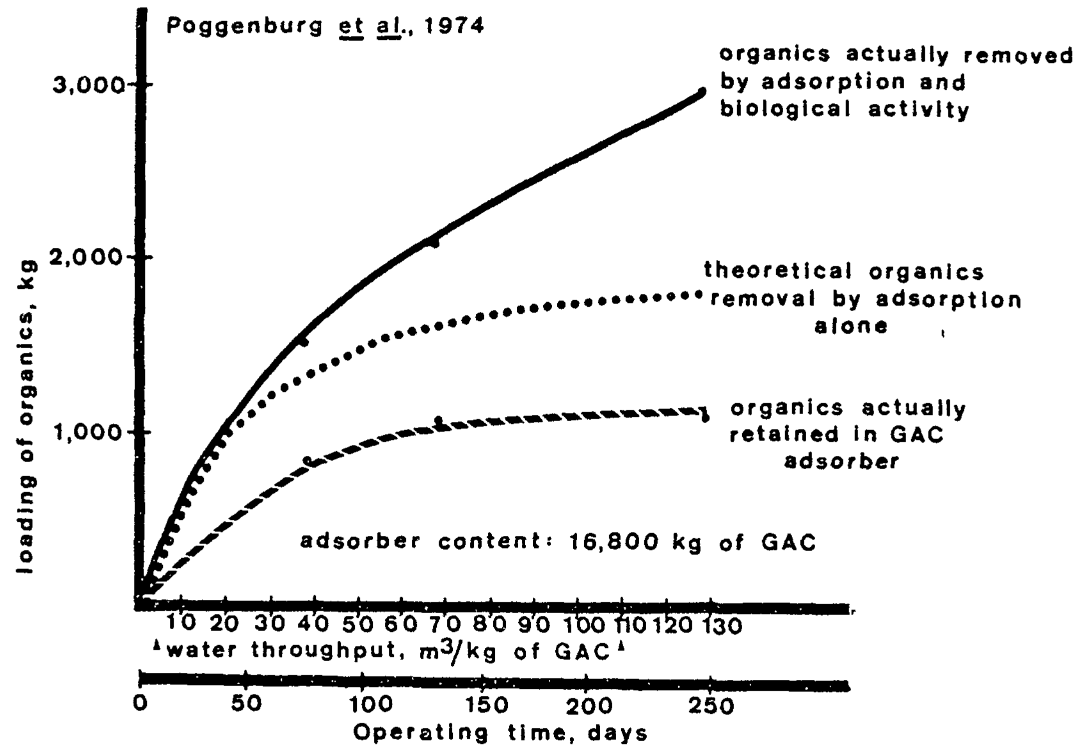


Figure 36. Organics removal in Düsseldorf GAC post-adsorber by adsorption and by adsorption + biological activity.

The lower curve in Figure 36 is the cumulative amount of adsorbed organics actually present (determined by DMF extraction). After 250 days of use, only 1,100 kg of adsorbed organic materials were shown to be present on the 16,800 kg of GAC. The difference between 2,900 kg (total organics removed from solution) and 1,100 kg which could be removed from the loaded GAC by DMF extraction represents the total amount of organic materials destroyed biochemically during the 250 days of use of this GAC. The difference between 1,800 kg of GAC capacity acting by adsorption only and the 1,100 kg actual organic loading after 250 days of use represents the adsorption capacity still available in this carbon adsorber after 250 days of use. Therefore, assuming that full saturation of this adsorption capacity can be attained, it can be concluded that the biological activity in the GAC medium extends the adsorption life of the GAC.

Perhaps more significantly, the total amount of organic materials which can be removed from the loaded GAC by extraction after 250 days reached a plateau, as did the adsorption-only curve. Therefore the available adsorption capacity (the difference between the two lower curves) became constant. However, the total rate of removal of organics from solution (the upper curve) still was increasing after 250 days of use. This is strong evidence to support the conclusion that some of the organic materials being destroyed biochemically are materials already adsorbed on the GAC. If this were not the case, the adsorption capacity of the GAC would have been expected to become completely saturated, and the cumulative organic removal curve would have reached a plateau at the same time as did the other two curves.

The difference between the 1,800 kg of organic materials removed by adsorption only, had the GAC been totally loaded, and the actual 1,1C0 loading (by CMF extraction) might be viewed as the amount of GAC adsorption capacity being reactivated biologically after 250 days of use. This figure (700 kg) is approximately 44% of the total adsorption capacity of the GAC being used.

Finally, it can be observed from Figure 36 that the contribution of biological activity to the removal of organic materials from solution became noticeable after 30 to 40 days of use.

Behavior of Düsseldorf Granular Activated Carbons With Respect to Removal of Organochlorine Materials

Relatively simple analytical methods were desired for controlling the performance and reactivation of the GAC adsorbers at Düsseldorf with respect to removal of chlorinated organic materials. To these ends, extraction methods were developed for these materials, followed by separation techniques which allow for subsequent gas chromatographic determinations of the individual compounds extracted. These procedures were developed by the Engler-Bunte Institute (Park, 1974; Park & Sontheimer, 1973) and involve initial extraction of the loaded GAC with dimethylformamide at 50°C. Microcoulometric titration of this extract gives the total amount of organochlorine compounds extracted. Pyrohydrolysis of the loaded GAC measures the total organochlorine materials present on the loaded GAC.

Water is added to the CMF extract and the solution then is extracted with n-hexane, which separates the non-polar organochlorine materials. The hexane solution then is dried and gas chromatographed. Polar organochlorine materials remain in the DMF-water solution.

In Figure 37 are plotted the total concentrations of organochlorine materials and those of tetrachloroethylene, hexachlorobutadiene and hexachlorocyclohexane at GAC bed depths of 0, 100 and 200 cm. These data were determined by the above procedures in two full scale operating GAC adsorbers at the Düsseldorf plant using different activated carbons (types L and F) being compared side by side. The data found were very similar for both carbons at the same bed depths.

About the same data were obtained for total non-polar organochlorine compounds when the initial extraction was performed with dioxane rather than with DMF, followed by hexane extraction of the DMF extract. Data shown in Figure 38 were obtained using a third full scale Düsseldorf GAC adsorber. From these results, it was concluded that only small differences in the data were measured using (1) DMF extraction, followed by addition of water and n-hexane extraction, (2) Soxhlet extraction of loaded GAC with dioxane and (3)

Soxhlet extraction of loaded GAC with dioxane, addition of water and extraction with n-hexane. Therefore, Poggenburg et al. (1974) concluded that extraction of loaded GAC with dioxane is a satisfactory method for determining the amount of non-polar organochlorine materials adsorbed by GAC. This method then was adopted for controlling Düsseldorf's GAC adsorbers, replacing the then-used UV absorption method.

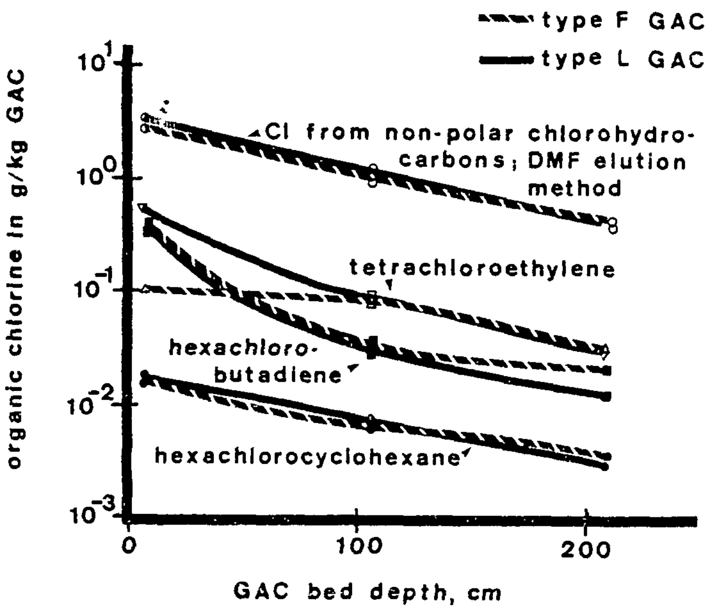


Figure 37. Distribution profiles for organically bound chlorine and some chlorohydrocarbons in Düsseldorf GAC beds

(Poggenburg et al., 1974)

Following adoption of the dioxane/hexane extraction method for determining non-polar organochlorine materials adsorbed, numerous additional data were obtained on operating full-scale plant GAC adsorbers. Some of these data are presented in Figures 39 and 40.

Figure 39 shows the values obtained for total extractable organics (E_g) with DMF, non-polar organics extractable with dioxane (E_d), the total amount of organochlorine compounds adsorbed on the activated carbon (by pyrohydrolysis), the amount of organochlorine compounds in the dioxane extracts (Cl_d) and the amount of organochlorine compounds in the hexane extracts of the dioxane extracts (Cl_h). Data in Figure 39 compare two different types of GAC (F and L), one operated at the Düsseldorf Holthausen plant, the other operated at the Duisburg Wittlaer plant (both using the same treatment process and sand bank filtered Rhine River water in the same general location) and after similar quantities of water had been passed through each adsorber.

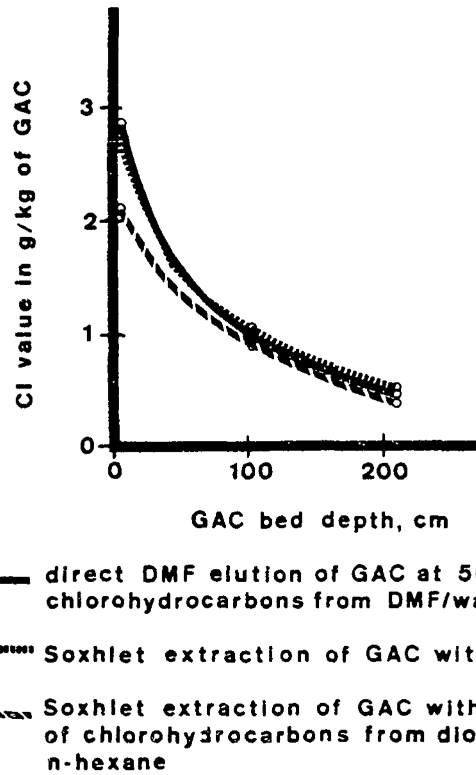
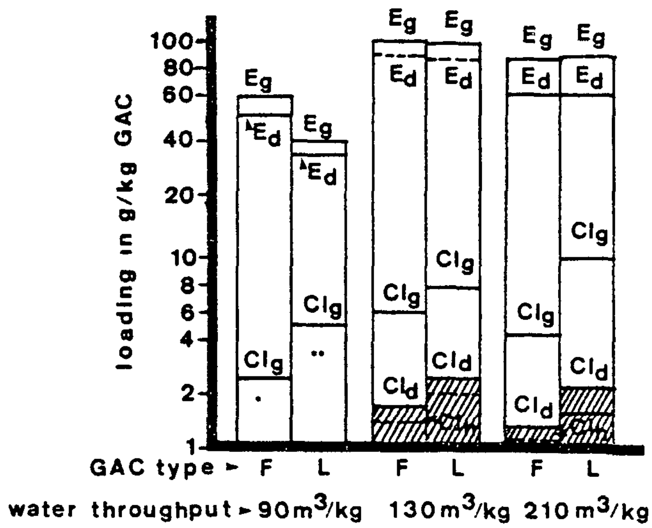


Figure 38. Distribution of organically bound chlorine in Düsseldorf GAC beds.

(Poggenburg et al., 1974)

After 90 cu m of water had been passed through the adsorbers per kg of GAC, the total organic materials extracted by DMF from GAC type F was about 60 g/kg and about 40 g/kg for type L. The non-polar organics extracted by dioxane were 50 and 35 g/kg, respectively, for types F and L, and the total organochlorine materials found were 2.5 and 5 g/kg, respectively, for types F and L. After passage of 210 cu m of water per kg of GAC through the adsorber, the total extractable organics were about 75 g/kg for the two types, total dioxane extractables were about 55 g/kg, and total organochlorine compounds found in the dioxane extracts were 4 and 8 g/kg, respectively, for types F and L.



E_g = total extractable organics

E_d = DMF extract (total non-polar extractable organics)

Cl_g = total Cl by pyrohydrolysis

Cl_d = Cl in dioxane extract

Cl_h = Cl in hexane extract

$^{\cdot}Cl_d = 0.43;\ Cl_h = 0.22$ $\quad$ $^{\cdot\cdot}Cl_d = 0.43;\ Cl_h = 0.64$

Figure 39. Organics removal with 2 types of GAC in 2 Düsseldorf treatment plants.

(Poggenburg et al, 1974)

These data confirmed the earlier pilot plant test data which showed that type F GAC had a slightly higher capacity to remove total organic materials, but that type L could remove double the amount of organochlorine materials.

The cross-hatched areas of Figure 40 show the total loadings of non-polar organochlorine materials on GAC samples taken from the upper, middle and lower regions of two of the plant operating GAC adsorbers at Düsseldorf, one using type L GAC and the other using type F. As would be expected, the loadings of total extractable organics and total organochlorine materials were higher in the upper regions than in the lower. The upper layer of Type F carbon showed total extractable organics levels of 103 g/kg of GAC and total organochlorine materials of 1.6 g/kg. In the upper layer of type L GAC, total extractable organics levels were 83 g/kg of GAC, but total organochlorine levels were 2.2 g/kg, about 40% higher.

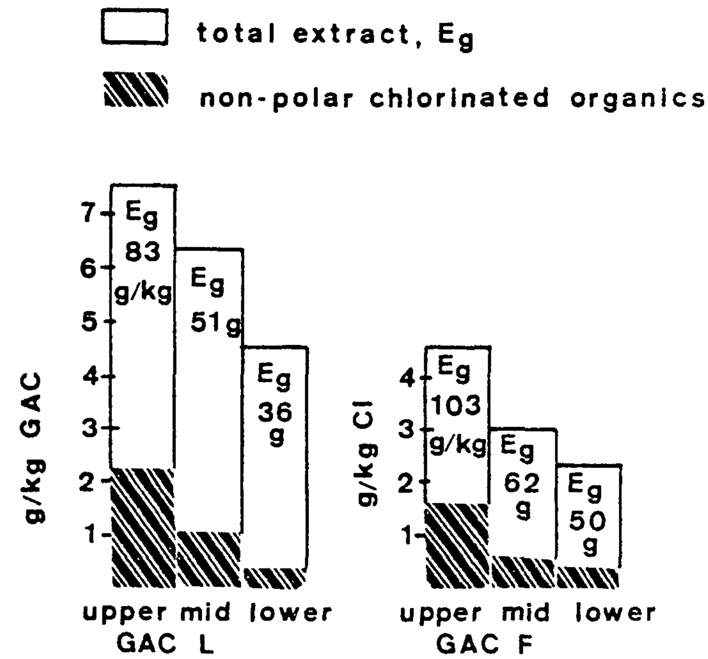


Figure 40. Change in loading of 2 types of GAC with polar and non-polar organic chlorine compounds at large Düsseldorf treatment plant.

(Poggenburg et al., 1974)

It should be noted also that when the upper layers of these GAC adsorbers reached these loadings of organochlorine compounds, the lower layers showed 0.25 to 0.3 g/kg loadings of organochlorine materials. During personal interviews in 1977 and again in 1978, Mr. Poggenburg advised that the technique of measuring the loading of organochlorine compounds as they progress down the GAC adsorber media by these analytical techniques is used to determine when the GAC should be regenerated. Whenever measureable levels of organochlorine materials are detected in the lower 20 to 25% of the Düsseldorf GAC adsorbers, the upper 80 to 75% of the GAC is removed and sent to reactivation. The remaining 20 to 25% of the GAC, containing little or no adsorbed organochlorine materials, is mixed with fresh or reactivated GAC and acts as a biological seed so that the GAC adsorbers can reattain biological equilibrium rapidly.

Prior to adopting these organochlorine analyses, Düsseldorf's GAC adsorbers were controlled by following organics removed (measured by UV absorption at 254 nm). This technique determines the aromatic and unsaturated organic materials. Reactivation of Düsseldorf's GAC was conducted once per year, using UV absorption as the control analysis. However, using organochlorine loadings as the controlling analytical procedure, Düsseldorf's GAC adsorbers now are reactivated every 5 to 6 months.

Biological activity in the Düsseldorf GAC adsorbers is considered by Mr. Poggenburg to be an essential part of the total Düsseldorf treatment process because the final treated water contains lower dissolved organics and is ammonia-free. Furthermore, there is no concern that non-chlorine containing organics will breakthrough before the organochlorine materials reach the lower portions of the GAC adsorbers. Nevertheless, UV absorption analyses still are conducted routinely at all three Düsseldorf plants (Engels, 1978). In addition, more sophisticated GC and GC/MS analyses also are conducted on Rhine River water and sand bank filtered treatment plant influents, so as to note the appearance of organic materials whose fates when processed by the Düsseldorf treatment techniques are not yet known.

<u>Bremen Pilot Plant Study</u>

The Auf dem Werder water plant of Bremen, Federal Republic of Germany has utilized the treatment process illustrated by Figure 41 to treat raw water from the River Weser. A comprehensive pilot plant program was carried out to determine if alternate treatment processes could be found to replace the slow sand filters, which required a large proportion of the site area.

A large pilot plant facility employing granular activated carbon with preoxidation and preaeration was constructed in 1969, and research was conducted on biological activated carbon over a three year period. The dissolved organic carbon (DOC) content of the raw water was 5 to 10 mg/l, and the permanganate consumption value numbers varied from 10 to 22 mg/l. For these tests, the rapid sand filtrate from the full-scale plant was used as the pilot plant feed water. All pilot plant data obtained were compared with those obtained after the slow sand filters of the full-scale plant.

Initial Process Screening Test--

Many initial screening tests were performed prior to the main pilot plant operation. A screening test facility providing a treatment process similar to that used in the Düsseldorf area to treat lower Rhine River water was utilized. The initial process screening test facility (Figure 42) consisted of an ozone contact chamber (0.7 m diameter, 3 m high), two holding tanks (each 2.5 cu m), a sand filter (0.7 m diameter, 3 m height) and an activated carbon filter (0.8 m diameter, 3 m height). Provision also was made to close off the flow of water through the carbon column periodically. At these times, the water in the carbon columns was recycled back through the carbon beds (adding oxygen continuously) and analytical parameters were measured. These included dissolved oxygen, DOC, carbon dioxide, ammonia, nitrate, etc. In this manner, material balances were determined at biological equilibrium. This was defined as the point at which the rate of consumption

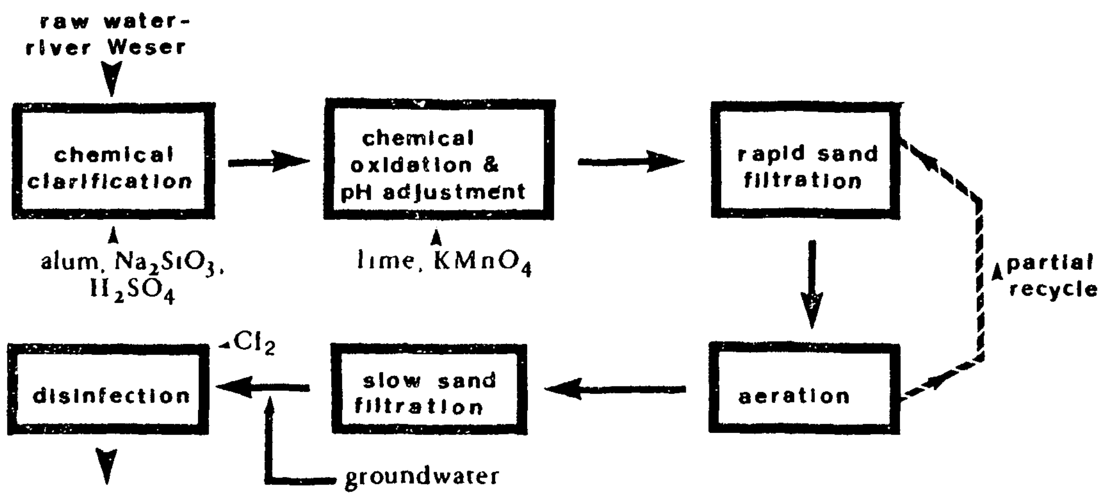


Figure 41. The Auf dem Werder water treatment process, Bremen, Federal Republic of Germany.

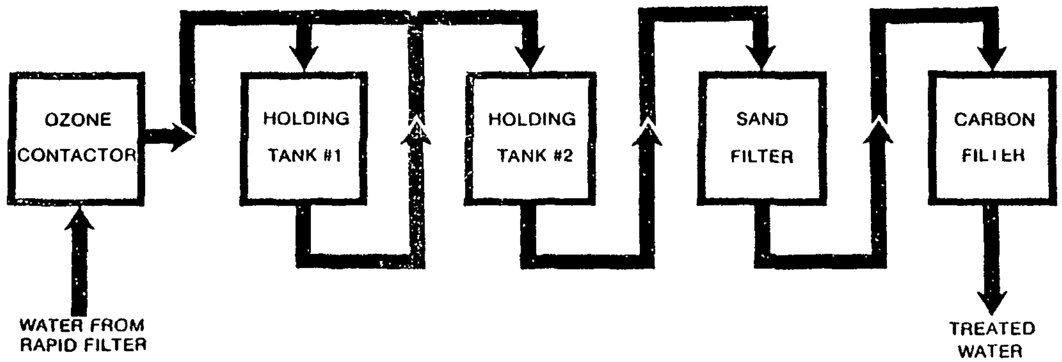


Figure 42. Bremen, Germany Water Works Pilot Plant

(Eberhardt, Madsen & Sontheimer, 1974)

of dissolved oxygen equaled the rate of formation of CO_2 (from degradation of DOC) in the absence of ammonia in the GAC column influent.

Initially, the depth of the granular activated carbon test bed was 1 meter and the filtration rate was such as to provide an empty bed contact time of 5 minutes. Ozone dosages were 1.5 to 2 mg/l. Under these conditions, ammonia was removed (biologically by nitrification) as efficiently as in the full-scale plant, but organics were removed less efficiently in the test unit. Increasing preozonation dosages to 4.7 mg/l and GAC empty bed contact times to 15 minutes (still 1 meter GAC bed depth) gave higher quality water than that obtained in the full-scale plant, with respect to removal of dissolved organic carbon (DOC), COD, oxygen consumption (by alkaline permanganate), ammonia and 48-hour colony counts. Pertinent data are listed in Table 19.

The testing unit used to gather the data of Table 19 was modified by incorporating a rapidly driven slow sand filter (RDSSF) after the GAC adsorber. This is merely a 1 meter deep slow sand filter operated at a filtration rate of 0.5 to 1 m/hr. This unit was installed to lower the very high 72 hour colony counts found after the biologically active GAC filter (see last column of Table 19).

Granular Activated Carbon Screening Test--

Rapid sand filtrate from the full-scale treatment process was used as influent to four granular activated carbon pilot plant units. Each pilot plant unit consisted of four columns connected in series as illustrated by Figure 43. Since each column contained 1.5 meters of granular activated carbon, it was possible to evaluate the treatment results achieved with 1.5, 3.0, 4.5 and 6.0 meters of GAC.

An initial 11 week GAC screening study was performed on the four GAC pilot plant units. Three units charged with GAC designated as Hydraffins BD, BR and LS were fed rapid sand filtrate from the full-scale plant. A fourth pilot plant unit charged with Hydraffin BD was fed prechlorinated rapid sand filtrate (dosage was not stated).

Review of the data obtained during this 11-week test period, summarized in Table 20, provided the following information:

1. Hydraffins BR and LS performed much better in removing dissolved organics (as measured by the permanganate oxygen demand values) than did Hydraffin BD. Therefore, Hydraffin BD was not tested further.

2. Prechlorination did not improve the ability of Hydraffin BD to remove dissolved organics. If anything, prechlorination was detrimental in this regard. Therefore, prechlorination was not continued in the long term pilot program.

3. Colony counts (48-hour incubation) and coliform counts in all activated carbon effluents were similar. However, 72-hour colony counts in the prechlorinated Hydraffin BD effluent were 3 to 6 times higher than in the filtrates of the other activated carbons tested.

TABLE 19. TESTS WITH OZONE AND ACTIVATED CARBON FILTERS (JANUARY 8 TO FEBRUARY 2, 1970)

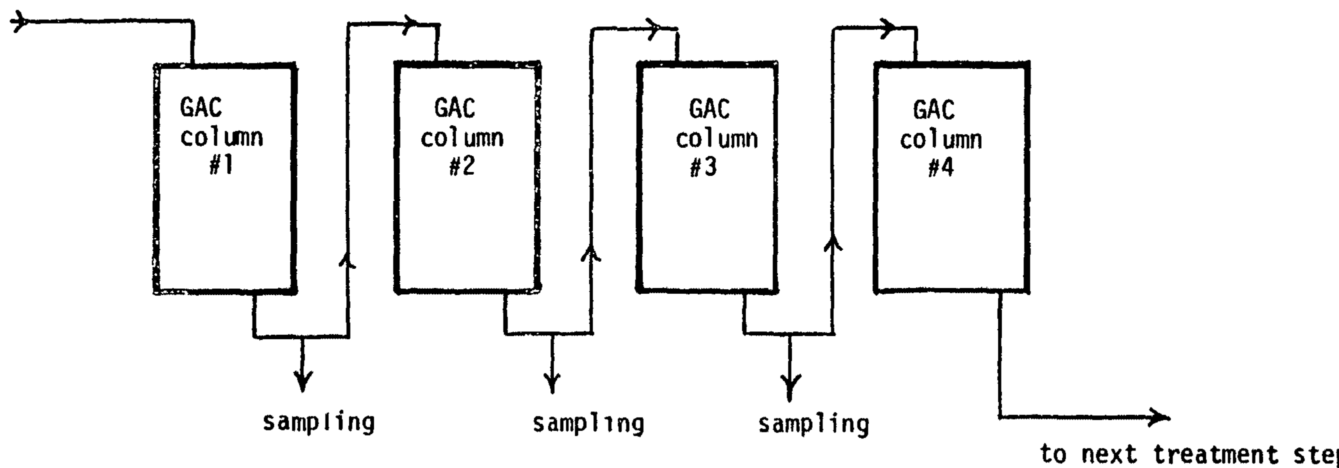
sampling point	pH	DOC mg/l	COD* mg/l	UV-abs. (Corr.) 240 nm, 1 cm	Permanganate oxygen demand mg/l** (COD)	Dissolved O_2 mg/l	NH_4^+ mg/l	turbidity x 10^{-3} abs.E.	Colony count/ml after	
									48 hrs	72 hrs
after clarification	7.75	4.3	12.9	0.278	21.4	11.7	2.68	4.54	6,600	-
rapid sand filtrate	7.63	3.7	11.4	0.257	18.4	10.5	2.37	0.92	2,700	-
after ozonation	7.59	4.1	10.6	0.163	15.9	16.9	2.16	0.99	0	-
after GAC	7.22	2.2	9.1	0.160	13.0	10.1	0.49	0.97	49	4,600
after RDSSF	7.18	2.4	7.9	0.151	11.7	8.8	0.21	0.90	9	320
after slow sand filter (for comparison)	7.30	3.2	9.5	0.225	16.5	6.7	1.41	0.89	114	-

Conditions:

Ozone dosage: 4.7 mg/l.
Flow rate, activated carbon filter: 2 m/hr at 1 m bed height (EBCT - 15 min). Flow rate, RDSSF: 0.5 m/hr at 1 m bed height (EBCT - 1 hr). Slow filter in large scale operation, as normal. DOC, COD and UV values sometimes from only two specimens. Mean water temperature 1.6°C.

* determined by the bichromate method
** determined by the alkaline permanganate method

Source: Eberhardt, Madsen & Sontheimer, 1974



Notes: Each column contains 1.5 meters of GAC bed depth

Effluent from GAC column #4 can be aerated and recycled to GAC column #1

Figure 43. Schematic of Bremen waterworks pilot plant GAC test units.

(Eberhardt, Madsen & Sontheimer, 1974)

TABLE 20. COMPARATIVE TESTS WITH DIFFERENT TYPES OF ACTIVATED CARBON FOR PURELY BIOLOGICAL TESTS. I = MAR. 24 - MAY 5, 1970 = 8.31°C; II = MAY 8 - JUNE 16, 1970 = 16.1°C.

Sampling point	Dissolved oxygen mg/l		Permanganate O_2 consmtn. mg/l		Δ($KMnO_4$ O_2 demand)**, mg/l		pH Value		Colony counts/ml after 48 hrs		Colony counts/ml 72 hrs	E coli & coli per 100 ml	
	I	II	I	II	I	II	I	II	I	II	II	I	II
rapid sand filtrate	11 1	8 6	11 5	11 1			7 64	7 69	278	242	800*	1	5
BD filtrate	9 3	6.8	6 6	8 0	4.8	3 1	7 80	7 65	364	61	1238	0	1
BR filtrate	9.0	5.3	2.5	3.6	9.0	7 5	8.02	7 54	382	70	2397	0	1
LS filtrate	8 6	6.0	2 0	2 8	9 5	8 3	7 73	7 56	122	68	1921	0	1
BD filtrate chlorinated	9.4	5.9	6 3	8 0	5 1	3 0	7 38	7 22	246	20	6545	0	0
slow sand filter for comparison	9.8	7.4	9 61	7 8	1 90	3 26	7 51	7 56	17	89		0	0
period: Mar 24 June 16, 1970 (overall)													
rapid sand filtrate	9 7		11.3				7 67		258			3	
BD filtrate	8.0		7 3		4 0		7 73		149			<1	
BR filtrate	6 9		3 0		8.3		7 78		164			<1	
LS filtrate	7 2		2.3		8 9		7.65		91			<1	
BD filtrate chlorinated	7.4		7 1		4 1		7 30		70			0	
slow sand filter for comparison	8.5		8.7		2 6		7 54		39			1	

* only 1 sample ** measured by the alkaline permanganate method

Source: Eberhardt, Madsen & Sontheimer, 1974

4. Hydraffins BR and LS, during the first six weeks of testing (Period I), reduced the permanganate oxygen demand values from 11.5 mg/l to 2.5 and 2.0 mg/l, respectively. During this period, adsorption appeared to be the dominant process removing dissolved organics, and biological activity within the GAC media was increasing. However, during the next five weeks (Period II), when significant biological activity appeared to be present, permanganate oxygen demand levels in the BR and LS effluents increased to 3.6 and 2.8 mg/l, respectively. In addition, the permanganate oxygen demands of Hydraffin BR and LS effluents were less than half those of the full scale plant.

Long Term Pilot Plant Operation--

Operation of the previously described Hydraffin BR and LS pilot plant units was continued for more than three years. During this time, the other two 4-column pilot GAC units were used to compare the effectiveness of other granular activated carbons and to test process parameters over shorter periods of time. The pilot plant units were backwashed every two weeks.

During the next 3 to 4 months, the performance of Hydraffin BR in removing dissolved organics decreased and reached a level which remained essentially constant for the balance of the more than three year test period. Figure 44 shows the overall performance of Hydraffin BR in this regard. After bioequilibrium had been attained in the GAC unit, about 4 to 6 mg/l of permanganate oxygen consumption was removed, irrespective of the value of the influent water, over the last two years of use. During this time, rapid sand filtrate from the full-scale plant contained 11.5 to 23 mg/l of permanganate oxygen demand. Therefore, the 4 to 6 mg/l of permanganate oxygen consumption removed during passage through the GAC was equivalent to 25 to 33% removal of dissolved organics. In addition, permanganate oxygen consumption values always were higher during summer than in the winter, probably because of increased biological activity during periods of higher water temperatures.

Long Term (3+ Years) Testing --

In Figure 45 are plotted the permanganate oxygen consumption values and the ratios of Δ(permanganate values)/Δ(dissolved oxygen consumed) obtained over the 3+ year period for the Hydraffin BR activated carbon adsorber. When the ratio was about 1 (which was the case most of the time), then adsorption and biodegradation of dissolved organics were occurring at about the same rates. On the other hand, when this ratio was greater than 1 (during winter), less dissolved organic material was being removed biochemically than was being removed from solution by adsorption. When the ratio was less than 1, the authors concluded that biochemical degradation of adsorbed organic materials was occurring faster than adsorption of organics from solution. These results again indicate that adsorptive sites on the granular activated carbon either still were available after three years of use, or were being regenerated biologically.

Data obtained for the Hydraffin LS GAC adsorber unit over the 38 month period of use were similar to those obtained with Hydraffin BR, except that a slightly longer initial adjustment period was required to reach biological equilibrium.

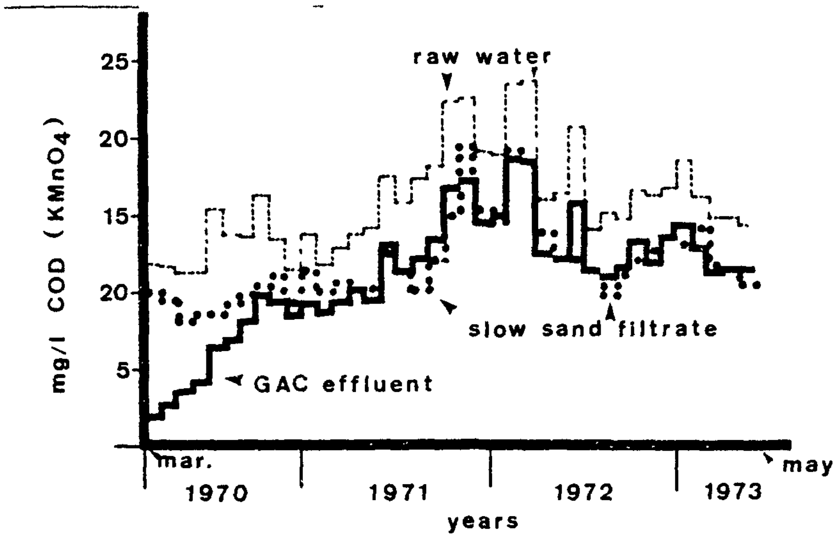


Figure 44. Comparison of chemical oxygen demand ($KMnO_4$) removal by slow sand filtration and BAC at Bremen, Federal Republic of Germany.

(Eberhardt et al, 1974)

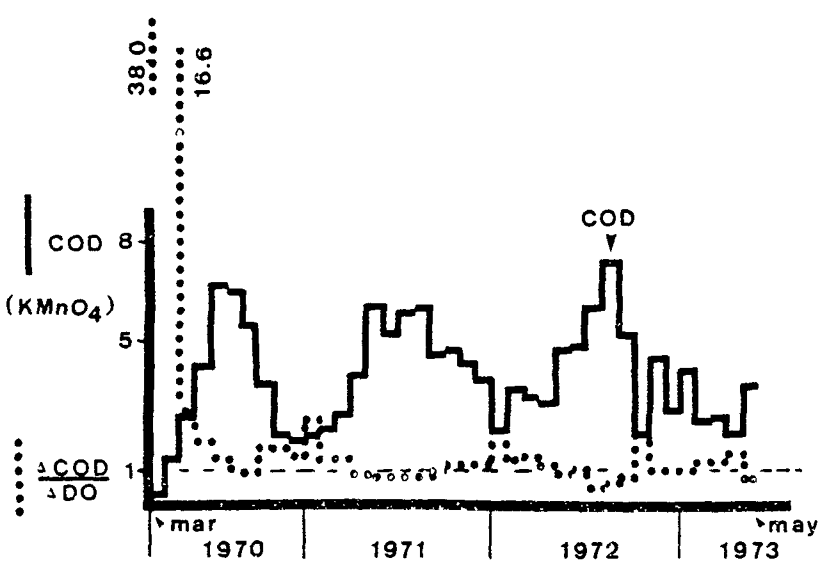


Figure 45. Variation of permanganate COD and Δ(COD/DO) with time of year.

Eberhardt et al., 1974

During the last 9 months of the 3+ year pilot plant test period, the amount of CO_2 produced during passage through the GAC columns was measured and the amount of inorganic carbon produced was calculated. Pertinent data are listed in Table 21. In all cases, the amount of inorganic carbon produced was greater than the amount of dissolved organics being removed (as measured by the permanganate oxygen consumption values). This behavior can be explained only by the biochemical decomposition of organic materials which had been adsorbed previously by the GAC.

Data listed in the lower half of Table 21 show that the biodegradation processes occur throughout the total 6 meter GAC column depth, and not just in the first 1.5 meters of GAC bed depth.

Further indication of biochemical regeneration of adsorption sites was obtained by extraction studies of loaded GAC samples. If biological regeneration occurs at a significant rate, then it would be expected that the loading of GAC after several years of use would not be as high as that of GAC columns acting as adsorbers only during the initial several months of use.

To confirm this hypothesis, samples of Hydraffin BR were removed from the adsorber columns after 3 years of use and compared with samples of Hydraffins LS Supra (LSS) and B-12 after only 4 months of use. All GAC samples were extracted first with dioxane in a Soxhlet apparatus and the solvent evaporated. The residue corresponds to the amount of non-polar organic material present on the GAC. The dioxane-extracted GAC then was extracted with dimethylformamide (DMF). The residue from evaporation of the DMF corresponds to the amount of polar materials present on the GAC. The sum of the two extracts is the total organic loading of the GAC at the time of sampling.

It can be seen from the extraction data (shown in Table 22) that the organic loadings of the first and fourth Hydraffin BR columns after 3 years of use were 28 to 30 g/kg of GAC. These loadings compare with 99 and 71 g/kg for the corresponding B-12 columns and 133 and 99 g/kg for the corresponding LSS activated carbon columns. Such large differences in GAC loadings were not a result of remarkably higher adsorption capacities of the B-12 and LSS activated carbons, but to the fact that biodegradation had not yet reached full swing in the B-12 and LSS carbons after only 4 months of use.

Table 22 also shows that after 4 months, the fourth GAC columns in the B-12 and LSS adsorber units had not yet become fully loaded with adsorbed organics, since the values measured upon extraction were lower than in the first columns. By contrast, the loadings of all 4 columns in the Hydraffin BR adsorber unit after 3 years of use all were about the same.

These data indicate that at Bremen's Auf dem Werder plant, removal of dissolved organic compounds in GAC filters occurs by a combination of adsorption and biological processes. Apparently through biological oxidation, a significant portion of the adsorbed organics are converted to CO_2 and water, and adsorption sites become available again to adsorb more dissolved organic materials.

TABLE 21. AVERAGES OF DATA OBTAINED DURING THE LAST 9 MONTHS OF THE 38-MONTH STUDY WITH BR ACTIVATED CARBON AT BREMEN, FEDERAL REPUBLIC OF GERMANY

Dates	raw water temp °C	oxygen consumption* mg/l			UV extinction at 240 mm × 10^3			DO consumption** mg/l		CO_2 increase mg/l		slow sand filtrate	
		raw water	F 2	F 4	raw water	F 2	F 4	F 1 2	1 4	F 1 2	1 4	$KMnO_4$ demand mg/l	UV extinction × 10^3
July 25 Sept 12, 1972	19 9	14 5	12 5	10 8	120	105	87	4 7	7 3	6 73	10 83	10 0	
Sept 26 Nov 14, 1972	11 3	16 4	14 5	13 0	135	126	144	0 7	2 4	1 96	3 70	12 3	103
Nov 28 Jan 23, 1973	5.3	16 5	14 9	12 9	141	130	122	1 8	4 9	2 29	4 13	12 8	120
Feb 6 April 3, 1973	7 0	15 4	13 3	11 2	131	116	116	1 1	2 5	2 79	3 87	12 3	119
April 17 May 22, 1973	13 1	14 0	12 3	11 1	111	103	98	1 4	2 9	2 70	5 08	10 6	92

	% reduction in oxygen consumption		DOC eliminated*** mg/l			inorganic C formed mg/l			DO consumption** mg/l			DO consumption / Inorganic C formed		
	F 1 2	1 4	F 1 2	3 4	1 4	F 1 2	3 4	1 4	F 1 2	3 4	1 4	F 1 2	3 4	1 4
July 25 Sept 12, 1972	13 8	25 5	0 39	0 47	0 86	1 84	1 11	2 95	4 7	2 5	7 3	2 60	2.32	2.49
Sept 26 Nov 14, 1972	12.8	20 7	0 24	0 32	0 55	0 53	0 48	1 01	0 7	1 6	2 4	1 40	3 52	2 41
Nov 28 Jan 1, 1973	9 7	21 8	0.29	0 21	0 50	0 62	0 51	1.13	1 8	3 1	4 9	2 94	6 20	4 41
Feb 6 April 3, 1973	7.1	23 4	0.39		0 39	0 76	0 30	1 06	1 1	1 3	2 5	1 57	4 47	2 39
April 17 May 22, 1973	12 1	20 1	0 21	0 13	0 34	0 74	0 65	1 39	1 4	1 4	2 9	1 54	2 28	2 12
geometric average.	10 8	11 1	0 29	0 21	0 50	0 81	0 57	1 38	1.62	2 05	3 67	2 00	3 60	2.70

* measured by the alkaline permanganate method
** higher in winter due to additional decomposition of ammonia
*** determined by UV extinction and assuming that each 0 038 UV extinction value corresponds to a DOC of 1 mg/l

The letter refers to "filtrate" and the following number to the GAC column Thus, F2 means "in the filtrate from the second GAC column", F4 the filtrate from column 4, F 1 2 the filtrate of columns 1+2, F 1 4 the filtrates of columns 1 + 2 + 3 + 4, etc.

Source: Eberhardt, Madsen & Sontheimer, 1974

TABLE 22. EXTRACTION OF ACTIVATED CARBON USED FOR DIFFERENT PERIODS

activated carbon filter	filter stage	water throughout m^3/kg	dioxane extract g/kg	DMF extract g/kg	total extract g/kg
BR (1-3 mm)	1	110	8.0	25.0	30.0
"	2	110	10.0	25.3	35.0
"	3	110	6.6	20.4	27.0
"	4	110	5.9	21.8	27.7
B-12	1	13.6	66.0	33.2	99.2
"	4	13.6	33.4	38.0	71.4
LSS(0.5-1.0 mm)	1	11.8	65.3	72.4	137.7
"	4	11.8	34.9	62.3	97.2
"	1	30.1	53.6	78.2	131.8
"	4	30.1	28.2	72.1	100.3

Source: Eberhardt, Madsen & Sontheimer, 1974

Colony Counts--Earlier tests in which the full-scale plant rapid sand filtrate was oxidized with ozone and then passed through GAC adsorbers showed abnormally high 72-hour colony counts. Installation of a rapidly driven slow sand filter (RDSSF) after GAC adsorption lowered the 72-hour colony counts to satisfactory levels. During the 3-year tests with Hydraffin BR, colony counts shown in Figure 46 were obtained. In most cases, colony counts were below 40/ml, but twice (during consecutive summers) they rose to very high levels. After September 1972 a RDSSF unit was installed after the BR test unit, and the high levels observed during the summers of 1970 and 1971 were not repeated. Bacterial data listed in Table 23 were obtained during the period October, 1972 to May, 1973.

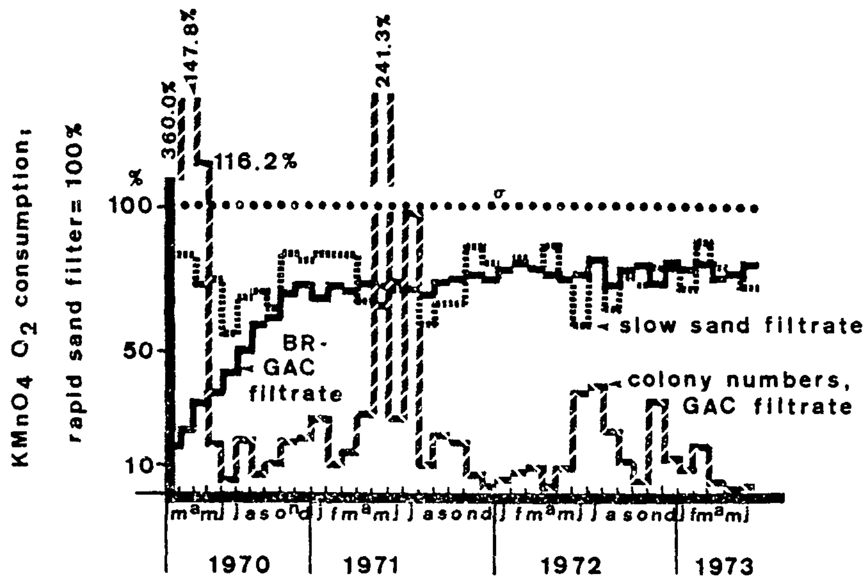


Figure 46. Percent decreases in colony numbers and permanganate oxygen consumption (COD) through GAC over 3+ years.

(Eberhardt *et al*., 1974)

During the 3-year tests with Hydraffin LS, abnormally high 48-hour colony counts were observed only once (May, 1971). A RDSSF was installed after the LS adsorber unit in September, 1970 and, after an initial 4 month adjustment period, the 48-hour colony numbers always were below 20/ml, except for the May, 1971 data which were very much higher (see Figure 47).

Eberhardt, Madsen & Sontheimer (1974) concluded that the quality of water following passage through biologically active GAC and a RDSSF was very high. At most, River Weser water processed in this fashion would require only safety chlorination (up to 0.3 mg/l chlorine dosage) to provide a stable free chlorine residual for the Bremen distribution system.

TABLE 23. BACTERIAL DATA IN RAW WATER, GAC FILTRATE AND RDSFF* FILTRATES

date	raw water		Colony and Coli numbers					
			after GAC column-2		after GAC column-4		after RDSSF*	
	colony nos/ml	E.coli & coliform bacteria/100 ml	colonies	colis	colonies	colis	colonies	colis
Oct. 3, 1972	1240	6	85	4	14	0	10	0
Oct. 17, 1972	320	8	40	4	22	0	10	0
Oct. 31, 1972	144	2	14	2	2	0	0	0
Nov. 14, 1972	96	30	34	8	41	0	3	0
Nov. 28, 1972	72	20	68	5	16	3	0	0
Dec. 12, 1972	170	28	39	10	4	4	0	0
Dec. 27, 1972	220	40	340	26	53	14	2	4
Jan. 9, 1973	600	18	44	6	36	4	4	0
Jan. 23, 1973	94	110	41	56	8	8	1	0
Feb. 16, 1973	200	32	47	6	35	3	0	0
Feb. 20, 1973	42	52	60	32	20	16	2	1
March 6, 1973	98	8	32	0	0	0	1	0
March 20, 1973	440	14	160	0	0	0	0	0
April 3, 1973	850	6	270	4	9	0	2	0
April 17, 1973	340	8	84	2	9	0	5	0
May 8, 1973	210	10	52	5	8	0	9	0
May 22, 1973	300	12	30	1	1	2	0	0
Geometric averages	217.6	15.3	59.1	3.8	6.7	0.56	1.20	0.14

*RDSSF = Rapidly driven slow sand filter

Source: Eberhardt. Madsen & Sontheimer, 1974

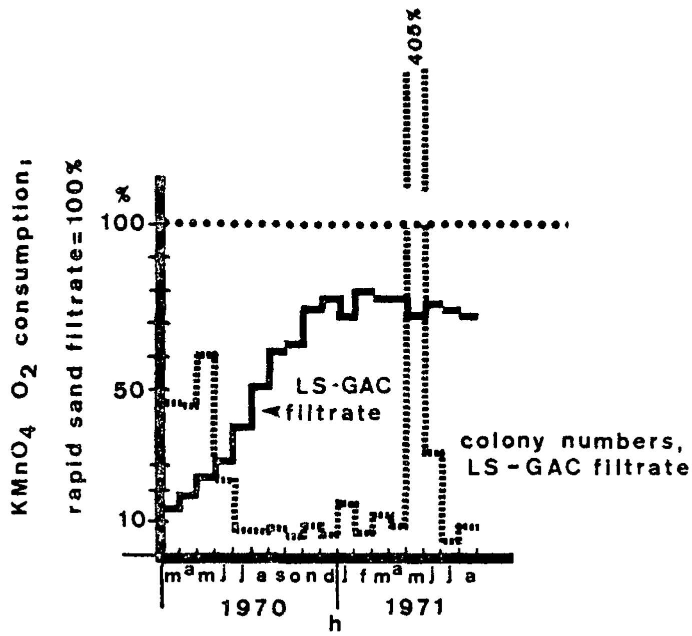


Figure 47. Percent reduction in colony numbers and permanganate oxygen consumption (COD) values in the Hydraffin LS-GAC filter, 1970-1971.

(Eberhardt et al., 1974)

Varying GAC Filtration Rates--Data listed in Tables 24 and 25 compare the performances of GAC columns of 3 and 6 meter depths and operated at 5 and 10 m/hr filtration rates. The 3 m column operated at 5 m/hr had the same empty bed contact time (EBCT) as the 6 m column operated at 10 m/hr. Data for the 6 m columns operated at 5 and 10 m/hr show the effects of increased EBCT. All data shown in Tables 24 and 25 were taken over an 8-month period, which began several months after startup of the GAC, to allow biological equilibrium to be attained.

From Tables 24 and 25, it can be seen that longer retention times in the GAC adsorbers resulted in higher consumptions of dissolved oxygen, but not significantly increased dissolved organic carbon removals (as measured by permanganate consumption). Lower colony numbers were obtained with longer retention times. Comparing data for the same bed depths but with different filtration rates showed that at the higher filtration rate, less dissolved oxygen was consumed, about the same degree of organic carbon removal was obtained and lower colony numbers were obtained. These data again indicate adsorption followed by biological regeneration as the operative mechanisms for removal of dissolved organic materials. The authors concluded that the increased consumption of dissolved oxygen during slower filtration

TABLE 24. COMPARISON OF VARIOUS FILTERING RATES (ACTIVATED CARBON LS)

1971	Temp. °C	pH value				DO (mg/l)				oxygen consumed* mg/l				Colony nos/ml	
		raw water	F 1/2	1/4	3/4	raw water	F 1/2	1/4	3/4	raw water	F 1/2	1/4	3/4	F1/4	3/4
Jan-Feb	5.1	7.87	7.71	7.59	7.65	11.6	9.9	8.7	9.7	12.6	10.2	8.6	9.5	17	16
March-April	8.3	7.91	7.77	7.62	7.67	11.0	8.9	7.0	8.5	13.1	11.2	9.0	10.2	32	29
May-June	17.4	7.95	-	7.40	7.52	8.7	-	1.9	4.5	15.8	-	10.4	11.8	67	85
July-August	20.6	8.03	-	7.44	7.53	7.9	-	1.3	3.4	16.4	-	11.1	12.0	50	11

Filter 1/2 and 1/4 with v_f = 5 m/hr   1/2 = 3 m bed depth

Filter 3/4 with v_f =10 m/hr   1/4 = 6 m bed depth

3/4 = 6 m bed depth

* measured by the alkaline permanganate method

Source: Eberhardt, Madsen & Sontheimer, 1974

TABLE 25. COMPARISON OF TWO ACTIVATED CARBON FILTERS OF THE SAME BED DEPTHS WITH DIFFERENT FILTERING RATES

parameter	rapid sand filtrate	activated carbon filtrate at v = 10 m/hr.	v = 5 m/hr.
pH	7.94	7.59	7.51
DO (mg/l)	9.7	6.0	3.5
oxygen consumption (mg/l)*	14.4	10.9	9.7
DOC (mg/l)	3.3	2.7	2.5
COD (mg/l)	12.7	9.5	8.9
UV extinction	0.139	0.110	0.109
no. of colonies	-	26	37

* measured by the alkaline permanganate method

Source: Eberhardt, Madsen & Sontheimer, 1974

rates must have been a result of biological decomposition of adsorbed organics, since total dissolved organic removal was about the same regardless of the filtration rates.

Varying GAC Grain Sizes--Two samples of Hydraffin LSS granular activated carbon having different average grain sizes (1 m and 1.8 mm) were compared over a period of 6 months. For this study, analyses were made at the start of the experiments using fresh GAC samples and data are listed in Table 26. It can be seen that although during the first month the larger grain size carbon removed more organics (as measured by the differences in $KMnO_4$ consumption values), for the subsequent 5 months, the smaller grain size GAC gave better organics removal. In addition, the differences between the two granular activated carbons in removing organics were widening in favor of the smaller grain sized GAC as time progressed.

Recycling Through GAC to Study Biological Regeneration--After two years of operation in a once-through mode, all of the effluent from the fourth column of the GAC adsorber unit containing Hydraffin LS was aerated and recycled back to the first column. This recycling was continued for the next two months, during which time the effluent from column #4 and the influent to column #1 were monitored for $KMnO_4$ consumption, CO, CO_2 formed and UV absorption. Data gathered over this period are listed in Table 27.

During the initial recycling period, the dissolved organic content of the effluent from column #4 increased, but then decreased after about 1 month to its original value. After the initial recycling period, the amount of CO_2 produced decreased to about 5 mg/l. During this time, however, the amount of dissolved organic material removed from solution per pass through the GAC (as measured by the permanganate consumption method) remained about the same. Also during this time, the amount of dissolved oxygen consumed was about equal to the amount of CO_2 produced (about 5 mg/l). The rate of CO_2 production (from biochemical oxidation) was always greater than the amount of organics removed from solution; thus biochemical degradation of adsorbed organics was occurring during the 2-month recycling period.

These data suggest that it may be possible to regenerate granular activated carbon columns in place, biologically, by employing this recycling technique. However, an estimated 6 month recycling period would have been required to attain total biological regeneration at the Bremen pilot plant, and this may not be practical. Nevertheless, these recycling data indicate strongly that biological regeneration does occur, and that it is at least technically feasible to consider biological regeneration in place, rather than by installing thermal reactivation facilities. Even partial biological regeneration processes could be effective in reducing thermal regeneration costs during times when the GAC is fully loaded with organic materials and the organic content of the raw water is low.

Granular Activated Carbons of Different Structures--It had been shown by Van der Kooij (1975) and by Klotz, Werner & Schweisfurth (1975) that bacteria are too large to fit into the micropores of granular activated carbon which comprise about 99% of the available surface area. Only the larger pores near the GAC outer surface are large enough to house the

TABLE 26. COMPARISON OF DIFFERENT GAC GRAIN SIZES (LS ACTIVATED CARBON)

Date	Temp. ^oC	pH value			DO content mg/l			oxygen consumption* mg/l		
		raw water	3/2	4/2	raw water	3/2	4/2	raw water	3/2	4/2
September 1971	16.65	7.83	7.88	7.91	8.5	7.1	7.2	18.0	3.4	2.8
October	12.93	7.89	7.78	7.77	9.2	7.3	7.3	22.1	11.4	11.8
November	7.16	7.84	7.68	7.66	10.1	8.1	8.1	22.1	15.9	16.6
December	7.23	7.77	7.61	7.59	9.3	7.3	7.0	18.9	14.0	14.4
January 1972	2.58	7.87	7.71	7.73	11.8	10.2	10.5	18.5	13.9	14.9
February 1972	4.06	7.84	7.59	7.61	10.3	7.1	7.6	23.2	18.5	19.7
Average, Sept. 1971-Feb. 1972	8.44	7.84	7.71	7.72	9.8	7.8	7.9	20.4	11.4	11.5
3/2 with 0.5 - 1.5 mm range 4/2 with 0.5 - 3.0 mm range										

* measured by the alkaline permanganate method.

Source: Eberhardt, Madsen & Sontheimer, 1974

TABLE 27. RESULTS OF RECYCLING TESTS AT BREMEN WATER WORKS

1972	pH	oxygen consumed* mg/l	DO mg/l	CO_2 mg/l	UV extinction 240 nm, 1 cm	Sampling Point
July 4	7.70	11.1	6.9	5.7	0.113	before filter 1
July 4	7.43	10.4	3.5	10.1	0.110	after " 4
July 5	7.67	12.0	5.3	7.1	0.148	before " 1
July 5	7.16	13.6	0.9	16.3	0.146	after " 4
July 7	7.40	18.0	5.8	5.5	0.177	before " 1
July 7	6.93	17.4	1.0	11.2	0.175	after " 4
July 18	8.05	14.2	8.2	3.1	0.165	before " 1
July 18	6.98	12.3	1.4	13.2	0.160	after " 4
July 19	7.30	14.2	6.1	6.6	0.172	before " 1
July 19	6.80	13.3	1.4	11.4	0.168	after " 4
July 21	7.15	17.1	5.6	6.6	0.206	before " 1
July 21	6.73	15.5	1.3	12.1	0.195	after " 4
July 25	7.30	13.6	5.8	7.0	0.174	before " 1
July 25	6.92	12.0	1.3	9.7	0.168	after " 4
August 1	7.42	10.1	6.1	7.6	0.155	before " 1
August 1	6.95	9.8	1.0	11.0	0.138	after " 4
August 15	7.40	10.8	6.0	6.6	0.154	before " 1
August 15	7.00	10.4	3.1	9.7	0.147	after " 4
August 29	7.27	10.7	6.8	7.0	0.140	before " 1
August 29	6.95	8.5	3.2	10.1	0.120	after " 4
Average-July 4-Aug. 29	7.47	13.2	6.4	6.3	0.160	before " 1
Average-July 4-Aug. 29	6.95	12.3	1.8	11.5	0.152	after " 4
difference	0.52	0.9	4.6	5.2	0.008	

* measured by the alkaline permanganate method

Source: Eberhardt, Madsen & Sontheimer, 1974

bacteria. Therefore, tests were conducted next with Hydraffin B-12, which contains a higher number of large inlet pores than do the other Hydraffins tested. Data obtained are listed in Table 28, and these were taken over an 8-month period.

During the first 4 months of use, more dissolved organic carbon was removed from solution (by adsorption) than was inorganic carbon produced. However, during the fifth month, the amount of inorganic carbon produced became about the same as the amount of organic materials being removed. After the sixth month, the amount of inorganic carbon produced was greater than the amount of dissolved organic carbon being removed. Comparing the results obtained with Hydraffin B-12 with those from other activated carbons, it is clear that the B-12 GAC removed a higher percentage of dissolved organic materials.

Further testing using fine grained (1 mm) Hydraffin LSS (which has a higher adsorption capacity for dissolved organics) was conducted for 11 months. Results from these tests and those shown in Table 24 are plotted in Figure 48. The ratios of Δ(DOC removed/cu m of GAC/hr) are plotted on the ordinate against time, and data obtained for Hydraffins BR, B-12 and LSS (0.5-1.0 mm grain size) are presented. Both B-12 and LSS gave better removals of dissolved organic materials than did Hydraffin BR. After the initial period of biology buildup, 32 to 38% of the influent DOC was biochemically decomposed at a steady rate in the Hydraffin B-12 adsorber. On the other hand, 50 to 53% DOC removal occurred in the Hydraffin LSS adsorber, but only after a somewhat longer initial adjustment period.

At the end of these 11-month long studies, samples of the different granular activated carbons were extracted with dioxane, then DMF, to determine their total organic loadings. An average loading of 115 g/kg of GAC was found for the fine grained LSS, and 85 g/kg for the B-12 carbon.

Summary of Bremen Pilot Plant Test Results --

1) Dissolved organic substances were first adsorbed by GAC resulting in high loadings on the GAC during the first 3 to 5 months of GAC use. Thereafter, biological activity reached a steady state, from which point a significant fraction of the adsorbed organics was degraded biochemically to CO_2 and water.

2) After the biological steady state had been attained, 100 to 140 g of dissolved organic carbon was bacterially oxidized/cu m of activated carbon per day. Consumption of dissolved oxygen averaged 360 g/cu m of granular activated carbon/day and 240 g/cu m/day during winter.

3) For 30 minute empty bed contact times, about 2 mg/l of DOC could be removed from solution. This corresponds to about 5 mg/l of dissolved organic materials removed.

4) Organic materials must be biodegradable. The amount of biodecomposable components present could be increased by preoxidation with ozone.

TABLE 28. TESTS WITH B-12 ACTIVATED CARBON

Date	Raw Water		% decrease in			ΔO_2	ΔCO_2	Δ DOC	Δ inorg. C
	oxygen consumed* mg/l	UV-extinction corr.	oxygen consumed* 1-2	oxygen consumed* 1-4	UV 1-4	mg/l 1-4	mg/l 1-4	mg/l 1-4	mg/l 1-4
Sept. 26 Oct. 17, 1972	16.6	0.126	60.3	67.2	69.8	3.5	1.92	2.31	0.52
Oct. 24-Nov. 14, 1972	16.5	0.150	39.1	56.2	49.2	3.6	2.98	1.94	0.81
Nov. 21-Dec. 12, 1972	14.1	0.125	27.5	48.4	47.8	2.6	2.07	1.56	0.56
Dec. 19-Jan. 9, 1973	15.3	0.126	24.6	45.1	36.2	4.1	3.40	1.20	0.43
Jan. 16-Feb. 6, 1973	19.3	0.173	18.6	36.7	31.3	4.6	5.85	1.42	1.47
Feb. 13-Mar. 13, 1973	14.8	0.133	17.2	36.9	33.3	2.4	3.85	1.16	1.05
Mar. 20-April 10, 1973	14.9	0.120	14.9	38.2	28.8	3.4	4.14	0.90	1.13
April 17-May 15, 1973	14.0	0.110	22.7	36.0	32.3	3.3	6.73	0.94	1.84
May 22-June 12, 1973	16.5	0.135	24.5	36.9	37.0	6.9	4.67	1.31	2.64

* measured by the alkaline permanganate method.

Source: Eberhardt, Madsen & Sontheimer, 1974

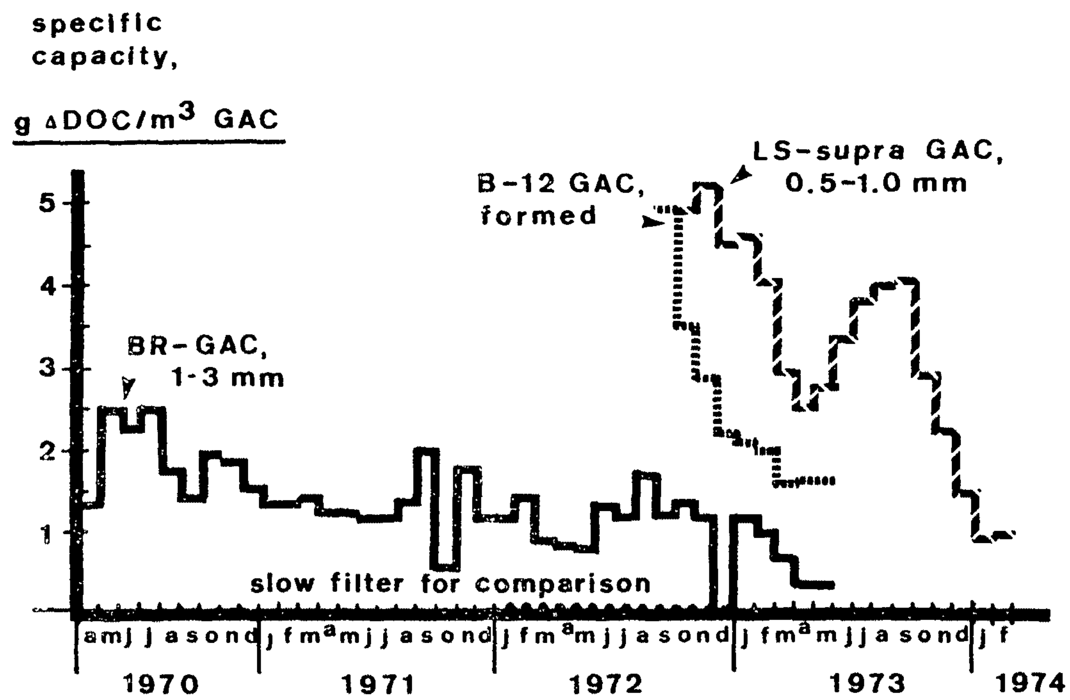


Figure 48. Variation in specific capacity for dissolved organic carbon (DOC) of a GAC filter with operating time for normal (BR) and more highly activated carbons.

(Eberhardt *et al.*, 1974)

Preozonation also increased the rate of DOC removal at low temperatures, during winter.

5) Biochemical regeneration of GAC was be followed by measuring the amount of CO_2 generated and relating this to the amount of DOC removed from solution. When the ratio Δ(DOC removed)/Δ(inorganic carbon produced) was less than 1, the source of the additional CO_2 must have been from organic materials previously adsorbed by the GAC. When this ratio was greater than 1, adsorption of organics was proceeding at a faster rate than biodegradation. When the ratio was about 1, the two processes were occurring at approximately the same rate.

6) During the 3+ years of testing at Bremen, the ratio Δ(DOC removed) to Δ(inorganic carbon produced) was about 1 most of the time. During periods of low water temperature (winter) the ratio was greater than 1; during summer the ratio was less than 1.

7) The maximum amount of DOC removal occurred during the initial period of GAC use, when adsorption was the dominating process. About 80% of the DOC was removed during the initial 6 week period. Thereafter, the DOC of the GAC effluent rose to a level which remained constant and was related to the influent DOC level. Under the best conditions found at the Bremen pilot plant (large inlet pore GAC, high initial adsorption capacity for the dissolved organic materials present in the Bremen raw water, fine grain size), about 50% of the influent DOC could be removed constantly after the biological steady state had been reached. For other granular activated carbons, the rate of DOC removal at the biological steady state was 20 to 33%.

8) Satisfactory 48- and 72-hour colony numbers/ml were obtained after passage through biologically active GAC. However, when the GAC influent had been preoxidized with ozone or with chlorine, the 72-hour colony counts rose to very high levels. Installation of a rapidly driven slow sand filter after the GAC adsorber lowered the 72-hour colony counts to acceptable values.

9) Coliform counts/100 ml were very low and acceptable in all GAC filtrates.

10) All GAC experiments conducted at the Bremen pilot plant utilized rapid sand filtrate from the full-scale plant, which had been pretreated with 1 to 3 mg/l of $KMnO_4$. No experiments were conducted to determine whether this permanganate pretreatment increased the biodegradation rates. Treatment of the plant rapid sand filtrate with chlorine (unreported dosage) did not increase the rate of biodegradation as did preozonation.

11) Ammonia levels in the River Weser raw waters remained low (below 2 mg/l) throughout the 3+ years of testing. Nitrification occurred in the rapid sand filters of the full-scale plant, in the biologically active GAC adsorbers and in the slow sand filters. The amount of dissolved oxygen required to satisfy the requirements for nitrification

in the GAC and following slow sand filters was sufficiently low that additional oxygen was not necessary.

Mülheim, Federal Republic of Germany

The Rheinisch-Westfälische Wasserwerksgesellschaft mbH has taken advantage of biological activated carbon to radically change the drinking water treatment process at the 48,000 cu m/day (12.7 mgd) Dohne plant in Mülheim, Germany (Sontheimer et al., 1978; Heilker, 1979). Raw water for this plant is the River Ruhr, which until mid-April, 1977 was treated by breakpoint chlorination for ammonia removal, flocculation, sedimentation, granular activated carbon for dechlorination, then ground filtration. Over the years, ammonia concentrations have increased, requiring prechlorination doses as high as 10 to 50 mg/l. In turn, these high chlorine doses produced large amounts of chlorinated organics (Table 29) which not only were incompletely adsorbed by the carbon columns and passed through the plant into the distribution system, but also caused frequent regeneration of the activated carbon columns (every 4 to 8 weeks).

TABLE 29. ORGANO-CHLOROCOMPOUNDS PRESENT AFTER BREAKPOINT CHLORINATION

Sampling Point	DOCl* ppb	DOClN** ppb	Sum of haloforms, ppb	$CHCl_3$ ppb
raw water (Ruhr river)	17	5	9	<1
after flocculation + sedimentation	---	--	15	6
after filtration	203	30	23	7
after GAC filters	151	17	21	7
after ground passage + safety chlorination	92	18	23	9

* DOCl = dissolved organic chlorine

** DOClN = dissolved organic chlorine, non-polar

Source: Sontheimer et al. (1978).

During a two year pilot study on the use of preozonation followed by activated carbon adsorption for removal of ammonia and of organics, it was found that breakpoint chlorination could be eliminated completely and the BAC operation could be relied upon totally for removal of ammonia. At the same time the DOC was reduced to the desired levels.

This process, involving ozonation ahead of sand filtration and granular activated carbon adsorption, was installed and began operating in mid-April, 1977. At the time, the GAC columns at this plant were 2 meters deep (EBCT =

5.5 minutes) and the GAC, exhausted during use under the old process, was used from mid-April until July, 1977. During late summer, 1977, the carbon bed depths were increased to 4 meters (EBCT = 11 minutes). Fresh GAC was charged to the deeper columns and these began operating in November, 1977. The process at Mülheim has been operating as predicted by the pilot studies and the carbon columns have not yet required regeneration. The performance of the full scale plant process is as effective as was the pilot process at the same stage of development (Sontheimer, 1978).

The newly installed process at Dohne involves preoxidation with about 1 mg/l of ozone with addition of poly-aluminum chloride and lime as flocculants. Preozonation oxidizes manganese and aids in flocculating the organics. After flocculation and sedimentation, 2 mg/l of ozone is added to oxidize dissolved organics. After a retention time of 15 to 30 minutes, the ozonized water initially was again preflocculated using 0.2 mg/l aluminum chloride and 0.1 mg/l polyelectrolyte, filtered through sand, then passed through biological activated carbon where the bulk of DOC and ammonia are removed.

During the period April-July, 1977, it was found that the preozonation step, coupled with high speed agitiation was so successful in removing suspended solids that the second $AlCl_3$ plus polyelectrolyte addition step was eliminated when the process was re-started in November, 1977. However, nitrification is promoted by addition of 20 mg/l of oxygen (obtained from liquid oxygen cylinders) before sand filtration (where most of the nitrification occurs). The ammonia content of the Ruhr River has risen to nearly 6 mg/l as of June, 1978. Addition of gaseous oxygen is controlled by a DO residual level of 7 mg/l monitored after the BAC columns.

Table 30 summarizes the the process changes which were made at the Dohne plant during the period 1977-1978. A comparison of the performance of the new process versus the old process is given in Table 31. The DOC of treated water today is less than half of that treated by the old process. Even lower DOC values are being obtained since the depths of the GAC columns have been increased. Finally, no chlorinated organics are being generated by prechlorination.

After activated carbon adsorption, the treated water is sent to ground infiltration (12 to 50 hours retention time), after which it is chlorinated (0.2 to 0.3 mg/l) and sent to the Mülheim distribution system. Ground infiltration at Dohne no longer is considered to be necessary, because of the high quality of water which the plant produces. It will be maintained, however, as a convenient and functional water reservoir (Heilker, 1978).

Table 32 shows the bacterial content of waters at the various points in the new treatment process. E. coli counts/100 ml are essentially zero after filtration and remain essentially zero after BAC filtration as well. There should be no concern for E. coli passing through the BAC media into the product waters because this strain of bacteria does not survive in the presence of the other bacterial strains present in the GAC (Van Der Kooij, 1978; Schweisfurth, 1978).

TABLE 30. PROCESS PARAMETERS AT THE DOHNE WATERWORKS (MÜLHEIM) BEFORE AND AFTER CHANGE OF TREATMENT

Treatment Step	Old Treatment (before 1977)	New Treatment (April-July 1977)	New Treatment (Nov. 77-June 78)
preoxidation	10-50 mg/l Cl_2	1 mg/l O_3	1 mg/l O_3
dosing	4-6 mg/l Al^{+3}	4-6 mg/l Al^{+3}	4-6 mg/l Al^{+3}
power input	0.1 kW/m^3	2.5 kW/m^3	2.5 kW/m^3
	Ret. time ≈ 0.5 min	Ret. time ≈ 0.5 min	Ret. time ≈ 0.5 min
flocculation	5-12 mg/l $Ca(OH)_2$	5-15 mg/l $Ca(OH)_2$	5-15 mg/l $Ca(OH)_2$
sedimentation	Ret. time ≈ 1.5 hr	Ret. time ≈ 1.5 hr	Ret. time ≈ 1.5 hr
ozonation	------	2 mg/l O_3	2 mg/l O_3
		Ret. time ≈ 5 min	Ret. time ≈ 5 min
filtration with preflocculation	v* - 10.7 m/hr	v* = 9 m/hr	20 mg/l
		0.2 mg/l Al^{+3}	liquid oxygen
		0.1 mg/l poly-electrolyte	
activated	v* = 22 m/hr	v* = 18 m/hr	v* = 28 m/hr
carbon filter	h** = 2 m	h** = 2 m (4 m)	h** = 4 m
ground passage	Ret. time 12-50 hr	Ret. time 12-50 hr	Ret. time 12-50 hr
safety chlorination	0.4-0.8 mg/l Cl_2	0.2-0.3 mg/l Cl_2	0.2-0.3 mg/l Cl_2

*v = filter velocity
**h = bed height

Sources: Sontheimer et al., 1978
Jekel, 1978 and 1979

TABLE 31. MEAN COC VALUES AFTER THE DIFFERENT TREATMENT STEPS (MÜLHEIM)

sampling point	1975 DOC, mg/l	1976 DOC, mg/l	April-July 1977, DOC, mg/l	Nov. 1977 - June 1978, DOC, mg/l
raw water (Ruhr river)	3.9	5.0	3.6	2.4 - 3.7
after flocculation + sedimentation	3.2	4.0	2.9	1.8 - 3.0
after filtration	3.2	3.8	2.6	1.7 - 3.1
after GAC filtration	3.0	3.7	2.3*	1.0 - 2.6**
after ground passage	1.8	2.1	0.9	---

* filters filled with fully loaded GAC, used in old treatment process
** filters doubled in height and filled with new GAC

Sources: Sontheimer *et al.*, 1978; Jekel, 1978

Pilot plant data are presented in Table 33 which show the effects of variation of activated carbons on removal of DOC, inorganic carbon, ammonia and dissolved oxygen. In addition, this table also compares the removal of these same parameters with carbon column depths of 2.5 m and 5.0 m for two different activated carbons.

Conversion of ammonia and dissolved oxygen consumption are fairly independent of carbon type or column depth. On the other hand, removals of DOC and inorganic carbon produced are affected by the carbon type. Most significant, the amount of DOC removed with 5.0 m columns is about 50% higher than with 2.5 m columns, although the amount of inorganic carbon measured increases only slightly.

During pilot studies at the Dohne plant with the BAC process, activated carbon columns were found to have operational lives of at least one year, and in some cases two years, without requiring regeneration. Life of the full scale carbon columns at Dohne now is estimated to be at least two years (Sontheimer, 1978). No signs of loss in performance of the activated carbon have been noted during the first year of operation, and the new carbon columns have not yet had to be regenerated (Jekel, 1978).

Additionally, preozonation has extended the running times of the sand filters from two to seven days before backwashing is required. Backwashing of the four GAC filters (each of which contains a different granular activated carbon being tested on full scale) varies, but was conducted during initial stages of plant operation every 10 days, on the average. However, during the summer of 1978, "a population explosion of nematodes" was observed in both the rapid sand filters and GAC adsorbers. These growths were caused by the long intervals between backwashes, during which the nematodes developed.

TABLE 32. GEOMETRIC MEAN VALUES OF BACTERIAL COUNTS FOR THE MÜLHEIM, GERMANY (DOHNE) PLANT USING OZONE

Sampling place	Total Bacterial Counts/ml		E-Coli/100 ml	
	M_g*	σ_g**	M_g*	σ_g**
Raw water (Ruhr)	14,490	2.0	1,620	1.7
After flocc'n + sediment'n	2,340	4.2	6.7	3.2
After filtration	6,010	4.9	<<1	---
After activated carbon	3,700	4.0	<<1	---
After ground passage	27	2.3	<<1	---

* M_g = geometric mean

** σ_g = geometric standard deviation

TABLE 33. PERFORMANCE OF BIOLOGICAL ACTIVATED CARBON FILTERS. MEAN VALUES FOR 6-MONTH OPERATION AFTER A 3-MONTH STARTING PERIOD (DOHNE PILOT PLANT, MÜLHEIM, GERMANY)

Activated carbon type	bed depth (m)	Δ DOC mg/l	Δ (inorg C) mg/l	Δ NH_4^+ mg/l	Δ O_2 mg/l
LSS	2.5	0.92	0.83	1.31	6.32
LSS	5.0	1.69	0.96	1.34	6.67
ROW	2.5	1.09	0.97	1.31	6.49
ROW	5.0	1.59	1.05	1.34	6.71
NK12	2.5	0.99	1.36	1.28	6.03
F40D	2.5	1.26	1.11	1.32	6.95
BKA	2.5	1.00	0.97	1.28	5.99

Source: Sontheimer *et al.*, 1978

When the backwashing intervals were reduced to 3 days (just below the time of the reproduction cycle of this genus of microorganisms), the nematodes disappeared (Heilker, 1979).

Elimination of breakpoint chlorination at the beginning of the Mülheim process eliminates formation of chlorinated organics which caused the activated carbon columns to have to be regenerated every 2 months under the old process. The 10 to 50 mg/l dosage of chlorine previously required for this step now has been replaced with 3 mg/l total dosage of ozone, applied in 2 stages. Additional cost-savings associated with this change include the labor which was required with breakpoint chlorination. Formerly, a technician was required to sample water every two hours and to analyze for chlorine and for ammonia. This labor requirement has been eliminated (Sontheimer, 1977a,b).

Increased algae levels occur in the Ruhr River near Mülheim in the spring and fall. These are compensated for at the Dohne plant simply by increasing the preozonation dosage from one to two mg/l until the algae bloom has subsided. The plant operating characteristics remain normal with this procedure (Nolte, 1978).

Because of the success of the BAC process in replacing breakpoint chlorination at the Dohne plant, the Rheinisch-Westfälische Wasserwerkgesellschaft mbH now is designing BAC into two of its other plants in the Mülheim area of Germany. Neither of these plants will employ ground infiltration of treated water.

It is important for the reader to realize that Dohne's raw water (the Ruhr River) does not contain significant amounts of of synthetic organic chemicals. TOCl levels are very low. In fact, the German government prohibits the discharge of industrial wastes into the Ruhr, because it is the source of drinking water for many cities in the area. There is considerable pollution in the Ruhr because of sewage discharges, but the components of this generally are biodegradable, or can be made so by oxidative pretreatment.

As a result, there is only a small chance for non-biodegradable organic materials to be present after ozonation, and most of the organics entering the BAC media are expected to be biodegradable. Therefore, the life of the BAC columns at the Dohne plant should be at least two years before regeneration is required, based on pilot studies of that length of time.

At the present time, the criteria to be used to determine when the GAC is to be regenerated at Dohne are the breakthrough of DOC and of the organic materials which absorb at 254 nm in the ultraviolet region. These criteria probably will be adjusted on the basis of overall plant performance and the changes which are noted in the water quality parameters currently being monitored. TOCl analyses are being conducted routinely at Dohne, and it is possible that this parameter can become a regeneration criterion, if pollutional levels of such halogenated organic materials increase in the future.

Rouen-la-Chapelle, France

At the 50,000 cu m/day (13.2 mgd) plant at la Chapelle St. Etienne de Rouvray in Seine Maritime (west of Paris near the Atlantic Ocean), well waters drawn from near the Seine contain 2 to 3 mg/l ammonium ion, 0 to 0.2 mg/l manganese, various micropollutants (detergents, phenols, Substances Extractable with Chloroform, etc.) and are practically devoid of dissolved oxygen. Since 1968, the ammonia content of the raw water has risen from an average of 0.3 mg/l to an average of 2.6 mg/l. This increase required that the treatment process be improved. Breakpoint chlorination was discarded because it would have required very large contact chambers (close to 7,000 cu m) and would have produced chlorinated organics which then would have to be removed.

After three years of pilot plant testing, the following process (Figure 49) was developed, was installed and began operating in February 1976 (Gomella & Versanne, 1977; Rice, Gomella & Miller, 1978):

- Pre-ozonation (0.7 mg/l) for Mn, organics and adding dissolved oxygen to the water
- Filtration through quartz sand
- Adsorption in GAC beds
- Ozonation for disinfection (1.4 mg/l)
- Post-chlorination (0.4 to 0.5 mg/l)

This single operation of preozonation assures the following:

- oxygen demands of the materials in water are satisfied,
- water is oxygenated,
- complex, biorefractory molecules are broken down and become biodegradable,
- the content of various micropollutants is lowered,
- manganese is oxidized and precipitates, to be retained on the sand filter so that it does not block adsorption sites on the biological activated carbon.

About 80% of the nitrification occurs in the sand filter beds (100 cm deep). Periodic backwashing of these sand filters to remove oxides of manganese does not upset the action of these bacteria. Similarly, bacterial activity on the activated carbon beds (75 cm deep) is not displaced during backwashing. The BAC beds are backwashed (by bumping with air, then using water) once each month, but have not yet had to be regenerated after 2.5 years of operation. However, one GAC bed was reactivated in early 1979 so

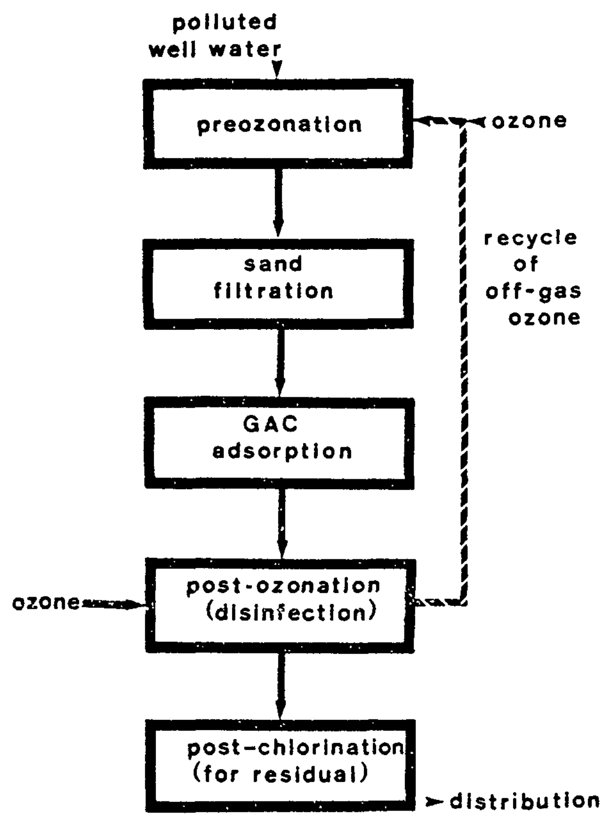


Figure 49. The Rouen-la-Chapelle process, Rouen, France.

as to allow plant personnel to become familiar with the operation (Schulhof, 1979).

This plant began operating in February, 1976 and showed the performances listed in Table 34 for the first two years of operation, respectively. During the first year the empty bed contact time for the carbon beds was 9 minutes. During the second year, this was increased to 18 minutes by decreasing the flow rate of water through the plant. The percent pollutant removals are somewhat better with the longer empty bed contact time.

TABLE 34. ROUEN-LA-CH^PELLE PLANT OPERATIONAL DATA (1976 AND 1977)

parameter	raw water	preozonized	filtered (sand & GAC)	post ozonized	% elimination 1976*	% elimination 1977**
turbidity (mastic drops)	4	-	-	2	--	--
ammonia (mg/l NH_4^+)	1.80	1.80	0.40	0.26	86%	95%
Mn (mg/l)	C.15	0.07	0.04	0.02	87%	90%
detergents (mg/l DBS)	0.12	0.09	0.06	0.03	75%	75%
phenols (microg/l)	6.5	4.0	1.5	0	100%	100%
SEC*** (microg/l)	590	470	250	150	75%	75%
substances extractable with cyclohexane (microg/l)	1,335	740	535	410	69%	70%

av. NH_3 content of raw water: 0.3 mg/l in 1968; 2.6 mg/l in 1975

* EBCT = 9 minutes
** EBCT = 18 minutes
*** SEC = Substances Extractable With Chloroform

Sources: * Gomella & Versanne, 1977
** Versanne, 1978

During a site visitation to the Rouen plant in June, 1977, it was learned that neither air nor oxygen are added after sand filtration or before GAC adsorption, and that the dissolved oxygen content of the water exiting the BAC beds is zero (Versanne, 1978). This would indicate the possibility that there may be incomplete nitrification or some denitrification occurring in the lower part of the 75 cm deep GAC beds.

Gomella & Versanne (1977) reported that even though 1 gram of ammoniacal nitrogen requires 4.57 g of oxygen to be converted to nitrate ion (stoichiometry not indicated), only 3.2 g are required at the Rouen plant. This is further indication of the occurrence of denitrification processes. In this situation, the oxygen source for the nitrifying bacteria would be the nitrate ion, and as oxygen is removed from the nitrate ions, both nitrite ions and nitrogen gas can form.

There should be no dangers from this practice at Rouen, however, because after BAC treatment, the product water is subjected to ozonation for disinfection. The French standard for this process involves first attaining a dissolved ozone residual of 0.4 mg/l, then maintaining that 0.4 mg/l residual ozone concentration for a minimum of 4 minutes. Under these conditions, Rouen's BAC-treated waters are disinfected, viruses are inactivated, any nitrite ions formed in the GAC beds are oxidized to nitrate ions and high dissolved oxygen levels are restored.

A case history of the Rouen plant has been published recently by Rice, Gomella & Miller (1978). At least 29 specific organic hydrocarbons and 16 oxygenated organics have been identified in Rouen's raw waters. Only chloroform, carbon tetrachloride, trichloroethylene and trichlorobenzene were identified as chlorinated organic impurities. Rouen does not monitor for TOCl, but is testing that procedure for possible use as a GAC reactivation criterion.

Under these circumstances, it is probable that most of the organic compounds present in the Rouen raw water are biodegradable after ozonation. The amounts of identified chlorinated organic compounds are very low. Therefore, it is to be expected that most of the organic pollutants present are being removed by the biologically active GAC, and the BAC should have a long useful life at Rouen. Nevertheless, the presence of some chlorinated organic compounds indicates that TOCl should be monitored frequently, as a check on the cumulative loading of these materials on the GAC. When this practice is instituted at Rouen, perhaps TOCl will be chosen as the key regeneration parameter, and the useful life of the BAC at Rouen may turn out to be shorter than indicated by the parameters listed in Table 34.

SECTION 10

EUROPEAN MICROBIOLOGICAL STUDIES IN ACTIVATED CARBON FILTERS & ADSORBERS

INTRODUCTION

Many investigators have observed the rapid growth of bacteria in activated carbon media used as filters and/or adsorbers in drinking water treatment (McCreary & Snoeyink, 1977, references cited therein; references cited throughout this sub-section). For purposes of differentiation, the term "activated carbon filter" will be used to describe the use of activated carbon in place of sand filters, when the primary function of the activated carbon is as a filtration medium. On the other hand, the term "activated carbon adsorber" will be used to describe the same activated carbon unit after sand or dual media filters.

High levels of bacteria also have been observed in the effluents from GAC filters and adsorbers used for periods of more than a few months. Several pertinent observations in this regard were presented at the Conference on Activated Carbon in Water Treatment held in England during April, 1973 and sponsored by the Water Research Association, Medmenham, England. The Proceedings of this conference provide valuable information regarding the status of activated carbon used for treating drinking water supplies at that time. In this sub-section we will discuss the status of European microbiological studies as it existed in 1973, as reported in five presentations made at that conference. Next, more recent European studies will be discussed. A portion of these later studies has been presented briefly in Section 6.

EUROPEAN STATUS AS OF 1973

Melbourne & Miller (1973) reported details of an extensive study conducted over the period 1968 to 1971 at the Colwick (England) plant which treats River Trent water. The plant treatment process consisted of biological sedimentation (for ammonia conversion), chemical addition, sedimentation, anthracite/sand filtration, GAC adsorption and post-chlorination. During this study the behavoir of the plant stream was compared with that of a second stream which was pretreated by chlorination or caustic soda softening.

Over the 3-year period of this study, it was found that the GAC adsorbers removed about 80% of the bacteria present in the plant stream entering the carbon beds under "normal conditions" (without prechlorination or presoftening). However, when prechlorination or presoftening were practiced, significantly increased growths of organisms across the GAC adsorbers were observed. On the average, waters from the sand filters containing no coliforms/100 ml, zero *E. coli*/100 ml and no 22°C plate counts/ml showed an average of about

10 coliforms/100 ml, zero to 9 E. Coli/100 ml, but 1,000 to 8,500 22°C plate counts/ml in the GAC effluents over an 8-week period (Table 35).

On the other hand, even when these high levels of organism growths occurred, final chlorination successfully eliminated them, except in a few instances.

Knoppert & Rook (1973) had studied the treatment of River Rhine water at the Rotterdam (The Netherlands) Waterworks with granular activated carbon over the period 1970 to 1972. At the time, this plant used the process consisting of microstraining, breakpoint chlorination, iron (III) coagulation, powdered activated carbon, flocculation, sedimentation and rapid sand filtration.

Knoppert & Rook (1973) stated, "The only objection to locating GAC beds at the end of the purification process is the generally-known bacterial growth in the beds, which may give rise to high bacterial counts in the delivered water". Therefore these investigators conducted a program to study the possibilities of diminishing this bacterial development by backwashing the GAC beds frequently.

Two equivalent GAC columns were operated in parallel and threshold odor numbers were monitored in the effluents. One column was backwashed daily and the other twice monthly. The column which was backwashed daily ran 52 weeks before taste breakthrough occurred. During this time, the measured 22°C bacterial count levels rose to 10,CCO/ml after 8 weeks, then diminished steadily to about 25/ml by the end of this run (52 weeks).

The second GAC column, backwashed twice monthly, ran only 40 weeks before taste breakthrough occurred. Bacterial counts in the effluents also rose to 10,000/ml after 8 weeks of operation, decreased to 100/ml after 24 weeks and then rose to nearly 1,000/ml at breakthrough (40 weeks).

The 37°C colony counts of both GAC beds remained at levels less than 10/ml throughout the test period. The 22°C colony counts of both GAC bed effluents were easily controlled by post-chlorination.

Ford (1973) reported studies conducted at the Foxcote Treatment Works of the Bucks Water Board (England), where GAC was introduced into the plant process for taste and odor control in 1960, after an 18-month pilot plant study conducted during 1957 and 1958. The treatment process at this 11,400 cu m/day (3 mgd) plant involved coagulation (ferric sulfate or alum), breakpoint chlorination (to 0.5 mg/l free residual chlorine), rapid sand filtration, GAC, rechlorination and ammoniation. The GAC adsorber bed was 0.91 m high x 2.44 m in diameter (volume 34.2 cu m) and had a 97 second actual contact time (assuming 30% interstitial voids in the carbon), or a superficial contact time of 325 seconds at a filtration rate of 2.8 mm/sec.

GAC filtrates at Foxcote frequently exhibited substantially higher plate counts (3-days incubation at 22°C on nutrient agar) than did the rapid sand filtrates. Figure 50 is a histogram of 22°C plate count data obtained for samples of the sand and GAC filtrates and of the final waters (rechlori-

TABLE 35 REMOVAL OF BACTERIA DURING CAUSTIC SODA SOFTENING AND PRECHLORINATION AT COLWICK, ENGLAND

sand filtered F 1			carbon treated G 1			disinfected H 1			sand filtered F 2			carbon treated G 2			disinfected H 2			
coli forms/ 100 ml	E coli per 100 ml	22°C plate count/100 ml	coli forms/ 100 ml	E coli per 100 ml	22°C plate count/100 ml	coli forms/ 100 ml	E coli per 100 ml	22°C plate count/100 ml	coli forms/ 100 ml	E coli per 100 ml	22°C plate count/100 ml	coli forms/ 100 ml	E coli per 100 ml	22°C plate count/100 ml	coli forms/ 100 ml	E coli per 100 ml	22°C plate count/100 ml	week no
			ferric sulfate coagulation									(1) caustic soda softening						
500	20	1,500	900	34	780	nil	nil	nil	<100	<10	30	450	74	6,500	50	nil	320	19
1,700	35	1,340	580	24	520	nil	nil	1	<5	<2	<10	10	2	700	nil	nil	12	20
3,200	150	3,900	490	8	730	nil	nil	5	30	nil	40	nil	nil	80	nil	nil	nil	20
3,400	50	2,460	290	4	226	nil	nil	nil	10	nil	220	<5	2	700	14	nil	250	21
11,000	455	2,400	290	6	70	nil	nil	nil	40	4	25	<5	<2	nil	1	nil	nil	21
3,600		5,400	550		64	nil		nil	10		4	630		900	220		1,200	22
2,600	45	410	270	2	72	230	2	60	335	6	1,360	860	90	2,500	nil	nil	nil	22
4,400	360	2,500	480	2	320	nil	nil	nil	2,400	92	650	80	32	6,800	250	15	nil	23
340	10	1,300	40	3	218	1	nil	nil	20	nil	8	120	18	>5,000	220	8	>5,000	23
160	4	80	80	1	43	nil	nil	7	250	nil	840	240	4	350	nil	nil	2	24
820	50	60	60	4	55	nil	nil	2	20	nil	121	80	2	100	1	nil	126	24
2,300	156	850	284	56	240	nil	nil	nil	225	10	130	860	20	680	37	6	156	25
2,400	90	>5,000	550	34	580	nil	nil	8	750	44	1,500	1,400	82	1,200	100	11	280	25
2,300	20	2,800	130	8	370	nil	nil	3	210	12	1,900	220	14	1,700	9	3	210	26
100	8	610	40	2	260	nil	nil	2	390	2	2,260	20	nil	1,160	nil	nil	150	27
			ferric sulfate coagulation									(2) prechlorination						
400	8		360	10		nil	nil		11	9		7	nil		19	nil		31
220	nil	190	120	nil	10	nil	nil	nil	nil	nil	nil	9	nil	700	4	nil	274	32
1,940	24	920	1,080	20	850	nil	nil	nil	12	8	280	1	nil	>5,000	nil	nil	29	32
960	20	80	100	5	40	nil	nil	nil	nil	nil	nil	3	nil	3,000	nil	nil	nil	33
2,600	130	6,000	1,390	46	<10	>500	21	850	nil	nil	nil	1	nil	>5,000				33
1,240	24	440	140	nil	31	nil	nil	nil	1	nil	nil	6	nil	8,600	nil	nil	nil	34
2,500	24	540	180	4	89	88	7	98	7	nil	<10	nil	nil	>2,000	3	nil	>2,000	34
580	240	3,200	560	30	1,000	35	12	800	nil	nil	9	70	6	6,000	nil	nil	560	35
2,400	124	4,000	10	nil	360	nil	nil	2	nil	nil	nil	4	nil	8,500	nil	nil	1,600	35
1,600	120	400	110	16	600	8	nil	2	nil	nil	nil	9	nil	>1,200	500	nil	>1,200	36
1,200	42	370	55	2	68	nil	nil	nil	nil	nil	nil	4	nil	>3,000	4	nil	>3,000	37
1,040	44	3,900	45	nil	380	nil	nil	nil	nil	nil	nil	2	nil	2,400	nil	nil	nil	37
500	4	820	25	nil	30	38	nil	30	nil	nil	1	5	nil	700	3	nil	630	38
7 000	168	6,400	60	nil	140	27	7	6	2	nil	9	190	48	3,200	nil	nil	nil	38
1,620	4	1,460	3,000	38	>5,000				1	nil	1	17	9	3,600	1	nil	nil	39
760	10	1,200	80	5	500	nil	nil	4	nil	nil	nil	3	nil	3,000	nil	nil	1	39

Source Melbourne & Miller, 1973

nated and ammoniated) over the 5-year period 1968 to 1972. In 71% of the cases, the GAC effluents showed higher plate counts than did the sand filtrates, and in 42% of the samples the GAC effluent count exceeded that of the sand filtrate by a factor of 10 or more. Rechlorination and ammoniation to a level of 0.45 mg/l of chloramine, did not restore the bacterial counts of the GAC effluents to the levels of the sand filtrates.

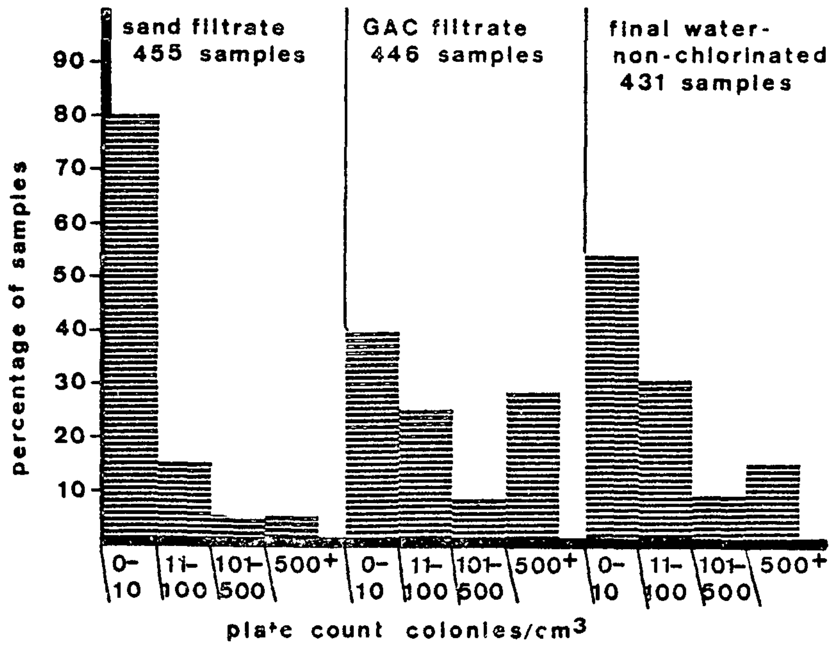


Figure 50. Histogram of agar plate counts, 3 days at 22°C.

(Ford, 1973)

The Water Research Association (England) examined samples of Foxcote water and tentatively identified the predominant microorganisms in the GAC filtrates as chlorine-forming Flavo bacteria, along with some spore-forming bacteria. Their work also demonstrated that three days incubation is too short a period of time for the development of easily visible colonies of these bacteria, and that much higher counts were obtained after 7 days incubation. Using 7 day incubation times, bacterial counts obtained with sand filtrates remained very low.

The occurrence of biological activity in the GAC adsorbers and their effluents in spite of approximately 0.5 mg/l free chlorine residuals in the influent waters thus was amply demonstrated.

Ford (1973) also noted that "animal infestation problems have occurred when (activated) carbon units have been taken out of service and left standing". Apart from this animal infestation tendency to occur in idle filters, Nais worms were found on only one occasion in the Foxcote activated carbon effluents. These were eradicated by addition of NaOCl to the backwash water to give a chlorine residual of 5 mg/l.

Richard (1973) reported on treatment studies of Seine River water at the Vigneux plant upstream of Paris, France. At this 1,500 cu m/hr (36,000 cu m/day; 9.5 mgd) treatment plant comparative tests were conducted using powdered and granular activated carbons. The Vigneux plant process at the time consisted of microstraining, clarification (with powdered activated carbon), filtration, breakpoint chlorination (with 6 to 8 mg/l of gaseous chlorine), coagulation (alum) and flocculation (activated silica). At the time of the reported study, 10 to 20 mg/l of powdered activated carbon was being injected upstream of the clarifiers. Chlorine dioxide (0.15 to 0.25 mg/l) was injected upstream of the reservoirs.

Three test processes were studied by Richard (1973):

1) clarification with powdered activated carbon, sand filtration;

2) clarification without powdered activated carbon, GAC filtration;

3) clarification without powdered activated carbon, sand filtration, GAC adsorption.

After 250 days of operation, a monitor was installed which controlled the breakpoint chlorination step to a free residual chlorine level of 0.25 to 0.40 mg/l from that point on. Under these conditions the pretreated plant water gave negative coliform (24 hours at 37°C) and E. coli counts.

Treatment without either powdered or granular activated carbon produced waters having very low plate counts. However, addition of powdered activated carbon to the clarifier produced filtered water showing less than 10 colonies/ml during cold weather and 10 to 100 counts/ml during summer. Passage through granular activated carbon, acting either as a filter or as an adsorber, gave colony counts of about the same order, although slightly higher. Final sterilization with chlorine dioxide (0.15 to 0.25 mg/l dosages) produced waters having zero plate counts/ml.

Kölle & Sontheimer (1973) discussed experiences with activated carbon in West Germany and specifically reviewed the role of biology in water pretreatment. They proposed that the action of microorganisms in granular activated carbon media is integrally connected with the enrichment of organic substances (by adsorption) which can result in improvement of substrate utilization by the bacteria. As waters containing organic materials pass through granular activated carbon columns or beds, some organics are adsorbed physically and/or are incorporated into the biomass and/or are oxidized to carbon dioxide. In addition, products and intermediates of biological assimilation had been observed (Koppe & Giebler, 1966) in the effluents from activated carbon media.

Kölle & Sontheimer suggested several experimental approaches to obtain more detailed information on the operable physical and biochemical processes occurring in activated carbon filters and adsorbers. These media can be operated and their efficiencies in eliminating organic materials from solution can be studied after exhaustion of their theoretical adsorption capacities. However, in operational water treatment plants, steady state conditions are difficult to establish, even over long operating periods, because compositions of raw waters being treated usually vary from day to day. Organic compounds which are rapidly adsorbed and tightly bound to the activated carbon surface will displace previously adsorbed organic compounds which are not as tightly held by the activated carbon surface.

A second approach is to follow, simultaneously, both the decrease in dissolved oxygen consumption and increase in carbon dioxide produced during passage of water through the activated carbon medium, comparing data measured in both the influents and effluents. The activated carbon filter or adsorber also can be used as a "bioassay bottle" by recycling effluent to become influent and following the changes in DO consumption and CO_2 production. Studies of this type were being conducted at the Auf-dem-Werder plant in Bremen, Federal Republic of Germany. Oxygen consumption upon passage through activated carbon rose to 7 mg/l during summer and dropped to 2 mg/l during winter, showing that surface water temperature variations affect biological activities significantly (Eberhardt, Madsen & Sontheimer, 1974).

Another factor complicating such studies is the kind of pretreatment applied before activated carbon treatment. Kölle & Sontheimer (1973) state, "There is practically no waterworks without pretreatment -- mostly using oxidation by ozone". Some laboratory tests have shown that it is desireable to add a flocculation step between oxidation (with ozone) and activated carbon filters or adsorbers, especially with respect to removing UV-absorbing organic substances (Kölle & Sontheimer, 1973).

Summary of European Studies in 1973

The status of published European knowledge of microbiological activity in activated carbon filters and adsorbers used in drinking water treatment as of 1973 can be summarized as follows:

1) Bacterial growths in activated carbon were known to occur in plant scale media to a significant extent, even when influent waters contained as high as 0.5 mg/l of free residual chlorine (after breakpoint chlorination).

2) Biological activity develops rapidly with fresh carbon charges. GAC units used for taste and odor control over a 1-year period developed maxima of 10,000 colony counts (22°C)/ml in the effluents in about 8 weeks. During this time the GAC influent waters contained zero colony counts/ml.

3) Prechlorination or presoftening of influent waters had been observed to increase the amount of biological growth in the GAC media in some cases.

4) Effluents from biologically active GAC media contain a much greater number of colonies than do effluents from slow sand filtrates.

5) Treatment of effluents from biologically active carbon media with chlorine or (0.15 to 0.25 mg/l dosage) chlorine dioxide lowered colony counts/ml to acceptable local biological standards.

6) Speciation studies of microorganisms in effluents from biologically active carbon media had shown the presence of chlorine-resistant flavobacteria (from waters which had been treated by breakpoint chlorination) along with some spore-forming bacteria.

7) Indications were that two and three day incubation periods were insufficient, even at 37°C, for development of easily visible colonies, and that 7 days of incubation gave much higher counts.

8) Animal infestation had been observed in activated carbon units which had been taken out of service and left standing for two days.

9) Bacterial activity was higher in the summer than in winter.

10) Products and intermediates from biological assimilation had been observed in effluents from activated carbon media.

CURRENT EUROPEAN MICROBIOLOGICAL STUDIES

At present, there are only two European groups known to have published results of continuing research into the microbiological aspects of activated carbon systems with respect to treatment of drinking water. These studies are being conducted at the KIWA (The Netherlands) by Dr. D. Van der Kooij and at the University of Saarlands (Federal Republic of Germany) by Professor Dr. R. Schweisfurth and his students. A third research program on this subject has been established recently at the Engler-Bunte Institut der Universität Karlsruhe during 1979.

Research Studies At The KIWA

Microbiological studies at the KIWA were published by Van der Kooij in 1975 and 1978. Additional unpublished information was provided by Dr. Van der Kooij in a personal interview during June 1978. These two published articles will be reviewed in this subsection and the discussion will be supplemented by the private communications supplied during June, 1978.

In work presented in 1975, Van der Kooij conducted side-by-side experiments with Norit ROW 0.8 Supra (the 0.8 refers to the particle size in millimeters) granular activated carbon (GAC), the same granular carbon but not activated (GNAC) and sand (0.85 to 1.00 mm particle size). Test columns containing each of these materials were fed with non-chlorinated tap water (13 to 17°C) at the rate 3.5 m/hr (3 minutes apparent contact times) over a period of 10 months. Colony counts in the columns were determined at intervals on diluted nutrient agar (0.36 g/l beef extract, 0.65 g/l peptone, 10 g/l agar) after 10 days of incubation at 25°C. The bacteria were removed from the sand, GNAC and GAC by subjecting the samples to ultrasonic energy. The numbers of bacteria found on the filtering materials were expressed as numbers/ml of filter volume and are shown in Figure 51.

This figure shows that the numbers of bacteria found on the activated carbon were always about 10 times higher than the numbers on the non-activated carbon and on sand. Using more refined measurements, Dr. Van der Kooij (1978a) showed that the numbers of bacteria on activated carbon were only 2 to 3 times higher than on the other two media.

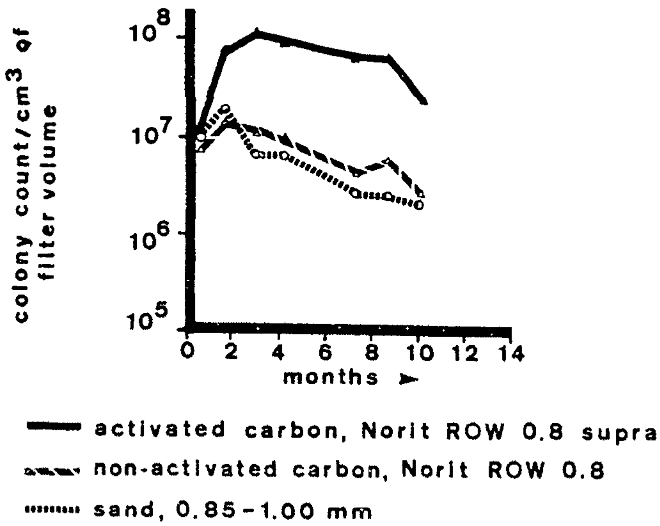


Figure 51. Bacterial numbers on GAC, granular non-activated carbon and sand, each fed with non chlorinated tap water.

(van der Kooij, 1975)

In a second experiment, samples of used GAC and GNAC (ROW 0.8 Supra) were taken from adsorbers fed with prefiltered river water for a period of one year. Wet carbon samples (150 ml) were treated with 50 ml of non-chlorinated tap water and aerated at 25°C. The numbers of coliforms, pseudomonads and actinomycetes proliferating in these carbons were determined weekly. The total numbers of viable bacteria were estimated by colony counts on diluted nutrient agar and expressed per cu m of filter volume. Oxygen consumption was expressed in mg of O_2/1 of filter volume/hr. Results are plotted in Figures 52 and 53. Table 36 shows the times to attain 50% reductions in the levels of bacteria present in the activated and non-activated carbons (50% reduction times).

Van der Kooij (1975) estimated that since the hypothetical cylindrical surface area of granular activated carbon is about 40 sq cm/cu cm of GAC present, when the colony count is 10^8/cu cm, then a single bacterium occupies, on the average, 40 sq microns of this available surface area. Since the available surface area of GAC is much higher than 40 sq cm/cu cm, it was concluded that there is only a low density of bacteria occupying the surface of the activated carbon, even allowing for the fact that colony count techniques measure only a portion of the bacteria present. Scanning electron microscope measurements made at the KIWA confirmed this conclusion, as did similar studies by Weber, Pirbazari & Melson (1978) on GAC samples contacted with chemically coagulated and settled sewage.

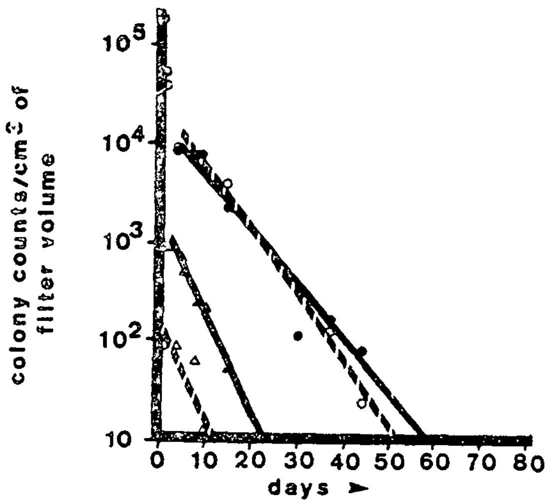


Figure 52. Numbers of pseudomonads (•○) and coliforms (▲△) on GAC ROW 0.8 supra (○▲) and on non-activated carbon ROW 0.8 (○△) during aeration at 25°C.

(van der Kooij, 1975)

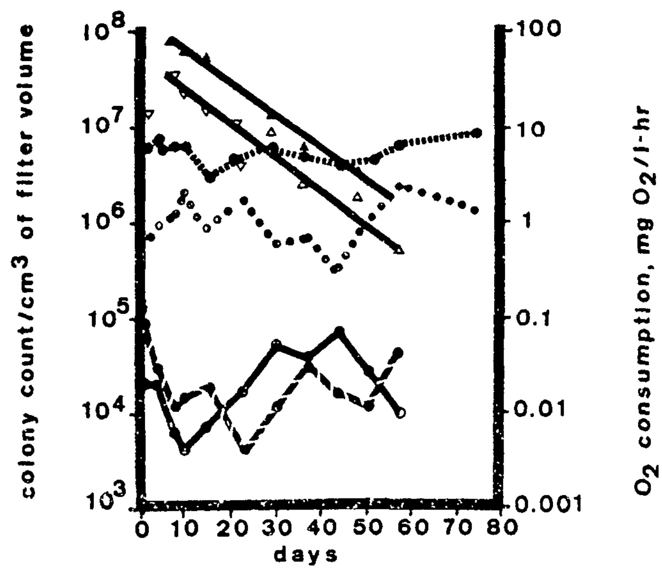
TABLE 36. 50% REDUCTION TIME (DAYS) OF DIFFERENT GROUPS OF BACTERIA ON ROW 0.8 SUPRA GAC AND ROW 0.8 GNAC

Type of Bacteria	ROW 0.8 Supra	ROW 0.8 not act.
Colony Forming Units (25°C, 10 days)	9	8.5
Coliforms	3	3.5
Pseudomonads	4.5	4.0
Actinomycetes	>50	>50

Source: Van der Kooij, 1975.

Based on these measurements, Van der Kooij (1975) concluded that adsorption processes operative in granular activated carbon are not hindered by the presence of bacterial growths on the activated carbon.

Figure 51 also shows that the number of bacteria on GAC samples decreased after reaching a maximum value. Van der Kooij (1975) concluded that this decrease is not caused by exhaustion of the adsorptive capacity of the GAC, since the same relative decrease also was noted with GNAC and sand. Van der Kooij points out that the decline also might be explained by a shift in the types of bacterial flora originally present to types of bacteria which do not participate in colony counts.



numbers of colony-forming units (▲△) and numbers of actinomycetes (•○) on ROW 0 8 Supra GAC (▲•) and non-activated ROW 0.8 (△○) during aeration at 25°C

O_2 consumption, mg O_2/l-hr:

ROW 0.8 Supra

ROW 0.8, *n.a.*

Figure 53. Numbers of bacteria and actinomycetes on GAC and GNAC; O_2 consumption with GAC and GNAC.

(van der Kooij, 1975)

Figure 52 shows that the numbers of both coliforms and pseudomonads, as well as the total colony forming bacteria, decreased rapidly on the GAC and GNAC. In 60 days the counts of pseudomonas bacteria dropped from 10,000 to

10/cu cm of filter volume and coliforms dropped to 10/cu cm in 23 days from 100 to 1,000.

On the other hand, the numbers of actinomycetes and the oxygen consumption rates did not show clear decreases during 60 days. Therefore, from the data of Figure 52 and of Table 36, it can be seen that the coliforms disappear faster than do other bacteria. Since there is hardly any difference in the 50% reduction times for the selected bacteria on GAC versus GNAC, Van der Kooij (1975) concluded that neither coliforms nor pseudomonas nor total colony-forming bacteria gained any advantage from the organic substances which were present on the activated carbon which had been in contact with river water for the one-year period.

The oxygen consumption rate during passage through either GAC or GNAC did not decrease with decreasing colony counts, nor did the number of actinomycetes (Figure 53). Van der Kooij (1975) therefore suggested that it is possible that the oxygen consumption values observed with both carbons were caused by chemical rather than bacterial processes. He also suggested that the relatively constant numbers of actinomycetes bacteria observed over the 60 day period might have been due to their ability to fragment into smaller organisms (to produce spores).

During June, 1978, Dr. Van der Kooij supplied the following additional information regarding his studies of biologically active filtration and adsorber media:

1) For sampling of filtration of adsorption media, 1 g samples of wet medium are taken into sterile, non-chlorinated tap water, then subjected to ultrasonics for 2 to 3 minutes. The supernatant liquid then is treated by normal dilution and plate counting. When water was added to the 1 g activated carbon sample treated once by ultrasonics and the ultrasonic exposure repeated, more bacteria were found in the second supernatant. The process was repeated 10 times on the same 1 g sample of activated carbon. About 40% of the total bacteria determined were found in the first supernatant, 20% in the second, 10% in each of the third and fourth extracts, etc. Even after the tenth ultrasonic treatment of the original 1 g sample, significant bacterial counts were being obtained. This indicates that bacteria are very tightly held by the activated carbon.

2) Samples from operational water treatment plant granular activated carbon filters or adsorbers were taken in 10 to 20 g quantities and at various depths.

3) A bioassay test for biologically assimilable organic carbon in raw waters has been developed by the KIWA at one of the large Dutch water treatment plants using river water. Pseudomonads were cultured in raw river water at 15°C and their rate of growth was determined. Next the river water was ozonized, then seeded with the same pseudomonad culture and their rate of growth again measured. The growth rate was found to be higher after ozonation than in the raw river water. Such a test again shows that ozonation converts some of the dissolved organics

present (which are not easily biodegraded) into organics which are more readily biodegradable. In addition, this procedure might be considered as a screening test at U.S. water treatment plants to determine whether detailed evaluation of an early stage biological processing step would be worthwhile. If no increase in biodegradability is observed after ozonation, then preoxidation of any sort will be ineffective in this regard.

4) Fresh samples of GAC have shown measureable levels of oxygen consumption before measureable levels of bacterial activity have built up in the medium. Therefore, GAC seems to cause some degree of surface catalyzed oxidation of dissolved organic substrates.

5) *E. coli* bacteria taken into a biologically active granular activated carbon filter or adsorber cannot survive in competition with the other species of microorganisms present. Therefore, in a properly sized and operated biologically active filter/adsorber medium, no *E. coli* bacteria are found in the filtrates. This is confirmed by long term experiences in Europe with slow sand filters.

In a paper presented in 1978(b), Van der Kooij reported continued studies of the microbiological processes occurring in granular carbon samples. In introducing the subject, Van der Kooij reported that "some investigators have concluded that an increased contact time between organisms and adsorbed organic substrates is allowing the microorganisms to adapt to the less readily biodegradable organic substances", thus allowing these harder-to-decompose organic compounds to be degraded during "biological regeneration" of the activated carbon adsorption sites.

In this more recent work, 6 cm diameter columns were filled with Norit ROW 0.8 Supra activated carbon (GAC), the same carbon but not activated (GNAC) and 0.8 to 1.0 mm sand. Again in side-by-side tests, the columns were treated with non-chlorinated tap water (14 to 18°C) containing an average of 3 mg/l of dissolved organic carbon at 3.5 m/hr filtration rates (3 minute apparent contact time) for a period of one year. Numbers of colony-forming units/ml were estimated by the surface spread technique on 8-fold diluted Lab-Lemco broth (Oxford CM 15) agar plates. Samples were exposed to ultrasonic energy for 3 minutes to detach the microorganisms, then samples were incubated for 10 days at 25°C. Removal of organic substances from solution was followed by measuring the ultraviolet absorption at 275 nm in 5 cm cuvettes.

Figure 54 shows the colony counts on the filter materials and in their filtrates measured over the one year period. Maximum values were attained in all three media during the first 20 to 30 days. After these maxima were reached, the adsorber effluents showed counts of 1,000 to 10,000/ml. Ultraviolet absorption measurements showed that immediate breakthrough of organic materials occurred with the GNAC and sand media. The GAC medium reached 80% of breakthrough in 30 days and 90% of breakthrough in 90 days, with respect to dissolved organic materials.

Figure 55 compares colony counts found on the three filter materials, which usually were higher on the GAC medium and reached a maximum of 7×10^7

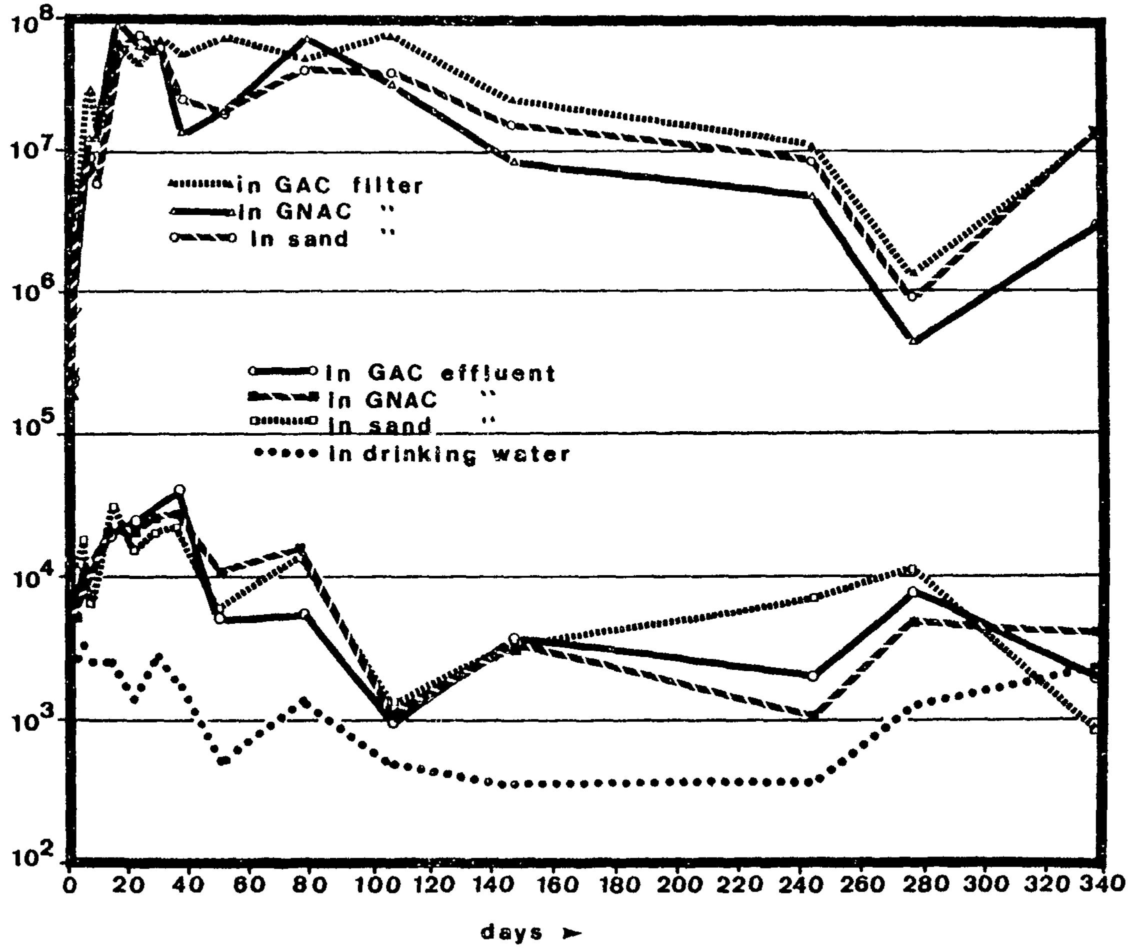


Figure 54. Colony counts in GAC, GNAC and sand filters and in their effluents over 340 days.

(van der Kooij, 1978)

cfu/ml. Colony counts on GNAC and sand were similar to each other. Figure 56 shows that the cfu/ml numbers found in all three effluents were about the same.

Van der Kooij (1978b) concluded that adsorption of organic materials by activated carbon therefore is not the cause of the high colony counts usually observed in the GAC filter/adsorbers. This was confirmed by noting that the majority of microorganisms isolated from the GAC were able to grow only on simple, non-adsorbing compounds like acetate, pyruvate and lactate, whereas adsorbing substances such as aromatic compounds (which are measured by ultraviolet absorption) were not utilized.

CH_3COO^-	CH_3COCOO^-	$CH_3CH(OH)CCO^-$
acetate	pyruvate	lactate

Effluents from the slow sand filters (which are known to remove bacteria) at the water treatment plant at the Hague (0.3 m/hr flow rate) were studied. Bacterial contents in these slow sand filters were 20,000 to 30,000 cfu/ml, but were less than 100 cfu/ml in the filtrates. Similar observations had been made earlier by Schmidt (1963). Comparing these slow sand filtrate counts with those of the side-by-side experiments (Figures 55 and 56) suggested that there was a relationship between flow rates and the number of microorganisms in the sand and in the filtrates. Therefore, colony counts in the GAC (Norit PKST) present on the slow sand filters of the Hague (probably a thin layer on top of the sand) were estimated in samples taken from 8 of the operational plant filters (Figure 57).

Comparison of the data of Figure 55 with those of Figure 57 shows that colony counts in samples of GAC taken from the top of the slow sand filters were 1 to 2 orders of magnitude lower than those observed in the experimental GAC filters supplied with non-chlorinated tap water. This confirmed the conclusion that flow rate through a filter bed strongly affects colony count levels in the filter materials.

Since the colony counts in GAC media usually were greater than those in GNAC and in sand, even though colony counts in the filtrates did not differ, Van der Kooij (1979) concluded that this behavior probably was due to the relatively large surface area/unit volume of GAC upon which microorganisms utilizing substrate from the passing water can attach. Therefore, Van der Kooij (1979) concluded that granular activated carbon is a favorable material for biological filtration processes.

Effects of microorganisms on adsorption of organics by GAC--

Some laboratory experiments next were conducted by Van der Kooij (1979) to determine the influence of bacterial cells attached to GAC on the adsorption of 4-nitrophenol (a readily adsorbed but difficult to biodegrade organic compound) and 4-hydroxybenzoate anion (a readily adsorbed and readily biodegradable organic compound) by Norit ROW 0.8 Supra granular activated carbon.

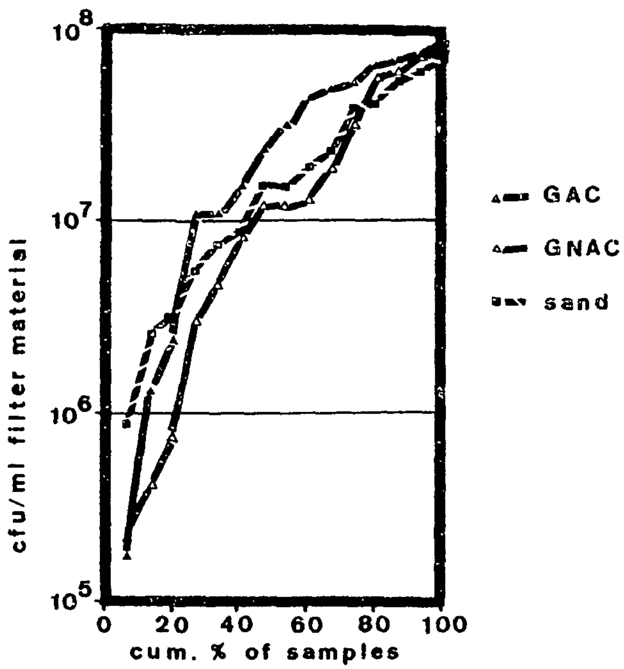


Figure 55. Colony counts in GAC, GNAC and sand.

(van der Kooij, 1978)

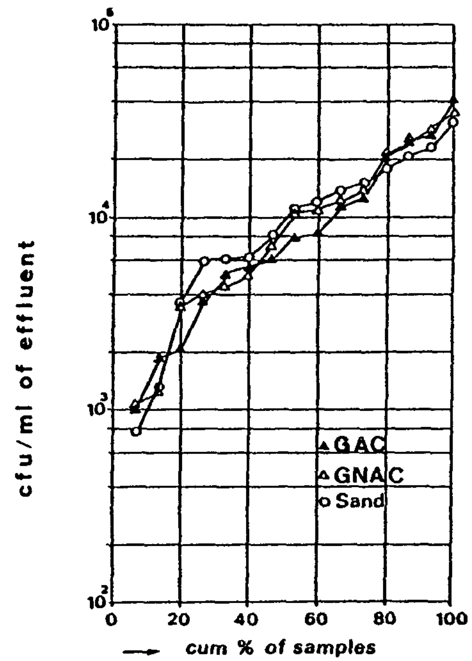
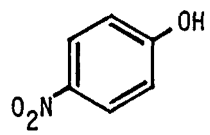
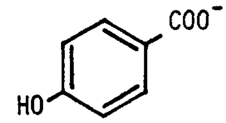


Figure 56. Colony counts in effluents from GAC, GNAC and sand filters.

(van der Kooij, 1978)



4-nitrophenol



4-hydroxybenzoate anion

Adsorption isotherms and rates of adsorption of these compounds were determined with growths of the bacteria Pseudomonas fluorescens (Strain 17) or Pseudomonas alcaligenes (Strain 131) being present on the GAC.

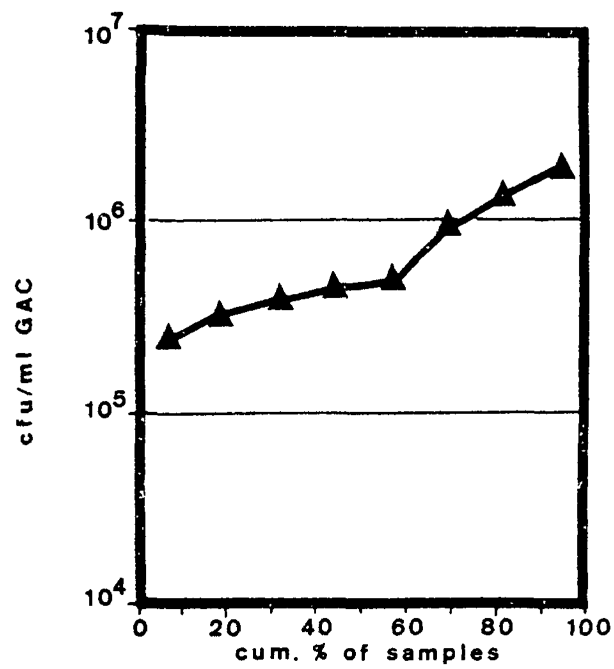


Figure 57. Colony counts in Norit PKST GAC in 8 slow sand filters at Den Hague.

(van der Kooij, 1978)

Strain 17 was found to grow on 4-hydroxybenzoate but not on 4-nitrophenol, whereas Strain 131 could not use either of the two organic substrates. For these studies, samples of GAC (0.1 g) were sterilized in bottles containing 200 ml of demineralized water with KH_2PO_4 (2.7 mg/l), $K_2HPO_4.3H_2O$ (5.3 mg/l) and $Na_2HPO_4.12H_2O$ (8.0 mg/l). The final pH after sterilization was 7.3.

To cultivate bacteria on the GAC, ammonium acetate was added to the sterilized solution to a final concentration of 10 mg/l of acetate carbon. Bottles were inoculated with either Strain 17 or 131 and incubated 3 days at 25°C in a rotary shaker (120 revolutions/minute). The bacteria developed to a maximum level of 4×10^7 cfu/ml of medium and the GAC contained about 2×10^8 cfu/ml (6×10^8 cfu/g) of GAC.

Under these conditions, either 4-nitrophenol or 4-hydroxybenzoate was added from sterilized solutions in final concentrations of 100, 50, 25 and 10 mg/l. These compounds also were added to bottles containing sterilized GAC without bacteria. The bottles were placed in a rotary incubator at 25°C and the concentrations of 4-hydroxyphenol and 4-hydroxybenzoate were measured by UV absorption at 254 and 269 nm, respectively in 5 ml of membrane filtered samples after 24, 48 and 144 hours of incubation. Ultraviolet absorption was measured every hour during the first 8 hours after addition in bottles containing an initial adsorbate (phenol or benzoate) concentration of 100 mg/l. All experiments were performed in duplicate.

Adsorption isotherms of 4-nitrophenol and 4-hydroxybenzoate on the activated carbon in the presence and absence of bacteria were calculated from measured concentrations and are presented in Figure 58. The disappearance of these compounds from solutions initially containing 100 mg/l of adsorbate is shown in Figures 59 and 60. Figures 58, 59 and 60 show that the phenol was better adsorbed by the GAC than was the hydroxybenzoate. With both compounds, however, the adsorption equilibrium was reached within 48 to 144 hours.

Results shown in Figure 58 indicate that the adsorption isotherms are not affected by the presence of bacteria. Moreover, adsorption of the adsorbates in the 100 ml bottles also was not affected by the presence of bacteria on the activated carbon. The adsorption rate of 4-hydroxybenzoate in the presence of bacteria could not be calculated because both bottles were infected by adsorbate-consuming microorganisms. Infection also occurred in some other bottles containing 4-hydroxybenzoate because this compound is so easily biodegraded, compared with 4-nitrophenol.

Van der Kooij (1979) concluded the following:

1) The number of microorganisms present on a filter/adsorber medium depends upon the flow rate of water through the medium, and is probably due to limited transport (diffusion) of the soluble substrate to the microorganisms.

2) Adsorption of organic compounds by GAC is not inhibited by the presence of a large number of bacteria on activated carbon.

3) Granular activated carbon adsorbers or filters in operational drinking water treatment plants sampled by Van der Kooij always contained lower colony counts than the levels applied in the laboratory experiments described in this paper. Therefore, in GAC adsorbers used to prepare drinking water, hindrance of adsorption of organic compounds by microorganisms is very unlikely.

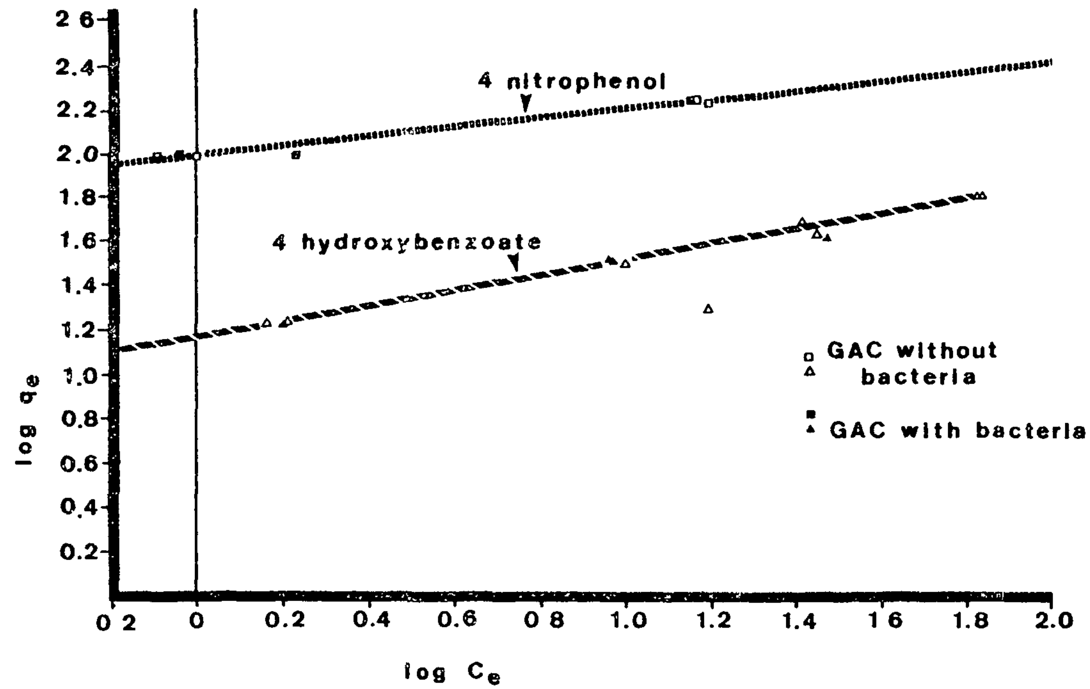


Figure 58. Adsorption isotherms of 4 nitrophenol and 4 hydroxybenzoate on ROW 0 8 Supra GAC, with and without bacteria.

(van der Kooij, 1978)

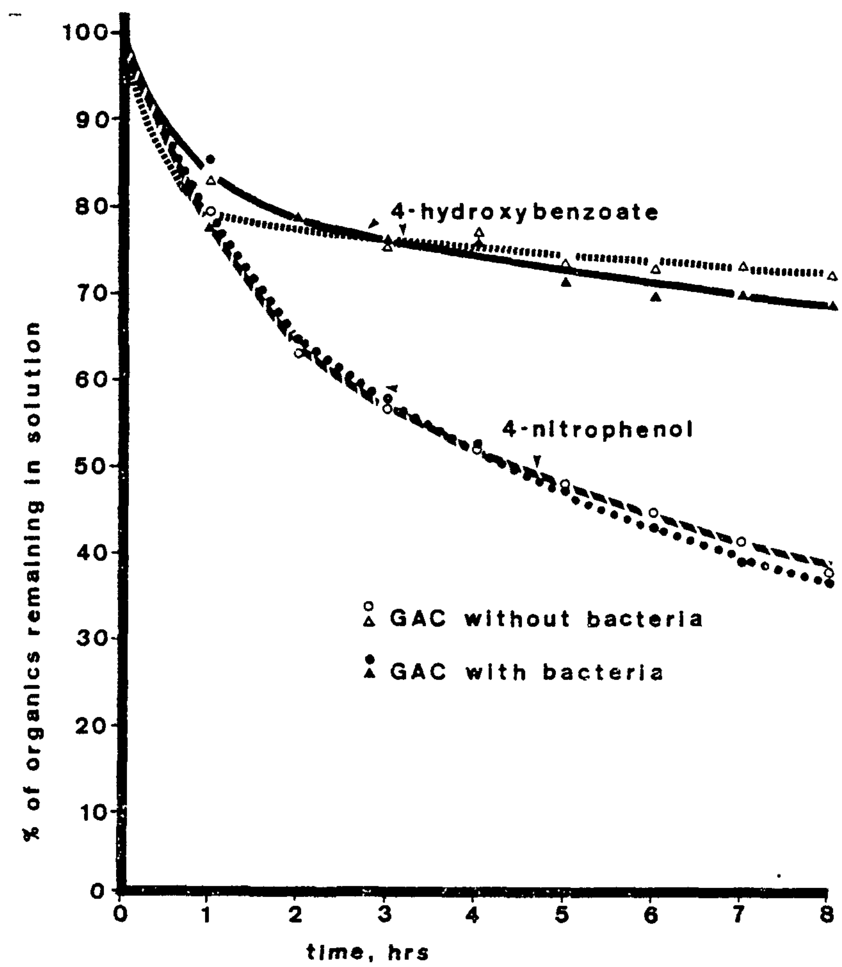


Figure 59. Removal of 4-nitrophenol and 4-hydroxybenzoate on passage through ROW 0.8 Supra GAC.

(van der Kooij, 1978)

On the other hand, Van der Kooij (1979) points out that hindrance of adsorption by microorganisms might occur when the influent water contains relatively large amounts of easily biodegraded materials. In these situations "extremely large numbers of microorganisms" develop on the activated carbon. Also, adsorption may be affected by the contamination of granular activated carbon by colloidal and suspended matter. These last two effects were not investigated during the 1979 study of Van der Kooij.

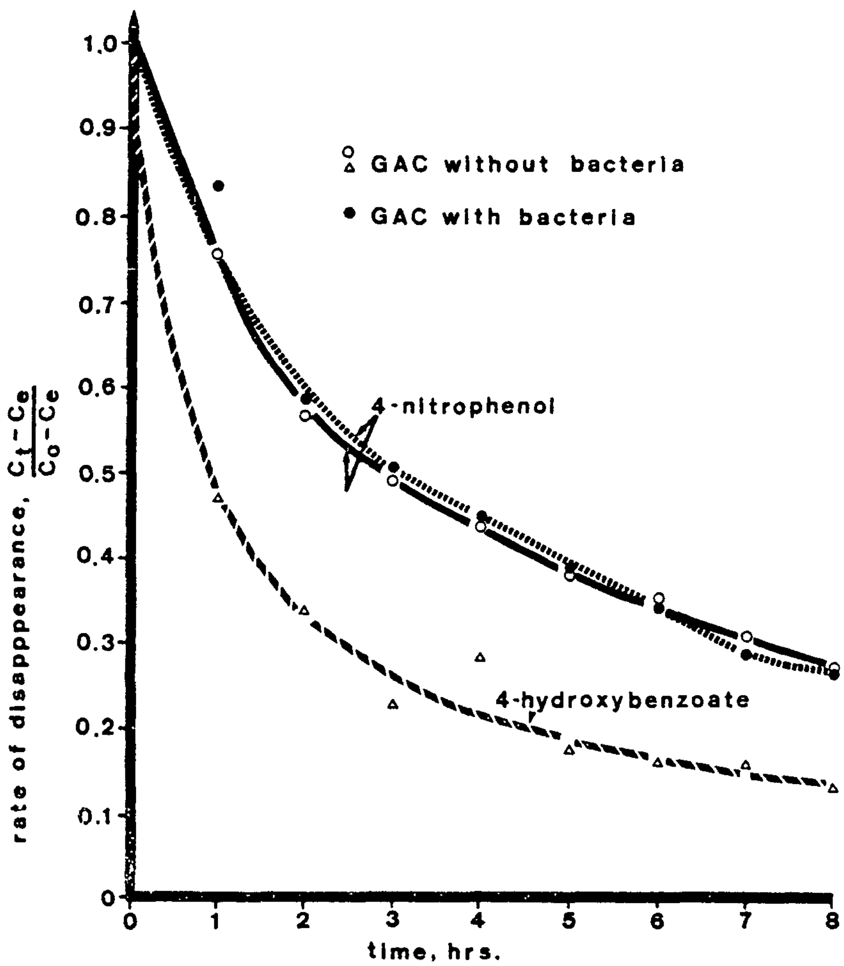


Figure 60. Rate of disappearance of 4-nitrophenol and 4-hydroxybenzoate on passage through ROW 0.8 Supra GAC.

(van der Kooij, 1978)

Research Studies at the University of Saarland

In 1972, a cooperative research program between the City of Wiesbaden and the University of the Saarlands (Federal Republic of Germany) was begun with the objective of studying the microbiology which was present in the GAC adsorbers at Wiesbaden's Schierstein water treatment plant. Two doctoral candidates at the University (P. Werner and M. Klotz) completed their Ph.D. thesis studies in 1979 based on these studies which were directed by Prof. Dr. Reinhart Schweisfurth. These scientists have published three progress reports of their studies, all of which will be reviewed here. In addition, all three investigators were interviewed in June, 1978 and provided additional information on their studies in the form of private communications.

In work presented in 1975, Klotz, Werner & Schweisfurth reported studies at the Schierstein water treatment plant at Wiesbaden, which had been conducted since 1972 on plant operating granular activated carbon columns and pilot plant columns. Initially, these investigators found that the determination of colony numbers as recommended by the DEV (Deutsche EinheitsVerfahren = German Standard Methods, 1962) (2 days incubation at 27°C) proved to be inadequate, because only a small portion of the microflora present are revealed by this technique. However, all nutrient media tested showed considerably increased colony numbers after breeding for 7 days, and this incubation time was used throughout this program and those which these investigators have reported subsequently.

The best medium for determination of microorganisms was found to be P-Agar which contained few nutrients and SPC-Agar which was rich in nutrients (Standard Methods, 1971). Both were incubated at 27°C for more than 7 days. The activated carbon samples were crushed in a simple mixer and the homogenized material then was processed for the determination of colony numbers in the same manner as were the water samples. The cell numbers (the total of all living and dead bacteria) were determined by counting microscopically after collecting on membrane filters and coloring. Apart from a few modifications (not delineated) all other tests were carried out as recommended by the DEV whenever possible.

The Schierstein Treatment Process--

At this plant, Rhine River water, not river sand bank filtered, is pretreated directly before ground infiltration to augment groundwater supplies. The treatment process involves aeration, settling, chlorination, flocculation, rapid sand filtration, activated carbon adsorption, then ground infiltration. During the course of this study some of the plant GAC adsorbers were operated as long as 3 years without being reactivated. At the end of this time, 30% of the influent dissolved organic carbon still was being removed from solution during passage through the GAC media.

In Figure 61 are shown the mean values of colony numbers determined at different points in the plant for the period March 1973 to March 1974. There was a decrease in colony numbers between the Rhine and the entrance to the activated carbon adsorbers, the largest effect being obtained following breakpoint chlorination. However, fresh populations of microorganisms were formed in the activated carbon media, such that very high colony numbers were found at the GAC media exits using the 7-day incubation method. By the 2-day incubation method normally applied for measuring colony counts, as recommended by the DEV for the control of drinking water, the water quality at this point in the process generally was satisfactory.

<u>Composition of microorganism populations in GAC effluents</u>--Populations were examined in freshly filled plant GAC adsorbers and in pilot plant test columns. The test columns consisted of four successive glass tubes each with an inside diameter of 4 cm and the total GAC bed depth was 3.2 m (4 x

0.8 m). Passage of water through each individual 0.8 m deep column is referred to as "a filter step".

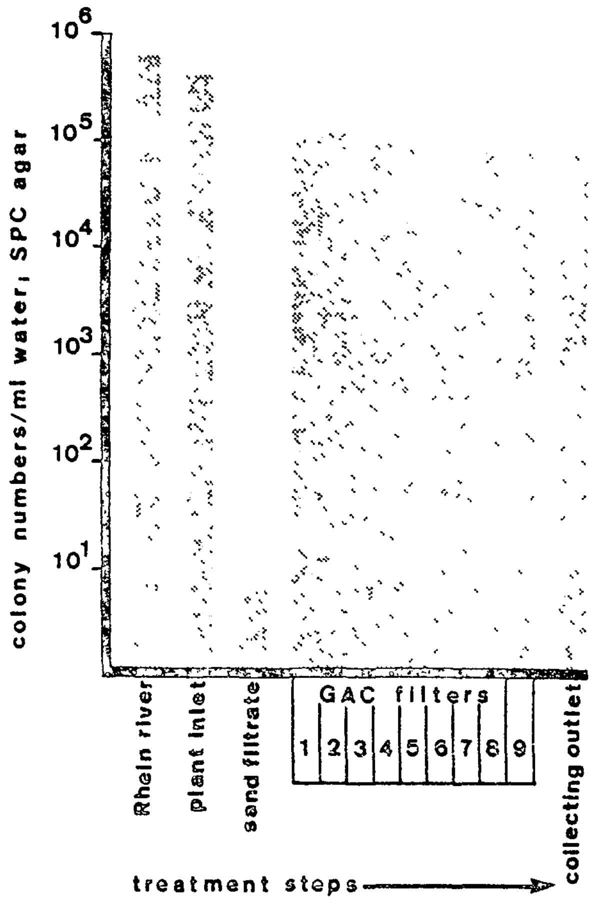


Figure 61. Mean colony numbers at various points in the Schierstein plant, March '73 - March '74.

(Klotz *et al.*, 1975)

The behavior of the microorganism populations was found to be the same in both the pilot plant test adsorbers and in the full scale plant adsorbers. During the first 20 days the colony numbers rose linearly and reached a maximum of 10^5 to 10^6/ml of water, after which they declined and remained at a slightly lower level closer to $1C^5$/ml. In the early stages of the pilot plant testing there were large differences in colony numbers between the individual filter steps, but these disappeared after about 30 days when the level stage (with respect to colony numbers) had been reached. Figure 62 shows the establishment of microorganism populations in the effluents from the pilot plant test adsorbers and Figure 63 shows similar microorganism establishments in the test adsorbers themselves.

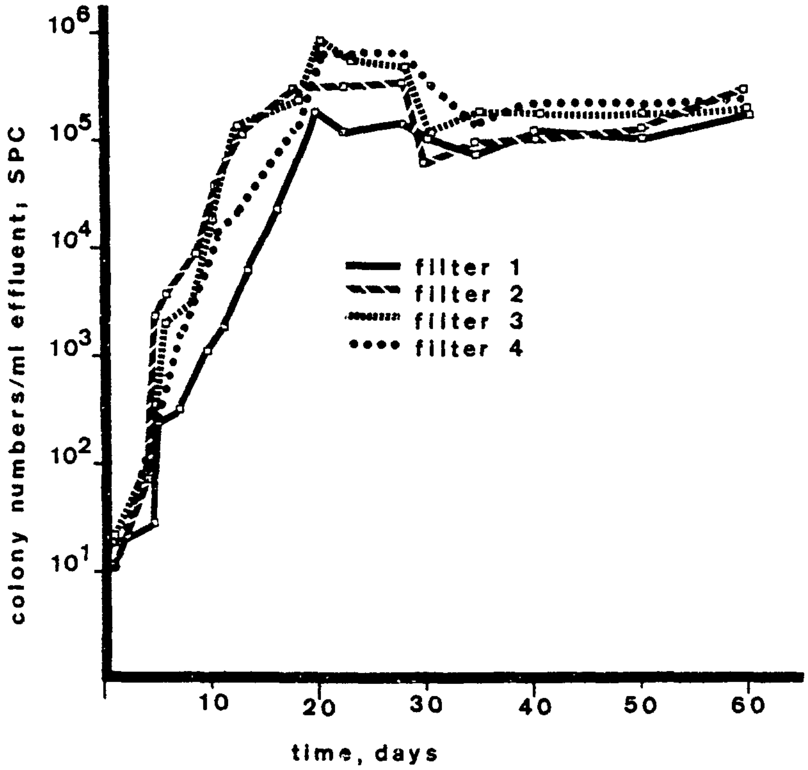


Figure 62. Development of colony counts in pilot plant GAC adsorber effluents at the Schierstein plant.

(Klotz et al., 1975)

Flow rate studies were conducted in the test columns using 4, 8 and 20 m/hr water velocities. The slope of the microorganism establishment curves (Figure 62) during the initial phase decreased with increasing velocity and with increasing column depth. The maxima were more pronounced as the velocity decreased. When the level stage was reached, there were only slight differences, however, the lowest colony numbers being observed at the lowest flow rate.

Microbiological & chemical conditions in a plant operating GAC adsorber--In Figure 64 are shown the colony numbers (living bacteria), cell numbers (living + dead bacteria) and free residual chlorine contents plotted against the adsorber depth (after an increasing number of filter steps). The low levels of colony numbers measured after the first two filter steps are explained by the low adsorber depth and the lack of sufficient contact time of the water passed through the GAC to destroy the free chlorine residual. The largest increase in colony numbers took place between steps 2 and 3 (after the free chlorine residual dropped to less than 0.1 mg/l), and there was no further increase between step 4 and the outlet.

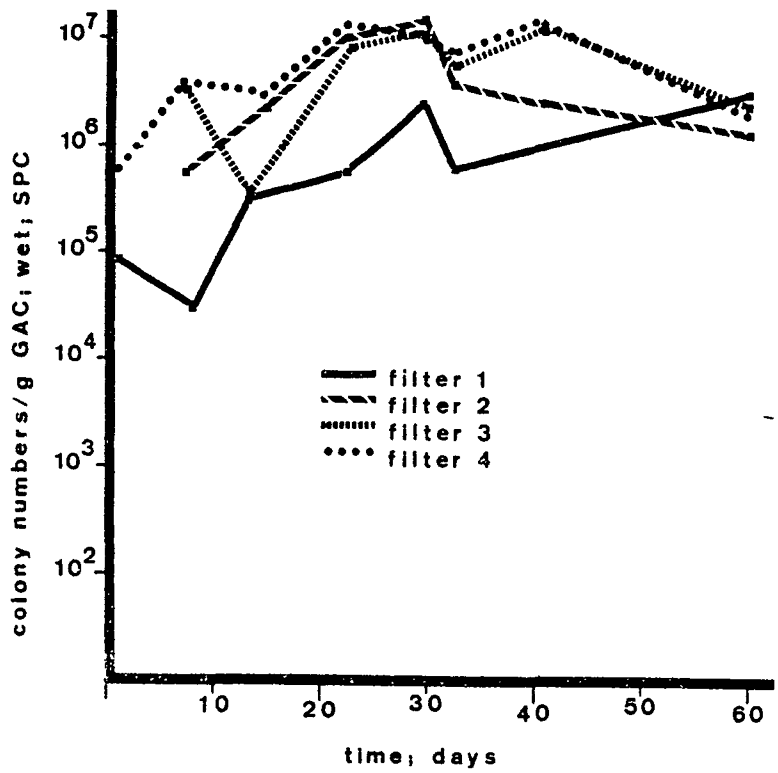


Figure 63. Development of colony counts in GAC of pilot plant adsorbers at Schierstein plant.

(Klotz et al., 1975)

In the uppermost activated carbon layers the residual chlorine content fell below 0.1 mg/l, where it no longer had any influence on the levels of living bacteria. Before the free chlorine concentration was lowered by the first GAC adsorber, the level of living bacteria was low, although the total cell numbers were high. After the chlorine content was lowered, the number of living bacteria increased rapidly, although the total cell numbers remained relatively constant.

Changes in dissolved oxygen and carbon dioxide contents of the water are indicators of the amount of microbial activity, as shown in Figure 65.

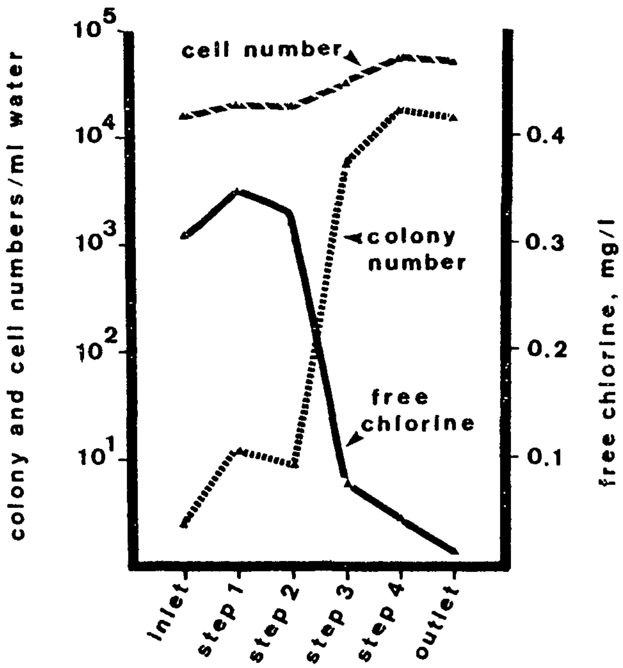


Figure 64. Colony & cell numbers and free chlorine contents as functions of GAC adsorber length.

(Klotz <u>et</u> <u>al</u>, 1975)

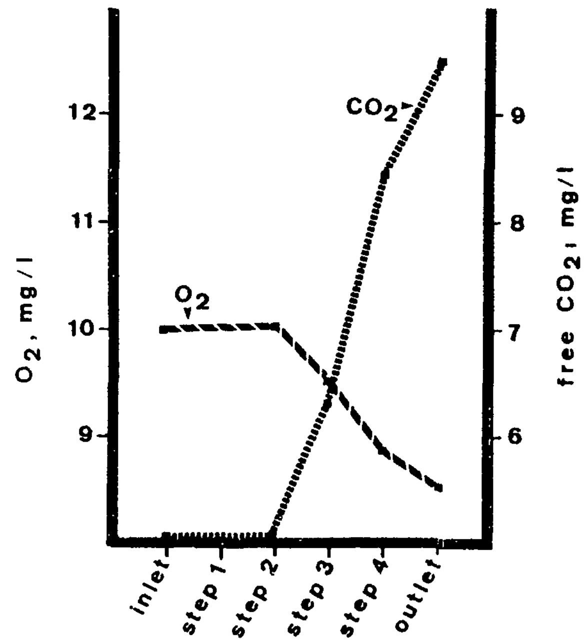


Figure 65 Oxygen and CO_2 contents of GAC effluents vs. adsorber depth.

(Klotz <u>et</u> <u>al</u>, 1975)

During passage through the GAC media there was an oxygen consumption of approximately 1.5 mg/l, most of which occurred after step 2, and a concurrent production of approximately 4.5 mg/l of CO_2, which also occurred mostly after step 2.

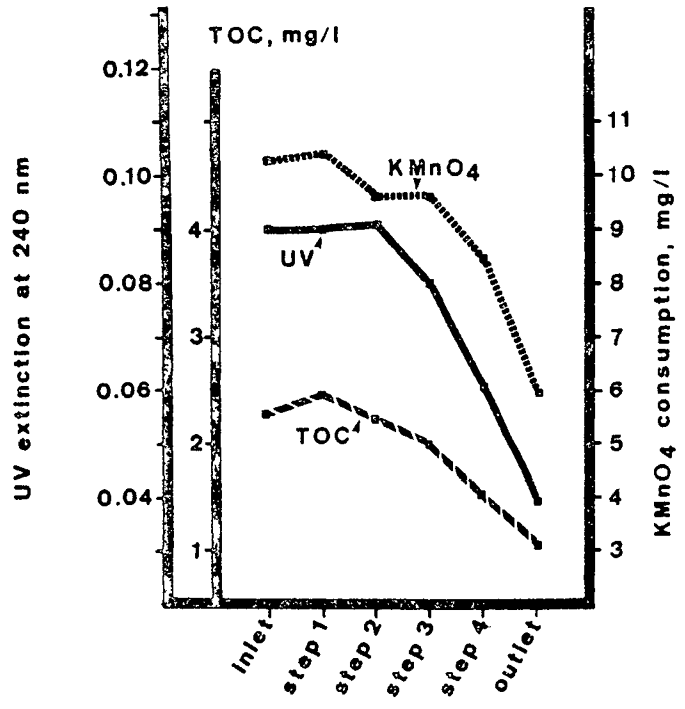


Figure 66. Organics content of GAC effluents vs. adsorber depth.

(Klotz *et al.*, 1975)

The change in organic content was followed (Figure 66) by three parareters. By UV absorption at 240 nm and TOC analyses, the content of organics decreased 55% after the fourth GAC filter step, and by about 45% as measured by the $KMnO_4$ consumption.

Behavior of microbial populations over a three year period--Figure 67 shows the colony counts/ml at the plant processing inlet (after aeration and settling), at the GAC adsorber inlet (after rapid sand filtration) and after passage through GAC adsorbers during the 3-year period May 1972 through August 1975. The numbers 1, 2 and 3 in this figure indicate changes in raw water qualities which resulted in distinct changes in colony numbers at the points indicated.

It appears noteworthy to the current reviewers of this work that there was an apparent breakthrough of colony counts through the GAC adsorbers after about three years of use. This indicates that there should be a GAC regeneration parameter based on colony counts as well as an organic component

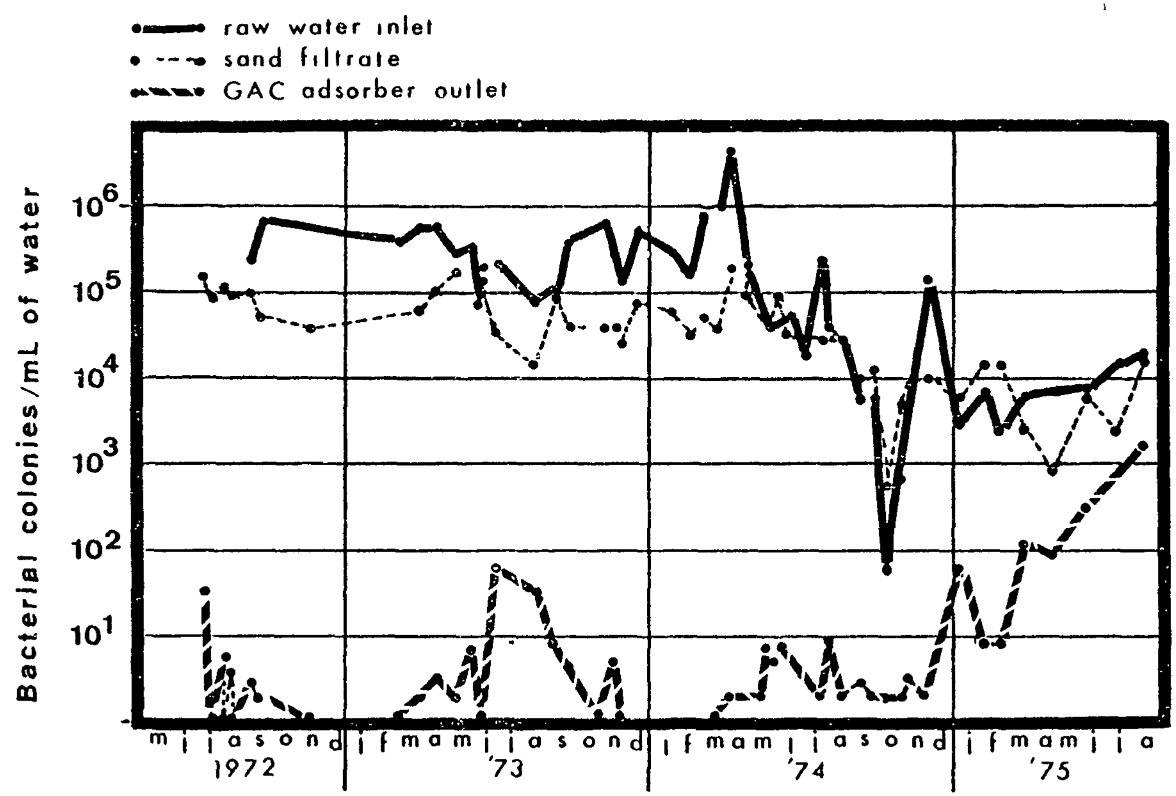


Figure 67. Behavior of microbial populations on GAC over 3 years at Wiesbaden, F. R. Germany.

(Klotz, Werner & Schweisfurth, 1975)

parameter, at least in plants opting to install a biological activated carbon process involving aeration and chlorination as the pretreatment steps. No data are available on microbial breakthrough, however, with processes using ozonation as the preoxidation step. This possibility of bacterial breakthroughs under BAC processing conditions should be evaluated.

Klotz, Werner & Schweisfurth (1975) also reported that they had determined large differences in colony numbers, as determined by the 7-day versus 2-day incubation technique, at five other German waterworks, each of which uses different treatment methods and utilizes different raw water qualities. They also stated that similar observations have been reported by scientists in Switzerland and the Netherlands, without giving supporting data or citing specific references.

Klotz, Werner & Schweisfurth (1975) also state that there seemed to be a tendency for decreased microbial activity in the Schierstein plant GAC adsorbers during winter, as indicated by lower oxygen consumption and CO_2 production data (which are not presented).

Activity of microorganism populations in the GAC adsorbers--In order to determine the relative contribution to removal of organic materials from solution by adsorption alone and by adsorption plus microbial activity, parallel tests were conducted using two pilot plant GAC adsorber test units. Each test unit consisted of four glass tubes connected in series (water passed through the tubes one after the other). Each glass tube had an inside diameter of 6 cm. The GAC bed depth in each glass column was 0.5 m, therefore the total GAC bed depth in each test unit was 2 m (4 x 0.5 m) and both 4-column pilot plant test units were operated under similar conditions. One of the test units was kept free of microorganisms by sterile filtration for more than two months, during which time about 15 cubic meters of water was passed through this sterile unit before it became bacterially contaminated. All other methods of keeping the test units sterile have the disadvantages of the presence of an additional bactericidal agent and of a large number of dead organisms.

In order to increase the amount of biodegradable organic substances, the inlet water was loaded with about 50 mg/l of phenol during the second phase of the test. This level of phenol is not toxic to the bacteria (Werner, Klotz & Schweisfurth, 1978).

Results of these tests are listed in Tables 37 and 38. When the GAC adsorber inlet was unloaded (the sand filtrate), the microorganism contribution to removal of organics was very small, as far as could be measured by UV absorption, dissolved organic carbon (DOC) and $KMnO_4$ consumption. On the other hand, the contribution of microorganisms to the decrease in easily biodegradable organics concentration was very high. This is of special importance because it means that the regrowth of bacteria, which can occur in distribution systems (feeding upon the easily biodegradable organics), now can be made to occur in the waterworks itself.

TABLE 37. PERCENTAGE OF BIOLOGICAL REMOVAL OF ORGANIC SUBSTANCES DURING PASSAGE THROUGH GRANULAR ACTIVATED CARBON

Raw Water Parameter	Sand Filtrate	Sand Filtrate Using Phenol-loaded Influent
DOC	<1.0%	6.0%
$KMnO_4$ consumption	3.7%	3.1%
UV Absorption, 240 nm	<1.0%	2.8%
UV Absorption, 254 nm	1.2%	6.2%
BOD_2	69%	---
BOD_5	46%	---
BOD_{20}	17%	---

Source: Klotz, Werner & Schweisfurth, 1975

TABLE 38. MICROBIOLOGICAL SHARE OF OXYGEN CONSUMPTION AND CO_2 PRODUCTION DURING PASSAGE THROUGH GRANULAR ACTIVATED CARBON

Raw Water Parameter	Sand Filtrate	Phenol-loaded Sand Filtrate
Oxygen Consumption	58%	68%
Carbon Dioxide Production	61%	64%

Source: Klotz, Werner & Schweisfurth, 1975

When the GAC adsorber inlet contained 50 mg/l of phenol, the activity of the microorganisms was slightly higher in the GAC media. It must be remembered, however, that the adsorption capacity of GAC for phenol is very high.

Electron-scan microscopic examination of GAC adsorber granules--During passage of water through GAC adsorbers, the concentration of microorganisms increases from about 10 colonies/ml to about 100,000/ml. Since the doubling period (under optimum conditions in the laboratory) for bacteria is about 20 minutes, this led to the conclusion that the increase in numbers of microorganisms actually measured has to emanate from the bacteria already present on the activated carbon. This is because the water remained in contact with the GAC for a short time only, which was insufficient to allow for the increases in colony numbers/ml actually measured.

Tests showed that there were colony numbers of up to 10^8/g of wet material on the activated carbon. The actual cell number, obtained by counting cells, could exceed these numbers by almost 100%.

A variety of electron-scan microscopic tests of activated carbon samples treated differently showed the same general distribution of the microorganisms on GAC adsorber granules. As a rule, the microorganisms were found to be sparsely scattered, and were always in the form of a single bacterial layer. The activated carbon surface area available (up to a pore diameter of 1 micron) was only fractionally utilized (about 1%). This was shown to be the case even when the activated carbon had been in contact with a nutrient solution for some time. These findings tend to confirm those of Van der Kooij (1975), who found that only a single bacterium was present, on the average, for each 40 sq microns of available surface area.

Adsorption of microorganisms onto activated carbon--Tests to determine the degrees of adsorption of microorganisms on activated carbon were conducted using starved and washed bacteria (mixed populations) in nitrogen-free environments. Figure 68 shows an adsorption isotherm of bacteria loaded on activated carbon as a function of the adsorptive concentration. At high colony numbers (above 10^{10}) the system tended toward saturation. At colony numbers of 10^7, 90% of the bacteria were adsorbed.

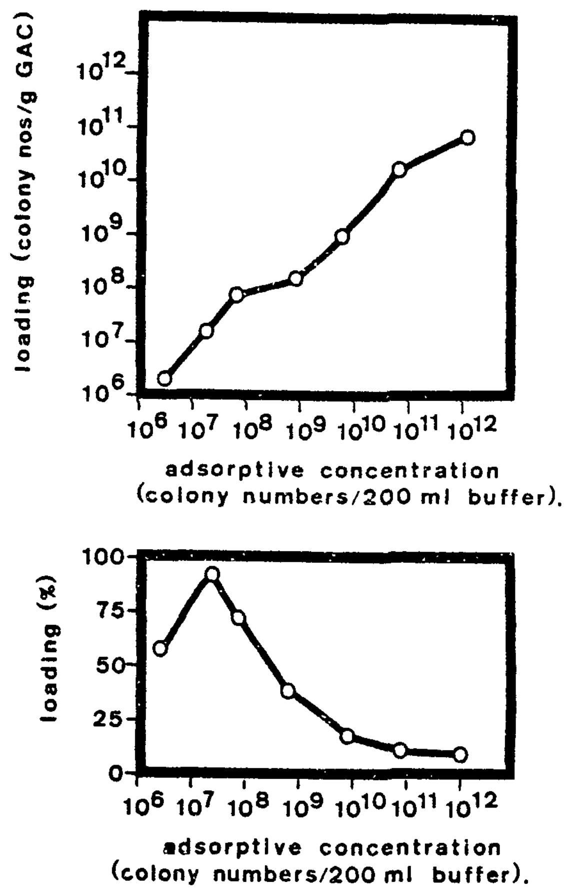


Figure 68. Microbiological loading of GAC--dependence on adsorptive capacity.

(Klotz, Werner & Schweisfurth, 1975)

Study of the influence of time on bacterial adsorption proved to be difficult, since it was impossible to avoid bacterial increase followed by bacterial extinction processes over extended periods of time (Figure 69). After an incubation period of 20 to 30 hours, adsorption and desorption of bacteria were nearing a steady state equilibrium condition. With increasing ion concentration (phosphate buffer at pH 7.2) the bacterial loading of the activated carbon increased as shown in Figure 70. No dependence of adsorption on temperature in the range of 5° to 37°C nor of pH over the range 5 to 8 was noted. Dead bacteria were found to be slightly better adsorbed by activated carbon than were living bacteria.

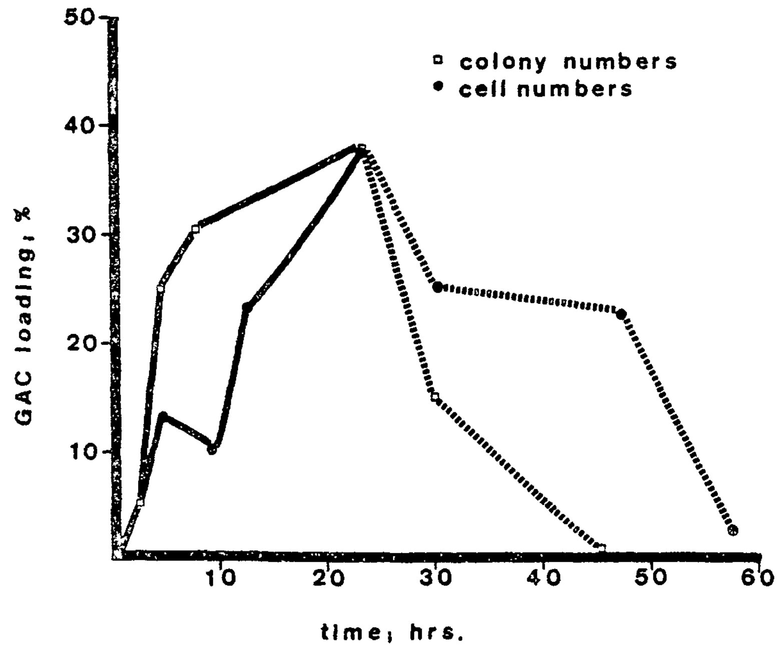


Figure 69. Dependence of microorganism loading of GAC with time.

(Klotz et al., 1975)

In a later report of continuing work at the Schierstein plant, Klotz, Werner & Schweisfurth (1976) pointed out that their technique for removing bacteria adhering to activated carbon samples was to mix them with water using a simple, domestic blendor (Braun MX 32) set at exactly the same rotational speed and for the same lengths of time for each sample. Both low nutrient P-agar (Wolters & Schwarz, 1956) and high nutrient SPC-agar gave the optimum numbers of colonies after 7 days of incubation at 27°C. Lower colony numbers were found using meat extract agar incubated at 27° and 37° as well as using gelatin incubated at 22°C (see German Unit Standards for Water, Wastewater and Mud Testing, 3rd Edition, 1960).

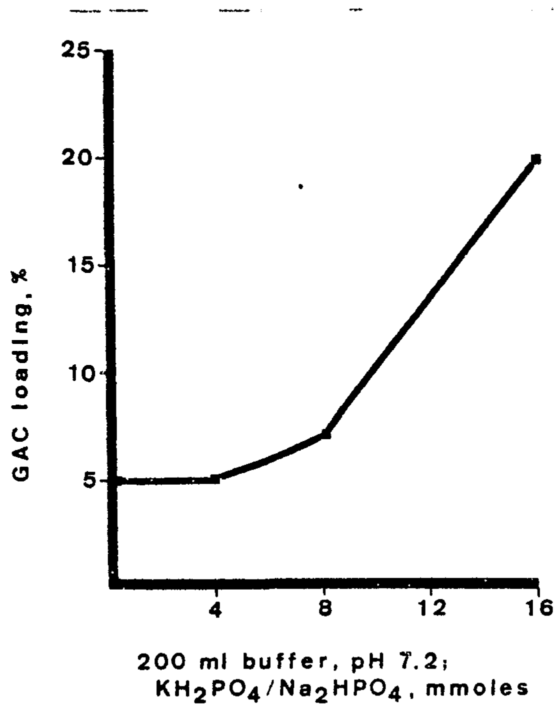


Figure 70. Dependence of microorganism loading of GAC with ion concentration.

(Klotz et al., 1975)

Colony numbers were measured using these three nutrient media at the outlet of the Schierstein plant GAC adsorbers for nearly one year (Figure 71). The colony counts/ml of the GAC adsorber influent were about 100/ml, but the effluents contained 1,000 to 100,000/ml, depending upon the season of the year (temperature) and upon changes in raw water quality.

When the full-scale pilot plant GAC adsorbers were used for the first time with new charges of GAC, colony numbers increased both in the adsorbers and in the new GAC effluents, even though the adsorber influent waters contained, as a rule, 0.5 to 1.0 mg/l of free residual chlorine, and sometimes contained even 4 mg/l (see Figure 72). The maximum colony numbers (10^5 to 10^6/ml of water in the effluents) were attained within 10 to 20 days after placing the GAC in service.

Different numbers of colonies were found at various GAC column depths, depending upon the length of time the particular carbon adsorber had been in service. This behavior was explained on the basis of free residual chlorine content. In the first of four pilot plant test columns connected in series, low colony numbers and greater than 0.1 mg/l concentrations of free residual chlorine were found. However a significant decrease in residual chlorine and an increase in bacterial numbers were measured after stage 2, which then remained constant after stages 3 and 4. Samples of spent GAC from the plant adsorbers were found to contain about 10^8 bacteria/g of wet weight carbon.

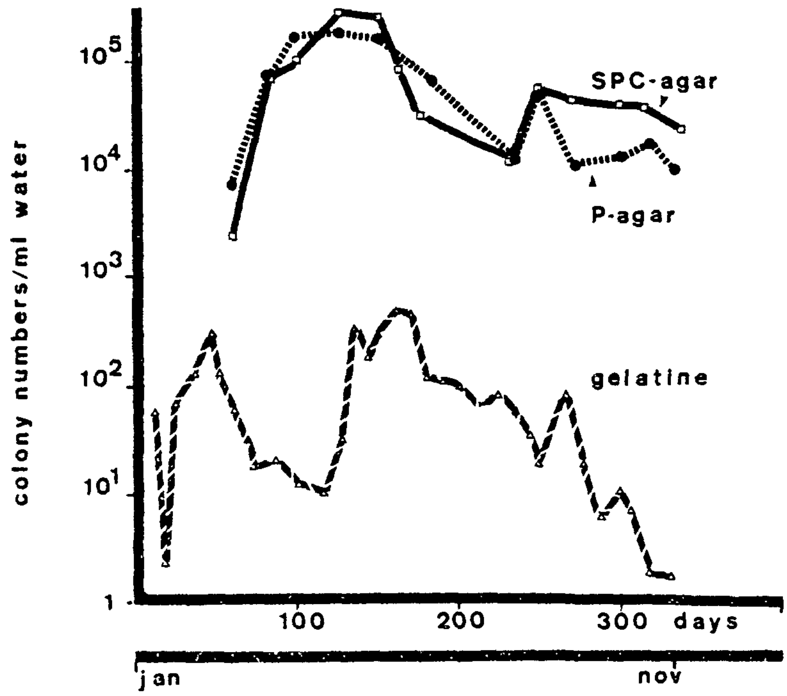


Figure 71. Fluctuation of colony numbers in GAC adsorber effluents at Schierstein plant during 1 year.

(Klotz et al., 1976)

Increasing the length of the adsorber columns (by connecting two or more in series) did not increase the number of colonies measured in adsorber effluents.

Short time reductions in the number of colonies present in the GAC adsorber effluents were brought about by backwashing using water from the adsorber outlets. The backwash water showed an increase in colony numbers after being used for backwashing (Figure 73), and these increases could result only from a lowering of the counts in the activated carbon adsorption media. This means that some of the bacteria were washed out of the activated carbon columns. However, the magnitude of the colony count lowering upon backwashing was not significant, in terms of decreasing the biochemical degradation efficiency for removing dissolved organics. Figure 73 shows that the numbers of colonies/ml in the activated cardon adsorber effluents at the steady state (before backwashing) was 5 to 8 x 10^4. This level rose above 10^5 just before backwashing and dropped to 10^3 to 10^4 just after backwashing. However, the steady state level of colony counts/ml was reattained after passage of 1,000 to 1,500 cubic meters (0.25 to 0.4 million gallons) of water. This required about 2 days.

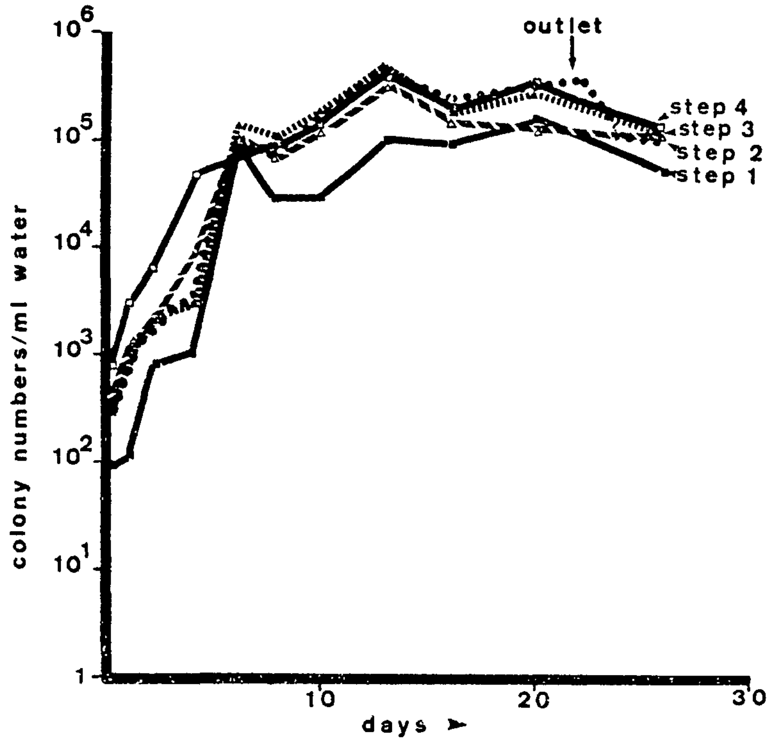


Figure 72. Development of microbiological activity in full scale adsorber with new GAC at Schierstein plant.

(Klotz et al., 1976)

In all investigations conducted by Klotz, Werner & Schweisfurth (1976) none of the effluents from any of the biologically operating activated carbon adsorbers showed the presence of any fecal indicators. Filamentous fungi and yeasts occurred randomly, but rarely in all investigations. Yeast numbers were lower than those of filamentous fungi. No substantial differences were found in comparing waters from the Wiesbaden (Schierstein) plant with those of the Frankfurt (Niederrad) Waterworks. Both of these plants are located near each other in the southern part of the Federal Republic of Germany. Schierstein draws water directly from the River Rhine and Frankfurt draws water from the River Main. It is important to recognize, however, that the quality of the River Rhine is much better than that of the River Main (Werner, 1979).

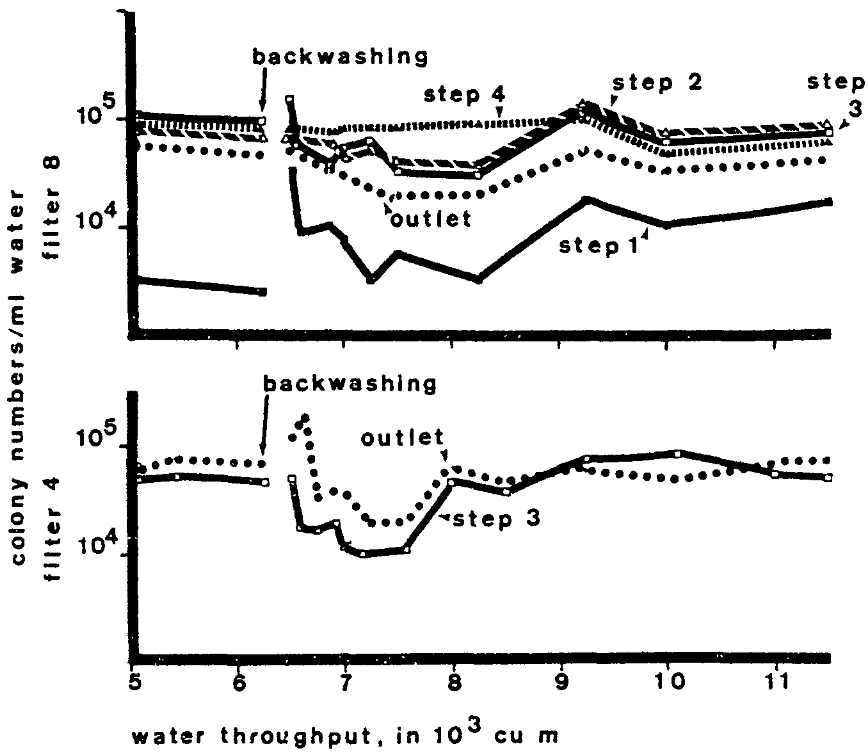


Figure 73. Changes in colony numbers at each GAC step and outlet in Schierstein plant.

(Klotz et al., 1976)

In all test results reported using the Schierstein plant GAC adsorbers, Klotz, Werner & Schweisfurth (1976) found correlations between microbiological and chemical/physical data only with respect to chlorine content and temperature.

In pilot plant tests conducted at the Schierstein plant, Klotz, Werner & Schweisfurth (1976) employed four identical glass tubes (4 cm diameter, 1.2 m in length) and connected in series, then filled with 80 cm of the same granular activated carbon used to charge fresh GAC into the full-scale Schierstein plant. This amount of GAC corresponded to a wet weight of about 1 kg. The adsorbers then were filled with chlorinated sand filtrate water from the main plant.

Flow velocities of water through the (fresh) GAC adsorbers (4, 8 and 20 m/hr) were found to influence the development of microbiological activities. The higher the velocity the more slowly the maximum values of colony counts/ml were reached in the filtrates (Figure 74). The maxima were highest for the slowest flow rate (4 m/hr) and they were attained faster at the slow flow rate. On the other hand, at the highest flow rate (20 m/hr), higher colony counts/g of GAC eventually resulted (Figure 75). Therefore, more bacteria were formed per unit time at such flow rates, which resulted in higher amounts of microbiological activity.

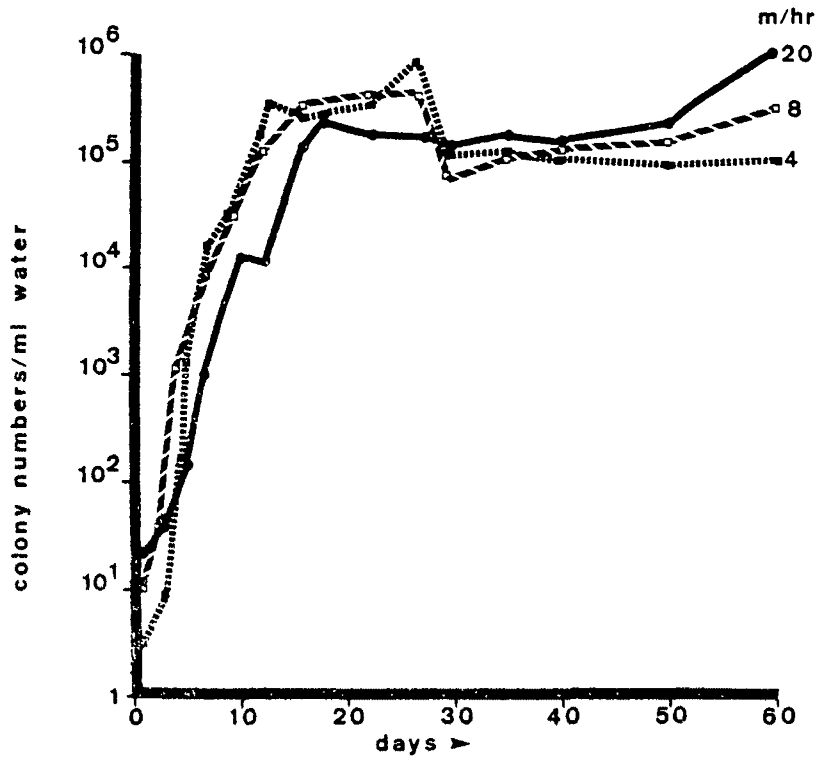


Figure 74. Development of colony numbers in effluents of new GAC pilot plant adsorbers as a function of flow rate at Schierstein plant.

(Klotz et al., 1976)

On the other hand, at slow flow rates, media conditions were created which had a favorable effect on the reproduction of filamentous fungi. Yeasts were found infrequently. Backwashing resulted in lowering the colony numbers in the adsorber effluents for a short period of time, and this effect was most pronounced for the adsorber group having the slowest throughput flow rate.

Similar behaviors with respect to bacterial growth rates in new batches of granular activated carbon were observed with LWS, ROW, ROW Supra and

F-100 carbons (Figure 76). LWS Carbon showed about one-half an order of magnitude lower colony counts/ml in the adsorber outlets than did the other three activated carbons tested.

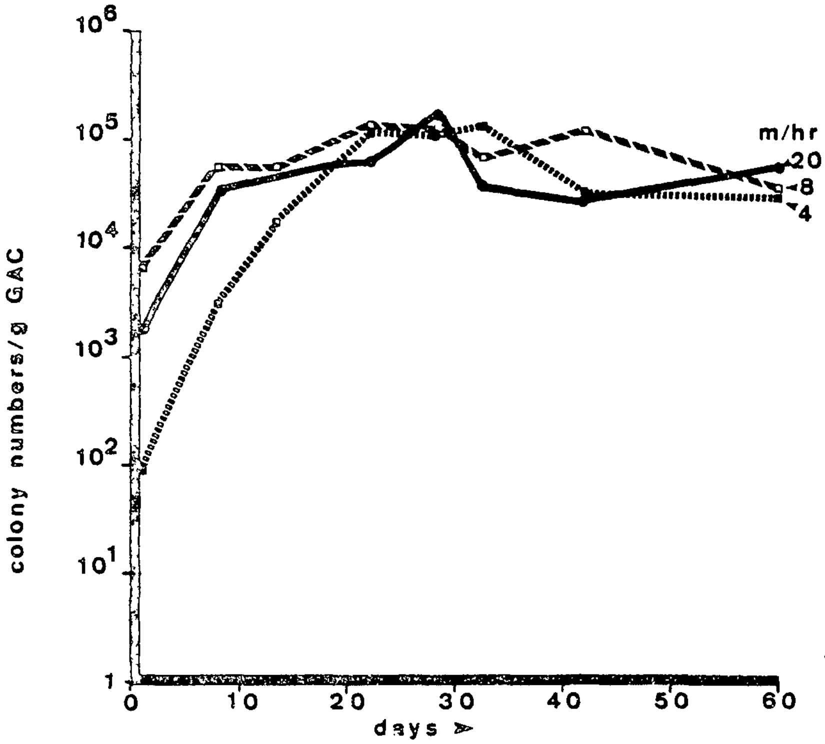


Figure 75. Development of colony numbers in new GAC charges in Schierstein pilot plant adsorbers as a function of flow rate.

(Klotz et al., 1976)

This work of Klotz, Werner & Schweisfurth (1976) confirmed that data obtained using the pilot plant test units could be related directly to data obtained using the full scale plant GAC adsorbers, with respect to colony numbers and the trends noted in these numbers with time.

Werner, Klotz & Schweisfurth (1979) presented additional data to substantiate their earlier conclusions regarding the extent of microbiological activity in the Schierstein (Wiesbaden) water treatment works granular activated carbon adsorbers. Raw water before chlorination generally contained 2 x 10^5 colony counts/ml and these decreased to about 1,000/ml before entering the activated carbon adsorbers. With high level prechlorina-

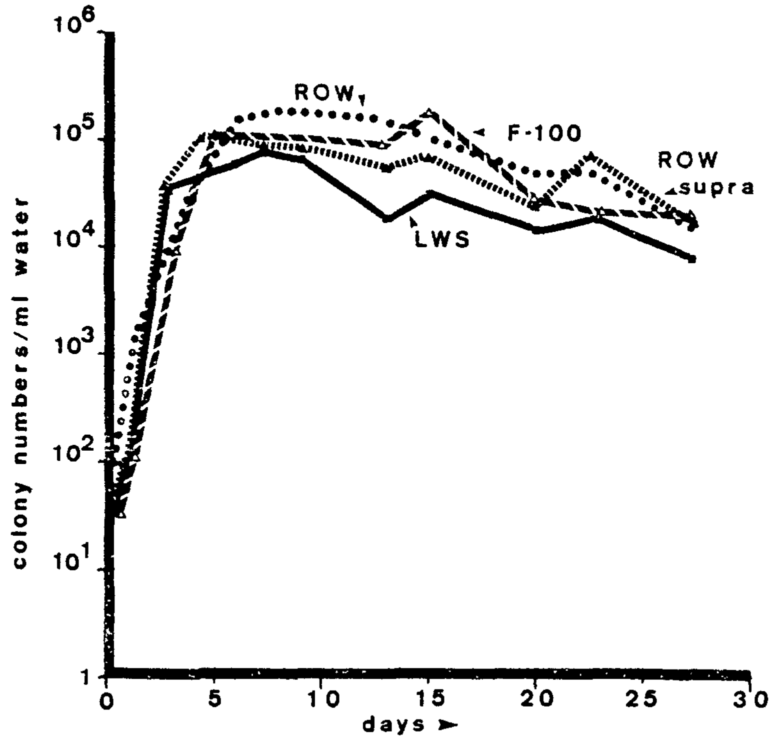


Figure 76. Development of colony numbers in effluents of pilot plant adsorbers with different types of GAC at Schierstein plant.

(Klotz *et al.*, 1976)

tion, almost all the bacteria originally present were killed and the GAC adsorber inlet waters contained very few colony counts.

In the activated carbon adsorbers the number of bacteria again increased to values around 7 x 10^4/ml. The activated carbon media were shown to contain about 1,000 times more bacteria per unit volume than did the carbon adsorber effluents.

The number of living cells was determined by enzymatic methods, rather than by culture methods, and the total number of cells (living plus dead bacteria) was determined microscopically by counting them after membrane filtration. Colony count determinations measured up to 20% of all living bacteria and up to 5% of the total (living + dead) cells.

Through a population comparison made by numerical taxonomy methods and comparison of the morphological and biochemical qualities of the bacterial strains identified as being present in the activated carbon media (using a computer program), it was found that:

1) The ability of the bacteria to adapt in the activated carbon adsorbers was less marked than their ability to adapt in raw water.

2) There was a higher percentage of pseudomonas bacteria present in the carbon adsorbers than in the raw water,

3) Bacterial populations can be differentiated clearly by the use of substrate, and especially by their reactions to toxic substances.

Based on these findings, Werner, Klotz & Schweisfurth (1979) concluded that a special microorganism population forms in the activated carbon adsorbers (at least those in use at the Schierstain water treatment plant).

Identification of microorganism populations--To date, 26 species of 11 genera of microorganisms have been isolated from the Schierstein plant GAC adsorber effluents by the University of Saarland scientists (Werner, Klotz & Schweisfurth, 1979), and these are listed in Table 38A. Most of the microorganisms present belong to the genera Pseudomonas. The families Bacillus and Azomonas also are represented to a considerable extent. These bacteria found to date are non-pathogenic in nature, and are generally found in water.

Table 39 lists the filamentous fungi and yeasts found in the effluents from the biologically-loaded granular activated carbon adsorbers of the Schierstein water treatment plant. These filamentous fungi and yeasts occurred rarely and irregularly in the effluents, hence their role in water treatment is considered by Werner, Klotz & Schweisfurth (1979) to be of secondary importance. The fungi identified to date all are apathogenic.

Performance of the bacteria--Activated carbon adsorbs dissolved organic substances, which can act as substrate for bacteria, but also adsorbs bacteria. Figure 77 shows the Freundlich adsorption isotherms for the adsorption of bacteria onto activated carbon.

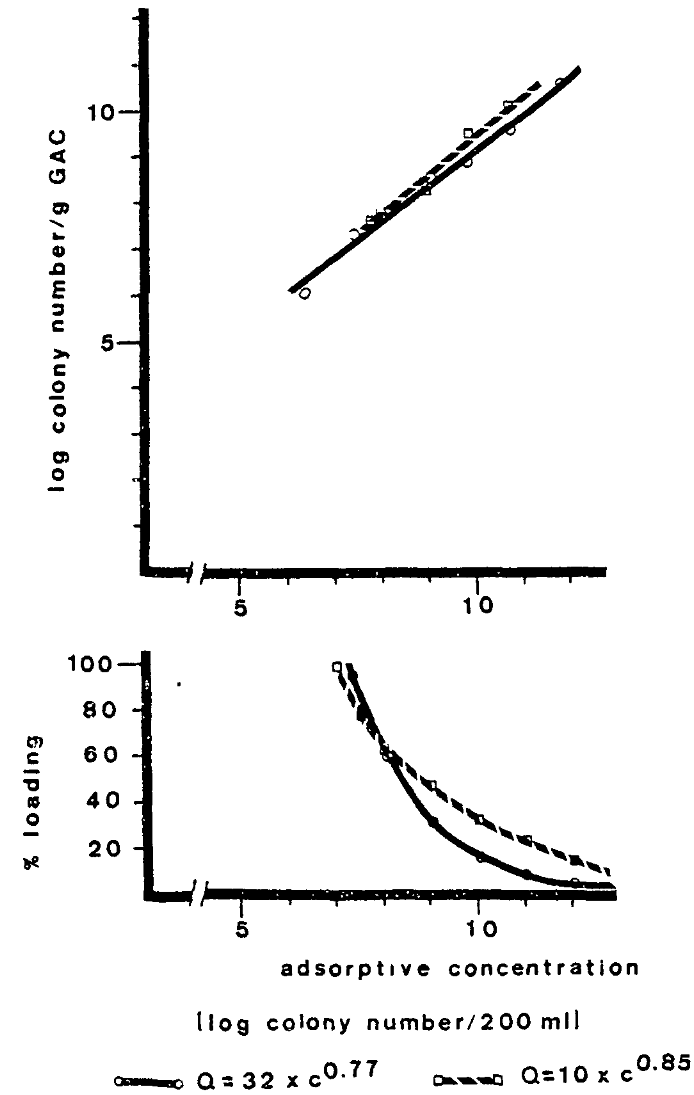


Figure 77. Bacterial adsorption on GAC.

(Werner et al., 1978)

TABLE 38A. BACTERIAL SPECIES FOUND IN EFFLUENTS OF GRANULAR ACTIVATED CARBON ADSORBERS AT THE SCHIERSTEIN (FRG) PLANT

Pseudomonas alcaligenes	Chromobacterium violaceum
Pseudomonas cepacia	Neisseria sicca
Pseudomonas facilis	Acinetobacter calcoaceticum
Pseudomonas fluorescens	Micrococcus luteus
Pseudomonas lemoignei	Staphylococcus saprophyticus
Pseudomonas mendocina	Bacillus cereus
Pseudomonas ruhlandii	Bacillus circulans
Pseudomonas stutzeri	Bacillus licheniformis
Pseudomonas spec.	Bacillus megaterium
Gluconobacter oxidans	Bacillus pumulis
Azomonas agilis	Bacillus thuringensis
Azomonas insignis	Corynebacterium spec.
Azomonas macrocytogenes	Micromonospora spec.

Source: Werner, Klotz & Schweisfurth, 1978

TABLE 39. TYPES OF FUNGI AND YEASTS FOUND IN EFFLUENTS OF GRANULAR ACTIVATED CARBON ADSORBERS AT THE SCHIERSTEIN (FRG) PLANT

Filamentous fungi	Phialophora hoffmannii
	Phialophora mutabilis
	Taphrina spec.
Yeasts	Rhodotorula minuta var. texensis
	Cryptococcus uniguttulatus
	Candida guillermondii var. guillermondii
	Hansenula anomala var. anomala

Source: Werner, Klotz & Schweisfurth, 1978

Because of the great difference in size between bacteria and organic molecules, the two are separated from each other after adsorption because of the porous structure of the activated carbon. The smaller, organic molecules are adsorbed mostly in the micropores of the activated carbon, which represent about 99% of the total available surface area. On the other hand, the much larger bacteria cannot be adsorbed in the micropores, but only on the surface and in the macropores, which make up about 1% of the total activated carbon surface area available for adsorption. This has a negative secondary effect on the metabolism of the bacteria.

In the absence of activated carbon, both bacteria and substrate are uniformly distributed in the aqueous medium.

As confirmation of these statements, Figure 78 shows plots of the metabolic activity of bacteria (measured by oxygen consumption) versus time. The initial colony counts/ml of bacteria with or without activated carbon being present were 1.2×10^8/ml and the water solution also contained 0.1

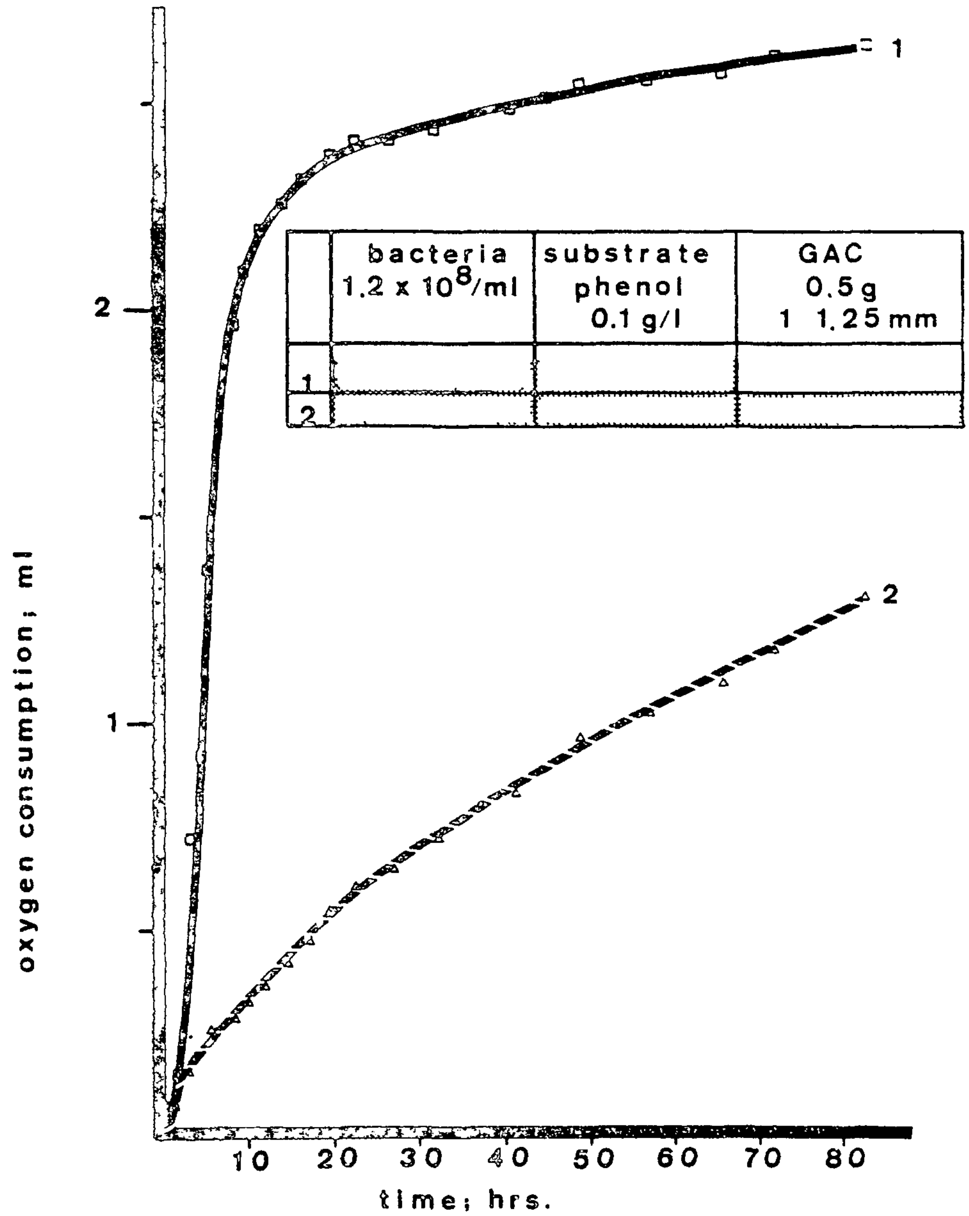


Figure 78. Effect of GAC on metabolic activity of bacteria.

(Werner et al., 1978)

g/l (100 mg/l) of phenol to act as a substrate for the bacteria. The upper curve (data obtained in the absence of activated carbon) shows that the phenol substrate was utilized rapidly by the bacteria (most within the first 24 hours). On the other hand, when 0.5 g/l (500 mg/l) of granular activated carbon (1 to 1.25 mm particle size) was added to a second solution containing the same number of colony counts/ml and the same amount of phenol, less than half of the substrate was utilized after 80 hours of contact than was utilized within 24 hours when activated carbon was absent.

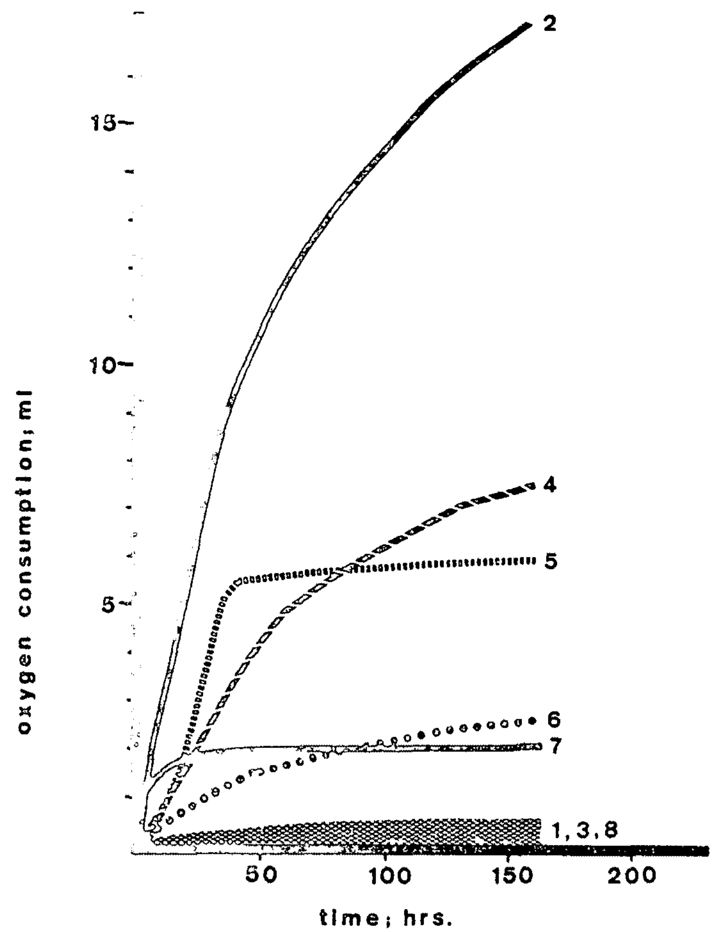
Activated carbon also provides a positive effect on the metabolism of bacteria, however. It enriches the concentration of organic substances in the adsorber media and increases their residence times in the adsorber. In addition, there is provided a "buffering action" of the system for organic substances which are toxic to the bacteria present. These effects are shown by the data plotted in Figure 79, in which 8 experiments were conducted with solutions initially containing 3.5×10^8 colony counts/ml. To four sets of two solutions were added 2.5, 1.0, 0.3 and 0.1 g/l quantities of phenol. In lower concentrations, phenol can serve as substrate (food) for the bacteria, but in the higher concentrations, phenol is toxic to the same bacteria.

To one of each of the four sets of solutions containing 3.5×10^8 bacterial colony counts/ml and added phenol now was added 0.5 g/l of granular activated carbon (1 to 1.25 mm particle size) and the rates of oxygen consumption were determined over a period of 200 hours.

At the highest phenol concentration (2.5 g/l -- 2,500 mg/l)) the solution without activated carbon showed no metabolic activity (zero oxygen consumption over 160 hours) (curve 1), proving that at this concentration phenol is toxic to the bacteria present. However, when 0.5 g/l of granular activated carbon was added to the duplicate solution containing 2.5 g/l of phenol, this sample showed the highest rate of oxygen consumption of all samples tested (curve 2). Therefore, it can be concluded that the activated carbon adsorbed the toxic quantity of phenol, rendering the aqueous solution harmless to the bacteria. This allowed the bacteria to remain viable. The adsorbed phenol then was slowly released into solution, in non-toxic concentrations (probably by desorption mechanisms), where it either passed through the activated carbon adsorber to the effluent and/or was captured and metabolized by the bacteria. Once adsorbed on the activated carbon, high initial concentrations of toxic materials, such as phenol, can become a slow releasing source of dissolved organic carbon substrate for the bacteria.

Similarly, the solution containing 1 g/l of phenol also was toxic to the bacteria (no oxygen uptake noted after 160 hours) and the duplicate sample treated with 0.5 mg/l of activated carbon showed the second highest oxygen consumption rate over 160 hours.

Data obtained at the lower phenol concentrations, however, seemed to conflict with the hypothesis developed for the higher phenol concentrations. The sample containing 0.3 g/l of phenol and no activated carbon consumed oxygen at more than twice the rate than did the duplicate sample containing activated carbon. This apparently reversed behavior can be explained, however, by considering that the adsorption capacity of the weight of



	bacteria 3.5 x 10^8 ml	phenol substrate 2.5 g/l	1 g/l	0.3 g/l	0.1 g/l	GAC; 0.5 g 1 1.25 mm
1						
2						
3						
4						
5						
6						
7						
8						

Figure 79. Effect of GAC on metabolic activity of bacteria.

(Werner et al., 1978)

activated carbon added was sufficient to adsorb the total amount of phenol present. In this case, even low levels of phenol were not released into solution, and the net effect was total removal of biodegradable substrate from solution.

This postulate is supported by the fact that the solution containing 0.3 g/l of phenol was not toxic to the bacteria; the oxygen consumption measured for this sample was the third highest of the eight samples tested.

Further confirmation of this hypothesis can be developed by considering the data obtained with the samples containing 0.1 g/l of phenol. Again, the sample to which activated carbon was added showed no metabolic activity (zero oxygen consumption after 160 hours) whereas the sample without added activated carbon rapidly attained a low level of oxygen consumption.

The rapid attainment of a constant level of oxygen consumption by the samples containing 0.1 and 0.3 g/l of phenol without added activated carbon shows that the oxygen uptake rates are independent upon the concentration of phenol (over this concentration range). With the sample containing 0.3 g/l of phenol, the fact that this amount of oxygen consumption was not attained until after about 40 hours can be explained either by there being an insufficient concentration of bacteria present initially or that this phenol concentration exerts some toxicity to the bacteria, which is overcome later either by adaptation or by the increase in bacterial populations over that period of time.

Contribution of Bacteria to Water Treatment--

The following merits were found by Werner, Klotz & Schweisfurth (1979) to hold true for the treatment of Rhine River water with high level chlorination prior to filtration and granular activated carbon adsorption. At the time this phase of the research program at the Schierstein plant was conducted, the efficiency of the activated carbon adsorbers in removing dissolved organic materials was about 80%. During this study the bacterial contributions to the removal of organic materials (as measured by consumption of dissolved oxygen and production of CO_2 compared with the total dissolved organic carbon removed) were found to be as follows:

- 5% reduction in levels of dissolved organic carbon,
- about 70% reduction in levels of easily decomposed organic substances (BOD_2),
- about 17% reduction in levels of difficult-to-decompose organic substances (BOD_{20}),
- about 60% of theoretical oxygen consumption,
- about 60% of theoretical production of carbon dioxide.

It was noted by Werner, Klotz and Schweisfurth (1979), however, that as the adsorption efficiency of the activated carbon for dissolved organic substances decreased, the bacterial contribution to removal of organics increased "considerably". At the Schierstein plant, the already low biodegradability of the organic components originally present in the raw water was further lowered by the high level chlorination step.

Lowering the amounts of easily biodegraded organic substances in biologically operating granular activated carbon adsorbers has a significant effect on the regrowth of bacteria in water supply distribution systems. Through biologically active activated carbon adsorbers these organic materials are at least partially removed in the plant, rather than in the distribution system. Furthermore, the bacterial activity present causes a continuing partial regeneration of the activated carbon, and thus prolongs its operating life before reactivation is required (Werner, Klotz & Schweisfurth, 1979).

During June, 1978, Prof. Dr. Schweisfurth and his students, Drs. Klotz and Werner were interviewed regarding some of the unpublished details of their 6 years of microbiological studies at the Schierstein plant. The following additional information was supplied by these scientists in the form of unpublished information:

1) Normal plate counting techniques measure only 5 to 10% of the living bacteria actually present. However, enzymatically, 20% of the total cell numbers can be counted. Total colony counts determined on culture media provide information only regarding those types of bacteria which grow on the media. Not all types of bacteria grow on specific culture media.

2) E. coli bacteria present in the influents of biologically active filter/adsorber media are not found in the effluents because other bacterial strains dominate in the media and E. coli cannot grow under these conditions. They simply die off.

3) The Schierstein plant in Wiebaden has an operating rule which does not allow a GAC column to stand idle and off-line for more than two days. Otherwise plate counts increase significantly and the biology changes.

4) The dissolved organic content of the Rhine at Wiesbaden is 3 to 4 mg/l, which is comprises mostly of municipal sewage. No industries discharge in the area. Wiesbaden recently has prolonged the residence time in reservoirs ahead of the Schierstein plant, to provide 3-day residence times for Rhine River waters, and which are biologically active. Before the reservoir residence time was increased, the 4 mg/l DOC level of the plant influent water was lowered to 2.5 at the inlet to the GAC media, and to 1 mg/l exiting the biologically active GAC adsorbers. Since the increased reservoir residence time, DOC levels in the inlet to the GAC adsorbers are even lower.

5) Although BAC media may seem to operate somewhat like trickling filters, they are not the same. Trickling filters must have a skin of slime (formed by multiple layers of bacteria) in order to be effective. BAC media remove about 3 times the amount of dissolved organics from solution as do trickling filters. In trickling filter operation, dissolved organics are adsorbed only by the slime coating, which is of very low

surface area, and then is degraded. In BAC operation, organics are adsorbed on the carbon surface, in the macropores and also in the micropores, then are degraded.

6) Only about 1% of the available GAC surface area (the macropores) is occupied by bacteria, which are all greater than 1 micron in particle size. Therefore, bacteria occupy only about 1 sq cm/cu m of GAC.

7) No clogging of the BAC media has been observed at the Schierstein plant during the past 6 years of use. On the other hand, the Rhine River at Wiesbaden does not contain nutrients which are optimum for good bacterial growths. If such optimal nutrients were present, it is possible that clogging could occur.

8) Waters passed through sterile, virgin GAC with no bacteria present contained measureable quantities of CO_2 and consumed measureable amounts of dissolved oxygen. This shows that GAC can participate in chemical oxidation reactions, and these <u>may</u> continue to occur even after bacterial activity has reached a steady state. In the experiment reported earlier (Klotz, Werner & Schweisfurth, 1975) in which a GAC column had been kept sterile for two months, CO_2 was produced, after which time the column became biologically active and the experiment was discontinued. The amount of CO_2 produced represented 1.5% of the total generated.

9) In Warburg apparatus studies (measuring metabolic bacterial activity by oxygen consumption and CO_2 production), the size of the GAC granules was important. The smaller the particle size the faster was the rate of oxygen consumption, until the carbon granule approaches 1 mm. At this point clogging became prevalent and the apparatus then could not be aerated or backwashed. With large GAC particle sizes the time for transfer of adsorbed organics to the bacteria becomes longer. The mechanism probably involves desorption of the organic material from the micropores, followed by diffusion to meet the bacteria. With larger GAC particles, the process is believed to become diffusion controlled; with smaller GAC particles the process is desorption controlled.

10) In considering biological mechanisms occurring during GAC operation, it is possible that some bacterially secreted enzymes can leave the bacterial cells, then may diffuse into the GAC micropores and act on the adsorbed organics, desorbing them so that they can diffuse out of the micropores and into the areas occupied by the bacteria.

11) In another water works (not Schierstein) the GAC was removing about 30% of the dissolved organics present in the adsorber influents after 5 years of operation.

12) For sampling of an operating pilot plant GAC adsorber, the containers are opened (at the top) and a 0.5 cm diameter sterile pipe is inserted into the carbon medium to the measured depth. The open end of the pipe is closed with the thumb of the person sampling and the filled tube is removed and emptied. The 0.5 cm sampling pipe allows 4 g samples to be

taken. The Schierstein plant GAC adsorbers are 4 meters high, 3 meters in diameter and contain 2 to 3 meters of GAC depth. When the full-scale plant GAC was charged, 10 to 20 g samples of used GAC were taken at 4 to 5 column depths. Samples also were taken from the center out to the periphery of each bed. The samples were found to be homogeneous (with respect to the bacterial parameters measured) at the same bed depth of GAC out to the peripheries, and also were homogeneous after the first 30 cm of depth.

13) GAC samples were homogenized in sterilized tap water using a Waring Blendor type of mixer. After establishing the optimum dilution to provide the best number of colonies for counting, the Blendor should be calibrated. This is done by plotting time of homogenization versus colony counts. The peak is taken as the optimum time of homogenization for that Blendor (which is always operated at the same speed).

14) The amount of dissolved organic carbon removed from solution bacterially is not precisely equivalent to the amount of CO_2 produced. This is because some organic carbon is used by the bacteria for self-synthesis, and does not become liberated as CO_2. However, some bacteria die and are attacked by living bacteria. When this occurs, some of the carbon contained by the dead bacteria is released as CO_2. These two effects of carbon consumption and carbon release tend to balance each other, and it should be possible to follow the biological degradation of organics reasonably quantitatively by measuring the rate of CO_2 formed as well as the rate of consumption of dissolved oxygen.

CONCLUSIONS REGARDING MICROBIOLOGICAL ASPECTS OF BAC SYSTEMS

From the published works and private communications described in this sub-section and elsewhere in this report, the following major conclusions can be drawn concerning the microbiology present in operational BAC systems in drinking water treatment plants:

1) Bacterial activity develops rapidly in fresh charges of granular activated carbon (within 5 to 12 days of initiation of flow) and reaches a peak of 10^4 to 10^6 colony counts per ml of water or 10^6 to 10^8 per g of GAC present in 10 to 20 days. At biological equilibrium, counts usually are higher in the GAC media than in the effluents.

2) Standard plate count techniques (incubation at 27°C over 2 days) show relatively low colony counts in the filter/adsorber media and their effluents. Incubation over 7 days shows much higher colony counts, and is the procedure being used by German microbiologists at the University of Saarlands in their studies.

3) These high bacterial activities occur even in the presence of free residual chlorine in the GAC media influents. There is an indication that when chlorinated influents (containing as high as 0.5 mg/l free residual chlorine after breakpoint chlorination) are passed through biologically operating activated carbon media, chlorine-resistant bacteria can be present in the effluents.

4) High bacterial levels in the activated carbon effluents can be destroyed using low dosage levels of chlorination (0.2 to 0.3 mg/l in Germany; up to 0.5 mg/l in France) or of chlorine dioxide (0.15 to 0.3 mg/l) provided that extraneous chlorine- or chlorine dioxide-demanding materials are absent.

5) At least 20 species of bacteria, 3 species of filamentous fungi and 4 species of yeasts have been identified in effluents from operating GAC units at the Schierstein plant at Wiesbaden. During the studies reported, this plant used aeration, breakpoint chlorination and rapid sand filtration as pretreatment before GAC adsorption. All microbial populations identified to date are non-pathogenic soil and water organisms.

6) *E. coli* bacteria do not appear to survive in competition with other types of bacteria present in biological activated carbon media used for treating drinking water. Therefore, *E. coli* bateria are not normally found in BAC media effluents. However, this conclusion must be based on the assumption that the BAC adsorber is properly sized (provides sufficient empty bed contact time) and is operated at a sufficiently slow throughput velocity.

7) No publications are known which deal with the question of endotoxins present in effluents from operational BAC systems.

8) Backwashing of operating BAC units lowers bacterial counts in the activated carbon media (and raises them in the backwash water), but not sufficiently to lower the degree of water treatment being sought (organic compound removal or nitrification). Counts return to normal within 2 days after backwashing.

9) GAC units containing microbiological growths taken off-line are not allowed to stand idle for more than two days, otherwise the microbiology changes and colony counts increase significantly.

10) There are no known incidents of biological fouling of operating BAC systems in Europe. If anything, the use of ozone as the preoxidant lengthens the time between backwashing of both the sand filters and GAC adsorbers (at the Dohne plant, Mülheim, FRG).

11) After 5 years of use, GAC adsorbers at another German water works (not Schierstein) were removing 30% of the dissolved organic carbon present in the adsorber influents.

12) On the other hand, results obtained by Van der Kooij (1979) showed that colony counts in the filtrates from sand, granular non-activated carbon and granular activated carbon filters were about the same. This indicates that the high colony counts usually observed in GAC filter/adsorbers are independent of the amount of organic materials adsorbed by the GAC.

13) The maximum removal of organic materials present in BAC adsorber influents (50% at biological equilibrium) was found during pilot plant studies at the Auf-dem-Werder plant at Bremen, FRG, but without the use of preozonation. In this case, a special GAC was employed which had a high percentage of macropores (to house a higher level of biological activity). In all other water treatment plants known to be utilizing BAC processes, the degree of removal of dissolved organic materials at the biological steady state is 25% to 35%, even with preozonation. It is worthy of noting that 30% removal of dissolved organics is found at Wiesbaden (the upper Rhine which is not so heavily polluted) using aeration and prechlorination without river sand bank filtration. On the other hand, the same 30% removal of organics is obtained in the lower Rhine area at Düsseldorf, where river sand bank filtration is followed by ozonation. BAC units can be allowed to remain on line at water works in southern Germany for longer times (up to several years) before reactivation is required, because of the absence of significant levels of halogenated organics in the Rhine at this point. On the other hand, in the Düsseldorf area, reactivation times of BAC media are controlled by the presence of halogenated organics progressing through the GAC.

14) At the Schierstein plant in Wiesbaden, bacterial breakthroughs were noted after 3 years of use of GAC columns for taste and odor control. This suggests that water utilities installing GAC systems should consider a bacterial monitoring test to use as a regeneration control parameter, in addition to whatever organic parameters are also adopted.

15) In operational BAC systems, bacteria occupy only the outer surface and macropores of the activated carbon granules. These account for 1 to 2% of the total GAC surface area in most activated carbons currently available. On the average, a single bacterium occupies 40 square microns per cubic meter of GAC surface area in operating BAC systems. This amount of bacteria present does not appear to interfere with dissolved organic adsorption processes in operational BAC systems.

16) High levels of phenol in the GAC adsorber influent(which are toxic to the bacteria present in the absence of GAC) are lowered by GAC adsorption to levels at which phenol can be utilized as bacterial substrate. Thus, BAC can be considered as a "sink" for adsorbable toxic (to bacteria) organic materials, which then may be biodegraded in the biologically active adsorber.

17) One postulated mechanism of BAC operation involves rapid adsorption of dissolved organics by the GAC micropores, followed by slow desorption and diffusion of the organics to areas where bacteria are present. The smaller the GAC particle size the greater is the rate of biochemical degradation of organics, possibly because the diffusion path is shortened and desorption becomes the rate-controlling step. This would imply that biologically active powdered activated carbon would be more efficient than granular activated carbon in removing dissolved organics from solution. On the other hand, GAC particle sizes below 1 mm cause problems of clogging and reducing attainable flow rates.

18) Bacterial activities are higher in BAC media during summer than during winter, probably because of higher water temperatures.

19) Samples of GAC known to be bacterially sterile cause some oxygen consumption and CO_2 production in waters being passed through such media. At biological steady state conditions, however, this amount of CO_2 produced represents only about 1.5% of the total produced.

SECTION 11

ESTIMATED COSTS FOR BAC SYSTEMS

It must be kept in kept in mind that the capital and operating costs for biologically enhanced granular activated carbon systems are determined by a number of factors:

- the type and amount of oxidative pretreatment required,
- the organic composition of the raw water (components which can and cannot be converted into biodegradable materials),
- the necessity to add oxygen,
- the necessity to maintain pH between 6 and 8 (to maintain optimal bacterial activity),
- the empty bed contact time of the GAC columns or beds,
- the necessity to pretreat the wastewaters to remove components which may be toxic to the bacteria.

In addition, the frequency of regeneration of the GAC will have a major impact on the GAC operating costs. In fact, one of the primary advantages of operating GAC media in biologically enhanced modes is the saving in reactivation costs (including attrition losses which occur during movement and handling of GAC during reactivation) which can be obtained in certain cases by installing a preoxygenation or preoxidation step. If the saving in GAC reactivation costs more than offset the installation of pretreatment to promote biological activity, then BAC will be cost-effective for the specific wastewater under consideration.

In this section, estimated costs for the major components of BAC systems will be discussed. These will include preoxidation with ozone (the highest cost preoxidation system), GAC adsorption contactors, initial loading of GAC to the contactors and GAC thermal regeneration equipment.

COSTS FOR OZONATION SYSTEMS

Oxidation with ozone will be the highest cost oxidation step, compared with using oxidants such as chlorine, chlorine dioxide, potassium permanganate, hydrogen peroxide, etc., adding pure oxygen or simply the addition of air. However, the most widely known biologically enhanced GAC systems to date utilize ozonation as the preoxidation step. Therefore, for purposes of this discussion, the costs for ozonation will be summarized. Those BAC systems which can utilize lower cost oxidants effectively, or simply oxygen or air, will be able to lower this portion of their total costs proportionately.

Capital Costs For Ozonation Systems

Major factors affecting the capital costs of ozonation systems include:

- Capacity of ozone generation system
- Number of stages of ozone use
- Type of ozone contactor off-gas destruction
- Type of ozone control system
- Space requirements
- Standby generation capacity required
- Use of air versus oxygen for ozone generation

Capital costs for ozone generation systems range from $850 to $1,150/lb of ozone generated per day when up to 100 lbs/day are required. This range drops to $300 to $500/lb of ozone per day when 1,000 lbs/day of ozone are required (Table 40; G.W. Miller, 1979). To these equipment costs must be added the costs for contacting, building space, control systems, contactor off-gas destruction, etc. Capital costs for fully installed ozonation systems are given in Table 41 (Gumerman, Culp & Hansen, 1978). Costs for construction of diffuser contactors (concrete columns, 18 feet deep with a length/width ratio of approximately 2/1) are listed in Table 42 for various sizes of chambers (Gumerman, Culp & Hansen, 1978).

TABLE 40. COST RANGE OF OZONATION SYSTEMS (FROM AIR)

Ozone Generation Capacity, lbs/day of ozone	Approx. Capital Cost, $/lb production cap./day
100	850 - 1,150
200	600 - 800
300	500 - 700
400	450 - 650
500	400 - 600
1,000	300 - 500

Source: G.W. Miller (1979)

Clark and Stevie (1978) assembled available capital cost data for ozonation systems and converted it into capital costs per mg/L of ozone dosage per 1,000 gallons of drinking water disinfected. These cost data are presented in Table 43 for plant sizes ranging from 1 mgd to 150 mgd. At the lower flow rates (10 mgd and below), the capital costs for generation of ozone from air are lower than those for generating ozone from oxygen. However, above 10 mgd, the capital costs for generating ozone from oxygen become less than those for air. For a 10 mgd treatment plant, the capital cost to provide an ozone (generated from air) dosage of 1 mg/L is estimated by Clark & Stevie (1978) to be on the order of 1.1¢/1,000 gal.

One year later, Hansen, Gumerman & Culp (1979) developed more detailed capital cost estimates for air-fed ozone generators capable of producing 0.5 to 10 lbs of ozone/day. These are given in Table 44, and include costs for

TABLE 41. CONSTRUCTION COST: OZCNE GENERATION SYSTEMS

	Ozone Generation Capacity, lbs/day					
	10	100	500	1,000	2,000	3,500
Mfgd. Eqpmt.	$32,250	143,610	511,960	685,810	1,075,540	1,523,240
Concrete	--	--	1,540	1,540	2,250	2,250
Steel	--	--	1,520	1,520	2,210	2,210
Labor	4,840	33,690	114,110	143,110	207,500	272,300
Housing	6,000	8,400	12,700	23,400	35,700	41,800
Subtotal	43,909	185,700	642,70C	855,380	1,318,200	1,841,800
Misc. & Conting'y	6,460	27,86C	96,410	128,310	197,730	276,270
Total	$49,550	213,560	739,110	983,690	1,515,930	2,118,070

Source: Gumerman, Culp & Hansen, 1978

TABLE 42. CONSTRUCTION COST: CCNCRETE OZONE CONTACT CHAMBERS

		Concrete Chamber Volume				
	cu ft	460	4,600	23,000	46,000	92,0C0
	gallons	3,441	34,413	1/2,063	344,126	688,252
Excavation & Sitework		$ 470	1,630	2,570	5,150	10,290
Concrete		850	4,950	8,280	15,450	29,810
Steel		1,470	8,400	13,570	23,330	48,550
Labor		2,150	12,200	19,510	36,120	69,330
Subtotal		4,940	27,180	43,930	82,050	157,980
Misc. & Contingency		740	4,080	6,590	12,310	23,700
Total		$ 5,680	31,260	50,520	94,360	181,680

basis: 18 ft deep; length/width ratio = 2/1

Source: Gumerman, Culp & Hansen, 1978

TABLE 43. CAPITAL COSTS FOR DRINKING WATER DISINFECTION WITH OZONE

Capital Costs, ¢/1,000 gal. (ozone generated from air or oxygen)	Design Capacity (mgd)				
	1	5	10	100	150
Capital Cost (from air)	2.90	1.36	1.11	0.76	0.73
Capital Cost (from oxygen)	4.46	1.50	1.08	0.61	0.58

Source: Clark & Stevie, 1978

TABLE 44. CONSTRUCTION COSTS FOR SMALL SCALE OZONE GENERATION SYSTEMS*

Cost Category	Ozone Generation Capacity (lbs/day)		
	0.5	5.0	10.0
Manufactured Equipment	$ 11,540	$ 19,880	$ 28,530
Labor	1,860	3,300	4,840
Housing	6,000	6,000	6,000
Subtotal	19,400	29,180	39,370
Miscellaneous & Contingency	2,910	4,380	5,910
TOTAL	22,310	33,560	45,280
Ozone Generating Equipment Costs ($/lb/day of O_3 generated)	23,080	3,976	2,853
Construction Costs ($/lb/day of O_3 generated)	44,620	6,712	4,528

* Assumes ozone is generated from air. Costs include ozone generator, dissolution equipment, electrical equipment, control instrumentation, but not contact chamber. Figures are not stated to include costs for air preparation equipment (which would add 20% to 25% to capital costs of manufactured equipment), nor for equipment to destroy ozone in contactor off-gases.

Source: Hansen, Gumerman & Culp, 1979

the ozone generator, dissolution equipment and all required electrical equipment and instrumentation, labor and housing, but not costs for the ozone contact chamber itself, since these are a function of water flow to be treated and contact time. These capital costs are not stated to include air preparation equipment or ozone destruction apparatus for contactor off-gas treatment. If not included, these costs must be considered to be somewhat low. For example, ozone generator suppliers normally estimate the capital costs for air preparation equipment to be about 20% to 25% of the total capital cost of the ozone generation system (Larocque, 1977, Private Communication).

Separate construction costs were estimated by Hansen, Gumerman & Culp (1979) for 18 ft high (water depth 16 ft) fiberglass reinforced plastic ozone contact chambers to be used in conjunction with ozone generation systems capable of producing 0.5 to 10 lbs/day. Costs for the contacting equipment itself are included with those of the ozone generation system. Contactor construction costs are listed in Table 45.

For larger sized ozone generation systems (10 to 3,500 lbs/day), Gumerman, Culp & Hansen (1979) estimated capital costs based upon air feed to the generator for up to 100 lbs/day of ozone generated and from oxygen above 100 lbs/day. They also assumed that all oxygen used for ozone generation would be generated on-site, and that although the ozonation equipment would be housed, the oxygen generation equipment would be located outside on a concrete slab.

These assumptions made by Gumerman et al. (1979) are not representative of current ozone generation practice, either for municipal water or wastewater treatment, for the most part. In drinking water treatment plants, Miller et al. (1978) have shown that of the approximately 1,100 plants which were using ozone during 1977, only 2 generate their ozone from oxygen. Only one of these plants (Duisburg, Federal Republic of Germany) recycles the oxygen-rich ozone contactor off-gases to the ozone generator. Even the largest and newest water treatment plants using ozone generate more than 5,000 lbs/day from air feed.

On the other hand, most of the newer and larger U.S. wastewater treatment plants using ozone also employ the oxygen activated sludge process. This means that the oxygen source for ozone generation comes from an on-site, oxygen generation plant which generates tons/day quantities of oxygen at the lowest cost, mostly for use in plant biological reactors. Therefore, oxygen is available at a lower cost than if oxygen generating equipment were to be sized simply to produce the volume necessary to feed the ozone generators alone.

In addition, in oxygen activated sludge plants using ozone, the oxygen-rich ozone contactor off-gases are not usually recycled to the ozone generator, but rather are passed into the biological reactor. This use of ozone contactor off-gases is referred to as a "once-through (the ozone generator) oxygen" system. In this manner, the only loss of oxygen in the system is that which is dissolved in the ozone-treated wastewater. Bhargava (1979) described an ozone generation system which uses partial recycle of oxygen

TABLE 45. CONSTRUCTION COST FOR OZONE CONTACT CHAMBERS (SMALL SCALE*)

Cost Category	Contactor Volume (gallons)				
	850	2,350	5,290	8,480	13,540
Manufactured Equipment	$ 690	$ 1,270	$ 3,160	$ 6,960	$ 8,640
Concrete	20	50	100	140	190
Steel	10	20	40	50	70
Labor	170	280	470	610	760
SUBTOTAL	890	1,620	3,770	7,760	9,660
Miscellaneous & Contingency	130	240	570	1,160	1,450
TOTAL	1,020	1,860	4,340	8,920	11,110

* for use with 0.5 to 10 lbs/day ozone generation capacity. Contact chambers are 18 ft high, fiberglass reinforced plastic.

Source: Hansen, Gumerman & Culp, 1979

and which has been installed in the 8 mgd sewage treatment plant at Murphreesboro, Tennessee. This oxygen activated sludge plant using ozone disinfection was scheduled to become operational by mid-1980. More details on the design of oxygen recycle systems for generation of ozone can be found in a paper by Lestochi et al. (1979).

Therefore, as with the estimates for small ozone generators, capital costs estimated by Gumerman et al. (1979) are considered to be low (in those cases in which large quantities of ozone are generated from air -- for most drinking water treatment purposes), but are high by the amount of oxygen recycle equipment which normally is not employed.

Capital costs for large scale ozone generation (10 to 3,500 lbs/day) estimated by Gumerman et al. (1979) are given in Table 46 and include equipment for gas preparation (assumed to be generation of oxygen), ozone generation (from oxygen at more than 100 lbs/day), dissolution, off-gas oxygen recycling (but may not include destruction of ozone in the contactor off-gases), electrical and instrumentation costs, all required safety and monitoring equipment, labor and housing costs.

The ozone contact chamber for large scale ozone generation was assumed by Gumerman et al. (1979) to be a covered, reinforced concrete structure, 18 feet deep and with a length/width ratio of approximately 2:1. Construction costs for such contact chambers are given in Table 47 (costs for the ozone dissolution equipment itself are included with the ozone generation equipment in Table 46).

It should be recognized that once an ozonation system has been installed for any single purpose, additional applications for ozone at the same plant will involve only the incremental costs for additional ozone generation capacity plus a second contacting system. All of the one-time costs associated with installing the initial ozone generation system (power, housing, controls, air treatment, off-gas destruction, etc.) already will be present, and the incremental cost per pound of ozone generated now will be less than those required for initial installation.

Operating & Maintenance Costs Of Ozonation Systems

Most of the operating expense to produce ozone is the cost of electrical power; this has been estimated to amount to about 80% of the total ozone generation costs. Much information on operating and maintenance costs stems from European drinking water treatment plants, some of which have been employing ozone since 1906. Miller et al. (1978) summarized the costs for ozone treatment of drinking water supplies in Europe and Canada. With ozonation doses ranging from 1.5 to 3.0 mg/L and with ozone generation capacities of 1,000 to 3,000 lbs/day (from air), ozonation costs ranged from 1.75 to 4.0 cents/1,000 gallons of water treated in 1977. These figures include the amortized capital costs (usually over 20 years at 8% interest) for air preparation equipment, ozone generation, ozone contacting, treatment of off-gases from ozone contacting, instrumentation and automation for the ozonation subsystem, and installation and housing for the ozonation system, operation and maintenance.

TABLE 46. CONSTRUCTION COSTS FOR OZONE GENERATION SYSTEMS (LARGE SCALE)

Cost Category	Ozone Generation Capacity (lbs/day)					
	10	100	500	1,000	2,000	3,500
Manufactured Equipment	$ 34,210	$152,350	$543,130	$ 727,560	$1,135,720	$1,615,980
Concrete	0	0	1,630	1,630	2,380	2,380
Steel	0	0	1,680	1,680	2,440	2,440
Labor	5,090	35,410	120,850	150,420	218,100	286,200
Housing	6,430	9,000	13,600	25,060	38,230	44,770
SUBTOTAL	45,730	196,760	680,890	906,350	1,396,870	1,951,770
Miscellaneous & Contingency	6,860	29,510	102,130	135,950	209,530	292,770
TOTAL	$ 52,590	226,270	783,020	1,042,300	1,606,400	2,244,540
Manufactured Equipment Cost, \$/lb/day of O_3 generating capacity	3,421	1,524	1,086	728	568	462
Construction Costs in \$/lb/day of O_3 generating capacity	5,259	2,263	1,566	1,042	803	641

Source: Gumerman, Culp & Hansen, 1979

TABLE 47. CONSTRUCTION COSTS FOR OZONE CONTACT CHAMBERS (LARGE SCALE*)

Cost Category	Contact Chamber Volume				
	cu ft 460 gallons 3,441	4,600 34,413	23,000 172,063	46,000 344,126	92,000 688,252
Excavation & Sitework	$ 490	$ 1,710	$ 2,700	$ 5,410	$ 10,820
Concrete	900	5,250	8,780	16,380	31,600
Steel	1,620	9,270	14,980	25,750	53,580
Labor	2,260	12,820	20,510	37,960	72,870
SUBTOTAL	5,270	29,050	46,970	85,500	168,870
Miscellaneous & Contingency	790	4,360	7,050	12,820	25,330
TOTAL	6,060	33,410	54,020	98,320	194,200

* Concrete chambers, 18 ft deep; length to width ratio = 2/1

Source: Gumerman, Culp & Hansen, 1979

The rather broad range of European ozonation system costs is affected mainly by the cost of housing for the ozonation system and variations in the local costs of electrical energy. If the ozonation system is housed in a separate building, as opposed to being retrofitted into an existing building, then the costs will be about 25% higher (Miller et al., 1978).

Small Scale Ozone Generation--

Hansen et al. (1979) developed operation and maintenance costs for generation of ozone at the rate of 0.5 to 10 lbs/day, from air. Electrical energy is required for building, heating, lighting and ventilating, as well as for ozone generation. It is not clear from the report by Hansen et al. (1979) whether costs for air preparation and for destruction of ozone in the contactor off-gases are included. Process energy for ozonation is based on 15 kWh/lb of ozone generated for the smallest system to 11 kWh/lb for the 10 lbs/day system. Maintenance costs were estimated to be 1% of the capital equipment costs. Annual operation and maintenance costs for small scale ozone generators are given in Table 48.

Large Scale Ozone Generation--

Gumerman, Culp & Hansen (1979) developed operation and maintenance costs for systems generating 10 to 3,500 lbs/day of ozone. Below 100 lbs/day, ozone is assumed by these authors to be generated from air; oxygen is the feed gas above 100 lbs/day and is generated on-site in a quantity necessary to feed the ozone generators. For air feed, power requirements were based on 11 kWh/lb of ozone generated, but 7.5 kWh/lb from oxygen. Annual operation and maintenance costs are estimated in Table 49.

LePage (1979) has reported the results of 8 months of operational experience at the 18 mgd Monroe, Michigan drinking water treatment plant which began operating with ozonation (for taste and odor control) in February, 1979. This plant is capable of generating 450 lbs/day of ozone from air and is designed to apply 3 mg/L of ozone to the raw water. After 8 months of operation, an average ozone dosage of 1.65 mg/l had been employed at an average ozonation cost of 0.634¢/1,000 gal of water treated.

Knorr (1979) reported that the new 10 mgd sewage treatment plant being constructed at El Paso, Texas will incorporate an average ozone dosage of 5 mg/l prior to GAC adsorption for an estimated operational cost of 4¢/1,000 gal of wastewater treated.

COSTS FOR GAC SYSTEMS

Major factors affecting the costs of installing and operating GAC systems include:

- empty bed contact time (EBCT) of water being treated
- regeneration frequency
- on-site versus off-site GAC reactivation

TABLE 48. OPERATION AND MAINTENANCE SUMMARY FOR SMALL SCALE OZONE GENERATION SYSTEMS*

Ozone Generation Rate (lbs/day)	Electrical Energy (kWhr/yr) Building	Process	Total	Maintenance Material ($/yr)	Labor (hrs/yr)	Total Cost** ($/yr)
0.5	6,570	2,560	9,130	$ 120	370	$ 4,090
5.0	6,570	21,900	28,470	200	550	6,550
10.0	6,570	40,150	46,720	290	550	7,190

* Ozone is generated from air

** Calculated using $0.03/kWh and $10.00/hr for labor

Source: Hansen, Gumerman & Culp, 1979

TABLE 49. OPERATION AND MAINTENANCE SUMMARY FOR LARGE SCALE OZONE GENERATION SYSTEMS*

Ozone Generation Rate (lbs/day)	Electrical Energy (kWh/yr) Building	Process	Total	Maintenance Material ($/yr)	Labor (Hrs/yr)	Total Cost** ($/yr)
10	5,750	40,150	45,900	$ 1,430	550	$ 8,310
100	9,850	401,500	411,350	3,060	550	20,900
500	16,420	1,368,750	1,385,170	10,770	910	61,430
1,000	30,780	2,737,500	2,768,280	14,270	1,830	115,620
2,000	71,820	5,475,000	5,546,820	22,120	2,190	210,430
3,500	123,120	9,581,250	9,704,370	31,150	2,920	351,480

* Assumes ozone is generated from oxygen, except for first line, which is ozone generated from air.

** Calculated using $0.03/kWh and $10.00/hr labor cost.

Source: Gumerman, Culp & Hansen, 1979

On the basis of information published to date, the empty bed contact times which have produced the most effective removals of ammonia and dissolved organics from aqueous solutions by combinations of adsorption and biological activity have been close to 10 minutes. However, longer empty bed contact times of 20 to 30 minutes have been recommended in some European drinking water treatment plants (Sontheimer, 1978b).

Regeneration of GAC normally is done on-site at large water and wastewater treatment plants, especially when the daily volumes of GAC to be regenerated or frequencies of reactivation warrant. On the other hand, when the GAC does not have to be regenerated frequently, then it usually is cost-effective for the plant to send its spent GAC back to the manufacturer for reactivation. Many of the larger European drinking water treatment plants using GAC do not have on-site GAC reactivation facilities (Rice *et al.*, 1979).

Culp (1980) points out that "good cost data are available from operating (GAC) installations at: (1) The South Lake Tahoe Public Utility District, South Lake Tahoe, California (13 years), (2) the Orange County Water District, Fountain Valley, California (4 years) and (3) the Upper Occoquan Sewage Authority, Manassas Park, Virginia (capital cost data only -- plant in operation only a few months)." In addition to these three plants, there are an additional 17 or so operating municipal advanced waste treatment plants which use GAC in the USA, and these plants also provide detailed cost information. However, Culp (1980) also cautions that "costs taken from wastewater cost curves which are plots of flow in mgd versus cost (capital or operation and maintenance costs) cannot be applied directly to drinking water treatment. Allowance must be made in the capital costs for the different reactivation capacity needed (for the two types of application), and in the operation and maintenance costs for the actual amount of carbon to be reactivated or replaced." These factors are site- and water- (or wastewater)-specific.

Capital Costs For GAC Systems

Components of capital costs for GAC systems include the contactor, site modifications, piping, pumps and valves, GAC fill, contingencies, fees and regeneration furnaces (assuming on-site reactivation). The summations of these capital costs for empty bed contact times of 9 and 18 minutes have been estimated by J.C. Clark (1979) and are presented in Figure 80 for flows up to 300 mgd. Of greatest significance is the fact that the GAC capital costs decrease sharply for plant flows up to 50 mgd, then decrease much more slowly up to 300 mgd.

Small Scale, Package GAC Columns--

Gumerman, Culp & Hansen (1979) developed construction costs for factory-assembled, package GAC columns, which were sized with 7.5 minutes empty bed contact time to treat volumes of 2,500 gal/day to 0.5 mgd. GAC bed depths were taken to be 5 feet and the surface hydraulic loading rate was taken to be about 5 gpm/sq ft. Conceptual design parameters for these package GAC units are listed in Table 50.

TABLE 50. CONCEPTUAL DESIGN PARAMETERS FOR PACKAGE GAC COLUMNS (7.5 min EBCT)*

Plant Flow		Flow Rate (gpm/sq ft)	GAC Columns			Housing Area (sq ft)
gpm	gpd		No.	Bed Area (sq ft)	Diameter (ft)	
1.7	2,500	5.1	1	0.34	0.67	60
17	25,000	5.4	1	3.14	2	150
70	100,000	5.6	1	12.6	4	300
175	250,000	5.1	1	34	6.5	375
350	500,000	5.5	1	64	9	450

* GAC columns are 5 ft deep; surface loading = 5 gpm/sq ft

Source: Gumerman, Culp & Hansen, 1979

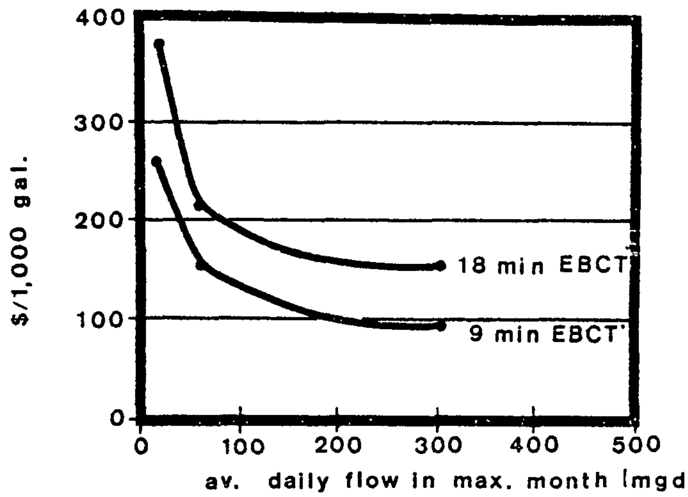


Figure 80. Capital costs for 9- and 18-min. GAC empty bed contact times.

(J.C. Clark, 1979)

Costs for these package GAC columns are based on the use of cylindrical, pressurized, downflow steel contactors designed to operate manually at 50 psi. Housing costs are included. Not included are supply piping to the GAC column and handling or conveyance systems for spent or regenerated GAC. Construction costs for this size GAC package unit (to handle plant flows of 2,500 gal/day to 0.5 mgd) are given in Table 51.

Large Scale GAC Contactors--

For plants treating larger flows (1 to 200 mgd), Gumerman, Culp & Hansen (1979) have developed cost estimates for gravity flow GAC contactors (concrete and steel construction) and for pressure GAC contactors.

Concrete construction--Gravity flow GAC contactors are assumed to be essentially identical to gravity flow filtration structures. Construction costs were developed for GAC bed depths of 5 ft and 8.3 ft, which provide empty bed contact times of 7.5 and 12.5 minutes, respectively, at a water application rate of 5 gal/min/sq ft (Tables 52 and 53, respectively). Costs of these facilities include the contactor structure, cylinder-operated butterfly valves, liquid and carbon handling piping with headers in a pipe gallery, flow measurement and other instrumentation, master operations panel and a housing building. Not included are costs for backwashing pumping, the initial GAC charge, spent or regenerated GAC handling outside of the contactor pipe gallery and GAC regeneration and preparation facilities. It was assumed that all GAC in a single contactor would be removed and replaced with regenerated GAC in a single operation. In turn, this requires that regeneration facilities be designed to store both spent and regenerated GAC in quantities equal to the amount in one contactor.

TABLE 51. CONSTRUCTION COSTS FOR PACKAGE GAC COLUMNS (7.5 min EBCT)

Cost Category	Plant Flow				
	1.7 gpm 2,500 gpd	17 gpm 25,000 gpd	70 gpm 100,000 gpd	175 gpm 250,000 gpd	350 gpm 500,000 gpd
Excavation & Site Work	$ 50	$ 50	$ 50	$ 80	$ 80
Manufactured Equipment	740	2,900	7,070	14,600	27,100
Concrete	100	250	480	580	700
Labor	1,100	3,900	6,240	9,500	13,000
Pumps, Valves & Piping	500	1,200	4,300	6,400	8,800
Electrical & Instrumentation	600	600	850	1,100	1,300
Housing	5,100	6,910	9,180	10,300	11,400
SUBTOTAL	8,190	15,810	28,170	42,560	62,380
Miscellaneous & Contingency	1,230	2,370	4,230	6,380	9,360
TOTAL COST	9,420	18,180	32,400	48,940	71,740

Source: Hansen, Gumerman & Culp, 1979

TABLE 52. CONSTRUCTION COSTS FOR CONCRETE GRAVITY CARBON CONTACTORS*

Cost Category	Total Contactor Volume (cu ft) and Area (sq ft)					
	(cu ft) 700 (sq ft) 140	3,500 700	7,000 1,400	35,000 7,000	70,000 14,000	140,000 28,000
Excavation & Sitework	$ 1,660	$ 3,050	$ 4,660	$ 13,670	$ 21,600	$ 36,630
Manufactured Equipment	29,000	62,660	86,130	335,690	582,300	1,080,360
Concrete	12,330	24,880	38,330	87,850	142,410	253,520
Steel	10,630	18,360	27,710	67,650	113,300	193,160
Labor	37,330	81,410	138,800	327,870	468,260	920,890
Pipe & Valves	33,570	108,700	206,130	597,380	863,970	1,463,150
Electrical & Instrumentation	14,730	42,250	42,250	109,050	185,720	291,840
Housing	17,400	40,480	70,590	291,940	514,330	968,520
SUBTOTAL	156,650	381,790	614,600	1,831,100	2,891,890	5,208,070
Misc. & Contingency	23,500	57,270	92,190	274,670	433,780	781,210
TOTAL	180,150	439,060	706,790	2,105,770	3,325,670	5,989,280
Volume/Single Contactor	350 ft^3	875 ft^3	1,750 ft^3	3,500 ft^3	5,000 ft^3	6,360 ft^3
Cost/Single Contactor	$90,070	$109,770	$176,700	$210,580	$237,550	$290,460

* 7.5 min EBCT; 5 ft GAC bed depth

Source: Gumerman, Culp & Hansen, 1979

TABLE 53. CONSTRUCTION COSTS FOR CONCRETE GRAVITY GAC CONTACTORS*

Cost Category	Total Contactor Volume (cu ft) and Area (sq ft)					
	(cu ft) 1,160 (sq ft) 140	5,810 700	11,620 1,400	58,100 7,000	116,200 14,000	232,400 28,000
Excavation & Site Work	$ 2,220	$ 4,080	$ 6,210	$ 18,240	$ 28,800	$ 48,770
Manufactured Equipment	29,000	62,660	86,130	335,690	582,300	1,080,630
Concrete	15,010	30,300	51,180	111,090	180,500	308,640
Steel	12,940	20,690	38,800	82,360	137,940	235,150
Labor	45,450	99,170	168,990	399,150	570,050	1,159,990
Pipe & Valves	33,570	108,700	206,130	597,380	863,970	1,463,150
Electrical & Instrumentation	14,730	42,250	42,250	109,050	185,720	291,840
Housing	17,400	40,480	70,590	291,940	514,330	968,520
SUBTOTAL	170,320	408,330	670,280	1,944,900	3,063,610	5,556,690
Misc. & Contingency	25,550	61,250	100,540	291,740	459,540	833,500
TOTAL	195,870	469,580	770,820	2,236,640	3,523,150	6,390,190
Volume/Single Contactor	580 ft^3	1,450 ft^3	2,905 ft^3	5,810 ft^3	8,300 ft^3	10,560 ft^3
Cost/Single Contactor	$ 97,940	$117,400	$192,710	$223,660	$251,650	$290,460

* 12.5 min EBCT, 8.3 ft GAC bed depth

Source. Gumerman, Culp & Hansen, 1979

Steel construction--These types of contactors are assumed by Gumerman, Culp & Hansen (1979) to be utilized when more than 30,000 cu ft of GAC contact volume is required. Costs were developed for such contactors (field-erected as opposed to factory-built) of 20 and 30 ft diameters, each with a GAC bed depth of 20 ft and an overall vessel height of 35 ft. System hydraulics were sized for an application rate of 5 gal/min/sq ft, which provides a 30 minute EBCT. Other conceptual design parameters are listed in Table 54.

Steel vessels are constructed of factory-formed steel plates, erected at the job-site. Units are provided with a nozzle-style underdrain; GAC is removed as required for regeneration through multiple carbon drawoff pipes in the underdrain support plates. Regenerated GAC is returned through a piping system to the top of each contactor. Costs presented are for a complete GAC contacting facility, including vessels, face and interconnecting piping, access walkways, cylinder-operated butterfly valves on all hydraulic piping and manually operated ball- or knife-type valves on the carbon handling system, flow control and other instrumentation, master operations control panel and a building to house the contactors.

Not included are costs for GAC supply pumping, surface wash and backwash pumping, the initial GAC charge, spent or regenerated GAC handling facilities (exclusive of the piping within the contactor building) or GAC regeneration or preparation facilities. Estimated construction costs for gravity flow steel GAC contactors are presented in Tables 55 and 56 for 20 and 30 ft diameter units, respectively, both providing 30 minute EBCTs.

Pressure GAC Contactors--Gumerman, Culp & Hansen (1979) developed construction costs for pressure GAC contactors constructed of shop-fabricated steel tankage. Bed depths of 5, 10 and 20 ft were estimated, providing empty bed contact times of 7.5, 15 and 30 minutes, respectively, at a hydraulic loading rate of 5 gal/min/sq ft. Conceptual design parameters are listed in Table 57. The practical upper limit plant size for this type of GAC contactor system is 20 to 25 mgd.

Costs are based upon downflow operation at a design working pressure of 50 psi using cylindrical ASME code pressure vessels, which are either 10 or 12 ft in diameter by 14, 23 or 33 ft in height, furnished with a nozzle-style underdrain and designed for rapid removal of spent GAC and recharge of virgin or reactivated carbon.

Estimated construction costs are presented in Tables 58, 59 and 60 for 7.5, 15 and 30 minute EBCTs, respectively, and are for complete GAC contacting facilities. These include vessels, cylinder-operated butterfly valves, liquid and GAC handling face piping with headers in the GAC contactor building, flow measurement and other instrumentation, master operation control panel and building. Not included are costs for contactor supply and backwash pumping, initial GAC charge, spent or regenerated GAC handling and GAC regeneration and preparation facilities. Housing requirements assume that the GAC columns are totally enclosed.

TABLE 54. CONCEPTUAL DESIGN PARAMETERS FOR STEEL GRAVITY FLOW GAC CONTACTORS; 20 FT GAC DEPTH*

Plant Flow (mgd)	Total Contactor Bed Area (sq ft)		No. of Contactors		Total GAC Volume, ft^3		Plant Area Requirements (sq ft)	
	20 ft diam	30 ft diam	20 ft diam	30 ft diam	20 ft diam	30 ft diam	20 ft diam	30 ft diam
10	1,570	--	5	--	31,400	--	6,500	--
50	7,850	7,065	25	10	157,000	141,300	33,000	26,000
100	15,700	14,130	50	20	314,000	282,600	66,000	50,000
200	31,400	28,260	100	40	628,000	565,200	126,000	95,000

* 30 minute EBCT

Source: Gumerman, Culp & Hansen, 1979

TABLE 55. CONSTRUCTION COSTS FOR STEEL GRAVITY FLOW GAC CONTACTORS*

Cost Category	Total Contactor Volume (cu ft) 31,400	157,000	314,000	628,000
Excavation & Site Work	$ 2,050	$ 6,560	$ 11,600	$ 21,760
Manufactured Equipment	340,970	1,619,750	3,170,980	6,137,800
Concrete	7,650	27,470	47,290	91,580
Steel	3,810	14,040	24,370	45,690
Labor	66,220	314,270	584,390	1,075,550
Pipe & Valves	140,730	675,500	1,437,110	2,644,620
Electrical & Instrumentation	50,460	207,800	406,820	787,250
Housing	169,000	792,000	1,584,000	3,024,000
SUBTOTAL	$ 780,890	3,657,390	7,266,560	13,828,250
Miscellaneous & Contingency	117,130	548,610	1,089,980	2,074,240
TOTAL	$ 898,020	4,206,000	8,356,540	15,902,490
Volume/Single Contactor (ft^3)	6,280	6,280	6,280	6,280
COST/SINGLE CONTACTOR	$ 179,600	168,240	167,130	159,020

* 20 ft diameter GAC tanks; 30 minute EBCT

Source: Gumerman, Culp & Hansen, 1979

TABLE 56. CONSTRUCTION COSTS FOR STEEL GRAVITY FLOW GAC CONTACTORS*

Cost Category	Total Contactor Volume (cu ft) 141,300	282,600	565,200
Excavation & Site Work	$ 7,150	$ 13,140	$ 25,020
Manufactured Equipment	1,327,160	2,595,980	5,139,970
Concrete	29,680	56,180	111,290
Steel	15,230	28,690	55,180
Labor	263,820	488,740	942,800
Pipe & Valves	565,490	1,092,710	2,111,020
Electrical & Instrumentation	170,640	332,910	659,530
Housing	624,000	1,200,000	2,280,000
SUBTOTAL	$3,003,170	$5,808,350	$11,324,810
Misc. & Contingency	450,480	871,250	1,698,720
TOTAL	$3,453,650	6,679,600	13,023,530
Volume/Single Contactor, cu ft	14,140	14,140	14,140
COST/SINGLE CONTACTOR	$ 345,370	$ 333,980	$ 325,590

* 30 ft diameter GAC tanks; 30 minute EBCT

Source: Gumerman, Culp & Hansen, 1979

Operating & Maintenance Costs Of GAC Systems

Major components of operating and maintenance costs include GAC replacement (for losses incurred during backwashing, handling and reactivation), GAC contactor operation, regeneration furnace labor and materials, fuel and miscellaneous expenses. Of these, costs for GAC replacement are the most significant (7% estimated losses during reactivation at more than 55¢/lb), followed by fuel (5,000 BTU/lb of GAC reactivated), regeneration furnace labor and materials, then contactor operation.

Package GAC Columns--

Hansen, Gumerman & Culp (1979) estimated operation and maintenance costs based on the conceptual design parameters given in Table 50, which assume that GAC adsorber units can be preceded by filtration and that the GAC would be replaced with virgin or regenerated carbon once per year.

TABLE 57. CONCEPTUAL DESIGN PARAMETERS FOR PRESSURE GAC CONTACTORS

Plant Flow (mgd)	No. of Contactors	Contactor Diam. (ft)	Total Contactor Area*** (sq ft)	Total Contactor Vol.* (cu ft @ detention times)			Plant Area** Requirements (sq ft)
				7.5 min	15 min	30 min	
1	2	10	157	780	1,570	3,140	1,750
10	12	12	1,357	6,790	13,570	27,140	4,800
50	60	12	6,786	33,930	67,860	135,720	21,000

* Volumes determined at bed depths of 5, 10 and 20 ft.

** Assumes that GAC contactors are totally enclosed.

*** GAC contactors sized for 5 gpm/sq ft application rates

Source: Gumerman, Culp & Hansen, 1979

Backwashing is assumed once per week, but the facilities otherwise operate essentially unattended, except for routine maintenance and monitoring the performance of the GAC column. No allowance for administrative or for laboratory labor (other than for minimal routine quality assurance testing) is included. Estimated operation and maintenance costs for the package GAC contactors are summarized in Table 61.

TABLE 58. CONSTRUCTION COSTS FOR PRESSURE GAC CONTACTORS*

Cost Category	Total Contactor Vol. (cu ft) & Area (sq ft)		
(cu ft)	780	6,790	33,930
(sq ft)	157	1,357	6,786
Excavation & Site Work	$ 530	$ 1,440	$ 6,180
Manufactured Equipment	49,010	409,290	1,944,170
Concrete	2,190	5,650	24,730
Steel	1,130	2,830	12,360
Labor	8,500	55,200	262,400
Pipe & Valves	15,250	135,310	679,880
Electrical & Instrumentation	15,630	82,910	429,660
Housing	32,550	125,160	512,400
SUBTOTAL	$124,790	817,790	3,871,780
Misc. & Contingency	18,720	122,670	580,770
TOTAL	$143,510	940,460	4,452,550
Volume/Single Contactor, ft^3	390	565	565
COST/SINGLE CONTACTOR	$ 71,760	78,370	74,210

* 5 ft GAC bed depth; 7.5 minute EBCT

Source: Gumerman, Culp & Hansen, 1979

Gravity Flow GAC Contactors - Concrete Construction--
Gumerman, Culp & Hansen (1979) estimated costs for this type of GAC contactor (5 and 8.3 ft depths, which equate to 7.5 and 12.5 minute EBCTs, respectively), which are given in Table 62. Building energy costs are for heating, ventilating and lighting. Process energy is required for backwashing

(once/day for 10 min at 12 gal/min/sq ft) and GAC slurry pumping during carbon removal and replacement (assumes regeneration frequency of every 2 months and a slurry concentration of 3 lb of GAC/gal of water utilized). Process energy requirements are essentially identical for the two different GAC depths.

TABLE 59. CONSTRUCTION COSTS FOR PRESSURE GAC CONTACTORS*

Cost Category		Total Contactor Vol. (cu ft) & Area (sq ft)	
(cu ft)	1,570	13,570	67,860
(sq ft)	157	1,357	6,786
Excavation & Site Work	$ 530	$ 1,490	$ 6,180
Manufactured Equipment	55,460	452,720	2,161,360
Concrete	2,190	5,650	24,730
Steel	1,130	2,830	12,360
Labor	8,990	58,570	280,050
Pipe & Valves	16,780	147,490	728,540
Electrical & Instrumentation	15,680	82,910	429,660
Housing	41,850	163,000	700,290
SUBTOTAL	$142,610	914,660	4,343,170
Misc. & Contingency	21,390	137,200	651,480
TOTAL	$164,000	1,051,860	4,994,650
Volume/Single Contactor, ft^3	785	1,130	1,130
COST/SINGLE CONTACTOR	$ 82,000	87,660	83,240

* 10 ft GAC bed depth; 15 minute EBCT

Source: Gumerman, Culp & Hansen, 1979

Maintenance material costs include costs for general supplies, backwash pump and GAC transport pump maintenance, instrumentation repair and other miscellaneous items. The cost for replacement of GAC (lost during contactor operation and GAC regeneration) is not included. Labor costs include the cost of operating the GAC contactors, backwashing pumps, GAC slurry pumps, instrument and equipment repairs and supervision.

Gravity Flow GAC Contactors - Steel Construction--

Operating and maintenance parameters are the same as for the GAC concrete contactors. Backwash frequency was assumed to be once/day for 10 minutes at 12 gal/min/sq ft and the GAC regeneration frequency was assumed to be every 2 months. Makeup carbon is not included in the annual operation and maintenance costs, listed in Table 63 for both 20 and 30 ft diameter columns (30 min EBCTs).

TABLE 60. CONSTRUCTION COSTS FOR PRESSURE GAC CONTACTORS*

Cost Category		Total Contactor Vol. (cu ft) & Area (sq ft)		
	(cu ft)	3,140	27,140	135,720
	(sq ft)	157	1,357	6,786
Excavation & Site Work		$ 530	$ 1,400	$ 6,180
Manufactured Equipment		77,300	749,560	3,560,370
Concrete		2,630	6,780	29,680
Steel		1,240	3,110	13,600
Labor		10,340	67,370	322,060
Pipe & Valves		18,500	221,730	1,120,350
Electrical & Instrumentation		16,420	87,100	451,200
Housing		79,050	303,420	1,332,250
SUBTOTAL		$ 206,010	1,440,460	6,835,690
Misc. & Contingency		30,900	216,070	1,025,350
TOTAL		$ 236,910	1,656,530	7,861,040
Volume/Single Contactor, ft^3		1,570	2,250	2,250
COST/SINGLE CONTACTOR		$ 171,520	154,140	143,960

* 20 ft GAC bed depth; 30 minute EBCT

Source: Gumerman, Culp & Hansen, 1979

Pressure GAC Contactors--

Electrical energy requirements were developed assuming that this type of GAC contactor serves both as a filter and adsorber. Backwashing requirements were assumed to be once/day for 10 minutes at a rate of 12 gal/min/sq

TABLE 61. OPERATION AND MAINTENANCE SUMMARY FOR PACKAGE GAC COLUMNS

Plant Flow		Energy (kWh/yr)			Maintenance	Labor	Total
gpm	gpd	Building	Process	Total	Material ($/yr)	(hrs/yr)	Cost* ($/yr)
1.7	2,500	6,140	120	6,260	$ 100	100	$1,290
17	25,000	15,400	1,200	16,600	275	100	1,770
70	100,000	30,800	4,840	35,640	1,000	160	3,670
175	250,000	38,500	9,690	48,190	2,650	210	6,200
350	500,000	46,170	24,210	70,380	4,880	260	9,590

* Calculated using $0.03/kWh and $10.00/hr for labor cost

Source: Hansen, Gumerman & Culp, 1979

TABLE 62. OPERATION AND MAINTENANCE SUMMARY FOR GRAVITY GAC CONTACTORS

Total Contactor Vol. (cu ft)	Electrical Energy (kWh/yr)			Maintenance Material ($/yr)	Labor (hrs/yr)	Total Cost* ($/yr)
	Building	Process	Total			
7.5 minute EBCT; 5 ft GAC bed depth						
700	44,120	690	44,810	800	900	11,140
3,500	151,850	3,410	155,260	2,510	1,500	22,170
7,000	279,070	6,820	285,890	4,020	2,100	33,600
35,000	1,190,160	34,080	1,224,240	13,200	4,600	95,930
70,000	2,165,890	68,150	2,234,040	21,600	9,000	178,620
140,000	4,123,490	136,540	4,260,030	36,700	18,000	344,500
12.5 minute EBCT; 8.3 ft GAC depth						
1,160	44,120	690	44,810	800	900	11,140
5,810	151,850	3,410	155,260	2,510	1,500	22,170
11,620	279,070	6,820	285,890	4,020	2,100	33,600
58,200	1,190,160	34,080	1,224,240	13,200	4,600	95,930
116,200	2,165,890	68,150	2,234,040	21,600	9,000	178,620
232,400	4,123,490	136,540	4,260,030	36,700	18,000	344,500

* Calculated using $0.03/kWh and $10.00/hr for labor cost

Source: Gumerman, Culp & Hansen, 1979

TABLE 63. OPERATION AND MAINTENANCE SUMMARY FOR STEEL GRAVITY GAC CONTACTORS*

Contactor Diam. (ft)	GAC volume (cu ft)	Electrical Energy (kWh/yr)			Maintenance Material ($/yr)	Labor (hrs/yr)	Total Cost** ($/yr)
		Building	Process	Total			
20	31,400	666,900	12,030	678,930	5,350	3,000	55,720
20	157,100	3,385,800	60,170	3,445,970	21,380	7,000	194,760
20	314,000	6,771,600	120,340	6,891,940	37,420	14,000	384,180
20	628,000	12,927,600	240,680	13,168,280	69,490	27,000	734,540
30	141,300	2,668,000	54,150	2,722,150	16,040	6,800	165,700
30	282,600	5,130,000	108,300	5,238,300	26,730	13,500	318,880
30	565,200	9,750,000	216,600	9,966,600	42,760	26,000	601,760

* 30 minute EBCT

** Calculated using $0.03/kWh and $10.00/hr for labor cost

<u>Source</u>: Gumerman, Culp & Hansen, 1979

ft. Energy requirements are for backwash pumping, for pumping of spent GAC to the on-site regeneration facilities and return. GAC was assumed to be removed and replaced every 2 months. Energy for supply pumping to the GAC contactors is not included, nor are costs for makeup GAC or on-site regeneration. The contactors are assumed to be completely housed. Other parameters are the same as for the preceeding types of large scale GAC contactors.

Annual operation and maintenance requirements for pressure GAC contactors are listed in Table 64.

COSTS FOR REPLACEMENT GAC

Costs were developed by Gumerman, Culp & Hansen (1979) for purchase and placement of virgin GAC for use in any of the above-discussed GAC contactors. Figure 81 shows a curve for the total costs of purchase, delivery and replacement of virgin GAC. This curve may be used to derive the complete cost of a GAC contactor and to determine the cost of makeup GAC lost during contactor operation and GAC regeneration.

COSTS FOR GAC REGENERATION

Gumerman, Culp & Hansen (1979) estimated costs for GAC reactivation both off-site (when space limitations or volumes of GAC being regenerated do not warrant installation of on-site equipment) and the several different types of on-site GAC regeneration equipment.

Off-Site Regional GAC Regeneration - Handling and Transportation

In addition to the capital equipment costs for ozonation and GAC adsorption discussed above, when GAC is to be reactivated off-site it will be necessary for the plant to have available carbon dewatering/storage bins. Two different design configurations were used by Gumerman, Culp & Hansen (1979) to develop cost estimates for these facilities. Storage bins of 2,000 cu ft and less are elevated, 12 ft diameter, 30 ft height, cylindrical tanks with conical bottoms, field-fabricated of braced, 0.25 inch, shop-formed steel plate protected by a suitable coating system. Bins of 5,000 cu ft volumes are elevated, 3-hopper, rectangular tanks. For larger storage requirements, multiple units would be used.

Construction costs for such GAC dewatering/storage facilities are listed in Table 65. Not included in these costs are paving for the access area nor for trucks necessary to haul dewatered GAC to the regional regeneration facility.

A summary of operation and maintenance costs for off-site GAC reactivation is presented in Table 66. The regeneration plant is assumed to be within 100 miles of the GAC-using facility. Annual fuel requirements for transportation are based on 3.5 miles/gal diesel fuel consumption, and maintenance materials for the trucks only were estimated at a unit cost of \$0.30/mile. Included in Table 66 are the costs for fuel, labor and maintenance to load spent GAC from dewatered GAC storage tanks to 30 cu yd semi-dump trailers, haul to the regeneration facility, unload, reload reactivated

TABLE 64. OPERATION AND MAINTENANCE SUMMARY FOR PRESSURE GAC CONTACTORS

Total Surface Area (ft^2)	Energy (kWh/yr)			Maintenance Material ($/yr)	Labor (hrs/yr)	Total Cost* ($/yr)
	Process	Building	Total			
157	916	179,550	180,470	1,600	2,000	27,010
1,357	7,967	492,480	500,450	8,020	3,500	58,030
6,786	39,746	2,154,600	2,194,350	37,420	7,500	178,250

* Calculated using $0.03/kWh and $10.00/hr for labor cost

Source: Gumerman, Culp & Hansen, 1979

GAC from bulk storage, return to the treatment plant and discharge either to on-site storage tanks or directly to the GAC contactors. It was also assumed that all these operations would be accomplished within an 8-hr day. The costs in Table 66 do not include the costs of regeneration at the regional facility. These would be charged by the owner/operator at a rate probably based on the reactivation equipment available, which are discussed below.

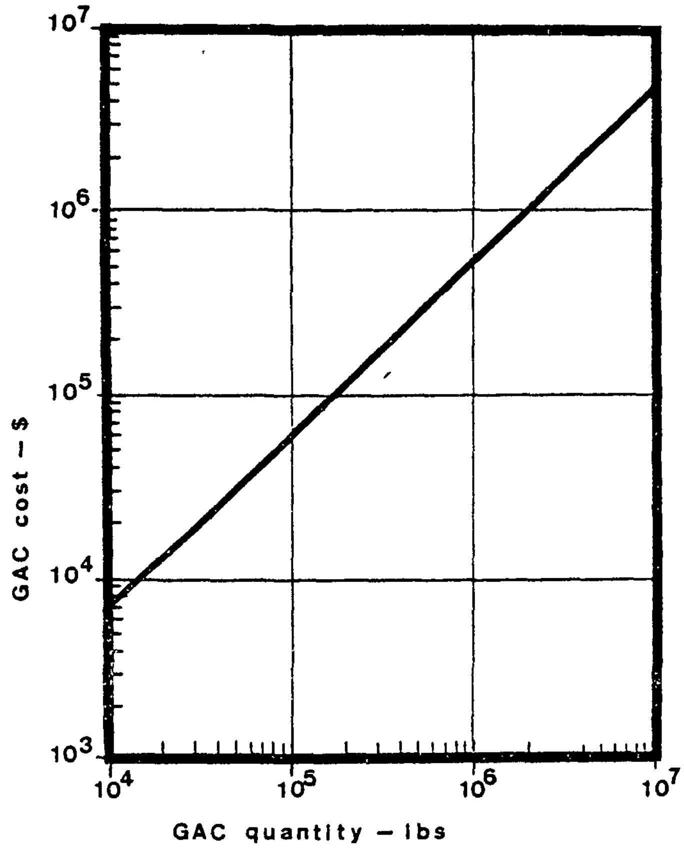


Figure 81. Material cost for GAC, including cost for purchase, delivery and placement.

(Gumerman, Culp & Hansen, 1979)

On-Site GAC Regeneration

Gumerman, Culp & Hansen (1979) present details of capital and operation and maintenance costs for multiple hearth, infrared and fluidized bed GAC regeneration equipment. Conceptual design parameters, construction costs and operation and maintenance costs are presented in Tables 67 through 75 for each of the 3 types of equipment. All regeneration furnaces are assumed to be inside buildings, and operation is assumed to be 24 hours/day, 365 days per year.

TABLE 65. CONSTRUCTION COSTS FOR OFF-SITE REGIONAL GAC REGENERATION -- ON-SITE HANDLING AND TRANSPORTATION FACILITIES

Cost Category	On-Site Storage Capacity (cu ft) 1,000	5,000	20,000
Excavation and Site Work	$ 210	$ 370	$ 1,470
Manufactured Equipment	3,240	13,050	50,600
Concrete	1,170	1,750	6,360
Steel	5,630	30,900	122,500
Labor	12,090	29,430	123,640
Pipe & Valves	1,380	3,830	14,990
SUBTOTAL	23,720	79,330	319,560
Miscellaneous & Contingency	3,560	11,900	47,930
TOTAL	$ 27,280	$ 91,230	$ 367,490

Source: Gumerman, Culp & Hansen, 1979

Kittredge (1980) summarized the economics of GAC regeneration and described the costs estimated for a fluidized bed GAC regeneration system which has been installed at the Manchester Water Works, Manchester, New Hampshire. This system has a designed operating capacity of 12,000 lbs/day (500 lbs/hr) of regenerated GAC and a projected total operating cost of 6.4¢/lb. The estimated annual operating costs for the Manchester system are presented in Table 76. Notice that the cost of makeup GAC represents nearly 54% of the total direct costs and 43% of the total annual operating costs. The need for makeup GAC is caused largely by losses incurred during regeneration. If the frequency of GAC reactivation could be lowered, a significant savings in GAC operating costs would be obtained.

Kittridge concluded that GAC can be regenerated by several different methods and options at costs ranging from 5¢ to 20¢/lb (for on-site regeneration systems) to the mid-30¢/lb range for off-site custom regeneration systems.

SUMMARY OF GAC TREATMENT COSTS

Clark, Culp & Gumerman (1980) summarized the most significant cost factors dealing with GAC treatment systems. Table 77 shows that the costs

TABLE 66. OPERATION AND MAINTENANCE SUMMARY FOR OFF SITE REGIONAL GAC REGENERATION -- HANDLING AND TRANSPORTATION ONLY

GAC Regenerated (lbs/yr)	Diesel Fuel* (gal/yr)			Maintenance Material ($/yr)			Labor** (hrs/yr)			Total Cost***($/yr)		
	10 mi+ haul	25 mi haul	100 mi haul	10 mi haul	25 mi haul	100 mi haul	10 mi haul	25 mi haul	100 mi haul	10 mi haul	25-mi haul	100 mi haul
30,000	5.7	14.3	57	6	20	60	6.8	11	14	80	140	230
150,000	28.6	71.4	286	30	90	320	34	55	70	380	670	1,150
500,000	97	243	971	110	280	1,090	116	187	238	1,310	2,260	3,910
1,000,000	194	486	1,943	210	550	2,180	232	374	476	2,620	4,510	7,810
3,000,000	582	1,430	5,829	650	1,640	6,540	780	1,200	1,428	8,710	14,280	23,440

* Based on 3.5 miles/gal for 30 cu yd semi-dump truck

** Labor for loading and unloading GAC and for hauling

*** Calculated using diesel fuel at $0.45/gal and labor at $10.00/hr

+ All distances are one way

Source: Gumerman, Culp & Hansen, 1979

of GAC treatment (18 min EBCT) including GAC regeneration, decreases from 13.3¢/1,000 gal at 20 mgd to 10.4¢/1,000 gal at 110 mgd. Table 78 shows a set of assumptions for installation of separate post-filter GAC adsorbers (18 min EBCT); Table 79 shows the costs for post-filter GAC adsorption in ¢/1,000 gal for drinking water treatment plants sized from 1 mgd (51.5¢) to 150 mgd (11.7¢). These costs are separated into amortized capital cost and operation and maintenance cost.

TABLE 67. CONCEPTUAL DESIGN PARAMETERS FOR MULTIPLE HEARTH GAC REGENERATION

Furnace Configuration			
Effective Hearth Area (sq ft)	I.D.	No. of Hearths	Building Area Requirements (sq ft)
27	30 inches	6	750
37	30 inches	6	750
147	39 inches	6	900
359	10 ft-6 in.	5	1,200
732	14 ft-6 in.	6	1,800
1,509	20 ft-0 in.	6	2,400

Source: Gumerman, Culp & Hansen, 1979

TABLE 70. CONCEPTUAL DESIGN PARAMETERS FOR INFRARED GAC REGENERATION FURNACE

Unit Capacity, lbs/day	Furnace Size, Width by Length, feet	Building Area Requirements, sq ft
2,400	4 x 20	480
16,800	7 x 48	2,500
38,400	8.5 x 72	3,900
60,000	9.5 x 100	6,000

Source: Gumerman, Culp & Hansen, 1979

Finally, Figure 82 shows the variation of total GAC treatment costs (GAC as post-filter adsorbers in drinking water treatment plants) in ¢/1,000 gal with the period of time between GAC reactivation (although the size of plant and EBCT are not given). It can be seen that reactivation periods of two months or less result in the highest costs (13¢ to 33¢/1,000 gal), but

TABLE 68. CONSTRUCTION COSTS FOR MULTIPLE HEARTH GAC REGENERATION

Cost Category	Furnace Hearth Area (sq ft)					
	27	37	47	359	732	1,509
Manufactured Equipment	$220,660	$275,830	$ 519,830	$ 647,140	$1,039,660	$1,304,880
Labor	117,720	147,150	273,280	346,850	557,060	704,210
Pipe & Valves	8,330	8,330	8,330	14,480	23,450	48,800
Electrical and Instrumentation	8,290	8,340	8,340	9,190	14,930	26,980
Housing	109,670	109,670	124,230	175,100	245,790	334,460
SUBTOTAL	$ 464,670	549,320	934,010	1,192,760	1,880,890	2,419,330
Misc. & Contingency	69,700	82,400	140,100	178,910	282,130	362,900
TOTAL	$ 534,370	631,720	1,074,110	1,371,670	2,163,020	2,782,230

Source: Gumerman, Culp & Hansen, 1979

TABLE 69. OPERATION AND MAINTENANCE SUMMARY FOR MULTIPLE HEARTH GAC REGENERATION

Effective Hearth Area, ft^2	Regenerated GAC, lbs/day	Electrical Energy, kWh/yr			Natural Gas ($scf/yr \times 10^6$)	Maintenance Material ($/yr)**	Labor (hrs/yr)	Total Cost* ($/yr)
		Building	Process	Total				
27	1,224	14,630	261,400	276,030	5.80	$ 2,990	900	$ 27,810
37	1,670	14,630	326,750	341,380	7.72	3,740	950	33,520
147	6,624	17,550	424,770	442,320	26.2	6,410	3,400	87,740
359	13,680	23,400	588,150	611,550	48.26	8,550	6,200	151,630
732	32,400	35,100	849,550	884,650	108.40	11,760	10,500	284,220
1,509	66,960	46,800	1,307,000	1,353,800	207.75	16,040	17,000	496,730

* Calculated using $0.03/kWh, $0.0013/scf and $10.00/hr for labor.

** Makeup GAC costs are not included

Source: Gumerman, Culp & Hansen, 1979

TABLE /1. CONSTRUCTION COSTS FOR INFRARED GAC REGENERATION FURNACES

Cost Category	Furnace Capacity (lbs/day)			
	2,400	16,800	38,400	60,000
Manufactured Equipment	$160,000	$360,000	$ 620,000	$ 940,000
Labor	48,000	100,000	174,000	235,000
Pipe & Valves	3,500	5,500	7,500	10,000
Electrical & Instrumentation	21,000	53,000	81,000	113,000
Housing	21,000	60,000	82,000	149,000
SUBTOTAL	$ 253,500	578,500	964,500	1,447,000
Miscellaneous & Contingency	38,030	86,780	144,680	217,050
TOTAL COST	$ 291,530	665,280	1,109,180	1,664,050

Source: Gumerman, Culp & Hansen, 1979

TABLE 72. OPERATION AND MAINTENANCE COST SUMMARY FOR INFRARED GAC REGENERATION FURNACE

GAC Regeneration Rate (lbs/day)	Energy (kWh/yr)			Maintenance Material ($/yr)	Labor (hrs/yr)	Total Cost* ($/yr)
	Building	Process	Total			
2,400	7,540	701,680	709,220	8,900	2,380	53,980
16,800	39,300	4,522,000	4,561,300	21,000	4,900	206,840
38,400	61,300	10,206,000	10,267,300	28,000	9,380	429,820
60,000	94,300	15,820,000	15,914,300	33,600	13,300	644,030

* Calculated using $0.03/kWh and $10.00/hr for labor

Source: Gumerman, Culp & Hansen, 1979

TABLE 73. CONCEPTUAL DESIGN PARAMETERS FOR GAC REGENERATION - FLUIDIZED BED PROCESS

GAC Regeneration Capacity (lbs/day)	Reactor Bed Area (sq ft)	Housing Requirements (sq ft)
6,000	4	1,400
12,000	8	1,800
18,000	12	2,200
24,000	16	2,600

Source: Gumerman, Culp & Hansen, 1979

TABLE 76. SUMMARY OF ESTIMATED OPERATING COSTS - FLUIDIZED BED GAC REGENERATION SYSTEM, MANCHESTER, N.H. WATER WORKS

Item Costs:	$/yr	¢/lb
Makeup GAC	115,500	2.75
Labor	9,450	0.22
Maintenance	13,000	0.31
Fuel	21,000	0.50
Power	7,560	0.18
Steam	11,740	0.28
Water	36,290	0.86
Total Direct Cost	$ 214,540	5.11 ¢/lb
Depreciation	39,250	0.92
Insurance & Taxes	7,850	0.19
Administration & Overhead	7,850	C.19
Total Indirect Costs	54,950	1.30 ¢/lb
Total Annual Operating Cost	$ 269,490	6.4 ¢/lb

Notes: 1. Estimate assumes 350 days/yr operation.
2. GAC transport system cost included, with depreciation.
3. Depreciation cost based on 20-year life expectancy.

Source: Kittredge, 1980

TABLE 74. CONSTRUCTION COSTS FOR GAC REGENERATION - FLUIDIZED BED PROCESS

Cost Category	GAC Regeneration Capacity (lbs/day) 6,000	12,000	18,000	24,000
Manufactured Equipment	$ 570,000	$ 650,000	$ 710,000	$ 755,000
Labor	180,000	205,000	225,000	240,000
Electrical & Instrumentation	10,000	11,000	11,000	12,000
Housing	60,000	75,000	90,000	106,000
SUBTOTAL	$ 820,000	$ 941,000	$1,036,000	$1,113,000
Miscellaneous & Contingency	123,000	141,150	155,400	166,950
TOTAL COST	$ 943,000	$1,082,150	$1,191,400	$1,279,950

Source: Gumerman, Culp & Hansen, 1979

TABLE 75. OPERATION AND MAINTENANCE COST SUMMARY FOR GAC REGENERATION - FLUIDIZED BED PROCESS

GAC Regeneration Rate (lbs/day)	Process Energy (kWh/yr)	Natural Gas (scf/yr)	Maintenance Material ($/yr)	Labor (hrs/yr)	Total Cost* ($/yr)
6,000	131,400	6,830,700	$ 15,540	2,400	$ 52,360
12,000	262,800	13,660,000	17,940	2,650	70,080
18,000	394,200	20,440,000	19,400	3,050	88,300
24,000	525,600	27,322,860	20,860	3,330	105,450

* Calculated using $0.03/kWh, $0.0013/scf for natural gas and $10.00/hr for labor

Source: Gumerman, Culp & Hansen, 1979

TABLE 77. COSTS OF GAC TREATMENT (18 MIN EBCT), INCLUDING REGENERATION

Type of GAC unit	Type of GAC Regeneration	Size of Treatment Plant, mgd	Total Annual Cost*	¢/1,000 gal treated
Pressure	off-site	2	$ 117,920	23.1 ¢
Pressure	on-site, IR furnace	20	$ 681,180	13.3 ¢
Gravity, steel	on-site, multiple hearth	75	$2,097,950	10.9 ¢
Gravity, steel	on-site, multiple hearth	110	$2,919,760	10.4 ¢

* Includes amortized capital costs @ 8% (20 yrs), labor @ $10.00/hr, electricity @ 3¢/kWh and maintenance materials; also natural gas cost @ 0.175 ¢/scf and diesel fuel @ 45¢/gal, when necessary.

Source: Clark, Culp & Gumerman, 1980

the total costs decrease much more slowly with reactivation periods from 3 months (11¢/1,000 gal) to 8 months (7¢/1,C00 gal). Thus, pretreatment concepts which can extend the GAC reactivation period beyond 2 months will have a significant cost-savings impact on the GAC treatment process.

TABLE 78. ASSUMPTIONS FOR 18 MINUTE EBCT GAC ADSORPTION

Item	Design Capacity (mgd)				
	1	5	10	100	150
Number of Contactors	3	6	12	40	60
Diameter of Contactors (ft)	8	12	12	20	20
Depth of Contactors (ft)	13	13	13	14	14
Volume of GAC/Contactor (cu ft)	653	1,469	1,469	4,396	4,396

Source: Clark, Culp & Gumerman, 1980

TABLE 79. AMORTIZED CAPITAL AND OPERATING & MAINTENANCE COSTS FOR GAC ADSORPTION (18-MINUTE EBCT), ¢/1,000 GALLONS

Item	Design Capacity (mgd)				
	1	5	10	100	150
Amortized Capital Cost	29.4	12.7	9.8	4.9	4.6
Operating & Maintenance	22.1	12.6	10.8	7.4	7.1
TOTAL COSTS	51.5	25.3	20.6	12.3	11.7

Source: Clark, Culp & Gumerman, 1980

COST SAVINGS WITH BAC SYSTEMS

As stated earlier, one primary benefit of optimizing biological activity in GAC adsorber systems involves extending the operating time of GAC adsorbers, thus effecting savings in costs for regeneration. In some BAC systems operating in European drinking water treatment plants, operating lives of GAC adsorbers are extended 2 to 5 times (Sontheimer, 1979) by incorporating chemical preoxidation with ozone before GAC adsorption. Schalekamp (1979) noted that in treating Swiss lake waters for potable purposes, the GAC operating time is only 6 months if preoxidation with ozone is not used. When ozonation is placed before GAC filtration/adsorption, the GAC can be used for about 3 years, an increase in longevity before thermal regeneration is required of a factor of five.

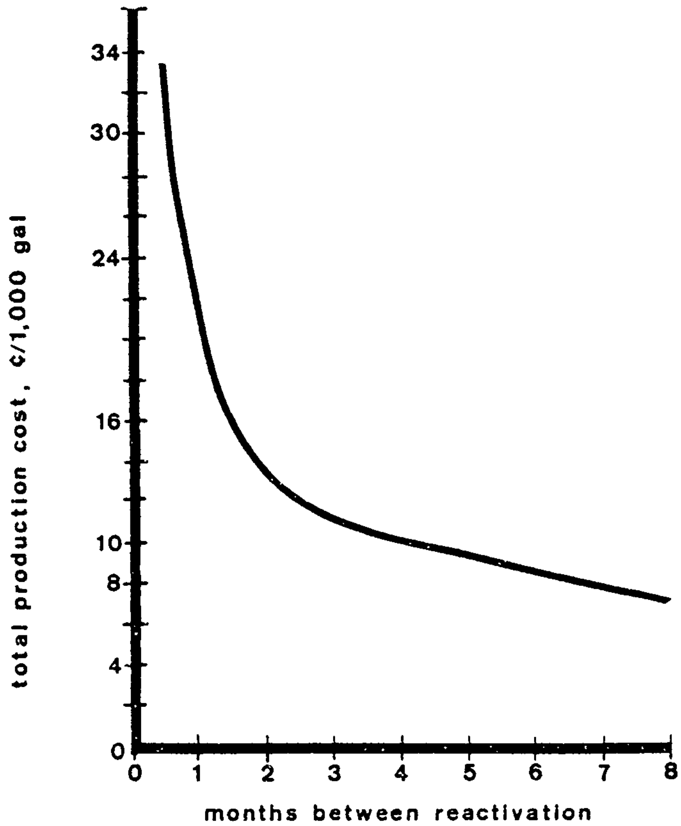


Figure 82. Production cost for GAC adsorbers vs period between reactivations.

(Clark, Culp & Gumerman, 1980)

The question arises, however, as to the cost-effectiveness of installing a high capital cost, energy-intensive ozonation system ahead of GAC adsorption to attain the cost savings which result from extending the period of GAC use. In order to quantify these savings in GAC regeneration, a basis for comparison and several operating assumptions was developed by J.C. Clark (1979).

The primary direct cost benefit of the BAC process relative to conventional use of GAC with frequent reactivation is the reduction in the number of reactivation cycles required per year. Temple, Barker & Sloane (1977) have shown that the majority of GAC operating expenses can be attributed to reactivation. For a typical United States water supply utility, reactivation costs account for approximately 70 to 75% of the GAC adsorber operating costs when six reactivation cycles are scheduled annually (2-month GAC life).

Accepting this cost basis and drawing upon the information about the performance of BAC presented above, a useful operating assumption for making these calculations is that the maximized biological activity in the carbon bed enhanced by chemical preoxidation with ozone (the highest initial cost chemical oxidant currently in use) will allow a reduction in the number of reactivation cycles from six to one annually for the attainment of comparable water quality (GAC useful life extended from 2 months to 1 year).

For the activated carbon adsorber operation, this decrease in number of reactivation cycles per year will cut annual operation costs by about 50%. This calculation is based on two key assumptions: first, that each of the six reactivation cycles adds about 12% (70 to 75% divided by 6) to the annual operating cost; second, that a utility required to reactivate its GAC fill only once per year will be unlikely to install a smaller, therefore less efficient, reactivation furnace and carbon transfer facility, and therefore will face higher costs for a single off-site reactivation cycle per year than a facility having its own on-site reactivation system and which reactivates six times per year. Instead, it is assumed that the utility requiring only one reactivation per year would choose to send its GAC out for reactivation.

The use of chemical preoxidation with ozone will increase the plant's operating costs, thereby offsetting to some extent the savings achieved by the reduction in reactivation frequency. The amount of this increase depends upon whether the plant treatment process already included ozone generation equipment and contact chambers before the introduction of GAC and also on the level of preozonation dosage required for the particular raw water quality to be treated prior to GAC adsorption.

<u>A Hypothetical Case Example</u> (J.C. Clark, 1979)

To illustrate the cost savings more accurately and to avoid the generalizations in the introductory section above, an example water treatment plant is used in this section to apply the principles directly. Since one objective of this report is to assess the potentials of transferring this recently developed European water treatment practice to the United States, a prototype U.S. water treatment plant is used as an example with the technical assumptions based upon successful European experiences with BAC.

The example plant is described fully in an EPA report (Temple, Barker & Sloane, 1977). Briefly, the plant supplies a community of 265,000 population with an average daily production of 50 mgd. The maximum plant capacity is 75 mgd and its treatment process includes conventional prechlorination, coagulation, sedimentation, rapid sand filtration and post-chlorination.

The capital costs for this plant to add GAC in a post-filtration adsorber/contactor mode to achieve 9 minutes empty bed contact times have been estimated at $10 million, whereas simply replacing the sand with GAC in existing filter beds would cost $5 million. These costs include carbon transfer systems and reactivation furnaces. The associated annual operating costs, assuming 6 reactivation cycles, are estimated to be $1.1 million for

GAC post-contactors and $1.3 million for replacement of sand by GAC, including debt service.

The capital costs of adding an ozone treatment system capable of applying ozone at dosages up to 2 mg/l at 50 mgd are shown in this same report (Temple, Barker & Sloane, 1977) to be $2.4 million. Operating costs for the full ozonation system (air treatment, ozone generation, contacting and off-gas destruction) are estimated to total $50,000 per year, including the savings likely to result from reduced chlorine dosage.

Applying the cost savings attributable to the combination of ozonation followed by GAC (post-contactor mode) to BAC, a new set of cost calculations can be made. The basic design assumptions are that the plant would install an ozonation system capable of applying up to 2 mg/l of ozone at 50 mgd and add GAC in the existing sand filter beds, providing a 9 minutes empty bed contact time. Moreover, the operating costs would include one annual reactivation cycle off-site rather than six cycles on-site.

The resulting capital cost for the ozonation + GAC system would be about $5.5 million, slightly more than the $5.0 million cost of the conventional GAC system using existing sand filter beds.

Even though the capital costs are a bit higher, the savings are substantial on the operating cost side. The annual GAC system operating costs would decrease by between $500,000 and $600,000, while the ozonation costs would increase by only some $50,000. Thus annual operating savings of between $450,000 and $550,000 would be achieved under the assumed conditions.

When both operating costs and the annual debt service expense on the capital expenditures are combined, the ozone/GAC system would add $1.1 million per year to the total annual costs of this typical water utility. This compares to $1.6 million per year for the conventional GAC system discussed above, showing the combined ozone/GAC system to be about 30% less expensive.

Energy Considerations (J.C. Clark, 1979)

Both the reactivation of GAC and the generation of ozone are energy intensive processes. Although the amount of energy needed to reactivate a pound of GAC varies according to furnace type and operating practice, most estimates are in the range of 3,500 and 7,000 BTUs per pound, with 5,000 BTUs per pound being a frequently estimated average. Estimates of electricity use for the generation of ozone are generally in a narrower range, with 10.5 kwhr per pound of ozone generated (from air) being a currently accepted figure. (This includes the energy required for air preparation, ozone generation, controls and instrumentation, but not contacting.) Since 11,000 BTUs are needed to generate one kilowatt-hour in a typical mixture of the various types of electric generating stations (which generate electricity at a fuel efficiency of about 33%), each pound of ozone generated requires the use of 115,500 BTUs of fossil fuel energy (although nuclear generation of electricity is a lower energy cost substitute).

The conventional use of GAC with 6 reactivation cycles per year and 2.6 million pounds of GAC per cycle would use 78 billion BTUs annually, plus the energy needed to produce the 1.1 million pounds of makeup GAC, which is estimated to require another 11 billion BTUs. Thus the total energy use by the conventional GAC system would be 89 billion BTUs annually.

By contrast, the example ozone/GAC system fuel use would consist of one annual reactivation cycle for the activated carbon, rather than six, plus the energy used by the ozonation equipment. The single GAC reactivation would account for 13 billion BTUs plus 2 billion BTUs for manufacturing the makeup GAC. The ozone generation would require 1.8 million kilowatt-hours annually, or 20 billion BTUs of primary fuel energy. The total fuel use for the example ozone/GAC system thus totals 36 billion BTUs annually.

By the measure of energy use, the ozone/GAC system clearly is more efficient under these assumptions. The use of 36 billion BTUs annually is only 40% of the use by the conventional GAC system of 89 billion BTUs. If the GAC reactivation can be prolonged to every two years (as is anticipated at the Dohne plant, Mülheim, Federal Republic of Germany), the total savings would be even more substantial. On the other hand, if the amount of ozone required for preoxidation should be 5 mg/l instead of 2 mg/l to prolong the GAC reactivation time to one year, then the energy costs for ozone/GAC would be about equal to those for GAC alone which would require 6 reactivations per year. In addition, if the types of organic materials present in the specific raw water to be treated already are biodegradable, such that chemical preoxidation with ozone is not required and a cheaper oxidant can be used to provide the same extension of GAC operating life before reactivation is required (one year), additional cost savings will be effected.

Sensitivity Analysis and Inflation Effects (J.C. Clark, 1979)

The preceding text has noted several assumptions about the operation and costs of a BAC system operated with chemical preoxidation using ozonation, as well as the conventional GAC system against which it is being compared. Since many of these assumptions may vary somewhat in future circumstances, the findings shown above need to be discussed in terms of their sensitivity to key assumptions. In addition, since it appears likely that inflation will continue, its effects on tradeoffs between capital investment and operating costs is important to consider in maximizing the benefits of biological activated carbon systems.

The basic conclusions noted above were that the ozone/BAC system was 30% less expensive on an annual basis than the conventional GAC system, and that the ozone/GAC design used 61% less fuel. More specifically, the annual costs were lower due to smaller operating and maintenance costs which, more often than not, offset the higher capital costs of the ozone/GAC combination. This offsetting effect then was annualized to show the combined effect of the capital, operating and maintenance costs in the first year of the project.

Although these cost estimates have been considered above as if they were exact figures, they are more accurately considered as midpoints of a range of likely future costs. This range depends largely on specific design assumptions which, in turn, depend upon regeneration frequencies, local differences in sites, existing plants, raw water quality, desired finished water quality, etc. The range of costs can vary under a typical set of characteristics to plus or minus 20% of the point estimates noted above. This range is enough to alter the comparison substantially, depending upon these factors.

A more likely influence on costs though, is the pace of inflation in coming years. The basic direction of inflation increases will influence the comparison between the ozone/GAC treatment combination and conventional GAC systems and favors the ozone/GAC system. Inflation will increase future operating costs, while capital costs will remain as fixed amounts based on investments made in a particular year.

More specifically, while the ozone/GAC system is 30% less expensive in the first year (as shown above), it would become 40% less expensive in the 10th year with an average 7% annual inflation rate. If inflation should rise at a higher average rate, the ozone/GAC combination will be favored even more substantially.

<u>Effect Of Operating Variables On GAC And BAC Treatment Costs</u>

Clark and Dorsey (1980) reviewed the cost data developed by Gumerman, Culp & Hansen (1978) to examine the influence of changes in the level of operating variables on the cost of GAC treatment (18 min EBCT). Losses of GAC per regeneration cycle of 6% were assumed. Most variables were found to have a greater impact on smaller than on larger treatment plant costs. The only exceptions to this finding were reactivation frequency and capital cost.

Those variables having the greatest effect on operation and maintenance costs are the system size, reactivation frequency, activated carbon loss and GAC cost. Power cost has a greater impact on smaller systems than do some of the other variables. Figure 83 shows a total GAC system cost versus GAC reactivation frequency for a 100 mgd post-filter GAC adsorption system at 3 different GAC costs. Assuming 60¢/lb for the GAC being reactivated at a frequency of 1.1 months, the total system operating cost is about 16¢/1,000 gal (point P_1). If GAC cost increases to 80¢/lb, the reactivation period would have to increase to 1.7 months (point P_2) for total costs to remain constant.

Figure 84 shows an analysis made by Clark & Dorsey (1980) in which ozone treatment is followed by GAC adsorption. Total production costs in ¢/1,000 gal are plotted against GAC reactivation frequency. These authors concluded that if the system initially requires regeneration each month without ozonation, then the addition of ozone would have to decrease the reactivation frequency to 2.6 months to break even (pay for the cost of installing ozonation facilities). However, if the system without ozonation has an initial GAC reactivation frequency of 2 months, Clark & Dorsey conclude that no break-even point exists to justify the costs of addition of ozonation.

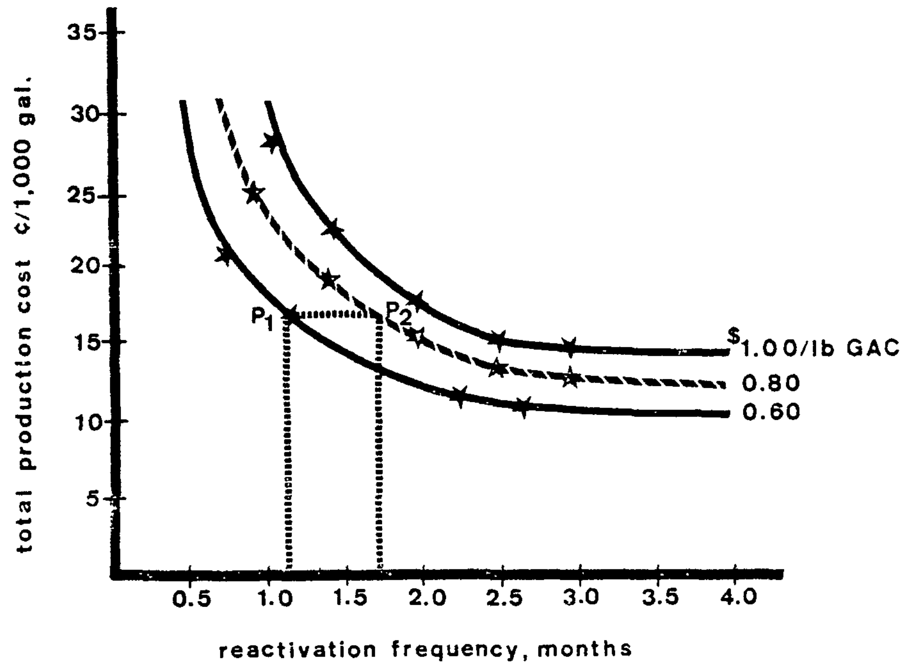


Figure 83. Total production cost vs. reactivation frequency for $0.60, 0.80 & 1.00/lb GAC for 100 mgd contactor system.

(Clark & Dorsey, 1980)

Practical Examples

Drinking Water Installations --

Dohne Plant, Mülheim, Federal Republic of Germany--Heilker (1979) has noted that a BAC process (preozonation, flocculation, sedimentation, ozonation, dual media filtration, GAC, ground passage and safety chlorination) has replaced the older process (breakpoint chlorination, flocculation, sedimentation, GAC, ground passage and safety chlorination). The older process used breakpoint chlorination for removal of ammonia; the newer process removes ammonia biologically.

Heilker's statement regarding cost comparisons between the two processes is as follows:

> "The treatment plants in the Dohne waterworks have been operating for more than 1.5 years using the revised process. The drinking water quality has been significantly improved without increasing treatment costs. The Dohne plant is less susceptible to disturbance and as a result can be operated with 50% of the former staff size. The activated carbon filter runs are 3 to 5 times longer than before."

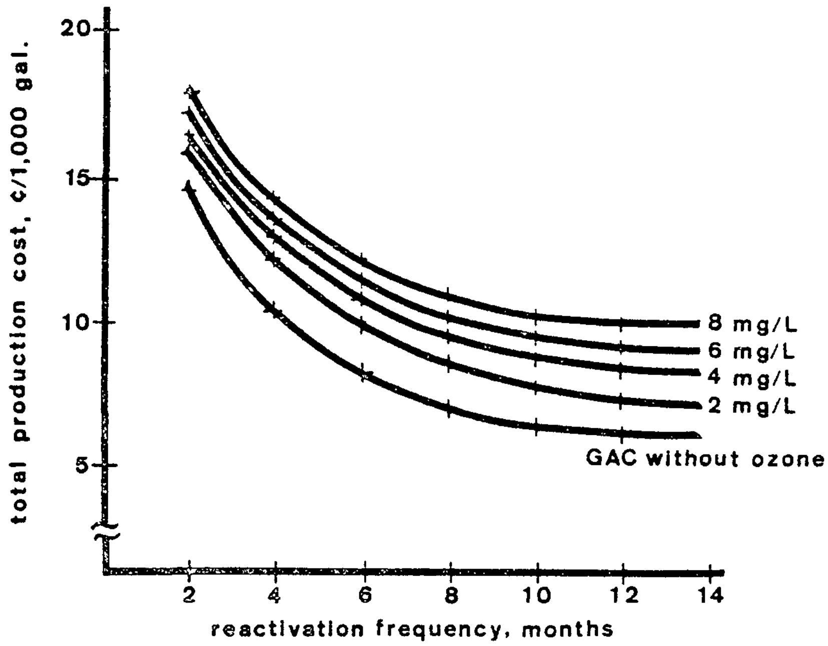


Figure 84. Cost of ozone and GAC in combination.

(Clark & Dorsey, 1980)

Dohne's new process required doubling the height of the GAC adsorbers, adding ozone generation facilities and pure oxygen evaporators (for addition of oxygen after filtration and before GAC adsorption), all of which increased costs. On the other hand, savings were obtained in the amount of chlorine used (10 to 15 mg/l dosages for prechlorination were eliminated), GAC regeneration costs (every 4 months with the old process, 1 to 2 years with the new process), and labor costs (half the former plant operating staff).

Windhoek Process, South Africa--Van Leeuwen (1979) has indicated that the 1 mgd process used at Windhoek, South West Africa to reclaim sewage for potable purposes, since 1968, involves breakpoint chlorination followed by 2-stage GAC adsorption. Under these circumstances, the GAC must be regenerated every 90 days. By contrast, when breakpoint chlorination was replaced by ozonation (8.5 to 10.5 mg/l applied dosage at 95% ozone transfer efficiency) in a 1 mgd pilot plant process, the GAC was operated for at least one year without requiring reactivation. This resulted in overall process cost savings of 13% at 1 mgd, and are projected to reach 24% at 10 mgd. These cost savings are dependent upon the clarification agent used, lime treatment being more costly than ferric chloride. Longer periods of GAC use without reactivation (greater than 1 year) are expected to result in even higher cost savings.

Inclusion of the ozonation unit process added 1.8 to 3.3¢/cu m (6.81 to 12.49¢/1,000 gal) in costs to the 1 mgd treatment line. This caused a decrease in GAC operating costs of 2.5 to 5¢/cu m (9.46 to 18.93¢/1,CCO gal. Costs by the old process versus those using ozonation are compared in Table 80 (Van Leeuwen, 1980).

CONCLUSION

Biological Activated Carbon processes can replace breakpoint chlorination for the removal of ammonia in treating drinking water supplies. As a result, generation of chlorinated organics is eliminated, along with the attendant increased difficulties associated with removing them once they are generated. However, the major cost savings associated with BAC processes involve less frequent necessity for thermal reactivation of the GAC. This produces two specific cost savings:

(1) savings in energy required with each reactivation cycle and

(2) savings in makeup GAC, which has been lost during the regeneration cycle.

In European drinking water treatment plants, promotion of biological activity by preoxidation with ozone extends GAC operating lives by 3 to 6 times. The amounts of ozone required to achieve extension of GAC operating life, or to optimize biological activity, must be determined for each water or wastewater to be so treated.

TABLE 80. COMPARISON BETWEEN TOTAL COSTS OF VARIOUS RECLAMATION PROCESS CONFIGURATIONS AT NATIONAL INSTITUTE FOR WATER RESEARCH, PRETORIA, SOUTH AFRICA

Process Configuration	Scale U.S. ¢/cu m		Scale $U.S./1,000 gal	
	4,000 cu m/day	40,000 cu m/day	1 mgd	10 mgd
1) Lime clarification, chlorination, 2-stage GAC (regenerated every 3 months)*	35¢	16.5 ¢	$1.32	$0.625
2) Lime clarification, ozonation, 2-stage GAC (regenerated every 12 months)	33¢	15¢	$1.25	$0.568
3) $FeCl_3$ clarification, ozonation, 2-stage GAC (regenerated every 12 months)	30¢	12.5¢	$1.14	$0.473

* Current process at Windhoek, South West Africa, plant

Source: Van Leeuwen, 1980

SECTION 12

ENGINEERING DESIGN CONSIDERATIONS FOR BAC SYSTEMS

INTRODUCTION

As a first step, the parameters to be considered in designing biologically enhanced GAC systems are the same as those which must be taken into consideration when designing granular activated carbon beds or columns to act purely as adsorbers. However, there are several additional parameters related to optimizing the biological aspects of specific organic materials present in the system being treated which must be considered. These include control of pH and DO levels, pretreatment to remove substances toxic to microorganisms, and possibly increased frequency of column backwashing because of increased biological growths.

Initially, adsorption isotherms should be measured for the organic components present in the wastewater and which are desired to be removed. This can be accomplished by the procedure described by Rodman, Shunney & Perrotti (1978). Several concentrations of the wastewater to be treated are allowed to come to equilibrium with weighed samples of pulverized GAC. The equilibrated mixtures are filtered and the filtrates are analyzed for the constituents of concern. Results are plotted on log-log paper, with the abscissa being in units of impurities remaining in solution and with the ordinate being in units of impurities adsorbed per unit weight of GAC.

The phrase "allowed to come to equilibrium" should not be viewed as a simple matter of several minutes, several hours, or even several days. Peel & Benedek (1980a) found that the adsorption of phenol required up to 3 weeks to attain equilibrium, and that o-chlorophenol required up to 5 weeks to attain equilbrium. Sufficient time must be allowed for equilibrium conditions to be attained, in order to result in an accurate measure of adsorption isothems. The required time to attain equilibrium conditions can vary, depending upon the nature of the specific organic materials present.

Adsorption isotherms provide a good estimate of the effectiveness of activated carbon to adsorb the impurities present in the wastewater to a given level. They also provide an indication of the maximum amount of impurities which can be adsorbed by the GAC being tested. Because of this, adsorption isotherms are helpful in selecting the most suitable type of GAC to adsorb specific impurities. However, it must be recognized that adsorption isotherms are equilibrium measurements, and will not indicate how the GAC will perform during continuous operation. Continuous flow studies on pilot plant scale are the best way to obtain data from which to design full scale plant adsorbers.

It should also be borne in mind that wastewaters which contain high levels of readily biodegradable organic materials usually can be treated biologically at much lower cost than by GAC adsorption. Appropriate biological treatment of high strength, highly biodegradable wastewaters also will lower the amount of GAC subsequently required for adsorption of refractory contaminants, thereby lowering overall system costs.

After adsorption isotherms have been determined, empty bed contact times can be developed for the type of GAC best suited to the adsorption of the particular pollutants to be removed from solution. At this point, those factors which will affect biological growth and proliferation should be considered.

PARAMETERS AFFECTING BIOLOGICAL GROWTH IN GAC MEDIA

The major parameters to be considered in optimizing BAC systems for treatment of industrial wastewaters are:

(1) Presence of materials which are toxic to biological growths (pesticides, heavy metals, etc.) -- if present, the wastewater must be pretreated to remove or destroy them,

(2) Chemical nature of materials to be removed (organics and/or ammonia) -- necessity for chemical preoxidation of organic constituents versus preaeration or preoxygenation,

(3) GAC pore size distribution -- presence of a high proportion of macropores to house bacteria,

(4) Necessity for sand or other "inert" media filtration before GAC adsorption -- for removal of insoluble materials generated by preoxidation and as support media for possible biological activity,

(5) Need for supplemental oxygenation before GAC adsorption -- to increase rate of formation of CO_2 and maintain aerobic conditions,

(6) Extension of empty bed contact time over that determined by adsorption isotherms -- usually 11 to 18 minutes EBCT will be required for BAC versus 5 to 15 minutes for GAC acting by adsorption only,

(7) Initial period of operation (several days) required to develop and establish biological growths. Nitrifying organisms require several weeks to develop, and may not develop at all if overpowered by other species which may be present. Necessity for biological seeding and/or adaptation of biological organisms to organic substrates to be removed from solution. Possible need to add nutrients (nitrogen and/or phosphorus) if feed solutions are deficient,

(8) pH must be maintained between 5 and 9 (preferably between 6 and 8) for optimum biological activity,

(9) Methods for controlling BAC media -- analytical monitoring for dissolved organic carbon, TOC, CO_2 (produced biochemically), dissolved oxygen, ammonia, nitrate, nitrite, bacterial levels in GAC effluents, etc.,

(10) Determination of GAC regeneration parameters -- breakthrough of surrogates or specific compounds,

(11) Backwashing of GAC and prefilters -- need for air scouring in addition to water backwashing,

(12) Materials of construction,

(13) Safety of GAC systems.

Each of these design parameters will be discussed in more detail below.

DISCUSSION OF SPECIFIC DESIGN PARAMETERS

Raw Water Composition

There are three important parameters of the raw water being considered for treatment by biologically enhanced granular activated carbon systems. These are:

(a) The toxicity of the organic materials present to the biological organisms present in the support media,

(b) The biodegradability of the organic materials present (with or without a preoxidation treatment step),

(c) The pH of the aqueous solution to be treated.

If materials are present which are toxic to biological growth, they must be removed from solution in order that biological growths in the inert media filters and GAC adsorbers may survive and proliferate. Common toxicants include heavy metals, cyanides and certain organics such as persistent pesticides (polyhalogenated materials).

If the organic materials present are not biodegradable but are adsorbable, they will be adsorbed by GAC. However, as soon as the GAC medium becomes saturated with these compounds, they will break through and reactivation will be necessary. On the other hand, if chemical oxidation will render these refractory organics even slowly biodegradable, then they can become nutrients for the bacteria present. As a result, the useful adsorption life of the GAC adsorbers will be extended.

Preliminary batch testing using ozonation will indicate whether a chemical preoxidation step will enhance the biological removal of organic contaminants. The biodegradability of the wastewater to be treated should be measured (say by oxygen uptake) before ozonation and then again after ozonation at various dosage levels. If the biodegradability does not increase upon oxidation, then biological activated carbon will be no more effective than treatment with GAC acting as an adsorber alone.

In conducting these preliminary biodegradation batch tests, care should be taken to use microorganisms which have become acclimated to the oxidized organic contaminants.

Biological growths occur best at pH 6 to 8 and not at all at high or low pH values. Therefore, acid or alkaline wastewaters will have to be adjusted to this pH range before passage through GAC. In addition, if pretreatment of the wastewater is necessary, this pH factor must be considered.

Type of GAC

The GAC utilized for treating the specific wastewater should have a high adsorptive capacity for the particular organic materials present. In addition to this, the work of Eberhardt, Madsen & Sontheimer (1974) at the Bremen, Federal Republic of Germany waterworks showed that GAC which contained a high proportion of macropores removed a higher proportion of DOC from solution than did GAC containing a smaller percentage of macropores. Normally, macropores in GAC constitute about 1% of the total surface area. The more effective GAC used by Eberhardt, Madsen & Sontheimer (1974) contained about 2% macropores. At biological equilibrium, the 2% macropore GAC removed about 50% of the DOC present, compared with only 25% to 33% DCC removal using GAC containing 1% macropores.

These data indicate that research should be conducted on GAC which has been designed to contain even higher levels of macropores.

Necessity For Filtration Before GAC Adsorption

In European drinking water treatment plants, it has been noted that ozone oxidation causes "microflocculation" of dissolved organic materials. This is explained on the basis of oxidative formation of carboxyl, alcohol and aldehydic groups, which are capable of forming hydrogen bonds with similar groups present in other organic molecules (Maier, 1979). Such hydrogen bonding effectively increases the molecular weights of dissolved organic materials present. If these molecular weights become sufficiently high, the materials will come out of solution in the form of flocs.

Furthermore, polar carboxyl groups are capable of linking with inorganic cations normally present in water, e.g., calcium, magnesium, iron, aluminum, etc. Such linkages with polyvalent inorganic cations also cause precipitation of dissolved organic materials.

Formation of such insoluble materials can be significant, and, therefore, can cause fouling of GAC adsorbers, blinding of the adsorption sites, or simply cause premature headlosses. As a minimum, buildup of such insoluble materials can require that the GAC adsorbers be backwashed more frequently than would be necessary in the absence of these insoluble materials. Thus, in those cases when chemical preoxidation is required, or when chemical flocculants are added in pretreatment, a filtration step should be inserted prior to GAC adsorption.

Need For Supplemental Oxygenation Prior To GAC Adsorption

When one atom of dissolved organic carbon is converted into 1 molecule of CO_2, 2 atoms of oxygen (1 molecule) are required. When 4 atoms of hydrogen (the maximum number which can be associated with the dissolved organic carbon atom) are converted to water, still another molecule of dissolved oxygen is required. To convert 1 molecule of ammonium ion to nitrate ion, hydrogen ion and water stoichiometrically requires at least 4.57 molecules of dissolved oxygen.

For these reasons, it is important that sufficient dissolved oxygen be present in solution so that biochemical oxidations can proceed as nearly to completion as feasible. The solubility of oxygen in water when added by aeration is between 6 and 10 mg/L, depending upon the water temperature. On the other hand, when pure oxygen is added to water, dissolved oxygen concentrations as high as 45 to 55 mg/L can be achieved, again depending upon the water temperature.

Therefore, it is important for the wastewater treatment chemist to know the biodegradability of his wastewater, so that sufficient oxygen can be provided to maintain the biological organisms in an aerobic condition. He should also know how much biodegradation occurs in the inert media filters, so that sufficient oxygen can be supplied prior to this treatment stage as well.

Dissolved oxygen requirements can be determined by measuring oxygen uptake in a Warburg type of apparatus. When conducting such measurements, however, it is important to be sure that the bacteria used have had time to adapt to the particular organics present. Depending upon the amount of biodegradable materials present in the wastewater, provision should be made to provide sufficient DO in the GAC influent so as to maintain a level of DO in the GAC effluent of at least 3 mg/L (Sontheimer, 1978). At the Dohne drinking water plant (Mülheim, Federal Republic of Germany), for example, the DO in the GAC column effluents is controlled at 7 to 8 mg/L (Heilker, 1979b).

If chemical preoxidation of the wastewater is required, the use of ozone generated from oxygen will provide a higher DO level than will ozone generated from air.

Empty Bed Contact Time

Adsorption of dissolved organics by GAC is a rapid process. Therefore, empty bed contact times of GAC columns which act strictly as adsorbers normally are on the order of 5 to 15 minutes. On the other hand, biological oxidation processes are slower than adsorptive processes, and longer EBCTs are required. In the Federal Republic of Germany, for example, GAC columns 2 meters high were first installed in drinking water treatment plants in Düsseldorf and in Mülheim for taste and odor control and for dechlorination, respectively. When the benefits of biological activity in GAC media were recognized, however, the depths of the Düsseldorf and Mülheim GAC columns were doubled to 4 meters. Not only did this produce longer EBCTs, but also provided greater adsorptive capacities for trace organics. On the other hand, capital costs for GAC are approximately doubled, as are costs for the initial charges of GAC.

On the basis of European drinking water treatment plants using BAC systems, it appears that EBCTs of 7 to 10 minutes are optimum for maximizing the benefits of biological activity.

Initial Period Of Biological Adjustment

From European drinking water experiences, virgin GAC columns require several days to a week of feeding with water to be treated in order for significant biological activity to develop which converts DOC to CO_2. Nitrifying organisms require even longer to develop, on the order of 2 to 3 weeks. It is probable that some industrial wastewaters will contain specific organic components which require even longer for adaptation of microorganisms. For example, Benedek *et al.* (1979) have shown that after ozonation, solutions of p-nitroaniline are not readily biodegradable (as measured by oxygen uptake rate) until after about 3 weeks of acclimation of the microorganisms. These microorganisms previously had been acclimated to p-nitroaniline.

Once the bacteria have adapted to the particular industrial wastewater, however, continuous operation of GAC systems should be easily maintainable.

Analytical Monitoring

Measurements for specific contaminants of the industrial wastewater being treated, COD, TOC, ammonia, dissolved oxygen, etc., in the influent and/or effluent of the GAC adsorbers are apparent. In addition to these determinations, however, it is also helpful to analyze effluents from biologically operating filtration or GAC adsorption media for carbon dioxide content (which can be followed in some cases by accurate determination of pH). By comparing the amount of inorganic carbon produced (the amount of elemental carbon contained in the CO_2 measured) with the amount of dissolved oxygen being consumed during the same period of time, one can determine that his treatment system is or is not in biological equilibrium. At biological equilibrium, the ratio of DO consumed to inorganic carbon produced will be close to 1.

Knowing the ratio of inorganic carbon produced to the amount of organic carbon removed from solution also is useful. If this ratio is greater than 1, more CO_2 is being produced than organic carbon is being removed from solution. This situation indicates that biological regeneration of some of the active adsorption sites of the GAC is occurring. Conversely, when the ratio is less than 1, this indicates that more dissolved organic carbon is being removed by adsorption than by biochemical decomposition.

As indicated in preceeding sections, it is important to provide sufficient DO to the solutions being treated to maintain the bacteria in an aerobic state. Since industrial wastewaters fed to GAC adsorbers are expected to contain considerably more DOC than drinking waters, it likely will be necessary to add pure oxygen before sand or other inert media filtration. This can be accomplished during ozonation, in the event that chemical preoxidation with ozone is chosen as a pretreatment step, by generating the required ozone from pure oxygen.

Monitoring the sand or inert medium filter influents and effluents for dissolved oxygen also will be necessary, so as to determine the amount of DO consumed biologically during filtration, as well as to determine the amount of additional oxygen necessary to be added prior to passage of the solution through biologically enhanced GAC.

GAC Regeneration Parameters

GAC regeneration parameters should be developed on the basis of the specific organic materials which must be removed from the wastewater and for which GAC was selected as the treatment process to deal with them. If chlorinated organics are the contaminants to be removed, for example, then GAC reactivation frequency should be based upon their breakthrough. Once the specific polluting contaminants to be removed have been identified, then specific or surrogate chemical analytical procedures can be developed for lower cost monitoring. The use of TOC as a surrogate analysis probably will be a useful procedure in this regard.

It should be recognized that the objective of GAC treatment is to remove those contaminants which can be removed by adsorption; the objective of promoting aerobic biological activity in the GAC is to remove as much of the biodegradable fraction as possible. Under ideal circumstances, breakthrough of the GAC system will be determined only by those chemicals which are adsorbed but which cannot be made biodegradable. If breakthrough of biodegradable organics occurs first, this means that the system has not yet been designed optimally.

Backwashing of Filtration Media and GAC Adsorbers

Air scouring is used initially during backwashing in all European drinking water treatment plants known to be using biologically enhanced GAC adsorption processes. Air scouring is required to loosen the biological growths adhering to the filtration or GAC media. In actuality, air scouring is more akin to "bumping", and as soon as the agglomerated filtration or GAC medium has been broken up by such bumping, then backwashing is continued with water.

Biologically operating European sand filters normally are backwashed first by air scouring, then with a mixture of air plus water, then with water alone. In backwashing GAC media, however, air scour then water backwashing is practiced. Apparently the density of GAC is too low to allow use of the (air + water) treatment without incurring significant losses of GAC.

Air scour or air backwash is a concept which has found considerable application recently in wastewater treatment, but little or no application in United States drinking water facilities. In water treatment practice, the combined effects of heavy prechlorination dosages as well as so-called surface washing have been sufficient to enable satisfactory filter cleaning during the backwashing cycle.

A report of the American Water Works Association Subcommittee on Backwashing of Granular Filters (Cleasby et al., 1977) recommends provisions for air scour or for surface wash when conditions exist such as those which occur with biological activity promoted in the beds. While surface wash units are common in modern U.S. water treatment plants, air scour systems are not. Cleasby et al. (1977) categorized backwashing methods as follows:

(1) High rate backwash - full bed fluidization and substantial bed expansion (20 to 50%) normally is preceeded and followed by a lower rate backwash. This backwash system can be used for single or multi-media filters.

(2) Low rate backwash with little or no bed fluidization or bed expansion - auxiliary scour is essential to low rate backwash. This backwash system can be used for single medium filters only.

(3) Water backwash with surface water wash only.

(4) Water backwash with air auxiliary:

    (a) Air scour followed by low rate water backwash - for use with single medium filters only.

    (b) Air scour followed by high rate water backwash - for use with single and multi-media filters.

    (c) Simultaneous air scour and low rate water backwash, followed by high rate water backwash alone - for use with single medium filters alone.

    (d) Simultaneous air scour and low rate water backwash, followed by high rate water backwash alone - for use with single and multi-media filters.

It appears that filter backwash techniques must be reviewed if chlorination ahead of filtration is discontinued. Based on the AWWA Filtration Committee's findings and European practice, provisions of either air scour or surface wash appear to be necessary. Provision of surface wash without prechlorination would appear to result in shorter filtration runs with associated increases in operating costs. For example, a midwest water treatment utility with filters equipped with surface wash estimated a reduction in backwash cycles from 60 hours to 30 hours. Conversion of a filtration system from water backwash to water backwash with air auxiliary would require complete reconstruction of existing filter bottoms to accomodate the air distribution systems.

In those European water treatment plants in which biologically enhanced GAC has been installed to replace breakpoint chlorination followed by GAC later in the process for dechlorination (for example, at the Dohne plant, Mülheim, Federal Republic of Germany), both the sand filters and the GAC adsorbers have been found to be able to operate nearly twice as long without breakpoint chlorination and with ozone preoxidation before backwashing becomes necessary. This is clear indication that the anticipated biological fouling of filters when prechlorination is eliminated may not occur, or, if it does, that it may be controlled by the low level preozonation required to promote aerobic bacterial activity in the filter and adsorber media.

The frequency with which backwashing of biologically enhanced filters or GAC adsorption media will be required usually is determined by headlosses. However, at the Dohne drinking water treatment plant (Mülheim, Federal Republic of Germany), filter runs as long as 1 week could be achieved before headlosses built up sufficiently to require backwashing. On the other hand, during the summer of 1978, a "population explosion" of nematodes was observed to occur in the rapid sand filters and GAC adsorbers. Since the reproduction cycle of these organisms is just over 3 days, it was concluded that nematode development was a result of the more than one week backwashing intervals. When backwashing intervals were lowered to 3 days, the nematodes disappeared completely (Heilker, 1979).

Valencia and Cleasby (1979) have recently published an excellent discussion of velocity gradients in granular filter backwashing, which provides the engineer with a valuable tool for analyzing shear forces in filter beds and their effects upon the media cleaning process.

Materials of Construction

Granular activated carbon systems will cause corrosion problems if they are not anticipated and provided for in the original design. It is not expected, however, that there will be any significant increase in corrosion behavior of GAC media as a result of operating with maximized biological activities. Perhaps the best source of information as to anti-corrosion measures to be taken is the carbon supplier himself, as well as operational plants where GAC has been in use.

At the new Kralingen drinking water treatment plant in Rotterdam, The Netherlands, the granular activated carbon adsorbers are constructed of carbon steel, but are coated on the inside with a proprietary coating. GAC is supported on a coated steel plate with plastic nozzles inset in the plate to provide flow distribution (Rice et al., 1979).

Heilker (1979) has described construction and corrosion inhibition aspects of the GAC adsorbers recently enlarged and rebuilt at the Dohne drinking water treatment plant in Mülheim, Federal Republic of Germany. Steel GAC adsorbers were selected initially, because they were better suited for overall process design and were easier to work with in modifying existing water treatment plants. However, corrosion problems caused high repair costs.

After 10 years of testing different adsorbers with additional cathodic corrosion protection, a method has been adopted at Mülheim which offers "nearly complete protection against defects". The 12 double-staged adsorbers are being modified as follows: all interior welded seams are being straightened and ground. Rust is being removed by sand blasting. Condensate is prevented by aeration during coating. Solvent-free epoxy resin, resistant to abrasion and to ozone, is used, and a 450 to 500 µm layer is applied. The poreless coating is tested with 1.5 to 2 kV.

Further experimentation has shown that the interior adsorber surfaces can be "completely protected" if a combined cathodic protection with sacrificial anodes is used and the electric power supply is transmitted over platinum-covered titanium anodes.

Costs for all corrosion protective devices being applied to GAC adsorbers at Mülheim amount to approximately 10% of the total cost of the treatment plant modifications required to convert the old (breakpoint chlorination) process to the BAC process recently installed (Heilker, 1979).

Mechanical Considerations

Culp (1980) reviewed GAC use in advanced wastewater treatment (AWT) systems and pointed out that the experience has varied from excellent to very poor. Culp also states that the failures of GAC systems in AWT applications have not stemmed from deficiencies in the basic GAC processes of adsorption of organics, but, rather, from mechanical problems, which have included:

- failure of GAC column linings due to improper installation or faulty material,
- corrosion of GAC storage tanks,
- corrosion of surface wash equipment and other metal parts in GAC contact tanks,
- numerous failures of GAC column underdrains, where the wrong type of sand filter type underdrains had been installed, or where the installation was defective,
- failure to make provisions for maintaining aerobic conditions at all times in the GAC column influent water,
- failure to provide means for excluding air or venting air from GAC column backwash lines prior to initiation of backwashing,
- lack of adequate means to dewater and feed measured amounts of spent GAC to the reactivation furnace,
- corrosion of furnace parts,

- installation of sub-standard or defective refractories in reactivation furnaces,
- improper installation of furnace refractories,
- inadequate pretreatment of wastewater prior to application of GAC,
- lack of adequate means for GAC movement and conveyance, apparently due to the lack of knowledge concerning the physical handling properties of GAC.

Culp (1980) concludes that any and all of these rather serious problems could have been avoided quite easily by proper application of the best current engineering design knowledge and practices for GAC systems.

Taking GAC Filter/Adsorbers Out Of Service

Plant personnel at European drinking water treatment plants which have been using granular activated carbon for some years advise that GAC columns or beds that have been in plant operation should not be allowed to stand idle or off-line for more than one day. If this caution is not heeded, the biomass in the activated carbon medium changes and when the unit is placed back in-line, contamination of the product drinking water occurs. When operating units are taken out of service, the activated carbon is sent for reactivation. If the units are to be taken off-line only for a few days, water is passed through the units continuously until they are placed back in line (Engels, 1978, Private Communication).

Safety Considerations of GAC Adsorbers

Strudgeon et al. (1979) have discussed several serious accidents which have occurred with GAC systems and which have resulted in at least two fatalities. These accidents occurred in adsorbers which contained wet GAC, which is an excellent adsorber of atmospheric oxygen. In two instances, workers apparently entered enclosed GAC adsorbers without positive pressure masks to provide oxygen and were suffocated because of the lack of sufficient oxygen.

Other potential hazards associated with GAC systems include the following:

(1) GAC in dry form contains significant quantities of fines and dust. As a result, all GAC handling systems pose the possibility for creating a dust explosion hazard, unless precautions are taken.

(2) If biological growths within GAC adsorbers are allowed to become anaerobic, and if sulfates are present, quantities of H_2S can be generated. This toxic gas also can pose a hazard to workers entering the adsorbers, although its presence usually can be readily detected nasally in small quantities.

(3) When dry and confined, GAC provides a relatively solid footing. However, after having been fluidized with the proper amounts of water, it has the characteristics of a mixture with virtually no support, thus allowing a heavier weight to sink within the mixture. The term "quicksand effect" has been applied to this meretricious behavior of GAC and similar systems.

(4) GAC also will "bridge", as soil does, and personnel entering a GAC vessel must insure that the bed is well drained and that bridging has not developed, which possibly could collapse and bury the individual.

Alternative GAC Adsorber Designs

Recently, Carnes and Burstein (1980) have addressed all of the engineering factors involved with designing GAC adsorption systems. This elegant treatise should be consulted by those wishing more detailed information on this subject. In addition, Bernardin (1980) has discussed the subject of problems and solutions of granular activated carbon operations.

REFERENCES

American Water Works Association, 1971, Water Treatment Plant Design, Am. Water Works Assoc., Inc., Denver, Colorado.

Anonymous, 1979, "Space-saving Wastewater Treatment", Chem. Engrg., July 2; p. 47-8.

Argo, D.G., Culp, R.L. & Hansen, S.P., 1978, "Ozone and Biological Activated Carbon", Presented at Am. Chem. Soc., 176th Natl. Meeting, Miami Beach, Florida, Sept. 11-15.

Arisman, R.K., Crase, T.C., Zeff, J.D. & Musick, R.C., 1979, "Destruction of PCBs in Industrial and Sanitary Waste Effluents by the Ultrox (UV-Ozone) Process", presented at AIChE 86th National Meeting, Houston, TX, April 1-5. Am. Inst. Chem. Engrs., New York, N.Y.

Baker, M.N., 1949, The Quest For Pure Water, Am. Water Works Assoc., Denver, Colorado.

Batchelor, J.S., 1977, "Activated Carbons for Effluent and Water Treatment", Effluent & Water Treatment J., April, 1977.

Benedek, A., 1977, "The Effect of Ozone on Activated Carbon Adsorption -- A Mechanistic Analysis of Water Treatment Data", Presented at Intl. Symp. on Advanced Ozone Technology, Toronto, Ontario, Canada, Nov., 1977. Intl. Ozone Assoc., Vienna, VA.

Benedek, A., Bancsi, J.J., Malaiyandi, M. & Lancaster, E.A., 1979, "The Effect of Ozone on the Biological Degradation and Activated Carbon Adsorption of Natural and Synthetic Organics in Water. Part II. Adsorption", Ozone Sci. & Engrg. 1(4):347-356. See also Stephenson, P., Benedek, A., Malaiyandi, M. & Lancaster, E.A., "Part I. Ozonation and Biodegradation", Ozone Sci. & Engrg. 1(3):263-280.

Benedek, A. & Richard, Y., 1980, "Advances in Biological Treatment", presented at the IWSA Congress, Paris, Sept.

Bernardin, F.E., Jr., 1980, "Granular Activated Carbon Operation: Problems and Solutions", in Proc. 8th Ann. WWEMA Indl. Poll. Conf., Houston, TX, June 4-6, p. 93-101.

Bhargava, P., 1979, "Ozone Disinfection of Pure Oxygen Activated Sludge Using Unique Partial Recycle System", presented at 52nd Ann. Conf., Water Poll. Control Fed., Houston, TX, Oct. 9.

Blanck, C.A., undated, ca. 1976, "Taste and Odor Control Utilizing Granular Activated Carbon in the Plains Region of The American Water Works System", Am. Water Works Service Co., Inc., Western Region.

Blue, P.T., 1979, Infilco Degremont Inc., Richmond, VA., Private Communication.

Brewer, W.S. & Carmichael, W.W., 1979, "Microbiological Characterization of Granular Activated Carbon Filter Systems", J. Am. Water Works Assoc. 71:738-740.

Cairo, P.R., McElhaney, J. & Suffet, I.H., 1979, "Pilot Plant Testing of Activated Carbon Adsorption Systems", J. Am. Water Works Assoc. 71:660-672.

Calgon Corp., undated, Basic Concepts of Adsorption on Activated Carbon, Filtrasorb Dept., Water Mgmt. Div., Calgon Corp., Pittsburgh, PA.

Carnes, B.A. & Burstein, D., 1980, "Alternative GAC Adsorber Design", presented at 8th Ann. Indl. Poll. Conf., Houston, TX, June.

Carswell, J.K., Jr., 1977, U.S. Environmental Protection Agency, Cincinnati, Ohio. Private Communication.

Characklis, W.G., 1973, "Attached Microbial Growths. I. Attachment and Growth", Water Research 2:1103.

Chédal, J., 1976, Cie. Générale des Eaux, Paris, France. Completed questionnaire for Public Technology Inc. survey describing Choisy-le-Roi plant.

Clark, J.W., Viessman, W. & Hammer, M.J., 1971, Water Supply & Pollution Control, 2nd Ed., The Intl. Textbook Co., Chapter 11, "Biological Treatment Processes".

Clark, J.C., Jr., 1979, "Economic Aspects of Controlling Synthetic Organics", presented at Seminars on Control of Organic Chemical Contaminants in Drinking Water, Jan. 16/17, Feb. 13/14 & March 13/14. U.S. EPA, Office of Drinking Water, Washington, D.C.

Clark, R.M. & Stevie, R.G., 1978, "Meeting the Drinking Water Standards: The Price of Regulation". Presented at the Nat'l. Conf. on Drinking Water Policy Problems. Resources For The Future, Washington, D.C., March 6-8, 1978.

Clark, R.M. & Dorsey, P., 1980, "Influence of Operating Variables on the Cost of Granular Activated Carbon Adsorption Treatment", U.S. EPA, Municipal Environmental Research Lab., Cincinnati, Ohio.

Clark, R.M., Culp, R.L. & Gumerman, R.C., 1980, "Cost of Granular Activated Carbon Adsorption in the USA", U.S. EPA, Municipal Environmental Research Lab., Concinnati, Ohio.

Cleasby, J.L., Arbolea, J., Burns, C.E., Prendiville, P.W. & Savage, E.S., 1977, "Backwashing of Granular Filters", J. Am. Water Works Assoc. 69(2):115-126.

Coco, J.H., Klein, E., Howland, D., Mayes, J.H., Myers, W.A., Pratz, E., Romero, C.J. & Yocum, F.H., 1979, "Development of Treatment and Control Technology for Refractory Petrochemical Wastes", EPA Report No. EPA-600/2-79-080. U.S. EPA, Robt. S. Kerr Env. Res. Lab., Ada, OK.

Coin, L., Hannoun, C. & Gomella, C., 1964, "Inactivation of Poliomyelitis Virus by Ozone in the Presence of Water", la Presse Médicale 72(37):2153-2156.

Coin, L., Gomella, C., Hannoun, C. & Trimoreau, J.-C., 1967, "Ozone Inactivation of Poliomyelitis Virus in Water", la Presse Médicale 75(38):1883-1884.

Culp, R.L., 1980, "GAC Water Treatment Systems", Public Works, Feb., pp. 83-87.

Directo, L.S., Chen, C.-L. & Kugelman, I.J., 1977, "Pilot Plant Study of Physical-Chemical Treatment", J. Water Poll. Control Fed. 49(10):2081-2098.

Dostal, K.A., Pierson, R.C., Hager, D.G. & Robeck, G.G., 1965, "Carbon Bed Design Criteria at Nitro, West Virginia", J. Am. Water Works Assoc. 57:663.

Eberhardt, M., 1975, "Experience with the use of Biologically Effective Activated Carbon", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, H. Sontheimer, editor. EPA Report No. EPA 600/9-76-030, Dec. 1976, pp. 331-347.

Eberhardt, M., Madsen, S. & Sontheimer, H., 1974, "Untersuchungen zur Verwendung Biologisch Arbeitender Aktivkohlefilter bei der Trinkwasseraufbereitung", Heft 7, Veröffentlichungen des Bereichs und des Lehrstuhls für Wasserchemie Leitung: Prof. Dr. H. Sontheimer, Univ. Karlsruhe, Germany. See also Wasser/Abwasser 116(6):245-247 (1975).

Edwards, R.W., 1979, "Control of Synthetic Organic Chemicals by Granular Activated Carbon - Theory, Application and Regeneration", presented at EPA seminar on Control of Organic Chemical Contaminants in Drinking Water, Philadelphia, Pennsylvania, January, 1979. Public Technology, Inc., Washington, D.C.

Engels, C., 1978, Düsseldorf Waterworks, Federal Republic of Germany, Private Communication.

Engler-Bunte Institut der Universität Karlsruhe, 1977, "Determination of the Organic Substances Dissolved in Water by Adsorption on Activated Carbon". From Practical Control Methods in the Treatment of Drinking

Water, published by EBI and DVGW Research Bureau, Richard Willstätter Allee 5, 7500 Karlsruhe, Federal Republic of Germany.

Fiessinger, F.M. & Monteil, A., 1980, "Case Studies for the Abandonment of Prechlorination", presented at Ann. Conf. of Am. Water Works Assoc., Atlanta, GA, June 18.

Flentje, M. & Hager, D.G., 1964, "Reevaluation of Granular Carbon Filters for Taste and Odor Control", J. Am. Water Works Assoc. 56(2):191-197.

Ford, D.B., 1973, "The Use of Granular Carbon Filtration for Taste & Odor Control", Proc. Water Research Assoc. Conf., Reading, England, pp. 263-278.

Froelich, E.M., 1978, "Control of Synthetic Organic Chemicals by Granular Activated Carbon -- Theory, Application and Reactivation Alternatives", presented at EPA seminar on Control of Organic Chemical Contaminants in Drinking Water, Cincinnati, Ohio, October, 1978. Public Technology, Inc., Washington, D.C.

Fry, J.C. & Staples, D.G., 1976, "Distribution of Bdellovibrio Bacteriovirus in Sewage Works River Water and Sediments", Appl. & Envmntl. Microbiology 31:469-474.

Fuchs, F. & Kühn, W., 1975, "The Use of Activated Carbon to Analyze Natural Waters With Regard to Their Behavior in Waterworks Filters", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, H. Sontheimer, editor. EPA Report No. EPA 600/9-76-030, Dec., 1976, pp. 182-207.

Gauntlett, R.B. & Packham, R.F., 1973a, "The Use of Activated Carbon in Water Treatment", Proc. Water Research Assoc. Conf., Reading, England, pp. 31-51.

Gauntlett, R.B. & Packham, R.F., 1973b, "The Removal of Organic Compounds in the Production of Potable Water", Chem. & Ind., Sept., 1973, pp. 812-817.

German Unit Standards for Water Testing, Wastewater Testing and Mud Testing, 1960, 3rd Edition, Chemie Publ., Weinheim, Federal Republic of Germany.

Gerval, R., 1978, "Ozonation of Raw Water Before Treatment in Drinking Water Plants", presented at Ozone Technology Symposium, Los Angeles, Calif., May, 1978. Intl. Ozone Assoc., Vienna, VA.

Gerval, R., 1979, "The Different Locations of Ozone in Treatment Lines. Study of the Operating Mechanisms According to These Locations", presented at 4th World Ozone Congress, Houston, TX, Nov. 26-29. Intl. Ozone Assoc., Vienna, VA.

Glaze, W.H., 1978, "A Comparison of Ozone and Ozone/Ultraviolet for the Destruction of Refractory Organic Compounds in Water". Presented at Ozone Technology Symposium, Los Angeles, Calif., May, 1978. Intl. Ozone Assoc., Cleveland, Ohio.

Gilbert, E., 1977, "Chemische Vorgänge bei der Ozonanwendung", in WASSER BERLIN '77 - Ozon und Wasser - Wasserchemie, p. 277-293. AMK Berlin or Intl. Ozone Assoc., Vienna, VA.

Gilbert, E., 1978, "Investigations on the Changes of Biological Degradability of Single Substances Induced by Ozonolysis", presented at Ozone Technol. Symp., Los Angeles, May 23-25. Intl Ozone Assoc., Vienna, VA.

Gomella, C. & Versanne, D., 1977, "Le Role de l'Ozone dans la Nitrification Bactérienne de l'Azote Ammoniacal -- Cas de l'Usine de la Chapelle Banlieue Sud de Rouen (Seine Maritime), France". Presented at Third Intl. Symp. on Ozone Technol., Paris, France, May, 1977. Intl. Ozone Assoc., Vienna, VA.

Gould, J.P. & Weber, W.J., Jr., 1976, "Oxidation of Phenols by Ozone", J. Water Poll. Control Fed. 48(1):47-60.

Grombach, P., 1975, "Reaktivierung von Aktivkohle im Wasserwerk", Gaz-Eaux-Eaux Usées 55(9):549-553.

Guirguis, W.A., Cooper, T., Harris, J. & Ungar, A., 1976a, "Improved Performance of Activated Carbon by Pre-Ozonation", Presented at 49th Annual Conf. of Water Pollution Control Fed., Minneapolis, Minn., Oct., 1976.

Guirguis, W.A., Hanna, Y.A., Prober, R., Meister, T. & Srivastava, P.K., 1976b, "Reaction of Organics Nonsorbable by Activated Carbon with Ozone", in Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, R.G. Rice & J.A. Cotruvo, editors. Intl. Ozone Assoc., Vienna, VA (1978), pp. 291-301.

Guirguis, W.A., Jain, J.S., Hanna, Y.A. & Srivastava, P.K., 1976c, "Ozone Application for Disinfection in the Westerly Advanced Wastewater Treatment Facility", in Forum on Ozone Disinfection, E.G. Fochtman, R.G. Rice & M.E. Browning, editors. Intl. Ozone Assoc., Vienna, VA, pp. 363-381.

Guirguis, W.A., Melnyk, P.B. & Harris, J.P., 1976d, "The Negative Impact of Industrial Waste on Physical-Chemical Treatment", presented at 31st Purdue Indl. Waste Conf., Lafayette, Indiana, May, 1976.

Guirguis, W.A., Cooper, T., Harris, J. & Ungar, A., 1978, "Improved Performance of Activated Carbon by Pre-Ozonation", J. Water Pollution Control Fed. 50(2):308-320.

Gumerman, R.C., Culp, R.L. & Hansen, S.P., 1978, "Estimating Costs For Water Treatment as a Function of Size and Treatment Efficiency", EPA Report

No. EPA-600/2-78-182. U.S. EPA, Municipal Environmental Research Lab., Cincinnati, Ohio.

Gumerman, R.C., Culp, R.L. & Hansen, S.P., 1979, "Estimating Water Treatment Costs", EPA Report No. EPA-600/2-79-162a (Vol. 1 - Summary) and -162b (Vol. 2 - Cost Curves Applicable to 1 to 200 mgd Treatment Plants). U.S. EPA, Municipal Environmental Research Lab., Cincinnati, Ohio.

Hagar, D.G. & Flentje, M., 1965, "Removal of Organic Contaminants by Granular Carbon Filtration", J. Am. Water Works Assoc. 57(11):1440 (1965).

Hagar, D.G. & Fulker, R.D., 1968, "Adsorption and Filtration with Granular Activated Carbon", J. Soc. Water Trtmt. & Examn., 17.

Handbook of Chemistry & Physics, 1975-1976, 56th Edition. CRC Press, Cleveland, Ohio, pp. C-141-143.

Hanna, Y., Slough, J., Jr. & Guirguis, W.A., 1977, "Ozone as a Pretreatment Step for Physical Chemical Treatment - Part II", Presented at Symposium on Advanced Ozone Technology, Toronto, Ontario, Canada, Nov., 1977. Intl. Ozone Assoc., Vienna, VA.

Hansen, S.P., Gumerman, R.C. & Culp, R.L., 1979, "Estimating Water Treatment Costs. Vol. 3. Cost Curves Applicable to 2,500 gpd to 1 mgd Treatment Plants". EPA Report EPA-600/2-79-162c. U.S. EPA, Municipal Environmental Research Lab., Cincinnati, Ohio.

Hasler, J.W., 1974, Purification With Activated Carbon, Chemical Publishing Co., Inc., New York, N.Y.

Heilker, E., 1978, Rheinisch-Westfälischen Wasserwerksgesellschaft mbH, Mülheim, Federal Republic of Germany. Private Communication.

Heilker, E., 1979a, "Design of Water Treatment Adsorption Systems", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA., Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, D.C.

Heilker, E., 1979b, "The Mülheim Process for Treating Ruhr River Water", J. Am. Water Works Assoc. 71(11):623-627.

Holluta, J., 1959, "Zwei Jahre Geruchsmessungen am Niederrhein", Kommunalwirtschaft 6:223-229.

Holluta, J., 1960, "Geruchs- und Geschmacksbeeinträchtigung des Trinkwassers. Ursache und Bekämpfung". Wasser-Abwasser 101:1018-1023 & 1070-1078.

Hopf, W., 1960, "Versuche mit Aktivkohlen zur Aufbereitung des Düsseldorfer Trinkwassers", Wasser-Abwasser 101(14):330-336.

Hopf, W., 1970, "Water Treatment With Ozone and Activated Carbon (The Düsseldorf Process), Part II. Notes on the Use of Ozone", Wasser-Abwasser 111(3):156-164.

Huisman, I.L., 1978, "Developments in Village-Scale Slow Sand Filtration", Progress in Water Technol. 11(1/2):159-165.

Hutchinson, M. & Ridgway, J.W., 1977, "Microbiological Aspects of Drinking Water Supplies", in Aquatic Microbiology, Soc. for Appl. Bacteriology, Symposium Series No. 6, F.A. Skinner & J.M. Shewan, editors, Academic Press, London & New York, pp. 179-218.

Jekel, M., 1977, "Biological Treatment of Surface Waters in Activated Carbon Filters", presented at Meeting of KIWA, Water Research Center & Engler-Bunte Inst., Univ. Karlsruhe, Federal Republic of Germany, Oct. 27-28, 1977.

Jekel, M., 1978, Engler-Bunte Institut, Univ. Karlsruhe, Federal Republic of Germany. Private Communications.

Jekel, M., 1979, "Experience With Biological Activated Carbon", presented at Intl. Conf. on Oxidation Techniques in Drinking Water Treatment, Karlsruhe, Federal Republic of Germany, Sept. 11-13. Engler-Bunte Inst. der Univ. Karlsruhe.

Jeris, J.S., Owens, R.W., Hickey, R. & Flood, F., 1977, "Biological Fluidized-Bed Treatment for BOD and Nitrogen Removal", J. Water Poll. Control Fed. 49(5):816-831.

Jüntgen, H., 1975, "Manufacture and Properties of Activated Carbon", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, op. cit., pp. 16-28.

Kittredge, D., 1980, "The Economics of Carbon Regeneration; State of the Art", J. New England Water Works Assoc. 94(1):1-23.

Klotz, M., Werner, P. & Schweisfurth, R., 1975, "Investigations Concerning the Microbiology of Activated Carbon Filters", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, op. cit., pp. 312-330.

Kappe, D.S., 1978, "Pretreatment of the Combined Industrial-Domestic Wastewaters of Hagerstown, Maryland. Vol. I". U.S. EPA Report No. EPA-600/2-78-043a, Robert S. Kerr Environmental Research Lab., U.S. EPA, Ada, OK 74820.

Klotz, M., Werner, P. & Schweisfurth, R., 1976, "Microbiolological Studies of Activated Carbon Filtering for the Treatment of Drinking Water: Research and Development in Water Works Practical Applications', Sci. Reports on Study and Planning of the City Works, Wiesbaden, A.G. 3:75-82.

Knoppert, P.L. & Rook, J.J., 1973, "Treatment of River Rhine Water With Activated Carbon", Proc. Water Research Assoc. Conf., Reading, England, pp. 109-125.

Knorr, D.B., 1979, "Direct Recharge For El Paso, Texas", in Proc. Water Reuse Symp., Washington, D.C., March 25-30. Am. Water Works Assoc. Research Foundation, Denver CO., pp. 212-238.

Kölle, W. & Sontheimer, H., 1973, "Experiences With Activated Carbon in West Germany", Proc. Water Research Assoc. Conf., Reading, England, pp. 347-367.

Kölle, W., 1974, "Suitability Testing of Water Works Activated Carbons on the Basis of Their Adsorption Characteristics for Organic Chlorine Compounds", Report of the Nuclear Research Center, Karlsruhe (KFK 1969 UF) of April, 1974, dealing with Water & Wastewater Chemistry Investigations, 1972/73.

Kölle, W., Sontheimer, H. & Steiglitz, L., 1975, "Eignungsprüfung von Wasserwerks-Aktivkohlenanlage Ihrer Adsorptionseigenschaften für Organische Chlorverbindungen", Vom Wasser 44:203-217.

Koppe, P. & Giebler, G., 1966, "Untersuchungen über die Ozonzehrung von Wässern", Wasser-Abwasser 107(8):196-200.

Kornegay, B.H., 1978, "Control of Synthetic Organic Chemicals by Activated Carbon -- Theory, Application and Regeneration Alternatives", presented at EPA seminar on Control of Organic Chemical Contaminants in Drinking Water, Los Angeles, Calif., Nov. 14-15, 1978. U.S. EPA, Office of Drinking Water, Washington, D.C.

Kühn, W., 1974, "Untersuchungen zur Bestimmung von Organischen Chlorverbindungen auf Aktivkohle", Dissertation, Fak. f. Chemie-Ing. Wesen, Univ. of Karlsruhe, Karlsruhe, Federal Republic of Germany.

Kühn, W. & Fuchs, F., 1975, "Untersuchungen zur Bedeutung der Organischen Chlorverbindungen und Ihrer Adsorbierbarkeit", Vom Wasser 45:217-232.

Kühn, W. & Sontheimer, H., 1973a, "Einige Untersuchungen zur Bestimmung von Organischen Chlorverbindungen auf Aktivkohle", Vom Wasser 41:65-79.

Kühn, W. & Sontheimer, H., 1973b, "Einfluss Chemischer Umsetzungen auf die Lage der Adsorptionsgleichgewichte an Aktivkohlen", Vom Wasser 40:115-123.

Kühn, W. & Sontheimer, H., 1974, "Zur Analytischen Erfassung Organischer Chlorverbindungen mit der Temperaturprogrammierten Pyrohydrolyse", Vom Wasser 43:327-341.

Kühn, W., Sontheimer, H. & Kurz, R., 1978, "Use of Ozone and Chlorine in Water Works in the Federal Republic of Germany", in Ozone/Chlorine

Dioxide Oxidation Products of Organic Materials, R.G. Rice & J.A. Cotruvo, editors. Intl. Ozone Assoc., Vienna, VA, pp. 426-441.

Kussmaul, H., 1978, "Efficiency of Ground Passage in Drinking Water Treatment", presented at Intl. Conf. on Oxidation Processes in Drinking Water Treatment, Karlsruhe, Federal Republic of Germany, Sept. 10-13, 1978. Engler-Bunte Inst. der Univ. Karlsruhe.

Latoszek, A. & Benedek, A., 1979, "Some Aspects of the Microbiology of Activated Carbon Columns Treating Domestic Wastewater", Environ. Sci. & Technol. 13(10):1285-1287.

Lawrence, C.H., 1968, "California Plant Uses Diatomite and Carbon Filters", Water & Wastes Engrg., Jan., 1968.

Larocque, R., CANOZONE, Montreal, Canada, 1977. Private Communication.

Lepage, W.L., 1979, "A Plant Operator's View of Ozonation", in Proc. Seminar On 'The Design and Operation of Drinking Water Facilities Using Ozone or Chlorine Dioxide', R.G. Rice, editor. New England Water Works Assoc., Dedham, MA., pp. 225-240.

Le Paulouë, J., 1978, TRAILIGAZ, Garges-lès-Gonesse, France. Private Communication.

Lestochi, L.J., Byrne, J.L. & Horg, S.N., 1979, "Generation of Ozone From Oxygen for Drinking Water Treatment", in Proc. Seminar On 'The Design and Operation of Drinking Water Facilities Using Ozone or Chlorine Dioxide', R.G. Rice, editor, New England Water Works Assoc., Dedham, MA, pp. 121-130.

Lurgi, 1976, Hydraffin, Aquaffin, Powdered and Granular Activated Carbon For Water Purification, Manufacturing, Application, Testing, Publicn. No. T-1188/3.76, Lurgi Apparate-Technik GmbH, Chemotechnik, Frankfurt/Main, Federal Republic of Germany.

Maier, D., 1971, "Untersuchungen zur Chemischen Regeneration von Erschöpften Wasserreinigungskohlen", Dissertation, Fak. f. Chemie-Ing. wesen, Univ. Karlsruhe, Federal Republic of Germany.

Maier, D., 1979, "Microflocculation By Ozone", in Oxidation Techniques in Drinking Water Treatment, W. Kühn & H. Sontheimer, editors, U.S. EPA Report No. EPA-570/9-79-020, pp. 394-417. U.S. EPA, Office of Drinking Water, Washington, D.C.

Maqsood, A. & Benedek, A., 1977, "The Effect of Low Temperature on Organic Removal and Denitrification in Activated Carbon Columns", J. Water Poll. Control Fed. 49:2107.

McCreary, J.J. & Snoeyink, V.L., 1977, "Granular Activated Carbon in Water Treatment", J. Am. Water Works Assoc. 69(8):437-444.

McElhaney, J. & McKeon, W.R., 1978, "Enumeration and Identification of Bacteria in Granular Activated Carbon Columns", presented at Am. Water Works Assoc. Technical Mtg., Louisville, KY, Dec. Am. Water Works Assoc., Denver, CO.

McElhaney, J., Coyle, J.T., Santo, J. & Burlingame, G., 1979, "The Effect of Bacterial Activity on TOC Removal Using Granular Activated Carbon", presented at Am. Water Works Assoc. Technology Conf., Philadelphia, PA, Dec. Am. Water Works Assoc., Denver, CO.

Melbourne, J.D. & Miller, D.G., 1973, "The Treatment of River Trent Water Using Granular Activated Carbon Beds", Proc. Water Research Assoc. Conf., Reading, England, pp. 73-108.

Metcalf & Eddy, Inc., 1972, Wastewater Engineering: Collection, Treatment, Disposal, McGraw Hill Book Co., New York, N.Y.

Miller, G.W., Rice, R.G., Robson, C.M., Scullin, R.L., Kühn, W. & Wolf, H., 1978, "An Assessment of Ozone & Chlorine Dioxide Technologies for the Treatment of Municipal Water Supplies". U.S. EPA Report No. 600/2-78-147. U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Cincinnati, Ohio 45268.

Miller, G.W., 1979, "Costs of Treating Drinking Water With Ozone", in Proc. Seminar On 'The Design and Operation of Drinking Water Facilities Using Ozone or Chlorine Dioxide', R.G. Rice, editor. New England Water Works Assoc., Dedham, MA, pp. 189-204.

Milliner, R., Bowles, D.A. & Brett, R.W., 1972, "Biological Pretreatment at Tewkesbury", Water Trtmt. & Examn. 21:318-326.

Moat, A.G., 1979, Microbial Physiology, John Wiley & Sons, New York, N.Y., Chapters 3 & 4.

Moser, R.H., 1978, Letter, dated July 25, 1978, to Fred E. Schlaegal, included as Attachment D of Comments and Recommendations Concerning EPA's Proposed National Interim Primary Drinking Water Regulations, Coalition For Safe Drinking Water, Indianapolis, Indiana, August, 1978.

Nolte, H., 1978, Rheinisch-Westfälischen Wasserwerksgesellschaft mbH, Mülheim, Federal Republic of Germany. Private Communication.

Osborne, D., 1979, "Experience at Wilne Treatment Works", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, 30 April - 2 May 1979, Reston, VA. U.S. EPA, Office of Drinking Water, Washington, D.C.

Park, Y.K. & Sontheimer, H., 1973, "The Transformation and Concentration of Pesticides From Dioxane Extracts Into n-Hexane", Vom Wasser 41:81-91.

Park, Y.S., 1974, "The Investigation of Polar Organic Chlorine Compounds in Waters and on Activated Carbons", Dissertation, Univ. Karlsruhe, Federal Republic of Germany.

Peel, R. & Benedek, A., 1977, "The Modelling of Activated Carbon Adsorbers in the Presence of Biooxidation", Water-1976. AIChE Symp. Series 166:25. Am. Inst. Chem. Engrs., New York, N.Y.

Peel, R. & Benedek, A., 1980, "Dual Rate Kinetic Model for Activated Carbon Adsorption, Parts I and II", accepted for publication in J. Am. Soc. Civil Engrs. Am. Soc. Civil Engrs., New York, NY.

Piet, G., 1979, "Behavior of Micropollutants in River Water During Ground Passage", presented at Intl. Conf. on Oxidation Processes in Drinking Water Treatment, Karlsruhe, Federal Republic of Germany, Sept. 10-13, 1978. Engler-Bunte Inst. der Univ. Karlsruhe.

Piet, G.J. & Zoeteman, B.C.J., 1980, "Organic Water Quality Changes During Sand Bank And Dune Filtration of Surface Waters in The Netherlands", J. Am. Water Works Assoc. 72(7):400-404.

Poggenburg, W., Engels, C., Weissenhorn, F.J., Fuchs, F. & Sontheimer, H., 1974, "Investigations on the Application of Activated Carbon for the Treatment of Filtrate From the Banks of the Rhine', Special Printing from the DVGW, Series, Water, No. 7, March 27-29, 1974, Duisburg. Deutscher Verein des Gas- und Wasserfaches e.V., 6236 Eschborn, Federal Republic of Germany.

Poggenburg, W., 1975, 'Activated Carbon Filters in Water Treatment Plants. Processing Techniques - Engineering - Operation", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, op. cit., pp. 74-97.

Poggenburg, W., 1977, Wasserwerk Düsseldorf, Düsseldorf, Federal Republic of Germany. Private Communication.

Poggenburg, W., 1978, Wasserwerk Düsseldorf, Düsseldorf, Federal Republic of Germany. Private Communication.

Prengle, H.W., Jr. & Mauk, C.E., 1978, ""Ozone/UV Oxidation of Pesticides in Aqueous Solution", in Ozone/Chlorine Dioxide Oxidation Products of Organic Materials, R.G. Rice & J.A. Cotruvo, editors. Intl. Ozone Assoc., Vienna, VA, p. 302-320.

Presecan, N.L., 1978, "Effects of Biological Growth on Granular Activated Carbon Adsorption Systems", presented at WWEMA Annual Indl. Poll. Control Conf., St. Louis, MO, 13 April. Water & Wastewater Equipment Mfgrs. Assoc., McLean, VA.

Rafelson, M.E., Brinkley, S.B. & Hayashi, J.A., 1971, Basic Biochemistry, 3rd Ed., McMillen Co., New York, NY.

Rice, R.G. & Miller, G.W., 1977, "Reaction Products of Organic Materials With Ozone and Chlorine Dioxide in Water", presented at Symp. on Advanced Ozone Technology, Toronto, Ontario, Canada. Intl. Ozone Assoc., Vienna, VA.

Rice, R.G., Gomella, C. & Miller, G.W., 1978, "Rouen, France Water Treatment Plant: Good Organics and Ammonia Removal with no Need to Regenerate Carbon Beds", Civil Engineering, May, 1978, pp. 76-82.

Rice, R.G., Miller, G.W., Robson, C.M. & Kühn, W., 1978, "A Review of the Status of Pre-Ozonation of Granular Activated Carbon For Removal of Dissolved Organics and Ammonia in Water and Wastewater Treatment", in Carbon Adsorption, P.N. Cheremisinoff & F. Ellerbusch, editors. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, p. 485-538.

Rice, R.G., Miller, G.W., Robson, C.M. & Hill, A.G., 1979a, "Ozone Utilization in Europe", presented at AIChE 86th Natl. Meeting, Houston, TX, April. In Water -- 1979, G.F. Bennett, editor, p. 117-134 (1980). Am. Inst. Chem. Engrs., New York, N.Y.

Rice, R.G., Robson, C.M. & Miller, G.W., 1979b, "Ozone For Drinking Water Treatment -- Current State Of The Art", in Proc. Seminar On 'The Design and Operation of Drinking Water Facilities Using Ozone or Chlorine Dioxide', R.G. Rice, editor. New England Water Works Assoc., Dedham, MA, p. 1-48.

Richard, Y., 1973, "Experience With Activated Carbon in France", in Proc. Water Research Assoc. Conf., Reading, England, pp. 313-346.

Richard, Y. & Fiessinger, F., 1977, "Emploi Complémentaire des Traitments Ozone et Charbon Actif", presented at 3rd Intl. Symp. on Ozone Technol., Paris, France, May, 1977. Intl. Ozone Assoc., Cleveland, Ohio.

Richard, Y., 1978, Soc. Degrémont, Rueil Malmaison, France. Private Communication.

Richard, Y., 1979, Soc. Degrémont, Rueil Malmaison, France. Private Communication.

Rodman, C.A., Shunney, E.L. & Perrotti, A.E., 1978, "Biological Regeneration of Activated Carbon", in Carbon Adsorption Handbook, P.C. Cheremisinoff & F.E. Ellerbusch, editors. Ann Arbor Science Publishers, Inc., Ann Arbor, MI, p. 449-483.

Romero, J.C., 1970, "The Movement of Bacteria Through Porous Media", Ground Water 8:37-48.

Rook, J.J., 1972, "Production of Potable Water From A Highly Polluted River", Water Treatment & Examn. 21:259.

Rook, J.J., 1974, "Formation of Haloforms During Chlorination of Natural Waters", Water Treatment & Examn. 23(2):234-243.

Rook, J.J., 1976, "Developments in Europe", J. Am. Water Works Assoc. 68(6):279-282.

Rook, J.J., 1978, Wasserwerk Kralingen, Rotterdam, The Netherlands. Private Communication.

Sala-Trepot, J.M., Murray, K. & Williams, P.A., 1972, "The Metabolic Divergence in the Meta Cleavage of Catechols by Pseudomonas Putida", Eur. J. Biochem. 28:347.

Schalekamp, M., 1975, "Use of Activated Carbon in the Treatment of Lake Water", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption. op. cit., pp. 128-159.

Schalekamp, M., 1979, "Swiss Experiences With Granular Activated Carbon (GAC) in the Treatment of Drinking Water", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA, Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, D.C.

Scheidtmann, W., 1975, "Investigations of the Optimization of Pretreatment When Using Ozone", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption. op. cit., pp. 98-111.

Schmidt, K.H., 1963, "Die Abbauleistungen der Bakterienflora bei der Langsamsandfiltration und ihre Beeinflussung durch die Rohwasserqualität und andere Umwelteinflüsse. Biologische Studien zur künstlichen Grundwasseranreicherung", Veröffentl. d. Hydrol. Forschungabt. der Dortmunder Stadtwerke AG, No. 5.

Schmidt, K.H., 1978, "Experience With Removal of Micropollutants in Slow Sand Filters", presented at Intl. Conf. on Oxidation Techniques in Drinking Water Treatment, Karlsruhe, Federal Republic of Germany. Engler-Bunte Inst. der Univ. Karlsruhe.

Schulhof, P., 1979, "French Experiences in the Use of Activated Carbon For Water Treatment", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA, 30 April-2 May. U.S. EPA, Office of Drinking Water, Washington, DC.

Schulhof, P., 1979, Cie. Générale des Eaux, Paris, France. Private Communication.

Schulhof, P., 1980, "Water Supply in the Paris Suburbs: Changing Treatment for Changing Demands", J. Am. Water Works. Assoc. 72(8):428-434.

Schweisfurth, R., 1978, Univ. of Saarlands, Homburg, Federal Republic of Germany. Private Communication.

Scott, C.D., Hancher, C.W., Holladay, D.W. & Dinsmore, G.B., 1975, "A Tapered Fluidized Bed Bioreactor for Treatment of Aqueous Effluents From Coal Conversion Processes", presented at Symp. on Environmental Aspects of Fuel Conversion-II, Hollywood, FL, 15-18 Dec.

Sontheimer, H. & Maier, D., 1973, "Untersuchungen zur Verbesserung der Trinkwasseraufbereitungstechnologie am Niederrhein (1. Bericht)", Wasser-Abwasser 113:187-193.

Sontheimer, H., 1975, "Considerations on the Optimization of Activated Carbon Use in Waterworks", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption. op. cit., pp. 208-214.

Sontheimer, H., 1977a, Engler-Bunte Institut, Univ. Karlsruhe, Karlsruhe, Federal Republic of Germany. Private Communication.

Sontheimer, H., 1977b, "Biological Treatment of Surface Waters in Activated Carbon Filters", presented at Seminar on Current Status of Wastewater Treatment & Disinfection With Ozone, Cleveland, Ohio, Sept. 15, 1977. Intl. Ozone Assoc., Vienna, VA.

Sontheimer, H., Heilker, E., Jekel, M., Nolte, H. & Vollmer, F.-H., 1978, "The Mülheim Process", J. Am. Water Works Assoc. 70(7):393-396.

Sontheimer, H., 1978, Engler-Bunte Institut, Univ. Karlsruhe, Karlsruhe, Federal Republic of Germany. Private Communication.

Sontheimer, H., 1979, "Development, Problems, Aims and Significance of the Oxidation Process in the Treatment of Drinking Water", in Oxidation Techniques in Drinking Water Treatment, W. Kühn & H. Sontheimer, editors, U.S. EPA Report No. EPA-570/9-79-020. U.S. EPA, Office of Drinking Water, Washington, DC.

Sontheimer, H., 1980, "Experience With Riverbank Filtration Along the Rhine River", J. Am. Water Works Assoc. 72(7):386-390.

Standard Methods for Examination of Water & Wastewater, 1971, 13th Edition, S.651, Am. Publ. Health Assoc., New York, N.Y.

Stephenson, P., Benedek, A., Malaiyandi, M. & Lancaster, E.A., 1979, "The Effect of Ozone on the Biological Degradation and Activated Carbon Adsorption of Natural and Synthetic Organics in Water. Part I. Ozonation and Biodegradation", Ozone Sci. & Engrg. 1(3):263-280.

Strudgeon, G.E., Lewis, B.J., Albury, W.W. & Clinger, R.C., 1980, "Safety Considerations in Handling Activated Carbon", J. Water Poll. Control Fed. 52(10):2516-2522.

Symons, J.H., editor, 1978, Interim Treatment Guide For Controlling Organic Contaminants in Drinking Water Using Granular Activated Carbon, U.S. EPA, Water Supply Research Division, Cincinnati, Ohio, Jan. 1978.

Temple, Barker & Sloane, Inc., 1977, "Economic Impact Analysis of a Trihalomethane Regulation for Drinking Water", U.S. EPA, Office of Drinking Water, Washington, D.C., August, 1977.

Temple, Barker & Sloane, Inc., 1978, "Revised Economic Impact Analysis of Proposed Regulations on Organic Contaminants in Drinking Water", U.S. EPA, Office of Drinking Water, Washington, D.C., July, 1978.

Tsezos, M. & Benedek, A., 1980, "Removal of Substances by Biologically Activated Carbon in a Fluidized-bed Reactor", J. Water Poll. Control Fed. 52(3):578-586.

U.S. Environmental Protection Agency, 1973, "Process Design Manual For Carbon Adsorption", Report No. EPA 625/1-71-002a. U.S. EPA, Washington, DC.

U.S. Environmental Protection Agency, 1978, "Proposed Regulations for Control of Organic Chemical Contaminants in Drinking Water', Federal Register, Feb. 9, 1978, 5756.

Valencia, J.A. & Cleasby, J.L., 1979, "Velocity Gradients in Granular Filter Backwashing", J. Am. Water Works Assoc. 71(12):732-738.

Van Der Kooij, D., 1975, "Some Investigations Into the Presence and Behavior of Bacteria in Activated Carbon Filters", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption. op. cit., pp. 348-354.

Van Der Kooij, D., 1978, Keuringsinstituut voor Waterleidingartikelen KIWA NV, Rijswijk (ZH), The Netherlands. Private Communication.

Van Leeuwen, J., 1979, "The Design and Application of Packed Column Adsorber for Ozonation in Water Reclamation", presented at 4th World Ozone Congress, Houston, TX, Nov. 26-29. Intl. Ozone Assoc., Vienna, VA.

Van Lier, W.C., Graveland, A., Rook, J.J. & Schultink, L.J., 1975, "Experiences With Pilot Plant Activated Carbon Filters in Dutch Waterworks", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption. op. cit., pp. 160-181.

Versanne, D., 1978, Cie. Gen. des Eaux, Rouen, France. Private Communication.

Wachs, A., Narkis, N. & Schneider, M., 1977, "Organic Matter Removal From Effluents by Lime Treatment, Ozonation, and Biologically Extended Activated Carbon Treatment", presented at Third Intl. Symp. on Ozone Technology, Paris, France, May, 1977. Intl. Ozone Assoc., Vienna, VA.

Water Pollution Control Federation, 1977, Wastewater Treatment Plant Design, A Manual Of Practice, WPCF, Washington, D.C.

Water Research Center, 1977, Water Purification In The EEC, A State Of The Art Review, Pergamon Press, Elmsford, New York.

Weber, W.J., Jr., 1972, Physico-Chemico Processes for Water Quality Control, Wiley Interscience, New York, N.Y.

Weber, W.J., Jr., 1974, "Adsorption Processes", Pure & Appl. Chem. 37(3). Intl. Union of Pure & Appl. Chem., Butterworth & Co. Ltd., London, England.

Weber, W.J., Jr. & Ying, W.C., 1977, "Integrated Biological and Physicochemical Treatment for Relamation of Wastewater", Proc. Intl. Conf. on Advanced Treatment & Reclamation of Wastewater, IAWPR, Johannesburg, So. Africa, June, 1977.

Weber, W.J., Pirbazari, M. & Melson, G.L., 1978, "Biological Growth on Activated Carbon: An Investigation by Scanning Electron Microscopy", Environmental Sci. & Technol. 12(7):817-819.

Weber, W.J., Jr., 1978b, Discussion of "Improved Performance of Activated Carbon by Preozonation", by W. Guirguis, T. Cooper, J. Harris & A. Ungar, J. Water Poll. Control Fed. 50(12):2781-2785.

Weber, W.J., Jr. & Van Vliet, B., 1978, "Fundamental Concepts for Application of Activated Carbon in Water and Wastewater Treatment", presented at Symp. on Activated Carbon Adsorption of Organics From the Aqueous Phase, Miami, FL, Sept. 1978. Am. Chem. Soc., Washington, DC.

Weissenhorn, F.J., 1977, "The Behavior of Ozone in the System and its Transformation", Wasser Berlin-1977, p. 140-147. AMK-Berlin, Federal Republic of Germany; Intl. Ozone Assoc., Cleveland, Ohio.

Werner, P., Klotz, M. & Schweisfurth, R., 1979, "Microbiological Studies of Activated Carbon Filtration", presented at Intl. Conf. on Oxidation Techniques in Drinking Water Treatment, Karlsruhe, Federal Republic of Germany, Sept. 11-13, 1978. Engler-Bunte Inst. der Univ. Karlsruhe.

Werner, P., 1979, Univ. of Karlsruhe, Federal Republic of Germany. Private Communication.

White, G.C., 1972, Handbook of Chlorination, Van Nostrand Reinhold Co., New York, N.Y.

Wolf, H.W., Camp, B.C. & Hawkins, S.J., 1979, "Pyrogenic Activity of Carbon Filtered Waters", U.S. EPA Report No. EPA-600/1-79-009, U.S. EPA, Health Effects Research Lab., Cincinnati, Ohio.

Wölfel, P. & Sontheimer, H., 1974, "Ein Neues Verfahren zur Bestimmung von Organisch Gebundenem Kohlenstoff im Wasser Durch Photochemische Oxidation", Vom Wasser 43:315-325.

Wolters, N. & Schwarz, W., 1956, "Untersuchungen über Vorkommen und Verhalten von Mikroorganismen", Arch. Hydrobiol. 51:500-541.

Woodward, R.L., Dostal, K.A. & Robeck, G.G., 1964, "Granular Activated Carbon Beds For Odor Removal", J. Am. Water Works Assoc. 56(3):287-295.

BIBLIOGRAPHY

Abram, J.C., 1973, "The Characteristics of Activated Carbon", Proc. Water Research Assoc. Conf., Reading, England, pp. 1-30.

Ackerman, R.A. & Cosentino, I.A., 1979, "Recreational Area Water Reuse System", in Proc. Water Reuse Symp., Washington, DC, 25-30 March. Am. Water Works Assoc., Denver, CO, pp. 1755-1761.

Ahlberg, N. & Rupke, J.W.G., 1974, "Modes of Activated Carbon Utilization in Wastewater Treatment", Proc. Physical-Chemical Treatment, Activated Carbon Adsorption in Pollution Control, Seminar held in Ottawa, Ontario, Canada, Oct. 24, 1974. Environmental Protection Service, Environment Canada.

Aldridge, J.L., 1973, "Design of Systems for Applying Powdered Activated Carbon", Proc. Water Research Assoc. Conf., Reading, England, pp. 145-158.

Anonymous, 1974, "Ozone-Carbon Dye Waste Treatment", Textile Ind. 138(10):-43, 45.

Argo, D.G., 1978, "Control of Organic Chemical Contaminants in Drinking Water", Presented at EPA Seminar on Control of Organic Contaminants in Drinking Water, Los Angeles, Calif., Nov. U.S. Environmental Protection Agency, Office of Drinking Water, Washington, D.C. 20460.

Argo, D.G., 1979, "Control of Organic Chemical Contaminants in Drinking Water", Presented at EPA Seminar on Control of Organic Chemical Contaminants in Drinking Water, Dallas, Texas, March. U.S. Environmental Protection Agency, Office of Drinking Water, Washington, D.C. 20460.

Argo, D.G., 1980, "Cost of Water Reclamation by Advanced Wastewater Treatment", J. Water Poll. Control Fed., 52(4):750-759.

Bailey, D.A., Bayley, R.W. & Waggott, A., 1973, "Treatment of Wastewaters With The Aid of Activated Carbon", Proc. Water Research Assoc. Conf., Reading, England, pp. 127-144.

Baldauf, G., Fritz, W. & Sontheimer, H., 1975, "Untersuchungen zur Adsorption von Adsorptivmischungen an Adsorbensgemischen", Vom Wasser 45:91-102 (1975).

Baldauf, G., Frick, B. & Sontheimer, H., 1977, "Berechnung des Sorptionsverhaltens von Gemischen", Vom Wasser 49:315-330.

Baldauf, G., 1977, "Competitive Adsorption Data in Bisolute Systems", presented at the Activated Carbon Meeting of KIWA, Engler-Bunte Institute and Water Research Center, Karlsruhe, Fedederal Republic of Germany, Oct. 30-31, 1977.

Baldauf, G., Frick, B. & Sontheimer, H., 1977, "A Model for the Description of Competitive Adsorption of Two-Solute Mixtures", presented at the Activated Carbon Meeting of KIWA, Engler-Bunte Institute and Water Research Center, Karlsruhe, Federal Republic of Germany, Oct. 30-31, 1977.

Baldauf, G., 1979, "Prediction of Organic Breakthrough Patterns From Laboratory Tests", Presented at NATO/CCMS Conf. on Adsorption Techniques in the Treatment of Drinking Water, Reston, Va., Apr. 30-May 2.

Becker, D.L. & Wilson, S.C., 1978, "The Use of Activated Carbon for the Treatment of Pesticides and Pesticidal Wastes", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F.C. Ellerbusch, editors, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, pp. 167-214.

Beebe, R.L., 1973, "Activated Carbon Treatment of Raw Sewage in Solids Contact Chambers", EPA Report No. EPA-R2-73-183, 98 pp. U.S. Environmental Protection Agency, Washington, D.C. 20460.

Benedek, A., 1974, "Carbon Evaluation and Process Design", Proc. Physical-Chemical Treatment, Activated Carbon in Pollution Control, Seminar held in Ottawa, Ontario, Canada, Oct. 24, 1974. Environmental Protection Service, Environment Canada, Ottawa.

Benedek, A. & Najak, A., 1975, "The Biological Regeneration of Activated Carbon", Presented at 48th Annual Conf. of Water Pollution Control Fed., Miami Beach, Fla. (Oct.). Water Poll. Control Fed., Washington, D.C.

Benedek, A., 1978, "Simultaneous Biodegradation and Activated Carbon Adsorption - A Mechanistic Look", presented at the Symposium on Activated Carbon Adsorption of Organics From the Aqueous Phase, Miami, Florida, Sept., 1978. Am. Chem. Soc., Washington, D.C.

Benedek, A., 1979, "The Effect of Chemical Oxidation on Activated Carbon Adsorption and Biodegradation", Presented at NATO/CCMS Conf. on Adsorption Techniques in the Treatment of Drinking Water, Reston, Va., Apr. 30-May 2.

Benedek, A., Stephenson, P., Malaiyandi, M. & Lancaster, E., 1979, "The Effect of Ozone on the Biological Degradation and Activated Carbon Adsorption of Natural and Synthetic Organics in Water", Presented at 4th World Ozone Congress, Houston, Texas, Nov. 26-29. Intl. Ozone Assoc., Vienna, VA.

Bernardin, F.E., 1973, "Cyanide Detoxification Using Adsorption and Catalytic Oxidation on Granular Activated Carbon", J. Water Poll. Control Fed. 45(2):221-231.

Berndt, C.L. & Meidl, J.A., 1979, "Startup and Operation of a 6.5 mgd PACT Process With Wet Air Regeneration", Presented at 53rd Annual Meeting of the Ohio Water Pollution Control Conf., Toledo, Ohio., June 20-22.

Bernhardt, H., 1970, "Entkeimung von Aktivkohlefiltern durch Erwärmung", Schriftenreihe der Vereins Wasser, Boden und Lufthygiene, Berlin, 31:165-169.

Bertrandy, M.C., 1974, "Filtrable Residual Organics From Biooxidation and Activated Carbon Adsorption of Domestic Wastewater", Master's Thesis, Wastewater Research Group, McMaster Univ., Hamilton, Ontario, Canada.

Besik, F., 1973, "High Rate Adsorption - Biooxidation of Domestic Sewage", Water & Sewage Works, June 1973, pp. 68-71.

Besik, F., 1975, "Simultaneous Removal of Nitrogen and Organics in New Activated Sludge Process", Special Conf. on Nitrogen As A Water Pollutant, Copenhagen, Denmark, Aug. 18-20, 1975. Intl. Assoc. of Water Poll. Research.

Bettens, L., 1979, "Powdered Activated Carbon in an Activated Sludge Unit", Effluent & Water Treatment J. 19(3):129-135.

Birkmeier, J.L., Sr., LaRocca, S.A. & Haulsee, R.E., 1978, "Activated Carbon Removes Pesticides From Wastewater At Research Facility", Indl. Wastes Sept./Oct., p. 20-24.

Bishop, D.F., et al., 1967, "Studies on Activated Carbon Treatment", J. Water Poll. Control Fed. 30:188.

Blanck, C.A., 1978, "End Taste and Odor Complaints With Granular Activated Carbon", The American City & County, Review Issue, pp. 9-10.

Blanck, C.A., 1979a, "Taste and Odor Control Utilizing Granular Activated Carbon in the Plains Region of The American Water Works System", Presented at Am. Soc. Civil Engrs. Mtg., Central Illinois Section, March 22. Am. Soc. Civil Engrs., New York, N.Y.

Blanck, C.A., 1979b, "Plant Operations as Related to Trihalomethanes", presented at 70th Annual Meeting, Illinois Section, Am. Water Works Assoc., Oak Brook, Ill., March 21.

Blanck, C.A., 1979c, "Trihalomethane Reduction in Operating Water Treatment Plants", J. Am. Water Works Assoc. 71(9):525-528.

Blanck, C.A., (date unknown), "In-Plant Control of Taste and Odors in the Plains Region of the American Water Works System". Am. Water Works Service Co., Inc., Fairview Heights, Ill.

Blanck, C., 1980, "GAC Value Exceeds Expectation", Water & Sewage Works, Jan., p. 40-42.

Boening, P.H., Beckmann D.D. & Snoeyink, V.L., 1980, "Activated Carbon Versus Resin Adsorption of Humic Substances", J. Am. Water Works Assoc. 72(1):54-59.

Bradley, K.C., 1974, "Design of an Activated Carbon Wastewater Treatment System for a Multi-Product Organic Chemical Plant", Proc. Physical-Chemical Treatment, Activated Carbon in Pollution Control, Seminar held in Ottawa, Ontario, Canada, Oct. 24, 1974. Environmental Protection Service, Environment Canada, Ottawa.

Brodtmann, N., DeMarco, J. & Greenberg, D., 1978, "Critical Study of Large Scale Granular Activated Carbon Filter Units for the Removal of Organic Substances from Drinking Water", presented at the Symposium on Activated Carbon Adsorption of Organics From the Aqueous Phase, Miami, Florida, Sept., 1978. Am. Chem. Soc., Washington, D.C.

Bull, R.J., Pereira, M.A. & Blackburn, K.L., 1979, "Bioassay Techniques for Evaluating the Possible Carcinogenicity of Adsorber Effluents", Presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, Va., Apr. 30-May 2.

Burns, D.E. & Shell, G.L., 1973, Physical-Chemical Treatment of a Municipal Wastewater Using Powdered Activated Carbon", EPA Report No. EPA-R2-73-264, 230 pp. U.S. Environmental Protection Agency, Washington, D.C. 20460.

Burns, D.E. & Shell, G.L., 1974, "Carbon Treatment of a Municipal Wastewater", J. Water Poll. Control Fed. 46:148-164.

Burley, M.J. & Short, C.S., 1973, "Economics of Activated Carbon Treatment", Proc. Water Research Assoc. Conf., Reading, England, pp. 203-240.

Cairo, P.R., McElhaney J. & Suffet, I.H., 1979a, "Design and Operational Experiences With Activated Carbon Adsorbers: Treatment of Delaware River Water", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, Va., Apr. 30-May 2.

California State State Water Resources Control Board, 1978, "The Effects of Advanced Wastewater Treatment on Trace Organic Compounds", Calif. State State Water Resources Control Bd., Publicn. No. 61, July, 147 pp.

Carnahan, R.P. & Keinath, T.M., 1973, "Competitive Adsorption From Heterogeneous Aqueous Solutions Onto Activated Carbon", Proc. Am. Chem. Soc. Natl. Meeting., April 8-13, General Papers, p. 101. Am. Chem. Soc., Washington, D.C.

Chédal, J. & Schulhof, P., 1979, "Reduction of the Content of Chlorine Compounds by a Treatment Combining Physico-Chemical and Biological Processes", in Oxidation Techniques in Drinking Water Treatment, W.

Kühn & H. Sontheimer, editors, U.S. EPA Report No. EPA-570/9-79-020. U.S. EPA, Office of Drinking Water, Washington, DC, p. 176-194.

Cheremisinoff, P.N. & Morresi, A.C., 1978, "Carbon Adsorption Applications", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, Ann Arbor Science Publishers, Inc., Ann Arbor, Mich., pp. 1-54.

Chian, E.S.K. & DeWalle, F., 1975, "Sequential Substrate Removal in Activated Sludge Systems Fed With Naturally Occurring Wastewater", Prog. Water Technol. 7:235-241.

Chian, E.S.K., Chang, Y., DeWalle, F.B. & Rose, W.B., 1975, "Combined Treatment of an Organic Chemical Water by Activated Sludge Followed by Activated Carbon, Proc. 30th Purdue Univ. Indl. Waste Conf., May 6-8, 1975. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, pp. 966-972.

Clark, R.M., Dorsey, P. & Adams, J.Q., 1979, "Influence of Operating Variables on the Cost of Treatment by Adsorption", Presented at NATO/CCMS Conf. on Adsorption Techniques in the Treatment of Drinking Water, Reston, Va., Apr. 30-May 2.

Cohen, J., 1974, "Introduction to Physical-Chemical Treatment", Proc. Physical-Chemical Treatment, Activated Carbon in Pollution Control, Seminar held in Ottawa, Ontario, Canada, Oct. 24, 1974. Environmental Protection Service, Environment Canada, Ottawa.

Consumer Product Safety Commission, 1979, "Home-Use Carbon-Only Water Filters", Federal Register 44(180):53559-53560.

Cookson, J.T., Jr., Ishizaki, C. & Jones, C.R., 1972, "Functional Surface Groups on Activated Carbon Responsible for Adsorption of Organics From Water", Water -- 1971, L.K. Cecil, Ed., AIChE Symp. Series 68(124):157-168.

Cookson, J.T., Jr., 1975, "The Adsorption Chemistry of Organics From Waters on Activated Carbon", Water -- 1975, G.F. Bennett, Ed., AIChE Symp. Series 71(151):376-386.

Cookson, J.T., Jr., 1978, "Adsorption Mechanisms: The Chemistry of Organic Adsorption on Activated Carbon", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, pp. 241-280.

Cooper, J.C. & Hagar, D.G., 1967, "Water Reclamation With Granular Activated Carbon", in Water Reuse, L.K. Cecil, editor. Chem. Engrg. Progress Symp. Series 63(78):185-192. Am. Inst. Chem. Engrs., New York, NY.

Culp, G.L. & Suhr, L.G., 1973, "State of the Art of Activated Carbon Treatment of Wastewater", Presented at the Physical/Chemical Treatment - Activated Carbon in Water Pollution Control Seminar, Environment

Canada, Environmental Protection Service, Technology Transfer Seminar, Vancouver, Canada.

Culp, R.L. & Hansen, S.P., 1980, "Carbon Adsorption Enhancement With Ozone", J. Water Poll. Control Fed. 52(2):270-281.

Culp/Wesner/Culp, 1978, "Estimating Costs for Granular Activated Carbon Systems in Water Purification -- Based on Experience in Wastewater Treatment", presented at meeting of Natl. Drinking Water Advisory Council, Washington, D.C., Aug. 22-23, 1978. U.S. EPA, Office of Drinking Water, Washington, D.C.

Cummins, B.B. & Nash, H.D., 1978, "Microbiological Implications of Alternative Treatment", Presented at AWWA Technol. Conf., Dec. 4., Louisville, Ky. Am. Water Works Assoc., Devner, Colo.

Daigger, G.T. & Grady, C.P.L., Jr., 1977, "A Model for the Bio-Oxidation Process Based on Product Formation Concepts", Water Research 11:1049-1057.

Daniels, S.L., 1972, "The Adsorption of Microorganisms Cnto Solid Surfaces", in Developments in Industrial Microbiology 13:211-253. Soc. Indl. Microbiology, Washington, D.C.

Davis, W.R., 1972, "Control of Stream Pollution at the Bethlehem Plant", Iron & Steel Engr. Year Book, p. 315.

DeJohn, P.B., 1974, "Factors to Consider When Selecting Granular Activated Carbon for Wastewater Treatment, presented at 29th Annual Indl. Waste Conf., Purdue Univ., W. Lafayette, Indiana, May 7-9, 1974.

DeJohn, P.B. & Adams, A.D., 1975, "Treatment of Oil Refinery Wastewaters With Granular and Powdered Activated Carbon", Proc. 30th Purdue Univ. Indl. Waste Conf., May 6-8, 1975. Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, pp. 216-232.

DeJohn, P.B., 1976, "Factors to Consider When Treating Dye Wastes With Granular Activated Carbon", Proc. 31st Purdue Univ. Indl. Waste Conf., May 4-6, 1976. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, pp. 375-384.

DeMarco, J. & P.R. Wood, 1978, "Design Data For Organics Removal by Carbon Beds", presented at Envmntl. Engrg. Div., Natl. Conf. on Engrg. Design, ASCE, Kansas City, MO, 10-12 July.

DeMarco, J., 1979, "Practical Application of Adsorption Techniques in Drinking Water", Presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, Va., Apr. 30-May 2.

DeWalle, F. & Chian, E.S.K., 1974, "Removal of Organic Matter by Activated Carbon Columns", Environ. Engr. Div., Am. Soc. Civil Engrs. 100:1085-1104.

DeWalle, F.B., Chian, E.S.K. & Small, E.M., 1976, "Organic Matter Removal by Powdered Activated Carbon Added to Activated Sludge Units", J. Water Poll. Control Fed., in Press.

DeWalle, F.B. & Chian, E.S.K., 1977, "Biological Regeneration of Powdered Activated Carbon Added to Activated Sludge Units", Water Research 11:439-446.

DiGiano, F.A. & Weber, W.J., Jr., 1972, "Sorption Kinetics in Finite Bath Systems", J. San. Engr. Div., Proc. Am. Soc. Civil Engrs. SA 6:1021.

DiGiano, F.A. & Weber, W.J., Jr., 1973, "Sorption Kinetics in Infinite Bath Experiments", J. Water Poll. Control Fed. 45(4):713-725.

DiGiano, F.A., 1979a, "General Considerations in Assessing the Beneficial Aspects of Microbial Activity on GAC", Presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, Va., Apr. 30-May 2.

DiGiano, F.A., 1979b, "Influence of Microbial Activity on the Performance of GAC", presented at AWWA Pre-Conference Seminar on Organics, San Francisco, CA, 24 June. Am. Water Works Assoc., Denver, CC.

Directo, L.S. & Chen, C.L., 1974, "Pilot Plant Study of Physical-Chemical Treatment", Presented at 47th Ann. Conf. of Water Poll. Control Fed., Denver, Colo.

Directo, L.S., Chen, C. & Miele, R.P., 1978, "Two-Stage Granular Activated Carbon Treatment", U.S. EPA Report No. EPA-600/2-78-170. U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

Dobbs, R.A., Middendorf, R.J. & Cohen, J.M., 1978, "Carbon Adsorption Isotherms For Toxic Organics", Municipal Environmental Research Laboratory, Office of Research & Development, U.S. EPA, Cincinnati, Ohio 45268. Unnumbered Report, dated May, 1978.

Dobias, J. & Starz, E., 1977, "Ozoneinsatz in Kleineren Trinkwasserversorgungsanlagen", Intl. Symp. on Ozone & Water, Wasser-Berlin - 1977, pp. 253-260. AMK-Berlin, Federal Republic of Germany; Intl. Ozone Assoc., Vienna, VA.

Dressman, R.C., McFarren, E.F. & Symons, J.M., 1977, "An Evaluation of the Determination of Total Organic Chlorine (TOCl) in Water by Adsorption Onto Granular Activated Carbon, Pyrohydrolysis and Chloride Ion Measurement", presented at Water Quality Technology Conf., Kansas City, Mo., Dec. 5-6, 1977. Am. Water Works Assoc., Denver, CO.

Eberle, S.H., Stöber, H. & Donnert, D., 1975, "Study on the Adsorption Properties of Aluminum Oxide and its Application for the Purification of Groundwater Containing Humic Substances", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, H. Sontheimer, editor. EPA Report No. EPA 600/9-76-030, Dec. 1976, pp. 405-413.

Elmaleh, S., LaBaquère, H. & Ben Aim, R., 1978, "Biological Filtration Through A Packed Column", Water Research 12:41-46.

English, J.N., Masse, A.N., Carry, C.W., Pitkin, J.B. & Haskins, J.E., 1971, "Removal of Organics From Wastewater by Activated Carbon", Water -- 1970, Chem. Engrg. Prog. Symp. Series 67(107):147-153.

English, J.N., Carry, C.W., Masse, A.N., Pitkin, J.B. & Dryden, F.D., 1974, "Denitrification in Granular Carbon and Sand Columns", J. Water Poll. Control Fed. 46(1):28-42.

Evans, F.L., III & Ryckman, D.W., 1963, "Ozonated Treatment of Wastes Containing ABS", Proc. 18th Indl. Waste Conf., Purdue Univ., Lafayette, Indiana, pp. 141-157.

Evans, T.M., Schillinger, J.E. & Stuart, D.G., 1978, "Rapid Determination of Bacteriological Water Quality by Using Limulus lysate", Appl. Env. Microbiol. 35:376.

Famularo, J., Pannu, A.S. & Mueller, J.A., 1978, "Prediction of Carbon Column Performance From Pure Solute Data", Presented at 51st Natl. Conf. of the Water Poll. Control Fed., Anaheim, Calif., Oct. 1978. WPCF, Washington, D.C.

Fenco Consultants, 1977, "The Removal of Organics From Potable Water Supplies By Ozonation and Activated Carbon; Biodegradation and Adsorption", proposal submitted to Dept. of Health and Welfare, Canada. Fenco Consultants Ltd., Toronto, Canada.

Ferguson, J.F., Keay, G.F.P., Merrill, M.S. & Benedict, A.H., 1979, "Powdered Activated Carbon in Contact Stabilization Activated Sludge", J. Water Poll. Control Fed. 51(9):2314-2323.

Ferrara, A.P., undated (but after 1975), "Replacement of Filter Media With Granular Activated Carbon". ICI United States, Inc.

Ferrara, A.P., undated (but after 1977), "Controlling Bed Losses of Granular Activated Carbon Through Proper Filter Operation". ICI United States Inc.

Ferrara, A.P., 1980, "Controlling Bed Losses of Granular Activated Carbon Through Proper Filter Operation", J. Am. Water Works Assoc. 72(1):60-63.

Fiessinger, F., 1978, "Large Scale Applications of Granular Activated Carbon for Potable Water Production in France", presented at Symp. on Activated Carbon Adsorption of Organics From the Aqueous Phase, Miami, Fla., Sept., 1978. Am. Chem. Soc., Washington, D.C.

Fiessinger, F., 1979a, "The Cost of Activated Carbon Treatment in France", Presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, Va., Apr. 30-May 2.

Fiessinger, F., 1979b, "Biological Activated Carbon....A Myth or A Promising Reality?", Aqua 2.

Fiore, J.V. & Babineau, R.A., 1977, "Effect of an Activated Carbon Filter on the Microbial Quality of Water", Applied & Environmental Microbiology 34:541-546.

Fisher, J.L., 1980, "How to Conduct a GAC Organics Removal Pilot Study", Public Works, June, p. 100-102.

Flotard, R.D., Ford, D.L. & Harrison, W., 1979, "Use of Granular Activated Carbon to Remove Trace Organics From the Effluent of a Class-B Refinery: A Case Study", Natl. Tech. Info. Service, Springfield, VA, Report No. CONF-7906120-1.

Flynn, B.P. & Barry, L.T., 1976, 'Finding A Home For Carbon: Aerator (Powdered) Or Column (Granular)", Proc. 31st Purdue Univ. Indl. Waste Conf., May 4-6, 1976. Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, pp. 649-660.

Flynn, B.P., Robertaccio, F.L. & Barry, L.T., 1976, "Truth or Consequences: Biological Fouling and Other Considerations in the Powdered Activated Carbon - Activated Sludge System", Proc. 31st Indl. Waste Conf., Purdue Univ., pp. 855-862. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan.

Flynn, B.P. & Stadnik, J.G., 1977, "Startup of a 38 mgd Powdered Activated Carbon - Activated Sludge (PACT) Treatment System at DuPont's Chambers Works", Presented at the 50th Annual Water Poll. Control Fed. Conf., Philadelphia, Pa., Oct. 3.

Fokken, B. & Kurz, R., 1979, "Removal of Purgeable Organic Chlorine Compounds by Activated Carbon Adsorption", Presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, Va., Apr. 30-May 2.

Ford, D.L. & Buercklin, M.A., 1972, "The Interrelationship of Biological-Carbon Adsorption Systems for the Treatment of Refinery and Petro-Chemical Wastewaters", Presented at the 6th Intl. Assoc. Water Poll. Research Conf., Jerusalem, Israel, June.

Ford, D.L., 1976, "Current State of the Art of Activated Carbon Treatment", in Proc. Open Forum on Management of Petroleum Refinery Wastewaters, F.S. Manning, editor. U.S. EPA, Robt. S. Kerr Environmental Research Labs., Ada, OK, p. 295-344.

Ford, D.L., 1977, "Putting Activated Carbon in Perspective to 1983 Guidelines", Indl. Water Engrg. 14(3):20-27.

Ford, D.L. & Manning, F.S., 1978, "Treatment of Petroleum Refinery Wastewater", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, pp. 687-732.

Frick, B., 1977, "Use of Adsorption Data For Characterization of Organics in Natural Water Systems", presented at Activated Carbon Meeting, WRC-KIWA-EBI, Karlsruhe, Federal Republic of Germany, 27-28 Oct. Engler-Bunte Inst., Univ. Karlsruhe, FRG.

Frick, B., Bartz, R., Sontheimer, H. & DiGiano, F., 1977, "Problems of Designing Filter Plants", presented at Activated Carbon Meeting, KIWA, Engler-Bunte Inst. & Water Research Center, Karlsruhe, Federal Republic of Germany, Oct. 30-31, 1977. Engler-Bunte Inst. der Univ. Karlsruhe.

Frick, B., 1979, "Prediction of Multicomponent Adsorption Behaviour in Activated Carbon Adsorbers - Equilibrium Aspects", Presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, Va., Apr. 30-May 2.

Fritz, W. & Schluender, E.-U., 1974, "Simultaneous Adsorption Equilibria of Organic Solutes on Activated Carbon", Chem. Engrg. Sci. 29:1279-1282.

Fulton, G.P., 1980, "New York City's Pilot Plant Filter Studies, Part One", Public Works, April, p. 62-64. "Part Two", Public Works, May, p. 85-88.

Gardiner, E.R., 1973, "Experience With Powdered Activated Carbon For Taste And Odor Control", Proc. Water Research Assoc. Conf., Reading, England, pp. 241-262.

Gardner, F.H., Jr. & Williamson, A.R., 1976, "Naval Stores Wastewater Purification and Reuse by Activated Carbon Treatment", EPA Report No. EPA-600/2-76-227, Oct., 1976. Industrial Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio 45268.

Garland, C.F. & Beebe, R.L., 1970, "Advanced Wastewater Treatment Using Powdered Activated Carbon in Recirculating Slurry Contactor Clarifiers", U.S. Fedl. Water Qual. Admin. Contract No. 14-12-400. U.S. Environmental Protection Agency, Washington, D.C. 20460.

Garrison, W.E., Gratteau, J.C., Hansen, B.E. & Luthy, R.F., Jr., 1978, "Gravity Carbon Filtration to Meet Reuse Requirements", J. Environ. Engrg. Div., Am. Soc. Civil Engrs., Dec. 1978, pp. 1165-1174.

Gasser, J.A., Chen, C.-l. & Miele, R.P., 1978, "Fixed Growth Nitrification of Secondary Effluent", J. Environ. Engrg. Div., Am. Soc. Civil Engrs. 104(1):77-92.

Glushchenko, V. Yu., Levagina, T.G. & Pershko, A.A., 1975, "Effect of the Nature of a Carbon Surface on the Adsorption of Nitro Compounds From Aqueous Salt Solutions", Kolloidnyi Zhurnal 37(1):134-136.

Goodall, J.B. & Hyde, R.A., 1979, "Current United Kingdom Practice in the Use of Granular Activated Carbon in Drinking Water Treatment", Presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, Va., Apr. 30-May 2.

Grandjacques, B.L. & Waller, G., 1973, "Design of Carbon Beds", Proc. Water Research Assoc. Conf., Reading, England, pp. 159-176.

Guarino, C.F., Radziul, J.V., Cairo, P.R., Blair, D.D., Pence, M.M., Aptowicz, B.S. & Weintraub, N., 1980, "Design and Economic Considerations of GAC Systems", Water & Sewage Works, Sept., p. 58-59, 63-64, 66-67.

Gulf South Research Institute, 1979, "Results From Phase 1 Report of GSRI on Home Water Treatment Units", U.S. EPA, Office of Drinking Water, Washington, DC.

Guy, M.D., McIver, J.D. & Lewis, M.J., 1977, "The Removal of Virus by a Pilot Treatment Plant", Water Research 11:421-428.

Halaby, D., Helm, J.M. & Zolin, P., 1978, "Economic Evaluation of Full Scale Carbon Regeneration Systems", presented at Symp. on Activated Carbon Adsorption of Organics From the Aqueous Phase, Miami, Fla., Sept. Am. Chem. Soc., Washington, D.C.

Hals, O. & Benedek, A., 1973, "Simultaneous Biological Treatment and Activated Carbon Adsorption", presented at 46th Annual Conf., Water Poll. Control Fed., Cleveland, Ohio, Oct.

Hals, O, 1974, "Biological Treatment and Activated Carbon Adsorption", M. Engr. Thesis, Water Research Group, McMaster Univ., Hamilton, Ontario, Canada.

Hanna, Y.A., Meister, T. & Slough, J., Jr., 1977, "Ozone as a Pretreatment Step for Physical-Chemical Treatment Process. Part I", Presented at Seminar on Current Status of Wastewater Treatment and Disinfection With Ozone, Cincinnati, Ohio, Sept. Intl. Ozone Assoc., Vienna, VA.

Hansen, K.H., Jr., 1979, "Control of Synthetic Organic Chemicals by Granular Activated Carbon -- Theory, Application and Reactivation Alternatives", presented at Seminar on Control of Organic Chemical Contaminants in Drinking Water, Dallas, Texas, March 13-14. U.S. EPA, Office of Drinking Water, Washington, D.C.

Hattori, T., 1973, Microbial Life in the Soil; An Introduction, M. Dekker, Publishers, New York, N.Y.

Hay, W.C., 1975, "Pilot Plant Studies of the Use of Radiation-Induced Oxidation for Treatment of Industrial and Municipal Wastewater", Proc. WWEMA 3rd Annual Indl. Solns. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, pp. 507-527.

Heath, H.W., Jr., 1977, "Combined Powdered Activated Carbon - Biological ("PACT") Treatment of 40 mgd Industrial Waste", presented at Symp. on Indl. Waste Poll. Control, ACS Natl. Meeting, New Orleans, LA, Mar. 24. Am. Chem. Soc., Washington, D.C.

Helfgott, T., Hunter, J.V. & Rickert, D., 1970, "Analytical and Process Classification of Effluents", J. Sanit. Engr. Div., Am. Soc. Civil Engrs. 96(SA3):779-803.

Heukelekian, H. & Heller, A., 1940, "Relation Between Food Concentration and Surface for Bacterial Growth", J. Bacteriology 40:547-558.

Heymann, E., 1975, "Practical Experiences in the Use of Flocculation and Filtration Connected in Series to Granular Activated Carbon Filters", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, H. Sontheimer, editor, op. cit., pp. 112-127.

Hiser, L.L. & Tarazi, D.S., 1971, "Application of Carbon Techniques to Biological Systems", Water -- 1970, Chem. Engrg. Prog. Symp. Series 67(107):267-278.

Hodges, W.E., 1978, "Filtration Pilot Studies for the City of Los Angeles", presented at Forum of Assoc. of Environ. Engrg. Profs., Atlantic City, N.J., June 28, 1978.

Hoigné, J. & Bader, H., 1978, "Ozone Initiated Oxidations of Solutes in Wastewater: A Reaction Kinetic Approach", Prog. Water Technol. 10(5/6):-657-671.

Holladay, D.W., Hancher, C.W., Chilcote, D.D. & Scott, C.D., 1976, "Biodegradation of Phenolic Waste Liquors in Stirred Tank, Columnar and Fluidized Bed Bioreactors", presented at 69th Ann. Meeting, AIChE, Chicago, Ill., Nov. 28-Dec. 2. Am. Inst. Chem. Engrs., New York, N.Y.

Holluta, J., et al., 1960, "Untersuchungen über Geruchsbildene Organische Stoffe im Wasser und Deren Isolierung und Identifizierung", Monatsheftbull. SVGW 40:105-112.

Holluta, J., 1964, "Organische Extraktstoffe in Oberfläschenwässern und Deren Bedeutung für die Trinkwasserversorgung", Forschung und Fortschritte 38(6):164-166.

Hölzel, G., 1977, "Control of Virgin and Reactivated Carbon for Drinking Water Treatment", presented at Activated Carbon Meeting of the KIWA, Engler-Bunte Inst. and Water Research Center, Karlsruhe, Federal Republic of Germany, Oct. 30-31, 1977. Engler-Bunte Inst. der Univ. Karlsruhe.

Hölzel, G., 1979, "Laboratory Activated Carbon Test Methods For Water Utilities", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, Va., Apr. 30-May 2.

Hopkins, C.B., Weber, W.J., Jr. & Bloom, R., 1968, "A Comparison of Expanded Bed and Packed Bed Adsorption Systems", U.S. EPA Report No. TWRC-2, 74 pp., U.S. Environmental Protection Agency, Cincinnati, Ohio.

Hopkins, C.B., Weber, W.J., Jr. & Bloom, R., 1970, "Granular Carbon Treatment of Raw Sewage", U.S. EPA Report No. ORD-10750 DAL 05/70. U.S. Environmental Protection Agency, Municipal Environmental Research Lab., Cincinnati, Ohio.

Horvath, R.S., 1972, "Microbial Co-Metabolism and the Degradation of Organic Compounds in Nature", Bact. Rev. 36:146-155.

Houston, C.W., 1978, "Bio-Regeneration of Hydrocarbon-Exhausted Activated Carbon", Tech. Completion Report, U.S. Dept. of Interior, Office of Water Resources Research Project No. A-C63-RI. Natl. Tech. Info. Service Report No. PB 288,651.

Huang, J-C. & Steffens, C.T., 1976, "Competitive Adsorption of Organic Materials by Activated Carbon", Proc. 31st Purdue Univ. Indl. Waste Conf., May 4-6, 1976. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, pp. 107-121.

Hutton, D.G., 1978, "Combined Powdered Activated Carbon - Biological Treatment", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, pp. 389-448.

Hutton, D.G., 1979, "Removal of Priority Pollutants by the DuPont 'PACT' Process", Presented at 7th Ann. Indl. Poll. Control Conf., WWEMA, Philadelphia, Pa., June 5-7. Water & Wastewater Equipmt. Mfgrs. Assoc., McLean, Va.

Hutton, D.G. & Temple, S., 1979, "Priority Pollutant Removal: Comparison of DuPont 'PACT' Process and Activated Sludge", Presented at 52nd Ann. Conf. Water Poll. Control Fed., Houston, Texas, Oct. 10. Water Poll. Control Fed., Washington, D.C.

Hutton, D.G., 1980, "Removal of Priority Pollutants", Indl. Wastes 26(2):22, 24, 26.

Jain, J.S. & Snoeyink, V.L., 1973, "Adsorption From Bisolute Systems on Active Carbon", J. Water Poll. Control Fed. 45(12):2463-2479.

Jain, K.K., 1978, "A Carbon Adsorption Process for Highly Concentrated Municipal Waste and Low Water Temperatures", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, pp. 627-660.

Jain, K.K. & Bryce, A.J., 1978, "Feasibility of Munitions Wastewater Treatment by Adsorption-Oxidation:, in Carbon Adsorption Handbook, loc. cit., pp. 661-686.

Janata, W., 1975, "Investigations Into the Control of Activated Carbon Filters at Waterworks", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, H. Sontheimer, editor, op. cit., pp. 230-237.

Jeris, J.S., et al., 1974, "High Rate Biological Denitrification Using a Granular Fluidized Bed", J. Water Poll. Control Fed. 46:2118.

Johnson, R.L. & Baumann, E.R., 1971, "Advanced Organics Removal by Pulsed Adsorption Beds", J. Water Poll. Control Fed. 43:8.

Johnson, W.R. & Jenkins, C.R., 1978, "A Study for Improving the Aerobic Media Trickling Filter for Wastewater Treatment", Final Report of Contract DI-14-31-0001-6051, Office of Rsch. & Technol., Dept. of Interior, Washington, D.C. Natl. Tech. Info. Service Report No. PB-288,775.

Jones, J.L., Kuo, M.C.T., Kyle, P.E., Radding, S.B., Semrau, K.T. & Somogyi, L.P., 1979, "Overview of the Environmental Control Measures and Problems in the Food Processing Industries", EPA Report No. EPA-600/2-79-C09, U.S. EPA, Cincinnati, Ohio.

Joschek, H.-I., Dehler, J., Koch, W., Engelhardt, H. & Geiger, W., 1975, "Formal Kinetic Model For The Biological Decomposition Of Industrial Wastewater", Chemie-Ing.-Techn. 47:422-428.

Joyce, R.S. & Sukenik, V.A., 1964, "Feasibility of Granular Activated Carbon Adsorption For Wastewater Renovation", Report No. AWTR-10, Env. Health Series, Water Supply & Poll. Control, U.S. Dept. of Health, Education & Welfare, Public Health Service, Cincinnati, Ohio.

Joyce, R.S., Allen, J.B. & Sukenik, V.A., 1966, J. Water Poll. Control. Fed. 38(5):813.

Juhola, A.J., 1973, "Regeneration of Activated Carbon", Proc. Water Research Assoc. Conf., Reading, England, pp. 177-202.

Jüntgen, H., 1975b, "Phenomena of Activated Carbon Regeneration", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, H. Sontheimer, editor, op. cit., pp. 269-283.

Kalinski, A.A., 1972, "Enhancement of Biological Oxidation of Organic Wastes Using Activated Carbon in Microbial Suspensions", Water & Sewage Works, p. 115.

Kawazaki et al., 1965, Water & Wastewater (Japan) 6:632-648, 778-780.

Keinath, T.M. & Weber, W.J., Jr., 1968, "A Predictive Model for the Design of Fluid-Bed Adsorbers", J. Water Poll. Control Fed. 40(5):741-765.

King, D.L. & Verma, R.D., 1968, "The Role of Particulate Substrates in Biotic Degradation", Proc. 23rd Indl. Waste Conf., Purdue Univ., Lafayette, Indiana.

Klein, J., 1975, "Comparative Assessment of Adsorbents", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorp-tion, H. Sontheimer, editor, op. cit., pp. 215-229.

Klemetson, S.L. & Scharbow, M.D., 1979, "Filtration of Phenolic Compounds in Coal Gasification Wastewater", J. Water Poll. Control Fed. 51(11):2752-2763.

Knopp, P.V., Gitchel, W.B., Meidl, J.A. & Berndt, C.L., 1978, "Wet Oxidation Regeneration", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, op. cit., pp. 539-626.

Knoppert, P.L., Oskam, G. & Vreedenburgh, E.G.H., 1980, "An Overview of European Water Treatment Practice", J. Am. Water Works Assoc. 72(11):592-599.

Kölle, W., 1975, "Use of Macroporous Ion Exchangers for Drinking Water Purification" in Translation of Reports on Special Problems of Water Technology, H. Sontheimer, editor, op. cit., pp. 405-413.

Koppe, P., Sebesta, G. & Herkelmann, H., 1974a, "Vorläufige Mitteilung Über die Biochemische Oxidation Einer Schwer Abbaubaren Substanz in Gegenwart von Aktivkohle", Gesundsheits-Ing. 95(2):33-35.

Koppe, P., Sebesta, G. & Herkelmann, H., 1974b, 'The Biochemical Oxidation of a Slowly Degradable Substance in the Presence of Activated Carbon: Biocarbon Unit", Gesundsheits Ingenieur 95:247-248.

Koppe, P., Imhoff, K.R., Herkelmann, H. & Sebesta, G., 1979, "Some Practical Aspects of the 'Biocarbon Process'", Water Research 13:865-871.

Kreissl, J.F. & Westrick, J.J., 1972, "Municipal Waste Treatment by Physical-Chemical Methods", in Application of New Concepts of Physical-Chemical Wastewater Treatment, W.W. Eckenfelder, Jr. & L.K. Cecil, eds., Pergamon Press, New York, N.Y.

Kühn, W., 1978, "Formation and Behavior of Polar Organochloro Compounds", presented at Intl. Symp. on Oxidation Techniques in Drinking Water Treatment, Karlsruhe, Federal Republic of Germany, Sept. 11-13, 1978. Engler-Bunte Inst. der Univ. Karlsruhe.

Kussmaul, H., 1979, "Purifying Action of the Ground in the Treatment of Drinking Water", in Oxidation Techniques in Drinking Water Treatment, W. Kühn & H. Sontheimer, editors, U.S. EPA Report No. EPA-570/9-79-020. U.S. EPA, Office of Drinking Water, Washington, DC.

Lang, E.W., Timpe, W.G. & Miller, R.L., 1975, "Activated Carbon Treatment of Unbleached Kraft Effluent For Reuse", U.S. EPA Report No. EPA-660/2-75-004, April, 1975. Industrial Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio 45268.

Lang, E.W., Stephens, J.W. & Miller, R.L., 1977, "Activated Carbon Treatment of Kraft Bleaching Effluents", U.S. EPA Report No. EPA-600/2-77-119, June, 1977. Industrial Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio 45268.

Latoszek, A. & Benedek, A., 1974, "Some Aspects of the Microbiology of Activated Carbon Columns Treating Domestic Wastewater", Water Research Group Report, McMaster Univ., Hamilton, Ontario, Canada.

Lawson, C.T. & Fisher, J.A., 1973, "Limitations of Activated Carbon For Upgrading Petrochemical Effluents", in Water - 1973, G.F. Bennett, editor. AIChE Symp. Series 70(136):577-584.

Lawson, C.T., 1976, "Cautions and Limitations on the Applications of Activated Carbon Adsorption to Organic Chemical Wastewaters", in Proc. Open Forum on Management of Petroleum Refinery Wastewaters, F.S. Manning, editor. U.S. EPA, Robt. S. Kerr Environ. Research Labs., Ada, OK, p. 345-358.

LeClair, B.P. & Wei, N., 1974, "The Use of Powdered Activated Carbon and Chemicals in the Treatment of Raw Sewage", Proc. Physical-Chemical Treatment, Activated Carbon in Pollution Control, Seminar held in Ottawa, Ontario, Canada, Oct. 24, 1974. Environmental Protection Service, Environment Canada, Ottawa.

Lee, D.D. & Scott, C.D., 1977, " A Tapered Fluidized-Bed Bioreactor for Treatment of Aqueous Effluents From Coal Conversion Processes", presented at 70th Ann. Meeting of AIChE, New York, Nov. 13-17. Am. Inst. Chem. Engrs., New York, N.Y.

Leuser, R.M., 1978, "Pulsed Bed Decolorizing System at the Pepsico Sugar Refinery - A Case History", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, op cit., pp. 779-818.

Li, A.Y.L. & DiGiano, F.A., 1980, "The Availability of Sorbed Substrate For Microbial Degradation on Granular Activated Carbon", presented at 53rd Annual WPCF Meeting, Research Symp., Las Vegas, Nev., Sept. Water Poll. Control Fed., Washington, DC.

Lindstrom, F.T., Haque, R. & Coshow, W.R., 1970, "Adsorption From Solution. III. A New Model for the Kinetics of Adsorption-Desorption Processes", J. Phys. Chem. 74(3):495-502.

Lipscombe, F., 1862, British Patent No. 2,887.

Lombana, L.A. & Halaby, D., 1978, "Carbon Regeneration Systems", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, op. cit., pp. 905-922.

Love, O.T., Jr., Robeck, G.G., Symons, J.M. & Buelow, R.W., 1973, "Experience With Activated Carbon in the USA", Proc. Water Research Assoc. Conf., Reading, England, pp. 279-312.

Love, O.T., Jr., Carswell, J.K., Stevens, A.A. & Symons, J.M., 1975, "Evaluation of Activated Carbon", U.S. EPA, Water Supply Research Lab., Cincinnati, Ohio, 3 Feb.

Love, O.T. & Symons, J.M., 1978, "Operational Aspects of Granular Activated Carbon Adsorption Treatment", Draft Paper, U.S. EPA, Water Supply Research Laboratory, Cincinnati, Ohio.

Lowry, J.D. & Burkhead, C.E., 1978, "The Role of Adsorption in Biologically Extended Activated Carbon Columns", presented at Symp. on Activated Carbon Adsorption of Organics From the Aqueous Phase, Miami, Fla., Sept. 1978. Am. Chem. Soc., Washington, D.C. Also, J. Water Poll. Control Fed. 52(2):389-398 (1980).

Lurgi Express Information, 1977, "Reactivation of Activated Carbon. Thermal Reactivation of Granular Activated Carbon in the Two-Stage Fluid Bed", Publicn. No. T-1191/2.77, Lurgi Apparate-Technik GmbH - Chemotechnik Division, D-6, Frankfurt/Main, Federal Republic of Germany.

Lyman, W.J., 1978, "Applicability of Carbon Adsorption to the Treatment of Hazardous Industrial Wastes", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, op. cit., pp. 131-166.

Lynch, W.O. & Potter, L.R., 1979, "Start-up and Initial Operation of Physical-Chemical Wastewater Treatment Facilities at Cortland, New York", presented at 52nd Annual WPCF Conf., Houston, TX, 10 Oct. Water Poll. Control Fed., Washington, DC.

Maier, D., Fuchs, F. & Sontheimer, H., 1976, "Bestimmung von Organischen Säuren in Wässern und auf Aktivkohle", Wasser/Abwasser 117(2):70-74.

Maqsood, R. & Benedek, A., 1973, "The Feasibility of the Physicochemical Treatment of Sewage at Low Temperatures", Proc. Intl. Symp., Research & Trtmt. of Wastewaters in Cold Climates, Univ. Saskatchewan at Saskatoon, Canada, Aug.

Maran, E. & Sulik, D.J., 1977, "Advanced Waste Treatment Design Protects Lake Alton", Water & Sewage Works, April, pp. 68-69.

Martin, R.J. & Iwugo, K.O., 1978, "Studies on Residual Organics in Biological Plant Effluents and Their Treatment by the Activated Carbon Adsorption Process", presented at Symp. on Activated Carbon Adsorption of Organics From the Aqueous Phase, Miami, Fla., Sept., 1978. Am. Chem. Soc., Washington, D.C.

Masschelein, W.J.. 1979, "Belgian Experiences in Practical Applications of Adsorption Techniques in Treating Drinking Water", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA., Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, DC.

Matsuoka, H., 1973, "Ozone Treatment of Industrial Wastewater", PPM 4(10):-57-69.

Matthews, J.E., 1978, "Treatment of Petroleum Refinery, Petrochemical and Combined Industrial-Municipal Wastewaters With Activated Carbon -- Literature Review", U.S. EPA Report No. EPA-600/2-78-200, Robt. S. Kerr Environmental Research Lab., U.S. EPA, Ada, Oklahoma 74820.

Mattson, J.S., Mark, H.B., Jr. & Weber, W.J., Jr., 1969, "Identification of Surface Functional Groups on Active Carbon by Infrared Internal Reflection Spectrophotometry", Anal. Chem. 41:355-358.

Mattson, J.S., Mark, H.B., Jr., Malbin, M.D., Weber, W.J., Jr. & Crittenden, J.C., 1969, "Surface Chemistry of Active Carbon: Specific Adsorption of Phenols", J. Colloid & Interface Science 31(1):250-264.

McCarty, P.L., Reinhard, M. & Argo, D.G., 1977, "Organics Removal by Advanced Wastewater Treatment", presented at the Annual Conf., Am. Water Works Assoc. Anaheim, Calif., May, 1977. AWWA, Denver, Colo.

McCarty, P.L., Argo, D. & Reinhard, M., 1979, "Operational Experiences With Activated Carbon Adsorbers at Water Factory 21", J. Am. Water Works Assoc. 71(11):683-689.

McCrodden, B.A., 1974, "Operation of a Refinery Wastewater Treatment Plant Using Filtration of Carbon Adsorption", in Proc. Physical-Chemical Treatment - Activated Carbon Adsorption in Pollution Control, Seminar held in Ottawa, Ontario, Canada, Oct. 24, 1974. Environmental Protection Service, Environment Canada, Ottawa.

McCrodden, B.A., 1979, "Treatment of Refinery Wastewater Using A Filtration-Activated Carbon System", U.S. EPA Report EPA-600/2-79-C66, Robt. A. Kerr Environmental Research Lab., U.S. EPA, Ada, Oklahoma 74820.

McGuire, M.J., 1978, "Feasibility Analysis and Implementation of Synthetic Organic Chemical Control Strategies", presented at Symp. on Activated Carbon Adsorption of Organics From the Aqueous Phase, Miami, Fla., Sept., 1978. Am. Chem. Soc., Washington, D.C.

McGuire, M.J. & Suffet, I.H., 1979, "Adsorption of Organics From Domestic Water Supplies", J. Am. Water Works Assoc. 70(9):621-636.

Meijers, A.P., 1979, "The Use of Carbon Filtration in The Netherlands", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, Va., Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, D.C.

Meijers, A.P., Rook, J.C., Schultink, B., Smeenk, J.G.M.M., van der Laan, J. & Poels, C.L.M., 1979, "Objectives and Procedures for GAC Treatment", J. Am. Water Works Assoc. 71(11):628-637.

Merk, W., 1979, "Prediction of Multicomponent Adsorption Behavior in Activated Carbon Adsorbers -- Kinetic Aspects", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA., Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, D.C.

Miller, G.W. & Rice, R.G., 1978, "European Water Treatment Practices -- The Promise of Biological Activated Carbon", Civil Engrg., Feb., 81-83.

Miller, G.W., Rice R.G., & Robson, C.M., 1978, "Large Scale Applications of Activated Carbon With Ozone Pretreatment", presented at Symp. on Activated Carbon Adsorption of Organics From the Aqueous Phase, Miami, Fla., Sept., 1978. Am. Chem. Soc., Washington, D.C.

Miller, R., 1979, "Treatment of Ohio River Water", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA, Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, DC.

Miller, S., 1980, "Adsorption on Carbon: Solvent Effects on Adsorption", Environ. Sci. & Technol. 14(9):1037-1049.

Miltner, R.J., 1979, "Results for Ohio River Valley Water Sanitation Commission (ORSANCO) Studies", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA, Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, DC.

Mizumoto, K. & Horie, M., 1974, "Dyeing Wastewater Treatment by Combination of Ozone and Activated Carbon", Japan Textile News 89:238.

Morris, J.C. & Weber, W.J., Jr., 1966, "Adsorption of Biochemically Resistant Materials From Solution. Adv. Waste Trtmt. Report-16. U.S. Environmental Protection Agency, Municipal Environmental Research Lab., Cincinnati, Ohio.

Morrison, T.J. & Edwards, L.L., 1978, "Ozonation of Water for Salmonid Fish Rearing Facilities. Pilot Plant Results", presented at Intl. Ozone Assoc. Workshop on Aquatic Applicns. of Ozone, Orlando, Florida, Nov., 1978. Intl. Ozone Assoc., Vienna, VA.

Moss, W.H., Schade, R.E., Sebesta, S.J., Scheutzow, K.A., Beck P.V. & Gerson, D.B., 1977, "Full-Scale Use of Physical/Chemical Treatment of Domestic Wastewater at Rocky River, Ohio", J. Water Poll. Control Fed. 49(11):2249-2254.

Mueller, J.A. & Mancini, J.L., 1975, "Anaerobic Filter - Kinetics and Application", in Proc. 30th Purdue Univ. Indl. Waste Conf., May 6-8, 1975. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, pp. 423-447.

Müller, G. & Bernhardt, H., 1976, "Comparative Bacteriological Investigations on an Experimental Activated Carbon Filter Used For Chlorinated and Ozonized Groundwater and Reservoir Water", Forum, Umwelt, Hygiene 2(27):393-396.

Murin, C.J. & Snoeyink, V.L., 1979, "Competitive Adsorption of 2,4-Dichlorophenol and 2,4,6-Trichlorophenol in the Nanomolar to Micromolar Concentration Range", Environ. Sci. Technol. 13(3):305-311.

Myers, L.H., 1976, "Pilot Plant Activated Carbon Treatment of Petroleum Refinery Wastewater", in Proc. Open Forum on Management of Petroleum Refinery Wastewaters, F.S. Manning, editor, 26-29 Jan. U.S. EPA, Robt. S. Kerr Environmental Research Labs., Ada, OK.

National Research Council, 1979, "An Evaluation of Activated Carbon For Drinking Water Treatment", NRC, Washington, DC. Natl. Tech. Info. Service, Springfield, VA, Report No. PB-299,968/8WP.

O'Brien, J.E. & Alsentzer, H.A., 1977, "Demonstration Plant for the Treatment of Wastewaters From Tank Truck Cleanings", AIChE Symp. Series 73(167): 189-192, Water-1976. Am. Inst. Chem. Engrs., New York, N.Y.

Oehler, K.E., 1977, "Development of a Method for Chemical Oxidation During Processing of Surface Waters", presented at Activated Carbon Conference, Oct., 1977, Karlsruhe, Federal Republic of Germany. Engler-Bunte Inst. der Univ. Karlsruhe.

O'Farrell, T.P. & Menke, R.A., 1978, "Operational Results for the Piscataway Model 5 MGD AWT Plant". U.S. EPA Report No. EPA-600/2-78-172, Sept., U.S. EPA, Cincinnati, Ohio, 91 pp.

Osborne, D.J., 1979a, "Activated Carbon Treatment", printed in On-Stream, No. 21, Winter Issue. Humphries & Glasgow, Ltd., 22 Carlisle Place, London SW1P 1JA, England.

Osborne, D.J., 1979b, "Experience With Multi-Hearth Furnace at Wilne Treatment Works, Nottingham, U.K.", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA, Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, DC.

Otte, G. & Rosenthal, H., 1978, "Water Quality During a One Year Operation of a Closed, Intensive Fish Culture System", presented at Intl. Ozone Assoc. Workshop on Aquatic Applications of Ozone, Orlando, Florida, Nov. 1978. Intl. Ozone Assoc., Vienna, VA.

Oulman, C.S., 1980, "The Logistic Curve as a Model for Carbon Bed Design", J. Am. Water Works Assoc. 72(1):50-53.

Pahren, H.R. & Melton, R.G., 1979, "Mutagenic Activity and Trace Organics in Concentrates From Advanced Wastewater Treatment Plant Effluents", in Proc. Water Reuse Symp., Washington, DC, 25-30 March. Am. Water Works Assoc. Research Foundation, Denver, CO, p. 2170-2186.

Parkhurst, J.D., Dryden, F.D., McDermott, G.N. & English, J., 1967, "Pomona Activated Carbon Pilot Plant", J. Water Poll. Control Fed. 35:R70.

Paulson, E.G., 1969, "Adsorption as a Treatment of Refinery Effluent", Calgon Corp. Report. No. C-623 for CCRW Subcommittee of Chemical Wastes, Am. Petroleum Inst., Washington, D.C.

Peel, R.G. & Benedek, A., 1980a, "Attainment of Equilibrium in Activated Carbon Isotherm Studies", Env. Sci. & Technol. 14(1):66-71.

Peel, R.G. & Benedek, A., 1980b, "Dual Rate Kinetic Model for Activated Carbon Adsorption, Part I. Prediction of Column Performance Using the Surface Diffusion Model", accepted for publication in J. Am. Soc. Civil Engrs. Am. Soc. Civil Engrs., New York, N.Y.

Peel, R.G. & Benedek, A., 1980c, "Dual Rate Kinetic Model for Activated Carbon Adsorption, Part II. A Simplified Driving Force Model", accepted for publication in J. Am. Soc. Civil Engrs. Am. Soc. Civil Engrs., New York, N.Y.

Reel, R.G. and Benedek, A., 1980d, "Dual Rate Kinetic Model of Fixed Bed Adsorber", J. Env. Engrg. Div., Am. Soc. Civil Engrs. EE4:797-813.

Pendygraft, G.W., Schlegel, F.E. & Huston, M.J., 1979, "The EPA-Proposed Granular Activated Carbon Treatment Requirement: Panacea or Pandora's Box?" J. Am. Water Works Assoc. 71(2):52-60.

Perrotti, A.E. & Rodman, C.A., 1974, "Factors Involved With Biological Regeneration of Activated Carbon", Water -- 1974, G.F. Bennett, Ed., AIChE Symp. Series 70(144):317-325. Am. Inst. Chem. Engrs., New York, N.Y.

Perry, D.L., Smith, J.K. & Lynch, S.C., 1980, "Development of Basic Data and Knowledge Regarding Organic Removal Capabilities of Commercially Available Home Water Treatment Units Utilizing Activated Carbon; Final Report, Phase 2", U.S. EPA, Office of Water Supply, Washington, DC.

Peyton, G.R., Burleson, J., Huang, F., Lin, S. & Glaze, W., 1979, "Treatment of Potential Drinking Water Supply Pollutants With Ozone and Ozone/UV", Presented at 4th World Ozone Congress, Houston, Texas, Nov. 26-29. Intl. Ozone Assoc., Vienna, VA.

Piet, G. & Morra, C.F., 1979, "Behavior of Micropollutants in River Water During Bank Filtration", in Oxidation Techniques in Drinking Water Treatment, W. Kühn & H. Sontheimer, editors. U.S. EPA Report No. EPA-570/9-79-020. U.S. EPA, Office of Drinking Water, Washington, DC, p. 608-619.

Pitkat, C.A. & Berndt, C.L., 1980, "Textile Waste Treatment at a Municipal PACT Facility", presented at 35th Annual Purdue Indl. Waste Conf., 12-14 May. Purdue Univ., School of Civil Engrg., Lafayette, IN.

Poels, C.L.M., undated, but after 1977, "Toxicological Quality of Rhine Water and Implications for Water Treatment Processes", KIWA, Rijswijk, The Netherlands.

Poon, C.P.C. & Shunney, E.L., 1973, "Have A Space Problem?", Water & Wastes Engrg. 10(3):B-2-B-6.

Popper, K., Camirand, W.M., Williams, G.S. & Mecchi, E.P., 1978, "Regeneration of Spent Activated Carbon With Formaldehyde", U.S. Patent, 4,073,747, Feb. 14, 1978.

Prengle, H.W., Jr., Mauk C.E. & Payne, J.E., 1977, "Ozone/UV Oxidation of Chlorinated Compounds in Water", in Forum on Ozone Disinfection, E.G. Fochtman, R.G. Rice & M.E. Browning, editors. Intl. Ozone Assoc., Vienna, VA, pp. 286-295.

Prober, R., Hanna, Y.A. & Guirguis, W.A., 1977, "Toward a Model for Activated Carbon Treatment in the Presence of Significant Bacterial Growth". Presented at WWEMA Meeting on Wastewater Treatment, Atlanta, Georgia, April, 1977.

Prosche, M.A., 1976, "Activated Carbon Treatment of Combined Storm and Process Waters", in Proc. Open Forum on Management of Petroleum Refinery Wastewaters, F.S. Manning, editor, 26-29 Jan. U.S. EPA, Robt. S. Kerr Environmental Research Labs., Ada, OK, p. 399-410.

Randtke, S.J., 1978, "Discussion of Guirguis, Cooper, Harris & Ungar, 1978", J. Water Poll. Control Fed. 50(11):2602-2603.

Reimers, R.S., Englande, A.J. & Miles, H.B., 1976, "A Quick Method for Evaluating the Suitability of Activated Carbon Adsorption for Wastewaters", Proc. 31st Indl. Waste Conf., Purdue Univ., May 4-6, 1976. Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, pp. 395-408.

Reynolds, T.D. & Hawkins, S.J., 1980, "Water Treatment Project: Observations on Use of GAC in Practice", U.S. EPA Report No. EPA-600/1-80-023, U.S. EPA, Health Effects Research Lab., Cincinnati, Ohio.

Rice, R.G., Miller, G.W., Robson, C.M. & Kühn, W., 1977, "Biological Activated Carbon", presented at Intl. Symp. on Advanced Ozone Technology, Toronto, Ontario, Canada, Nov., 1977. Intl. Ozone Assoc., Vienna, VA.

Rice, R.G., Miller, G.W. & Robson, C.M., 1978a, "Potentials of Biological Activated Carbon for the Treatment of Industrial Wastewaters", presented at WWEMA Annual Indl. Poll. Control Symp., St. Louis, Mo., April, 1978. Water & Wastewater Equipment Mfgrs. Assoc., McLean, Va.

Rice, R.G., Miller G.W. & Robson, C.M., 1978b, "European Drinking Water Treatment Practices", presented at the Annual Meeting of the Natl. Assoc. of Water Cos., Baton Rouge, La., Oct., 1978. Natl. Assoc. of Water Cos., Washington, D.C.

Rice, R.G., 1979a, "Biological Activated Carbon", presented at EPA Seminar on Control of Organic Chemical Contaminants in Drinking Water, Dallas, Texas, March, 1979. Public Technology, Inc., Washington, D.C.

Rice, R.G., 1979b, "Biological Activated Carbon - A Status Report", presented at 4th World Ozone Congress, Houston, Texas, Nov. 26-29. Intl. Ozone Assoc., Vienna, VA.

Rice, R.G., 1980, "Ozone Gives Boost To Activated Carbon", Water & Sewage Works, April, pp. 40-82.

Rice, R.G., Robson, C.M. & Miller, G.W., 1981, "Biological Activated Carbon and its Potentials for Treating Industrial Wastewaters", Final Report of Grant No. R-804385-01 to Public Technology, Inc. U.S. EPA, Office of Environmental Engrg. & Technol., Washington, DC.

Richard, Y., 1972, "Experiment on the Industrial Treatment of Drinking Water by Activated Carbon", Degrémont S.G.E.A., Rueil Malmaison, France, 5 Dec.

Richard, Y. & Fiessinger, F., undated, but after 1972, "Le Traitement Industrielle Des Eaux Potables par le Charbon Actif", Degrémont, S.G.E.A., Rueil Malmaison, France.

Richard, Y. & Blue, P., 1978, "Ozone Pretreatment of Drinking Water", presented at IOI Ozone Technology Symposium, Los Angeles, Calif., 23-25 May. Intl. Ozone Assoc., Vienna, VA.

Richard, Y., Brener, L. & Leblanc, C., 1979, "Optimization of Potable Water Treatment Lines With A View to Halogenous Compound Reduction", Presented at 4th World Ozone Congress, Houston, Texas, Nov. 26-29. Intl. Ozone Assoc., Vienna, VA.

Rizzo, J.A., 1976a, "Activated Carbon Clears Effluent", Oil & Gas J. 74(22):-52-56.

Rizzo, J.A., 1976b, "Case History: Use of Powdered Activated Carbon in an Activated Sludge System", in Proc. Open Forum on Management of Petroleum Refinery Wastewaters, F.S. Manning, editor, 26-29 Jan. U.S. EPA, Robt. S. Kerr Environmental Research Labs., Ada, OK, p. 359-374.

Robeck, G.G., 1978, "Progress Report, July 1 to Sept. 30, 1978, EPA Drinking Water Research Activities, p. 1. U.S. EPA, Water Supply Research Lab, Cincinnati, Ohio 45268.

Robertaccio, F.L., Hutton, D.G., Grulich, G. & Goltzer, H.L., 1972, "Treatment of Organic Chemical Plant Wastewater with the DuPont PACT Process", presented at AIChE Natl. Meeting, Dallas, AIChE Symp. Series No. 125, Vol. 65.

Roberts, P., Gujer, W. & Eugster, J., 1977, "Reinigung von Kommunalem Abwasser Mittels Aktivkohle Nach Schwach Belasteter Biologischer Reinigung und Filtration, Vom Wasser 48:47-70.

Rodman, C.A. & Shunney, E.L., 1970, "A New Concept For The Biological Treatment of Textile Finishing Waters", Water -- 1970, Chem. Engrg. Prog. Symp. 67(107):451-457.

Rodman, C.A., 1971, "Bio-Regenerated Activated Carbon Treatment of Textile Dye Wastewater", EPA Report No. 12090 DWM. U.S. Environmental Protection Agency, Indl. Environ. Research Lab., Cincinnati, Ohio 45268.

Rodman, C.A. & Shunney, E.L., 1971, "New Concepts For Treating Coloured Organic Contaminated Wastewater", Presented at Symp. on Environ. Engrg. Aspects of Pollution Control, London, England, June 22-23, Soc. Environmental Engrs., London.

Rom, D., Wachs, A.M. & Rotel, M., 1980, "Pilot Plant Studies of Water Renovation in a System Combining Ozonation With Activated Carbon Treatment", presented at 53rd Annual WPCF Conf., Las Vegas, Nev., 1 Oct. Water Poll. Control Fed., Washington, DC.

Rosenthal, H. & Sander, E., 1975, "An Improved Aeration Method Combined Waste Foam Removal in a Seawater Recycling System", Intl. Council for the Exploration of the Sea, Mariculture Committee, E:14, 1-16 (Fisheries Improvement Committee).

Rosenthal, H., von Westernhagen, H. & Otte, G., 1978, "Maintaining Water Quality in Laboratory Scale Sea Water Recycling Systems", Intl. Council for the Exploration of the Sea, Mariculture Committee Report, C.M. 1978/F:10.

Rosenthal, H. & Otte, G., 1979, "Ozonation in an Intensive Fish Culture Recycling System", Ozone Sci. & Engrg. 1(4):319-327.

Sander, R., 1977, "Formation and Removal of Chlorinated By-Products in a Pilot Plant Unit", presented at Seminar on Activated Carbon, Karlsruhe, Federal Republic of Germany, Oct. 30-31, 1977. Engler-Bunte Inst. der Univ. Karlsruhe.

Sander, R., 1979, "Effect of Prechlorination on Activated Carbon Adsorption", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA, Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, DC.

Savage, P.R., 1979, "Waste Disposal With An Energy Bonus", Chem. Engrg., May 21, p. 116-117.

Scaramelli, A.B. & DiGiano, F.A., 1970, "Upgrading the Activated Sludge System by Addition of Powdered Carbon", Water & Sewage Works 120(9):90-94.

Schalekamp, M. & Bakker, S.P., 1978, "Use and Thermal Regeneration of Activated Carbon in Switzerland", Effluent & Water Trtmt. J. 18(1):28-32.

Schalekamp, M., 1979, "The Use of GAC Filtration to Ensure Quality in Drinking Water From Surface Sources", J. Am. Water Works Assoc. 71(11):-638-647.

Scherm, M. & Lawson, C.T., 1977, "Pilot Demonstration of Renovation and Reuse of Wastewaters From Organic Chemical Manufacturing", Indl. Water Engrg., Oct./Nov. issue, p. 16-22.

Schulhof, P., 1979, "An Evolutionary Approach to Activated Carbon Treatment", J. Am. Water Works Assoc. 71(11):648-659.

Schuliger, W.G., 1974, "Equipment Design Considerations", in Proc. Physical-Chemical Treatment Activated Carbon Adsorption in Pollution Control, Seminar held in Ottawa, Ontario, Canada, Oct. 24, 1974. Environmental Protection Service, Environment Canada, Ottawa.

Schuliger, W.G., 1978, "Purification of Industrial Liquids With Granular Activated Carbon: Techniques For Obtaining and Interpreting Data and Selecting the Type of Commercial System", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, op. cit., pp. 55-84.

Semmens, M.J. & Goodrich, R.R., Jr., 1977, "Biological Regeneration of Ammonium-Saturated Clinoptilolite. I. Initial Observations", Environ. Sci. & Technol. 11(3):255-265.

Semmens, M.J., 1977, "The Feasibility of Using Nitrifying Bacteria To Assist The Regeneration of Clinoptilolite", in Proc. 32nd Purdue Univ. Indl. Waste Conf., May 10-12, 1977. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, pp. 733-744.

Semmens, M.J., Wang, J.T. & Booth, A.C., 1977, "Nitrogen Removal by Ion Exchange: Biological Regeneration of Clinoptilolite", J. Water Poll. Control Fed. 49(12):2431-2444.

Semmens, M.J. & Porter, P.S., 1979, "Ammonium Removal by Ion Exchange: Using Biologically Restored Regenerant", J. Water Poll. Control Fed. 51(12):2928-2940.

Shelby, S.E., Koon, J.H., Marks, D.R. & Scott, H.A., Jr., 1980, "Adsorption of Chlorinated and Non-Chlorinated Organics From a Pesticide Manufacturing Plant Waste Stream", presented at 53rd Natl. Conf. WPCF, Las Vegas, Nev., 1 Oct. Water Poll. Control Fed., Washington, DC.

Sharma, B. & Ahler, R.C., 1977, "Nitrification and Nitrogen Removal", Water Research 11:897-925.

Shuckrow, A.J., Bonner, W.F., Presecan, N.L. & Kazmierczak, E.J., 1972, "A Pilot Study of the Physical-Chemical Treatment of Raw Wastewater at the Westerly Plant in Cleveland, Ohio", Water Research 6:619.

Shunney, A.L., Perotti, A.E. & Rodman, C.A., 1971, "Decolorization of Carpet Yarn Dye Wastewaters", Am. Dyestuff Reporter 60(6):32, 34-36, 38, 40.

Siemak, R.C., Trussell, R.R., Trussell, A.R. & Umphres, M.D., 1979, "How to Reduce Trihalomethanes in Drinking Water", Civil Engrg., Feb. 1979, pp. 49-51.

Skovronek, H.S., Dick, M. & des Rosiers, P.E., 1977, "Selected Uses of Activated Carbon for Industrial Wastewater Pollution Control", Indl. Water Engrg., 14(3):6-13.

Skovronek, H.S. & Becker, D.L., 1977, "Pollution Control by Adsorption", presented at 70th Annual Meeting of the Am. Inst. Chem. Engrs., New York, N.Y., Nov. 13-17, 1977. AIChE, New York, N.Y.

Skovronek, H.S., 1978, "Industrial Case Histories", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, op. cit., pp. 85-130.

Slade, J.S., 1978, "Enteroviruses in Slow Sand Filtered Water", J. Inst. Water Engrs. & Scientists 32(6):530-536.

Smith, J.K., Lynch, S.C., Gebhart, J.E. & Monteith, C.S., 1979, "Development of Basic Data and Knowledge Regarding Organic Removal Capabilities of Commercially Available Home Water Units Utilizing Activated Carbon - Preliminary Report - Phase I", U.S. Environmental Protection Agency, Office of Water Supply, Washington, DC.

Smith, S.A., Chapman, R.L. & Butterfield, O.R., 1979, "Tahoe-Truckee Water Reclamation Plant First Year in Review", Proc. Water Reuse Symp., Washington, D.C., Mar. 25-30, pp. 1435-1445. Am. Water Works Assoc. Research Foundation, Denver, Colo.

Smith, S.B., 1974, "Techniques of Activated Carbon Regeneration", in Proc. Physical-Chemical Treatment Activated Carbon Adsorption in Pollution Control, Seminar held in Ottawa, Ontario, Canada, Oct. 24, 1974. Environmental Protection Service, Environment Canada, Ottawa.

Smithson, G.R., 1978, "Regeneration of Activated Carbon: Thermal, Chemical, Solvent, Vacuum and Miscellaneous Regeneration Techniques", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, op. cit., pp. 879-904.

Snoeyink, V.L., McCreary, J.J. & Murin, C.J., 1977, "Activated Carbon Adsorption of Trace Organic Compounds", U.S. EPA Report No. 600/2-77-223, U.S. EPA, Indl. Environ. Research Lab., Cincinnati, Ohio 45268.

Snyder, A.J. & Alspaugh, T.A., 1974, "Catalyzed Bio-Oxidation and Tertiary Treatment of Integrated Textile Wastewaters", U.S. EPA Report No. 660/2-74-039, June, 1974. U.S. EPA, Indl. Environ. Research Lab., Cincinnati, Ohio 45268.

Sontheimer, H., 1975a, "The Importance of Adsorption Processes in Drinking Water Treatment", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, H. Sontheimer, editor, op. cit., pp. 1-15.

Sontheimer, H., 1975b, "Basic Principles of Adsorption Process Techniques", in Translation of Reports on Special Problems of Water Techology, Vol. 9, op. cit., p. 29-66.

Sontheimer, H., 1975d, "Realistic Laboratory Test Methods for the Evaluation of Activated Carbon", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, H. Sontheimer, editor, op. cit., pp. 250-268.

Sontheimer, H., 1975e, "Theory and Practice in the Use of Adsorption Processes", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, H. Sontheimer, editor, op cit., pp. 414-417.

Sontheimer, H., Wölfel, P. & Safert, F., 1977, "Verbesserung der Biologischen Abbaubarkeit der Organischen Stoffe in Biologisch Gereinigten Abwässern Durch Fine Ozonbehandlung", presented at 3rd Intl. Symp. on Ozone Technology, Paris, France, May. Intl. Ozone Assoc., Vienna, VA.

Sontheimer, H., 1978a, "Biological Treatment of Surface Waters in Activated Carbon Filters", OZONews, July, 1978, Part 2 - Technical Paper Section. Intl. Ozone Assoc., Cleveland, Ohio.

Sontheimer, H., 1979a, "Process Engineering Aspects in the Combination of Chemical and Biological Oxidation", in Oxidation Techniques in Drinking Water Treatment, W. Kühn & H. Sontheimer, editors. U.S. EPA Report No. EPA-570/9-79-020. U.S. EPA, Office of Drinking Water, Washington, pp. 702-714.

Sontheimer, H., 1979b, "Biologisch-Adsorptive Trinkwasseraufbereitung in Aktivkohlefiltern -- Das Mülheimer Verfahren", Rheinisch-Westfälische Wasserwerksgesellschaft mbH (Mülheim a.d. Ruhr) & DVGW-Forschungsstelle am Engler-Bunte Institut der Universität Karlsruhe, Feb.

Sontheimer, H., 1979c, "German Experience in Activated Carbon Treatment", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA, Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, DC.

Sontheimer, H., 1979d, "Applying Oxidation and Adsorption Techniques: A Summary of Progress", J. Am. Water Works Assoc. 71(11):612-617.

Sontheimer, H., 1979e, "Design Criteria and Process Schemes for GAC Filters", *J. Am. Water Works Assoc. 71(11):618-622.*

Spahn, H., Brauch, V., Schlünder, E.U. & Sontheimer, H., 1974, "Auslegung von Aktivkohlefiltern zur Wasserreinigung. Teil I: Untersuchung der Adsorption am Eizelkorn", Verfahrenstechnik 8(8), 8 pp.

Spahn, H., Brauch, V., Schlünder, E.U. & Sontheimer, H., 1975, "Auslegung von Aktivkohlefiltern zur Wasserreinigung. Teil II. Theoretische und Experimentelle Bestimmung der Beladungsfelder in Aktivkohlefestbetten", Verfahrenstechnik 9(1), 5 pp.

Stephenson, P., 1979, "The Effect of Ozone on the Biodegradability of Refractory Organics in Water", M. Engr. Thesis, McMaster Univ., Hamilton, Ontario, Canada.

Stevens, A.A., Seeger, D.R., DeMarco, J. & Moore, L., 1979, "Removal of Higher Molecular Weight Organic Compounds by the Granular Activated Carbon Adsorption Unit Process", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA, Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, DC.

Stewart, D.R. & Sierka, R.A., 1979, "Effects of Preozonation of Domestic Wastewater on Activated Carbon Adsorption", presented at 52nd Annual WPCF Conf., Houston, TX. Water Poll. Control Fed., Washington DC.

Strack, B., 1975, "Operation, Problems and Economy of Activated Carbon Regeneration", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, op. cit., pp. 284-311.

Suffett, I.H., Brenner, L., Coyle, J.T. & Cairo, P.R., 1978, "Evaluation of the Capability of Granular Activated Carbon and XAD-2 Resin to Remove Trace Organics From Treated Drinking Water", Env. Sci. & Technol. 12(12):

Suffett, I.H., McGuire, M.J., Josephson, J. & Ember, L.R., 1978, "Cleanup: That Old Black Magic Works Again!", Environ. Sci. & Technol. 12(10):-1138-1149.

Suffet, I.H., 1980, "An Evaluation of Activated Carbon for Drinking Water Treatment: A Report From the National Academy of Science", J. Am. Water Works Assoc. 72(1):41-50.

Suidan, M.T., Cross, W.H. & Khan, K., 1979, "Treatment of Phenolic Wastewater with Activated Carbon Filters. Technical Completion Report, Sept. 1977 - Sept. 1979. Natl. Tech. Info. Service, Springfield, VA, Report No. FE-2756-T1.

Suzuki, J., 1976, "Study on Ozone Treatment of Water-Soluble Polymers. I. Ozone Degradation of Polyethylene Glycol in Water", J. Appl. Polymer Sci. 20:93-103.

Suzuki, J., Nakagawa H. & Ito, H., 1976, "Study on Ozone Treatment of Water-Soluble Polymers. II. Utilization of Ozonized Polyethylene Glycol by Bacteria" J. Appl. Polymer Sci. 20:2791-2797.

Suzuki, M., Tada, Y. & Kawazoe, K., 1977, "Comparison of Treatment Processes for Strong Wastewater From Chemi-Mechanical Pulp Mill", Pacific Chem. Engrg. Congr. (PAChEC '77) 2:1322-1329. Am. Inst. Chem. Engrs., New York, N.Y.

Symons, J.M., 1976, "Summary of Granular Activated Carbon Practice Data", Report dated Feb. 17, 1976. U.S. EPA, Water Supply Research Laboratory, Concinnati, Ohio 45268.

Symons, J.M., 1979, "Practical Applications of Adsorption Techniques in Drinking Water Treatment", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA, Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, DC.

Symons, J.M., Carswell, J.K., DeMarco, J. & Love, O.T., Jr., 1979, "Removal of Organic Contaminants From Drinking Water Using Techniques Other Than Granular Activated Carbon Alone - A Progress Report", Drinking Water Research Div., Municipal Environmental Research Lab., Office of Research & Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

Taylor, R.H., Allen, M.J. & Geldreich, E.E., 1979, "Testing of Home Use Carbon Filters", J. Am. Water Works Assoc. 71(10):577-579.

Thibault, G.T., Steelman, B.L. & Tracy, K.D., 1978, "Enhancement of the Refinery Activated Sludge Process With Powdered Activated Carbon", Presented at 6th Ann. Indl. Poll. Control Conf., WWEMA, St. Louis, Mo., April 13. Water & Wastewater Equipment Mfgrs. Assoc., McLean, VA.

Tien, C., 1978, "Bacterial Growth and Adsorption in Granular Activated Carbon Columns", presented at Symp. on Activated Carbon Adsorption of Organics From The Aqueous Phase, Miami, Florida, Sept. Am. Chem. Soc., Washington, D.C.

Tifft, E.C., Jr. & Tamays, T.A., 1979, "Drinking Water Treatment With Ozone/Granular Activated Carbon", Presented at 4th World Ozone Congress, Houston, Texas, Nov. 26-29. Intl. Ozone Assoc., Vienna, VA.

Timpe, W.G. & Lang, E.W., 1974, "Activated Carbon Treatment of Kraft Mill Effluent For Reuse", Water -- 1973, G.F. Bennett, ed., AIChE Symp. Series 70(136):585-591. Am. Inst. Chem. Engrs., New York, N.Y.

Tomlinson, T.G. & Snaddon, D.H., 1966, "Biological Oxidation of Sewage by Films of Microorganisms", Air & Water Poll. Inst. J. 4:865.

Van Der Kooij, D., 1978, "Processes During Biological Oxidation in Filters", presented at Intl. Conf. on Oxidation Techniques in Drinking Water Treatment, Karlsruhe, Federal Republic of Germany, Sept. 11-13, 1978. Engler-Bunte Inst. der Univ. Karlsruhe.

Van Leeuwen, J. & Prinsloo, J., 1980, "Ozonation at the Stander Water Reclamation Plant", Water SA 6(2):96-102.

Van Vuuren, L.R.J., Clayton, A.C. & Van Der Post, D.C., 1978, "Current Status of Water Reclamation at Windhoek", Presented at 51st Ann. Conf. of the Water Poll. Control Fed., Anaheim, Calif., 1-6 Oct. WPCF, Washington, D.C.

Von Dreusche, C., Jr., 1978, "Process Aspects of Regeneration in a Multiple Hearth Furnace", in Carbon Adsorption Handbook, P.H. Cheremisinoff & F. Ellerbusch, editors, op. cit., pp. 923-954.

Waggott, A. & Bayley, R.W., 1972, "The Use of Activated Carbon for Improving the Quality of Polished Sewage Effluent", Water Pollution Control, p. 417.

Wallace, R.N. & Burns, D.E., 1976, "Factors Affecting Powdered Carbon Treatment of a Municipal Wastewater", J. Water Poll. Control. Fed. 48(3):511-519.

Waller, G., 1976, "Granular Activated Carbon and its Re-Use in Water and Waste Treatment", Prog. Water Technology 8(2/3):39-45.

Wallis, C., Stagg, C.H. & Melnick, J.L., 1974, "The Hazards of Incorporating Charcoal Filters Into Domestic Water Systems", Water Research 8:111-113.

Warner, H.P. & English, J.N., 1978, "Wastewater Treatment For Reuse and its Contribution to Water Supplies", U.S. EPA Report No. EPA-600/2-78-027, March, 40 pp.

Wasserlauf, M., 1974, "Toxicity Removal From Kraft Mill Effluents by Activated Carbon", in Proc. Physical-Chemical Treatment Activated Carbon Adsorption in Pollution Control, Seminar held in Ottawa, Ontario, Canada, Oct. 24, 1974. Environmental Protection Service, Environment Canada, Ottawa.

Weber, W.J., Jr. & Morris, J.C., 1964, "Equilibrium and Capacities for Adsorption on Carbon", J. Sanit. Engr. Div., Am. Soc. Civil Engrg. 90:SA3, 79.

Weber, W.J., Jr., 1964, "Competitive Interactions in Adsorption From Dilute Aqueous Bi-Solute Solutions", J. Appl. Chem. 14:565-572.

Weber, W.J., Jr. & Gould, J.P., 1966, "Sorption of Organic Pesticides From Aqueous Solution", in Organic Pesticides in the Environment, Advances in Chemistry Series, No. 60, A,. Chem. Soc., Washington, D.C., pp. 280-304.

Weber, W.J., Jr. & Keinath, T.M., 1967, "Mass Transfer of Perdurable Pollutants From Dilute Aqueous Solution in Fluidized Adsorbers", Chem. Engrg. Progress Symp. Series 63(74):79-89.

Weber, W.J., Jr., Hopkins, C.B. & Bloom, R., Jr., 1970, "Physico-Chemical Treatment of Wastewater", J. Water Pollution Control Fed. 42:83-99.

Weber, W.J. Jr., 1970, "Discussion of High Quality Reuse Water By Chemical-Physical Wastewater Treatment, J. Water Poll. Control Fed. 42(3):456-463.

Weber, W.J., Jr., Hopkins, C.B. & Bloom, R., Jr., 1971, "Expanded Bed Adsorption Systems For Treatment of Sewage Effluents", Water -- 1970, AIChE Symp. Series 67(107):541-553. Am. Inst. Chem. Engrs., New York, N.Y.

Weber, W.J., Jr., 1973, "The Prediction of the Performance of Activated Carbon For Water Treatment", Proc. Water Research Assoc. Conf., Reading, England, pp. 53-72.

Weber, W.J., Jr., Friedman, L.D. & Bloom, R., 1973, "Biologically Extended Physicochemical Treatment", in Proc. 6th Intl. Conf. on Advances in Water Poll. Research, Jerusalem, June 8-23, 1972, S.H. Jenkins, editor. Pergamon Press, Oxford, England and New York, N.Y., pp. 641-649.

Weber, W.J., Jr. & Crittenden, J.C., 1975, "MADAM I - A Numeric Method For Design of Adsorption Systems", J. Water Poll. Control Fed. 47(5):924-940.

Weber, W.J., Jr., 1977, "Integrated Biological & Physical-Chemical Treatment for Reclamation of Wastewater", Indl. Water Engrg. 14:20-27.

Weber, W.J., Jr., Pirbazari, M. & Herbert, M.D., 1978, "Removal of Halogenated Organic and THM Precursor Compounds From Water by Activated Carbon", Environmental & Water Resources Engrg. Dept., Univ. of Michigan, Ann Arbor, Michigan.

Weber, W.J., Jr., 1978, Discussion of "Improved Performance of Activated Carbon by Preozonation", by W. Guirguis, T. Cooper, J. Harris & A. Ungar, J. Water Poll. Control Fed. 50(12):2781-2785.

Weissenhorn, F.J., 1975, "Testing of Activated Carbon Filters in Waterworks", in Translation of Reports on Special Problems of Water Technology, Vol. 9 - Adsorption, H. Sontheimer, editor, op. cit., pp. 238-249.

Werner, P., Klotz, M. & Schweisfurth, R., 1978, "Microbiological Studies of Activated Carbon Filtration", in Oxidation Techniques in Drinking Water Treatment, W. Kühn & H. Sontheimer, editors, U.S. EPA Report No. EPA-570/9-79-020, p. 678-688.

Werner, P., Klotz, M. & Schweisfurth, R., 1979, "Investigations Concerning the Microbiology of GAC Filtration for Drinking Water Treatment", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA, Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, DC.

Wilson, S.C. & Krantz, G.E., 1978, "Source Listing for the Application of Activated Carbon Technology", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, op. cit., pp. 955-1022.

Wölfel, P. & Sontheimer, H., 1977, "Amelioration de la Degradation Biologique des Eaux Residuaires par un Traitment a l'Ozone", presented at 3rd Intl. Symp. on Ozone Technol., Paris, France, May. Intl. Ozone Assoc., Vienna, VA.

Wood, P.R. & DeMarco, J., 1978, "Effectiveness of Various Adsorbents in Removing Organic Compounds From Water. Part I - Removing Purgeable Halogenated Organics", presented at Symp. on Activated Carbon Adsorption of Organics From the Aqueous Phase", 176th ACS Mtg., Miami Beach, Fla., 10-15 Sept. Am. Chem. Soc., Washington, DC.

Wood, P.R. & DeMarco, J., 1978, "Effectiveness of Various Adsorbents in Removing Organic Compounds From Water. Part II - Removing Total Organic Carbon and Trihalomethane Precursor Substances", presented at Symp. on Activated Carbon Adsorption of Organics From the Aqueous Phase, 176th ACS Mtg., Miami Beach, Fla., 10-15 Sept. Am. Chem. Soc., Washington, DC.

Wood, P.R., 1979, "Treatment of Contaminated Ground Water", presented at NATO/CCMS Conf. on Adsorption Techniques in Drinking Water Treatment, Reston, VA, Apr. 30-May 2. U.S. EPA, Office of Drinking Water, Washington, DC.

Wood, P.R., Jackson, D.F., Gervers, J.A., Waddell, D.H. & Kaplan, L., 1980, "Removing Potential Organic Carcinogens and Precursors From Drinking Water", U.S. EPA Report No. EPA-600/2-80-130a. U.S. EPA, Municipal Environmental Research Lab., Cincinnati, Ohio.

World Health Organization, 1975, "Health Effects Relating to Direct and Indirect Reuse of Wastewater for Human Consumption", Report of an Intl. Working Meeting, held at Amsterdam, The Netherlands, Jan. 13-16, 1975. Tech. Paper No. 7.

Ying, W.C. & Weber, W.J., Jr., 1978, "Bio-Physicochemical Adsorption Systems for Wastewater Treatment: Predictive Modeling for Design and Operation", in Proc. 33rd Annual Purdue Univ. Indl. Waste Conf., 9-11 May. Ann Arbor Science Publishers, Inc., Ann Arbor, MI, p. 128-141.

Ying, W.C. & Weber, W.J., Jr., 1979, "Bio-Physicochemical Adsorption Model Systems For Wastewater Treatment", J. Water Poll. Control Fed. 51(11):-2661-2677.

Zaidi, S.A. & Tollefson, E.L., 1976, "The Physical-Chemical Treatment of Sour Gas Plant Process Wastewaters", J. Can. J. Petrol. Technol., April-June, 1976, pp. 39-47.

Zanitsch, R.H. & Stenzel, M.N., 1978, "Economics of Granular Activated Carbon Water and Wastewater Treatment Systems", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, op. cit., pp. 215-240.

Zeff, J.D., Leitis, E. & Crosby, D.G., 1979, "Study of the Chemistry of the UV-Ozonation of Refractory Organic Compounds in Water", Presented at 4th World Ozone Congress, Houston, Texas, Nov. 26-29. Intl. Ozone Assoc., Vienna, VA.

Zobell, C.E., 1937, "The Influence of Solid Surfaces Upon the Physiological Activities of Bacteria in Sea Water", J. Bact. 33:86.

Zogorski, J.S. & Faust, S.D., 1978, "Operational Parameters for Optimum Removal of Phenolic Compounds From Polluted Waters by Columns of Activated Carbon", in Carbon Adsorption Handbook, P.N. Cheremisinoff & F. Ellerbusch, editors, op. cit., pp. 753-778.

Zuckerman, M.M. & Molof, A.H., 1970, "High Quality Reuse Water by Chemical-Physical Wastewater Treatment", J. Water Poll. Control Fed. 42(3):437-456.

APPENDIX A

AUBERGENVILLE PLANT (SUBURBS OF PARIS, FRANCE)

BACKGROUND

The Aubergenville water treatment plant of the Société Lyonnaise des Eaux et de l'Eclairage (SLEE) produces approximately 100,000 cubic meters of water per day (26.4 mgd) from 23 wells which are situated along the south side (left bank) of the Seine River downstream of Paris, between Les Mureaux and Epône.

1961 CONSTRUCTION

The plant was designed to treat groundwater drawn from an area between the Seine River and the Alluets Forest by means of wells driven in the Senonian limestone strata. The groundwater initially contained only a small amount of ammonia and iron with iron bacteria. The original treatment plant which was placed in service in 1961 included the following process steps:

(a) cascade aeration
(b) biological nitrification
(c) filtration
(d) post-disinfection with chlorine dioxide.

A few months of operation caused a drawdown of the groundwater level of the originally high quality water source. This resulted in an intrusion of groundwater from other sources, particularly from the Seine River. The quantity of flow from the Seine was accentuated by increases in the river level due to the construction of reservoirs and locks to allow passage of larger barges in the Seine. As a result, water from certain wells developed unpleasant tastes and exhibited increased levels of organic matter, detergents and bacteria. In particular, there was a large increase in the number of filamentous iron bacteria.

1969 ADDITIONS

Major additions to the treatment plant were made operational in 1969. These modifications included chemical clarification ahead of nitrification. Chemical addition ahead of clarification included aluminum sulfate for coagulation, activated silica for flocculation and powdered activated carbon for elimination of detergents, organics and bad tastes. Facilities were provided to enable ozonation of the water after the filtration step. Ozone addition is for taste and odor elimination, virus inactivation, removal of micropollutants and detergents.

Since 1969, the treatment process has been as follows: chemical clarification, cascade aeration, biological nitrification, ozonation and post-disinfection with chlorine. In Figure 85 the treatment process schematics of this plant are compared from 1961 to 1969, then from 1969 until 1978.

DETAILED PLANT DESCRIPTION

(a) Twenty-three, 30-meters deep wells, each producing 30 to 40 cubic meters per hour of water.

(b) Chemical Addition:

Aluminum sulfate	-	10 mg/l
Activated silica	-	2 mg/l
Powdered activated carbon	-	10 mg/l

(c) Four, 1,5CO cubic meters/hour Pulsator flocculator-clarifier units. Each unit is 22.3 x 21.6 x 5.1 meters water depth.

(d) Cascade aeration.

(e) Twenty-one biological nitrification units (described in detail below).

(f) Gravity sand filtration - 5 cubic meters/sq m/hr.

(g) One ozonation system, consisting of the following components:

Two, 440 cu m/hr variable speed, positive displacement blowers.

One, water-cooled, heat exchanger type, after-cooler.

One, Freon refrigerant-cooled drier to reduce air temperature to 5°C.

One, 2-cell, activated alumina desiccator drier to reduce air dew point to minus 60° C.

One, 550 tube, horizontal tube, Welsbach water-cooled ozone generator operating at 50 Hertz, with a production capacity of 22 kg of ozone per hour.

One, 2-compartment, countercurrent flow (ozone/water), 5 meters water depth, porous tube diffuser, ozone contactor. Each compartment provides 6 minute ozone contact tires, with an overall ozone contact time of 15 minutes. Total ozone dosage - 0.5 mg/l.

One, 200°C contactor off-gas ozone destructor.

(h) Post-disinfection - Chlorine is added at a booster pump station 189 meters from the plant.

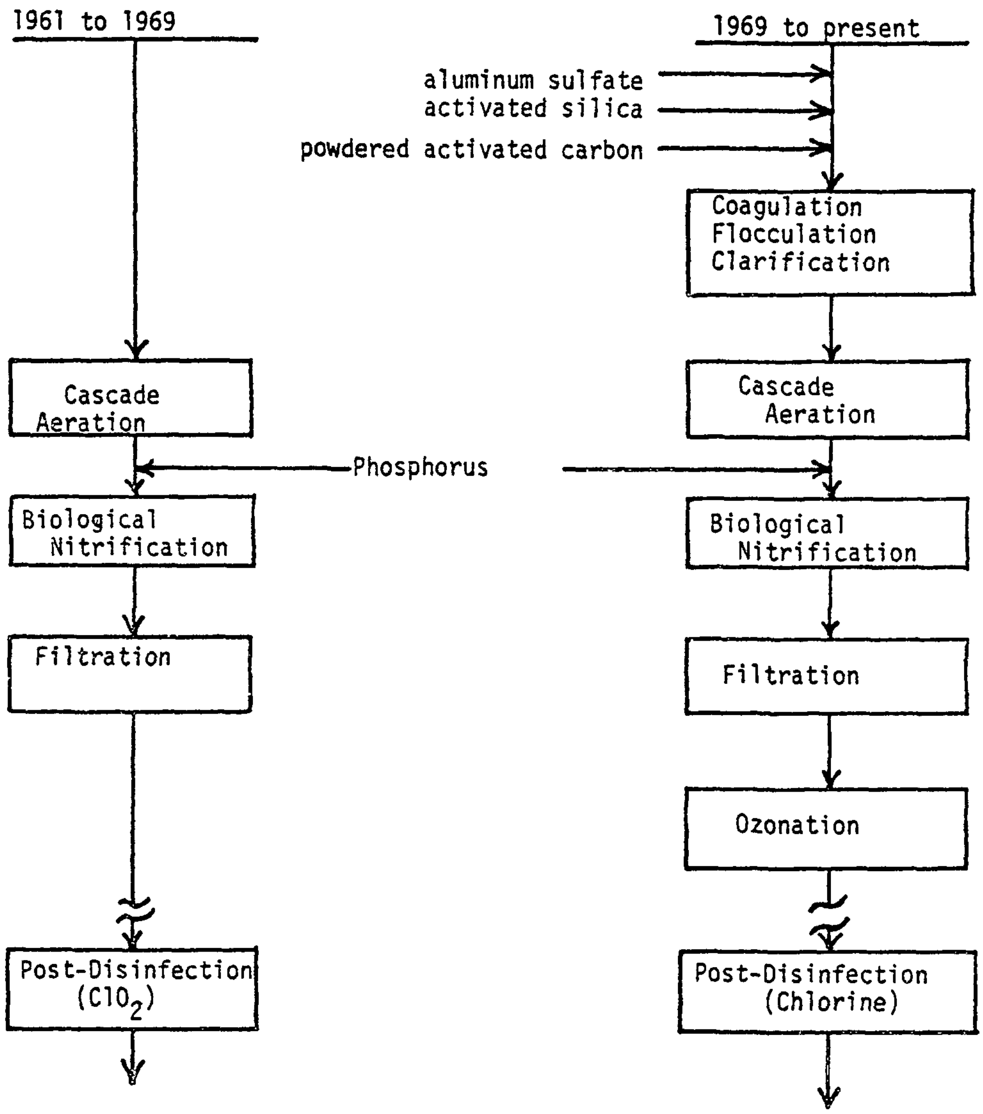


Figure 85. Aubergenville water treatment plant. Process Diagrams.

Biological Nitrification System

The details of biological nitrification at Aubergenville are as follows:

There are 21 nitrification beds at the Aubergenville plant, each with dimensions of 4.9 m (16.1 ft) by 5.9 m (19.3 ft) for a surface area of 28.9 m (311 ft). They have the following characteristics:

Bed depth is 2.5 m (8.2 ft).

Filtration rate at design flow is 11.65 m/hr (4.76 gpm/sq ft).

Upflow type.

Intermittent aeration, on for 2 minutes and off for 6. This 6 minute aeration time is less than the time required for water to pass across the filters. This mode of aeration decreases the bicarbonate equilibrium by decreasing the quantity of CO_2 eliminated by stripping and does not hinder nitrification.

The filter material used is pozzolanic (volcanic stone) with a grain size of 0.5 to 0.15 cm.

Aeration is accomplished by blowing air through the bed.

The quantity of phosphorus added is between 0.1 and 0.2 mg/l, expressed as P_2O_5. A phosphorus residual is not detected at the outlet.

Nitrification beds are backwashed with water, once per week.

Once every six months, the media are dosed with hypochlorite to eliminate filamentous bacteria. This dosing is carried out for 24 hours. Reseeding of the filter then requires one week.

Once every two years the media are removed from the beds, washed in media scour and put back in place. Reseeding then is immediate.

Efficiency: An influent ammonia concentration of 3 mg/l is reduced further to only trace quantities of ammonia after sand filtration.

APPENDIX B

CHOISY-le-ROI (EDMOND PEPIN PLANT), SUBURBS OF PARIS, FRANCE

BACKGROUND

This plant currently is designed to treat 800,000 cubic meters per day (211 mgd) of River Seine water and has an average daily flow of 470,000 cu m/day (124 mgd). In 1961 the first 300,000 cu m/day leg of the plant was installed, and by 1969 the balance of the 800,000 cu m/day treatment capacity was operational. Ozonation was installed in 1967 for color removal, taste and odor control, removal of phenols, detergents, polyaromatics, micropollutants (dissolved organic materials) and for bacterial disinfection and viral inactivation. The plant is owned by the Syndicat des Communes de la Banlieue de Paris pour les Eaux, a public agency, but is operated under contract by the Compagnie Générale des Eaux.

ORIGINAL PROCESS (Chédal, 1976)

Seine River water (which commonly contains 6 to 10 mg/l of total organic carbon), is chemically treated with flocculant (hydrolyzed aluminum chloride), powdered activated carbon, then by breakpoint chlorination (for ammonia removal), with sodium hydroxide for pH correction and chlorine dioxide for destruction of organic manganese complexes. Following addition of these chemicals, the water is treated by sedimentation and rapid sand filtration, dechlorinated by addition of sodium bisulfite, then ozonized (2 to 5 mg/l applied dosage, average dosage 4 mg/l) and treated with chlorine to provide a residual disinfectant for the distribution system.

In 1977, the post-disinfectant was changed to chlorine dioxide to provide a more stable distribution system residual.

This process has the disadvantage of producing chlorinated organic materials which are not readily removed during subsequent processing nor by the dechlorination step.

BIOLOGICAL REMOVAL OF AMMONIA

Gerval (1978) has described experiments which have led to replacement of the breakpoint chlorination step by a biological process for the conversion of ammonia to nitrate. This is done by preozonizing the raw Seine River water as it enters the plant raw water reservoirs. After preozonation, the water is retained about two days in the raw water reservoirs before being treated further by addition of the same chemicals as used in the old process, with the exception of chlorine and sodium bisulfite.

The preozonation step itself involves addition of low levels of ozone (up to 1.25 mg/l) over a short contact time (2 minutes). In Table 81 are listed values obtained for detergents, organic carbon, COD and ammonium ion concentrations contained by the raw water, by the water after 2-day storage with no preozonation, and by the water after preozonation (1.25 mg/l ozone dosage) plus 2-day storage. The contents of detergents and COD are nearly halved, the organic carbon content is lowered from 8 to 7 mg/l and the ammonium content is lowered from 4 to 3.2 mg/l by preozonation followed by 2-day retention. Nitrification now also can occur in the sand filters.

Several advantages have been realized from the preozonation treatment which produce savings in both chemicals and processing costs, as well as producing a higher quality finished water. First, the post-ozonation dosage, required for viral inactivation, can be lowered by at least 20%. According to French public health standards, whenever ozone is used for disinfection purposes, it must be applied under the following conditions: after satisfying the initial ozone demand and attaining a 0.4 mg/l of residual ozone in the water, this 0.4 mg/l residual then must be maintained for a minimum of 4 minutes. In plant practice, this residual normally is maintained 6 to 12 minutes, to be certain of meeting the 4 minute requirement. This treatment standard for viral inactivation is based on the pioneering work of Coin _et al._ (1964; 1967) and is further described by Miller _et al._, (1978).

Gerval (1978) states that by the old treatment process, without preozonation, the average ozone dosage necessary to provide viral inactivation (to attain and maintain 0.4 mg/l of dissolved ozone) was 4.2 mg/l. During the period of time the pilot plant studies were conducted employing 1.25 mg/l of preozonation, the average amount of ozone required for post-ozonation was halved, to 2.1 mg/l. Thus the total amount of ozone dosage required was 1.25 mg/l preozonation plus 2.1 mg/l post-ozonation, or 3.35 mg/l, a savings of about 20%.

Preozonation also was found to lower the amount of process chemicals normally added, not only by eliminating the need for chlorine (used in the breakpoint step) and sodium bisulfite, but also because of the flocculation effect caused by ozone oxidation which lowers the amount of flocculant, powdered activated carbon and chlorine dioxide required. In addition, the time between backwashings of the sand filters was doubled. Finally, when the ammonium ion concentration in the inlet water was not greater than 1 mg/l, the ammonia level in the sand filter outlet did not exceed 0.1 mg/l.

As a result of these process improvements, it is now possible for the Choisy-le-Roi plant to employ very low levels of chlorine for post-disinfection and formation of residual for the distribution system. Using the modified process which includes the preozonation technique, organic halogen compounds (probably trihalomethanes) were less than 10 microg/l in the pilot plant work reported by Gerval (1978).

Preozonation of raw water followed by retention over a period of time to allow biological activity to lower the contents of ammonia and organic carbon, as well as to allow reductions in levels of chemicals added and reduction in the amount of ozone required for viral inactivation has been practiced for several years at the Moscow, Russia water treatment plant (Schulhof, 1979). Based on the successful use of the process in Moscow, preozonation is being installed to replace breakpoint chlorination at the Choisy-le-Roi plant in the Paris suburbs. The process is scheduled for full-scale operation in 1980 (Schulhof, 1979). In addition, pilot plant studies are being conducted at other water treatment plants in the Paris suburbs and at most of the large scale water treatment plants operated by Compagnie Générale des Eaux (Le Pauloué, 1978).

Figure 86 shows the comparative schematic diagrams of the treatment process used at Choisy-le-Roi in 1978 and the modified process which includes preozonation.

TABLE 81. EFFECT OF PREOZONATION (1.25 mg/l) BEFORE STORAGE

	Detergents (mg/l)	Organic C (mg/l)	COD (mg/l)	$[NH_4^+]$ (mg/l)
Raw water	0.16	8.3	19	6.2
2-day storage (no preozonation)	0.13	8	11	4
2-day storage with preozonation	0.08	7	6	3.2

Source: Gerval, 1978

A recent article by Schulhof (1980) gives more details of the benefits of preozonation at Choisy-le-Roi and two other suburban Paris plants and the improvements being incorporated at these three plants to maximize biological removal of pollutants in (1) preoxidized reservoirs ahead of the treatment processes (2) in biologically operating sand filters and (3) in biologically operating GAC adsorbers.

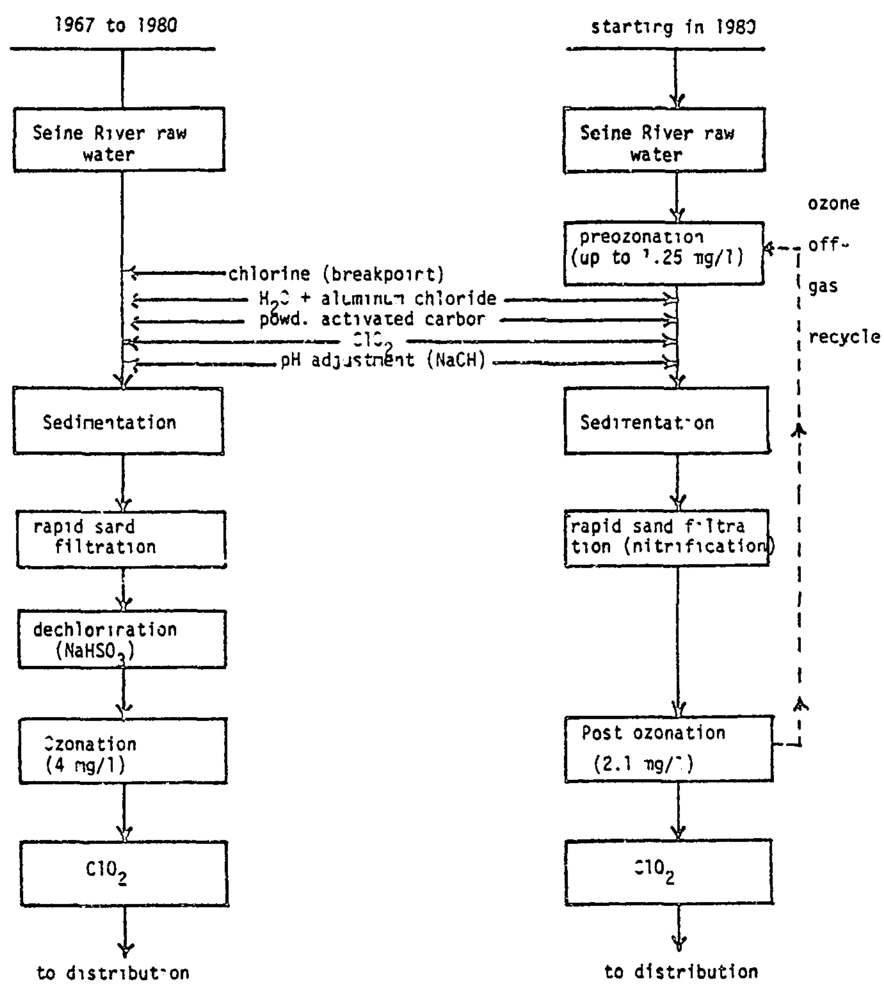


Figure 86. Choisy le Roi water treatment plant Process Diagrams.

APPENDIX C

DÜSSELDORF, FEDERAL REPUBLIC OF GERMANY

BACKGROUND

Three water treatment plants are operated by the City of Düsseldorf currently, and include the Flehe (88,000 cu m/day), Am Staad (119,200 cu m/day) and Holthausen (192,000 cu m/day) installations. These three plants use the identical process to treat river sand bank filtered water from the River Rhine, and which is described below. The Am Staad plant has been using the process of ozonation followed by GAC since 1961, and is the longest operating water treatment plant known to use this sequential combination of water treatment steps.

However, there are at least two other water treatment plants in the vicinity of Düsseldorf which also draw water from the same region of the Rhine and use closely similar treatment processes. These are the Duisburg Wittlaer III Wasserwerk and the Wuppertal Benrath plants. Plant data presented in this section of the report for unnamed water treatment plants utilizing river sand bank filtration was obtained from one or more of the plants noted above.

A detailed discussion of the Düsseldorf water treatment process was presented in Section 9 of this report, along with pertinent data showing the effectiveness of the various process steps. These will not be duplicated here. Instead, additional plant performance data will be presented and discussed.

RIVER SAND BANK FILTRATION

The five plants noted above make excellent use of the natural aquifers adjacent to the River Rhine. Figures 32 and 33 illustrate that the majority of water treatment is achieved in the so-called bank filtration (German: Uferfiltration) step. On the other hand, a disadvantage of using this method of pretreatment of organics is the necessity for subsequent ozone treatment for removal of iron and manganese.

Water is drawn from 10 m (32.8 ft) to 30 m (98.4 ft) deep wells situated 50 m (164 ft) to 250 m (820 ft) from the banks of the River Rhine. The aquifers in which the wells are located consist of sand and gravel deposits. Removal of turbidity and associated pollutants in the sand bank treatment results in a high quality sand bank filtered water. Additional treatment removes iron, manganese, taste, odor and dissolved organics.

OZONATION

Ozone is generated by means of horizontal tube, water cooled, ozone generators manufactured by Gebruder Herrmann of Köln (Cologne), Federal Republic of Germany. Each of the ozone generators contains 432 glass tubes and generates ozone from dried air by the application of power at 50 Hertz and voltages ranging from 9,000 to 16,000 volts. These tube-type generators were installed in the early 1970s and replaced the water-cooled, Otto plate units originally installed in 1961. Cooling of the ozone generators is by means of a closed loop cooling water system using chemically treated boiler feed water. The cooling water is cooled, in turn, by passing it through a heat exchanger located in the raw water supply line.

Ozonized air is drawn from the ozone generator by means of the negative pressure induced by passing treated water (approximately 1% of the total plant flow) through a venturi nozzle situated near the top of a vertical pipe having 10 meter submergence. The ozonized water mixes with the sand bank filtrate which passes down the vertical pipe and discharges into the contact chamber. The 10 meter submergence and overall contact chamber size provides a retention time of five minutes. The ozonized water from the contact chamber proceeds to a holding tank which provides an additional 30 minutes retention time.

Over the life of the Am Staad plant (since 1961), the ozone dosage necessary to produce the desired quality of finished water has had to be increased from an average of 1 mg/l to an average of 3 mg/l. This ozone dosage is set manually to maintain approximately 0.1 mg/l of ozone in the off-gases from the 30-minute detention tanks. This level of ozone is determined both by the potassium iodide wet chemistry procedure and by plant personnel "sniff-testing" the off-gases. Residual ozone in the off-gases from the contact chambers and the holding tanks is destroyed by passage through wet granular activated carbon. However, catalytic destruction of the ozone-containing off-gases has been tested at Düsseldorf plants and will be installed to replace the wet GAC procedure (Weissenhorn, 1977).

FILTRATION AND GAC ADSORPTION

Water is pumped at pressures of 6 bars (87 psi) to 7 bars (101 psi) from the ozonation holding tanks to the bilevel filtration/adsorption units. These units are constructed of steel, 8 meters high and 5 meters in diameter. Water flows downward through an upper 1.5 meter deep filter layer and then downward through a 2.5 meter depth of granular activated carbon. Both the filter layer and the adsorption layer rest on layers of support gravel, each based on a steel support plate containing plastic nozzles (approximately 31 per sq m). Each layer can be backwashed separately.

The hydraulic loading rate in the filtration/adsorber units has been 20 cu m/sq m/ hr (m/hr), or 8.8 gpm/sq ft, but recent plant expansions have reduced the loading rate to 12 m/hr (4.8 gpm/sq ft). The older coated steel units have been on-line since 1961 with satisfactory service from the coating, with the exception of physical wear in the vicinity of the media removal and changing fittings.

The filtration medium is a so-called "preactivated" carbon having the following characteristics:

Granule size	-	0.9 to 2.5 mm
Mean granule diameter	-	1.7 mm
Bulk weight	-	580 kg/cu m

Biological nitrification, as well as high degrees of removal of manganese, iron and turbidity, is achieved in the filtration stage with provision of 1.5 meters of filter media.

The adsorption medium consists of a mixture of Lurgi LS Supra and Chemviron (Calgon) F-300 granular activated carbons having the following characteristics:

Granule size	-	0.5 to 2.5 mm
Mean granule size	-	1.4 to 1.6 mm

Filtration layer runs of approximately 24 to 48 hours are observed. Backwash cycles for the adsorption stage are 4 to 6 weeks, with periods between regeneration ranging from 5 to 6 months. Initial air scouring, followed by a 5-minute water backwash, is the procedure used for both the upper and lower layers.

FINAL TREATMENT STEPS

The final treatment steps include the addition of sodium hydroxide for pH control (to neutralize CO_2 produced biochemically) and 0.1 to 0.3 mg/l of chlorine dioxide to disinfect and to maintain a residual within the distribution system.

The three City of Düsseldorf water treatment plants are unique in that there is very little reservoir storage for finished water. As a result, all three plants are designed to operate on demand.

GRANULAR ACTIVATED CARBON REGENERATION

Over the years since the ozone/GAC process was installed in Düsseldorf, the increased GAC levels of halogenated organics (TOCl) in the Rhine (which are not removed during river sand bank filtration) has shortened the GAC regeneration cycles to such a point (every 5 to 6 months) that it became economical to install reactivation facilities at the Düsseldorf plants. Spent GAC now is transported from the Am Staad and Flehe facilities to the fluidized bed regeneration furnace situated at the Holthausen plant. This furnace, which was in shakedown during a site visit in May, 1977, was fully operational in June 1978.

The GAC regeneration furnace was supplied by Lurgi and has a GAC regeneration capacity of 6 metric tons per day. It is to be the central regeneration facility for Düsseldorf, and space is available for two additional furnaces to be installed if and when needed. Spent GAC is flushed from a storage hopper to a dewatering screw which regulates the carbon to the upper or drying stage of the fluidized bed furnace which is maintained at a temperature of 200° to 300°C by means of natural gas heating. The dried GAC passes to the lower or reactivation stage where steam is injected into the chamber which is maintained at a temperature of 600°C to 800°C, again using natural gas heating. The GAC enters a quench tank from which it is flushed to a storage hopper. The furnace off-gas is treated by means of a cyclone after-burner and heat exchanger.

Another fluidized bed granular activated carbon regeneration furnace is installed at the Wuppertal Benrath water treatment plant. While this plant was not inspected by the 1978 site visitation team, it is known that the unit was designed and constructed by WABAG, a design/construction engineering firm headquartered in Kulmbach, Federal Republic of Germany. The Wuppertal regeneration facility was installed in January, 1978 but was still in shake-down in June, 1978. The maximum capacity of the unit is 240 kg of GAC/hr, but the recommended rate of application is 100 to 150 kg of GAC/hr.

A third fluidized bed GAC regeneration furnace is in operation at the Zürich (Switzerland) Lengg water treatment plant (Grombach, 1975).

It has also been reported (Water Research Center, 1977) that there is a multiple hearth GAC regeneration furnace at the Alelyckan water treatment plant at Goteberg, Sweden. This same reference notes that "one granular activated carbon regeneration plant is currently in use at Church Wilne, England." This English regeneration unit has been discussed by Osborne (1979).

PLANT OPERATIONAL DATA

Operational data from the individual plants in and around Düsseldorf are not readily available either from the plants or from the Engler-Bunte Institute of the University of Karlsruhe, which conducts research for many German waterworks. The Institute places great emphasis on the confidentiality of the raw and/or unpublished analytical data developed by and for their client waterworks. However, information was provided for unnamed plants on the lower Rhine which utilize the same treatment process as does Düsseldorf. Similar data for other water plants treating river waters in the Federal Republic of Germany were provided as well, identifying only the river source and the treatment process.

Table 82 contains actual plant operational data showing the degree of purification obtained at the various stages of treatment of River Rhine waters in the Düsseldorf area. Table 83 lists DOC and halogenated organics data obtained during a single day of operation at one of the five plants in the region.

Table 84 shows data obtained at a lower Rhine water treatment plant which uses a process consisting of river sand bank filtration, permanganate (oxidation)/polymer sedimentation, filtration and GAC treatment. These data were determined from the three operating trains in the plant, and are averages of data obtained throughout 1977.

TABLE 82. LOWER RHINE RIVER WATER TREATMENT DATA FOR PLANTS UTILIZING RIVER BANK FILTRATION/OZONATION/FILTRATION/GAC ADSORPTION. AVERAGES FOR 1977

Parameter	Raw Rhine River Water	After River Bank Filtration	After Ozonation & Filtration	After GAC
PLANT #3				
DOC (mg/l)	4.55	1.8	1.70	1.15
COD (mg/l)	12.7	4.88	--	3.33
UV	11.62	3.95	2.83	1.23
PLANT #4				
DOC (mg/l)	4.46	2.16	2.03	1.45
COD (mg/l)	13.11	5.54	--	3.47
UV	11.07	5.13	2.41	1.47
PLANT #5				
DOC (mg/l)	4.03	2.17	1.90	1.43
COD (mg/l)	11.13	6.07	--	3.19
UV	11.20	5.10	3.30	1.87

Note: DOC = dissolved organic carbon
COD = chemical oxygen demand
UV = relative absorbance at 250 nm

Table 85 shows data obtained at a plant utilizing river sand bank filtration, followed by GAC adsorption directly. Data presented are the averages obtained during 1977.

Table 86 shows average data for 1977 at a River Danube plant (without river sand bank filtration) using ozonation, filtration and GAC adsorption.

The following conclusions may be drawn from the data of Tables 82 through 86:

1) River sand bank filtration is an effective method of removing waterborne pollutants, as measured by DOC, COD and UV adsorption. The degree of pollutant removal is variable, however, as is seen by comparing data from Plants No. 3, 4 and 5 with those from Plants 2 and 6.

2) Data from Plants No. 3, 4 and 5 are in general agreement as to the levels of treatment attained after river sand bank filtration. Percentage removals of DOC, COD and UV absorbing materials by the treatment process consisting of ozonation/filtration/GAC adsorption is as follows:

TABLE 83. PLANT #4. CHLORO-ORGANIC MATERIAL DATA FROM A SINGLE DAY'S SAMPLING IN 1977

Water Treatment Process	Parameter									
	DOC	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	CCl_4	$C_2H_4Cl_2$	C_2HCl_3	C_2Cl_4	$C_2H_2Cl_4$
	mg/l	μg/l								
Rhine River raw water	4.7	3.9	--	--	--	2.4	--	0.8	1.1	--
river bank filtration	2.2	1.4	--	--	--	0.03	--	0.9	0.7	--
ozonation	2.0	0.9	--	--	--	0.02	--	0.2	0.3	--
filtration + GAC adsorption	1.6	1.1	--	--	--	0.04	--	0.1	0.05	--
0.2 mg/l chlorination	1.3	1.3	0.1	0.2	0.8	0.04	--	0.2	0.06	--

	% Reduction in Levels of DOC	COD	UV
Plant No. 3	36	32	69
Plant No. 4	33	37	71
Plant No. 5	34	47	63

TABLE 84. LOWER RIVER RHINE WATER TREATMENT DATA FOR PLANTS USING RIVER BANK FILTRATION/$KMnO_4$/POLYMER SEDIMENTATION/FILTRATION/GAC. AVERAGES FOR 1977

Parameter	Raw Rhine River Water	After River Bank Filtration	After $KMnO_4$ & Sedimentation	After GAC
PLANT #6				
TRAIN #1				
DOC (mg/l)	4.64	2.46	2.07	0.96
COD (mg/l)	14.10	7.17	--	--
UV	11.07	6.37	3.75	0.95
TRAIN #2				
DOC (mg/l)	4.64	2.46	2.05	1.26
COD (mg/l)	14.10	7.17	--	--
UV	11.07	6.37	3.78	1.63
TRAIN #3				
DOC (mg/l)	4.64	2.46	2.24	0.99
COD (mg/l)	14.10	7.17	--	2.50
UV	11.07	6.37	3.81	0.81

TABLE 85. LOWER RHINE RIVER WATER TREATMENT DATA FOR PLANT UTILIZING RIVER BANK FILTRATION/GAC ADSORPTION. AVERAGE FOR 1977

Parameter	Raw Rhine River Water	After River Bank Filtration	After GAC
PLANT #2			
DOC (mg/l)	4.25	0.88	0.74
COD (mg/l)	11.23	2.77	2.47
UV	9.13	1.47	1.16

TABLE 86. UPPER DANUBE RIVER WATER TREATMENT DATA FOR PLANT UTILIZING SEDIMENTATION/OZONATION/FILTRATION/GAC. AVERAGE FOR 1977

Parameter	Raw Danube River Water	After Treatment
PLANT #1		
DOC (mg/l)	2.26	1.61
COD (mg/l)	5.51	--
UV	4.98	1.49

COSTS

Only limited cost data were made available during the site visit to the Düsseldorf waterworks. This brief information is presented below.

Total revenues for the waterworks in 1976 were about 73 million Deutsch marks (DM), up from 55 million DM in 1974. The average rate charged for water was 0.9 DM per cubic meter in 1978, with the flat residential customer rate set at 1.2 DM/cu m, approximately equivalent to $2.20/1,000 gallons.

Treatment costs (exclusive of distribution and administration) were reported (Poggenburg, 1978) to comprise somewhat less than 40% of the total annual Düsseldorf water utility costs. The figure of 0.28 DM/cu m was mentioned as the total water cost in a recent year, excluding returns on capital. Costs at Düsseldorf should not be compared with those of nearby Mülheim, for example, because the Düsseldorf Water Works pays more for street usage.

The waterworks provides capital for new projects from its own funds set aside in previous years and from new bond issues. Bonds were sold recently (prior to 1978) at an interest cost of about 6.5%. The waterworks is a private stock company, with the City of Düsseldorf owning 100% of the stock. Due to its private status, its revenues are drawn entirely from rates charged for water and its financing is separate from other city capital projects.

The new fluidized bed furnace for reactivating spent GAC from all three Düsseldorf water treatment plants has been operating for over a year. The two-stage furnace operates at 200° to 300°C at the first stage for drying and at 600° to 800°C at the second stage for reactivation. An afterburner (which attains 600°C outlet temperatures) prevents air pollution and prevents even a visible steam plume. Absence of a visible steam plume is required by local air pollution control regulations. A cyclone removes particulates to a level of 75 parts per billion.

Energy requirements are 55 to 65 cu m/hr of natural gas (ΔH_{gas} = 8,400 kcal). At present, the furnace is operating with 4 to 5% GAC losses in the furnace, with a total loss of 8 to 9% (the difference is lost in transporting GAC from the adsorber to the furnace and returning). However, the 4 to 5%

furnace losses depend to some degree on the quality of the GAC and the temperature and precision of the furnace operations. The regeneration capacity is 6 tons/day (250 kg/hour).

Although no cost figures were made available on either the capital invested in the furnace or its operating costs, the total cost of regeneration was said to be a bit less than 30% of the cost of virgin GAC. With European GAC prices in the range of 70 to 80¢/lb, this percentage suggests a reactivation cost on the order of 20¢/lb.

Capital costs for a single GAC column at Düsseldorf were said to be 120,000 DM, without outside piping. The installed total capital cost for water treatment was 3,000 DM/cu m of water treated per hour. For each 1,000 cu m/hr of installed treatment capacity, the capital cost was 1,0C0 x 3,000 = 3,000,000 DM.

The City of Düsseldorf treats 400,000 cu m/day of water and pumps 500,000 cu m/day from the wells. The additional 100,000 cu m/day of well water is sent to industries and nearby cities for local treatment. The staff at Düsseldorf totals 375 people, but only 2 people operate the plants around the clock.

APPENDIX D

MORSANG-SUR-SEINE (SUBURBS OF PARIS)

GENERAL CHARACTERISTICS

The Morsang plant is located on the Seine River, 35 km upstream of Paris near the new town of Evry and supplies water to Evry as well as to the Paris suburbs. In concept and when completed about the year 2000, Morsang is expected to produce about 1,000,000 cu m/day (264.2 mgd) of drinking water from the Seine River.

Morsang is being constructed in successive, star-shaped plant stages, with each star being capable of producing 225,000 cu m/day (59.4 mgd). Each star at Morsang will be constructed around a central station with each treatment stage occupying one point of an imaginary three pointed star. At the center of each star will be the central station, which will house chemicals, activated carbon and ozonation equipment. Laboratories, pumping station and administration are housed in a separate building. The general plant layout is shown in Figure 87.

The first stage of the first 3-pointed star began operating in 1970. In 1975 the second stage of the first star was completed, and construction of the third stage of the first star will depend upon results obtained from a detailed pilot plant testing program, which was to be completed during 1979.

The Morsang plant is owned and operated by the Société Lyonnaise des Eaux et de l'Eclairage, one of two large, integrated water making companies in France.

Raw Seine River water at Morsang is fairly clean: TOC is about 3 mg/l, humic acids about 7 mg/l, ammonia about 0.5 mg/l and taste threshold about 12.

PLANT OPERATION

Raw Seine River water is coarse screened (1.5 mm mesh), then is subjected to breakpoint chlorination (for removal of ammonia, usually less than 0.5 mg/l) with 3 to 6 mg/l of chlorine added as the gas. Prechlorinated water then is pumped to the center of the first star where it is split into two streams. One stream of 50,000 cu m/day (13.2 mgd) is sent to the first stage of the star, and the second stream of 75,000 cu m/day (19.8 mgd) is sent to the second stage of the star.

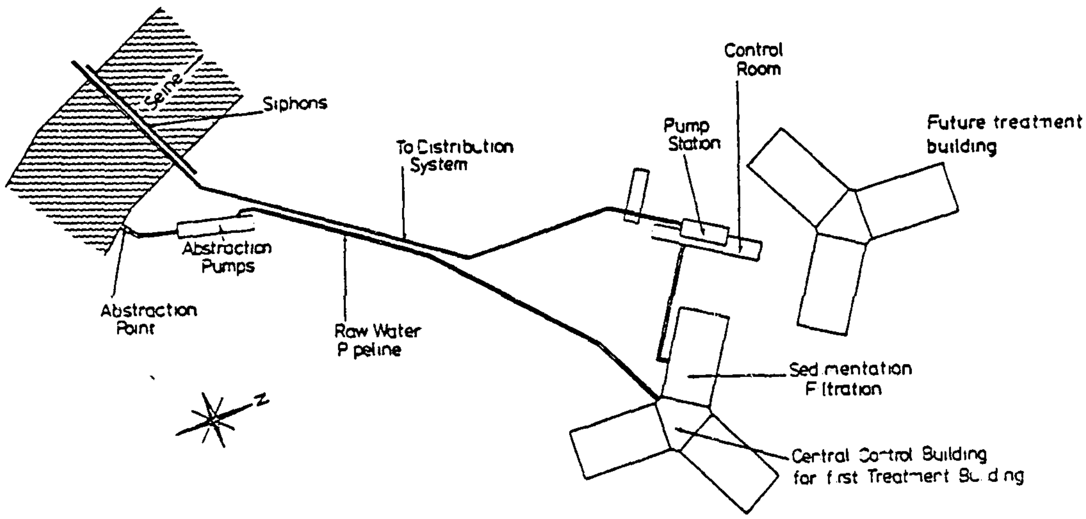


Figure 87. General layout of the Morsang-sur-Seine treatment works.

First Stage of the Star (Maximum flow: 3,300 cu m/hr -- 871,860 gal/hr)

Prechlorinated water is settled and clarified using a 665 sq m sludge blanket Pulsator clarifier (Degrémont) operated at an hydraulic loading rate of 3.15 cu m/sq m/hr (m/hr), then filtered through six type T Aquazur V (Degrémont) sand filters. Coagulation is accomplished with addition of 60 to 80 g/cu m of aluminum sulfate and is monitored by flocculation tests and zeta potential measurements. Activated silica (1 to 2.5 g/cu m) is made by adding sulfuric acid to alkaline sodium silicate, and its dosage depends upon the measured sludge cohesion coefficient. Powdered activated carbon normally is added ahead of the clarifier at 15 to 25 g/cu m.

Water is passed through the sand filters, each having an area of 60 sq m, at an hydraulic rate of 6 cu m/sq m/hr (m/hr). After sand filtration, the water is ozonized in two baffled contact chambers, each having a volume of 215 cu m (10.5 m long and 4.5 m high) and designed to achieve a contact time of 8 minutes at peak flow. About 67% of the total ozone generated is added to the first contact chamber in which the initial ozone demand is satisfied and a residual ozone concentration of 0.4 mg/l is attained. The remaining 33% of the total ozone dosed is added in the second chamber, where the level of residual dissolved ozone is maintained at 0.3 to 0.4 mg/l. The contact time in each chamber is 4 minutes at maximum flow (8 minutes total ozonation at peak flow). Water flow in each chamber is countercurrent to the direction of the upward flow of ozone-containing air (see Miller et al., 1978, p. 120). The residual dissolved ozone is monitored at the outlet of both contact chambers at 0.3 to 0.4 g/cu m.

This treatment sequence will be referred to subsequently as Process #1.

Second Stage of the Star: (Maximum flow: 3,300 cu m/hr -- 871,860 gal/hr)

Settling and clarification of the prechlorinated water are conducted with a 208 sq m Superpulsator clarifier (Degrémont). Filtration is through four Aquazur sand filters, each having a unit surface area of 63 sq m, at an average hydraulic loading of 8.75 m/hr and a peak hydraulic loading of 13 m/hr.

Ozone is produced (for the first two stages of the star) by two Degrémont generators, each having a production capacity of 6.6 kg/hr. Contact times (8 minutes at maximum flow) and other ozonation conditions are identical with those of the first stage.

Following ozonation is GAC adsorption through 1 m deep beds of Chemviron F-400 carbon, using four Aquazur filters each having a surface area of 63 sq m. These are operated at a filtration velocity of 13.1 m/hr at maximum flow. These Aquazur filters are especially designed for activated carbon and are called Mediazur filters.

After sand filtration and before ozonation, the water is divided into two equal portions. The first fraction is ozonized before GAC adsorption and the second is passed through the GAC adsorbers then ozonized. These two sequences of treating water in the second stage of the star (termed Process #2 and Process #3, respectively) have been monitored full-time since October, 1975 and the water qualities compared with those of Process #1 conducted over the same period of time. Initial results of this comparative study (obtained over the period October, 1975 through December, 1976) were reported by Richard & Fiessinger (1977) and are discussed below. The three processes are shown schematically in Figure 88, along with a fourth pilot plant process (Process #4) which will be discussed later.

Parameters studied during the 15-month program reported by Richard & Fiessinger (1977) for Processes #1, #2 and #3 included:

(a) Organic matter -- expressed as mg/l of oxygen consumed as measured by $KMnO_4$ oxidation in an acid medium,

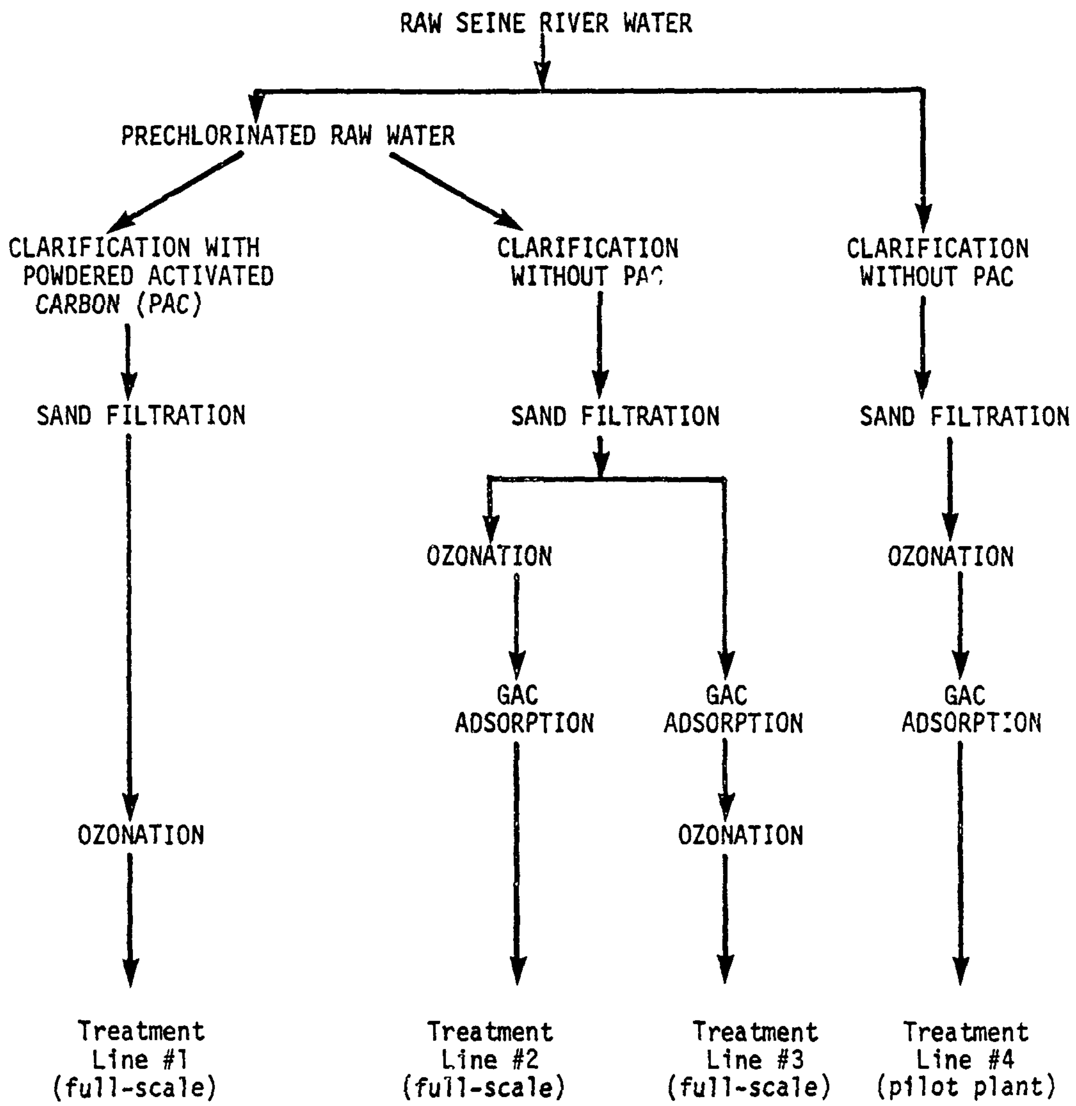
(b) Taste threshold -- measured at 30°C by the dilution method,

(c) Organo-halogen derivatives -- detected by gas chromatography combined with an electron capture detector. These were extracted with Uvasol pentane (Merck). Results given by Richard & Fiessinger (1977) were limited to chloroform and dichloromethane only.

RESULTS OF 15 MONTH STUDY COMPARING PROCESSES #1, #2 & #3

Organic Matter

Figure 89 shows the percent reduction in concentration of organic matter obtained by each of the three processes.



Note: all treated water leaving the plant is chlorinated for residual

Figure 88. Morsang-sur-Seine water treatment plant--processes operating in 1977.

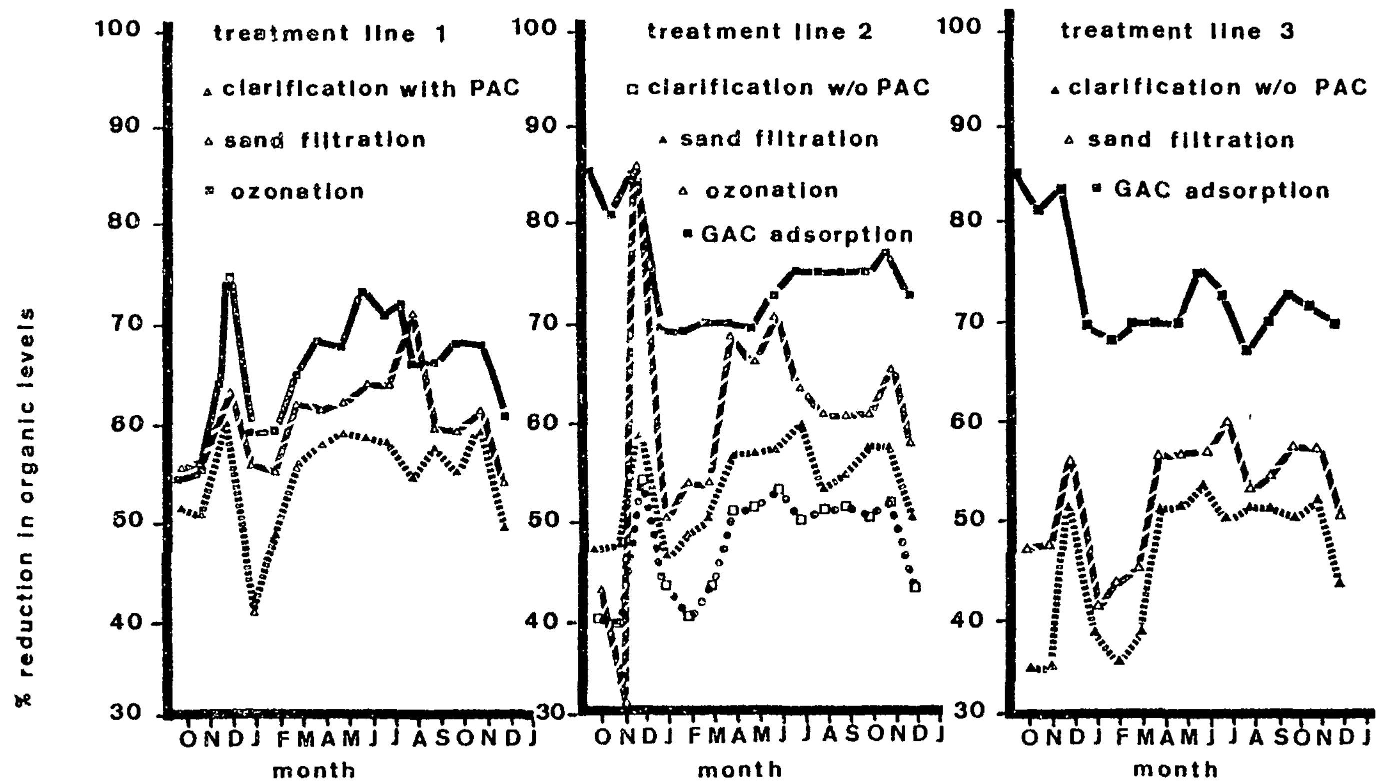


Figure 89. Percent reduction in levels of organic materials at Morsang.

(Richard & Fiessinger, 1977)

Process #1--

Starting with a raw water level of 3 mg/l, some 30 to 60% of the organic material is eliminated by clarification with 10 to 20 mg/l of powdered activated carbon. During the summer of 1976, this dose was increased to 25 to 30 mg/l. Sand filtration removed all carbon fines and increased overall organics removal to 55 to 65%.

The dosage rate of ozonation was found to affect the organics removal greatly. During the first three months, the ozonation dosage was too low and the organic content was the same as or higher than that obtained after sand filtration. Increasing the ozone dosage to 1.2 mg/l raised the total percent removal of organic matter to 60 to 70%, an additional 8% over sand filtration.

Processes #2 and #3--

Clarification at the rate of 8.75 m/hr without powdered activated carbon removed 40 to 50% of the organic material and sand filtration removed an additional 5% (total organic removal by powdered activated carbon and sand filtration: 45 to 55%.

Process #2--During the first three months of the study the ozone dosage again was too low, but when this was increased to 1.2 mg/l, the total removal of organic material increased to 55% to 70%. However, water treated with powdered activated carbon by Process #1 was of higher quality, with regard to organic matter content, after ozonation (1.4 mg/l of ozone) than that obtained from Process #2 (1.6 mg/l ozone).

During the first three months, GAC adsorption (after sand filtration and ozonation) increased the overall percent removal of organic materials to 80 to 85%. This figure fell to 70% when the water was cold and rose to 75% when the water was warm. The increased organics removal observed during warm weather could have been a result of bacterial activity in the GAC adsorbers. The 80% to 85% levels of organics removal were obtained after the first three months period and indicates that the additional 5% to 10% removal also may have been a result of bacterial activity in the GAC beds.

Process #3--Sand filtered water was passed through granular activated carbon. This increased the total organics removal to 80 to 85%, but this level fell to 70% when the water was cold.

A drought occurred during this test program, and the level of organics removal fell to 67% by Process #3 but was 75% by Process #2. This higher rate of organics removal by Process #2 was attributed to "the intense oxygenation of the ozonized water and the biological oxidation which it causes in the water".

When the drought ended, the quality of water which passed through the GAC adsorbers in Process #3 improved, but was still slightly lower (about 50%) than that obtained by Process #2.

Taste Threshold

During the 15 month study the raw water taste threshold rose from 10 up to a level of 20 to 30 units during the drought.

Process #1--

Clarification with powdered activated carbon followed by sand filtration lowered taste thresholds to two units in most cases. Upon ozonation, however, "new, unpleasant tastes" were formed, and the threshold level rose to three units. During the drought the taste threshold of clarified water rose to 4 to 10 units (even with powdered activated carbon dosages being increased to 20 to 25 mg/l) and the level in sand filtered water rose from 3 units to 6 units. During this period, the level in ozonized water remained at 2 to 3 taste units. This level was considered to be "not perfect, but acceptable to customers".

Process #2--

After ozonation and GAC adsorption, the taste threshold remained consistently at 1 unit over the 15 month period.

Process #3--

Sand filtration followed by GAC adsorption without ozonation produced taste threshold values of 1 for the first 10 months, then the carbon "completely lost its capacity for removal of taste" and the threshold value rose to 2 units.

The difference in activated carbon performances (with ozonation in Process #2 and without ozonation in Process #3) was attributed to "the dual role of ozone":

a) Ozone oxidized non-polar, or taste-causing, organic molecules into polar molecules which have a less powerful taste; and

b) Ozonation aerates the water and stimulates biological activity in the GAC adsorbers.

Formation and Elimination of Halogenated Organic Derivatives

The chloroform content of the Seine raw water at the Morsang plant is well below 1 microg/l. Chlorination at the clarifier (with 3 to 6 mg/l of chlorine) produces chlorinated organics, and chloroform levels of 5 to 15 microg/l are found routinely at this point. Figure 90 shows results of chloroform analyses obtained during the 15 month study.

Process #1--

Powdered activated carbon treatment lowered the chloroform content 40 to 50%, leaving 0.1 mg/l of total chlorine in the clarified water. Additional chlorine (0.2 mg/l) had to be added to the filter inlet to protect it from algae and zooplankton, but this additional chlorine dose produced "no more than 1 microg/l of additional chloroform". After clarification and sand filtration, chloroform levels found were 5 to 7.5 microg/l.

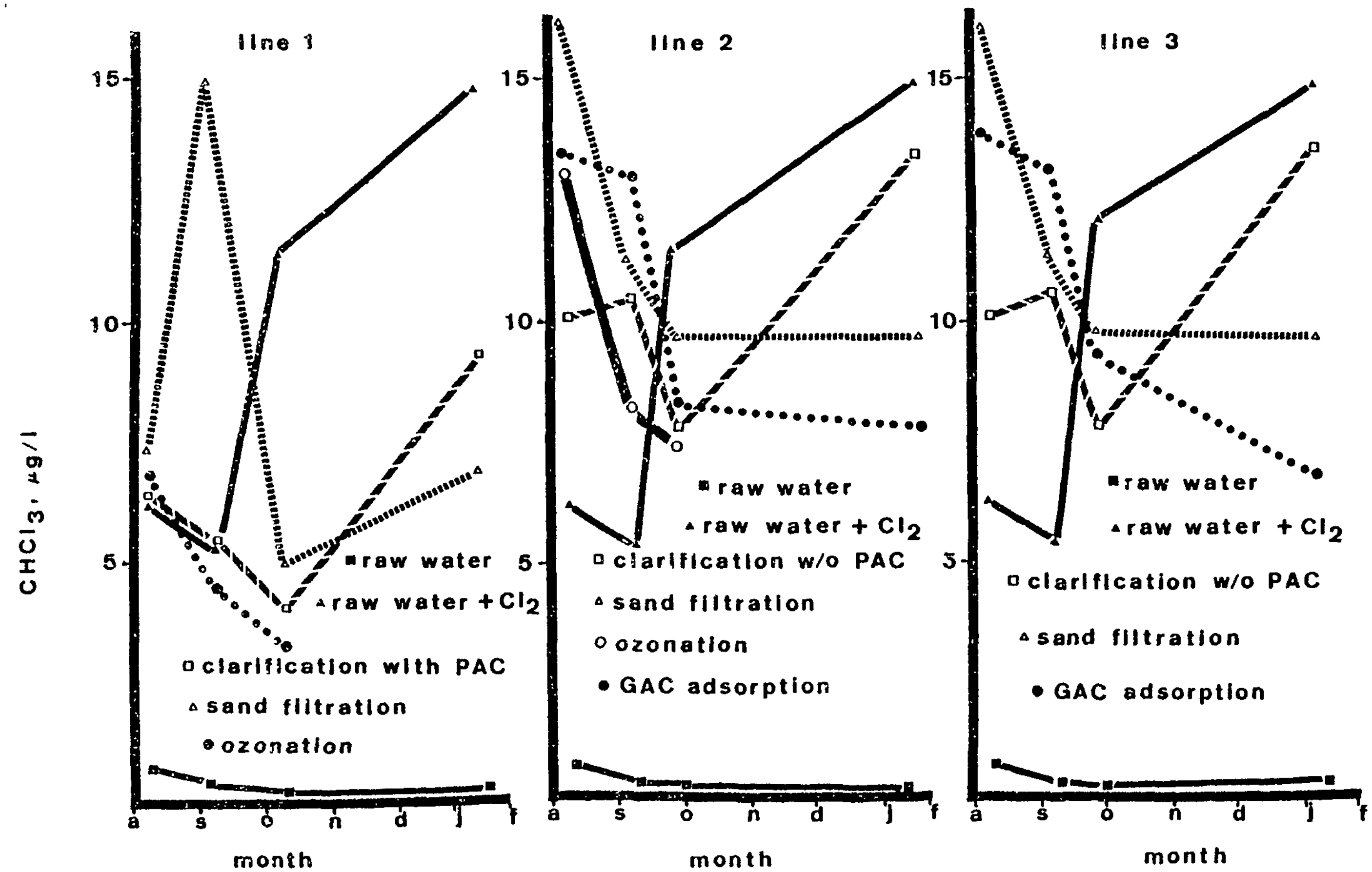


Figure 90. Evolution of $CHCl_3$ in Morsang waters.

(Richard & Fiessinger, 1977)

Ozonation lowered the chloroform level to 3.5 to 6.5 microg/l, but by air stripping, not by chemical oxidation.

Processes #2 and #3--

Prechlorinated water was clarified without addition of powdered activated carbon. The amount of chloroform produced tended to increase with longer retention times in the clarifier, and vice-versa. After sand filtration, the average chloroform concentration was 10 microg/l.

Process #2--After ozonation followed by GAC adsorption, the chloroform concentration varied between 7 and 13 microg/l. (It is apparent that the 1 meter deep GAC beds had been saturated with chloroform and that breakthrough had been attained early in the 15 month study).

Process #3--The same chloroform range (7 to 13 microg/l) was obtained after sand filtration followed by GAC adsorption (no ozonation). Thus, ozonation followed by GAC adsorption should have no capability to remove chloroform after the adsorption capacity of the GAC for chloroform has been exceeded.

Conclusions From the 15-Month Study of Processes #1, #2 and #3

Richard & Fiessinger (1977) drew the following conclusions from this 15-month comparative study:

1) Formation of chloroform can be reduced by optimizing the coagulation step (before chlorination), which lowers the humic content to a minimum.

2) After prechlorination, powdered activated carbon (PAC) removes residual chlorine from the water, adsorbs chloroform precursors and reduces the level of chloroform by about 50%.

3) Over the 15-month period, sand filtration followed by GAC adsorption at 10 m/hr (no ozonation) removed 40% of the chloroform.

4) Ozonation before or after GAC adsorption removed some chloroform, but by air stripping, not by chemical oxidation.

5) Chloroform concentrations at Morsang have never exceeded 16 microg/l.

6) Process #1 (clarification with powdered activated carbon, final treatment with ozone) produces "less than perfect" organoleptic qualities, which will be affected directly by any change in the amount of raw water pollution.

7) Process #3 [clarification (without powdered activated carbon), sand filtration, GAC adsorption, post-ozonation] produces water with "very good organoleptic qualities". With sudden surges of raw water pollution, however, it is better to use powdered activated carbon so as to prolong the useful life of the GAC.

8) Process #2 [clarification (without powdered activated carbon), sand filtration, ozonation, GAC adsorption] gave "very appreciably improved

results". Ozone aerates the water and oxidizes non-polar compounds which cause unpleasant tastes. This "increases the activity of the carbon and prolongs its useful life considerably".

(No data are reported by Richard & Fiessinger, 1977, regarding the criteria measured to determine the useful life of the GAC adsorbers. However, these are presumed to be organoleptic parameters, such as taste threshold, in order to maintain low taste thresholds.)

9) Biological phenomena in the GAC appear to be stimulated by ozonation of the water before passage through the GAC adsorbers.

The next phase of the research program at Morsang-sur-Seine was a pilot plant study of the treatment of raw Seine water by a process in which break-point chlorination was eliminated (Process #4). This pilot plant study began in early 1977 and was to have been completed during 1979, after which a decision was to be made as to the treatment process to be installed on full-scale in the third stage of the first star. Very recent data (Fiessinger & Montiel, 1980) presented at the 1980 Annual American Water Works Association Conference indicates that the decision will be to install Process #4.

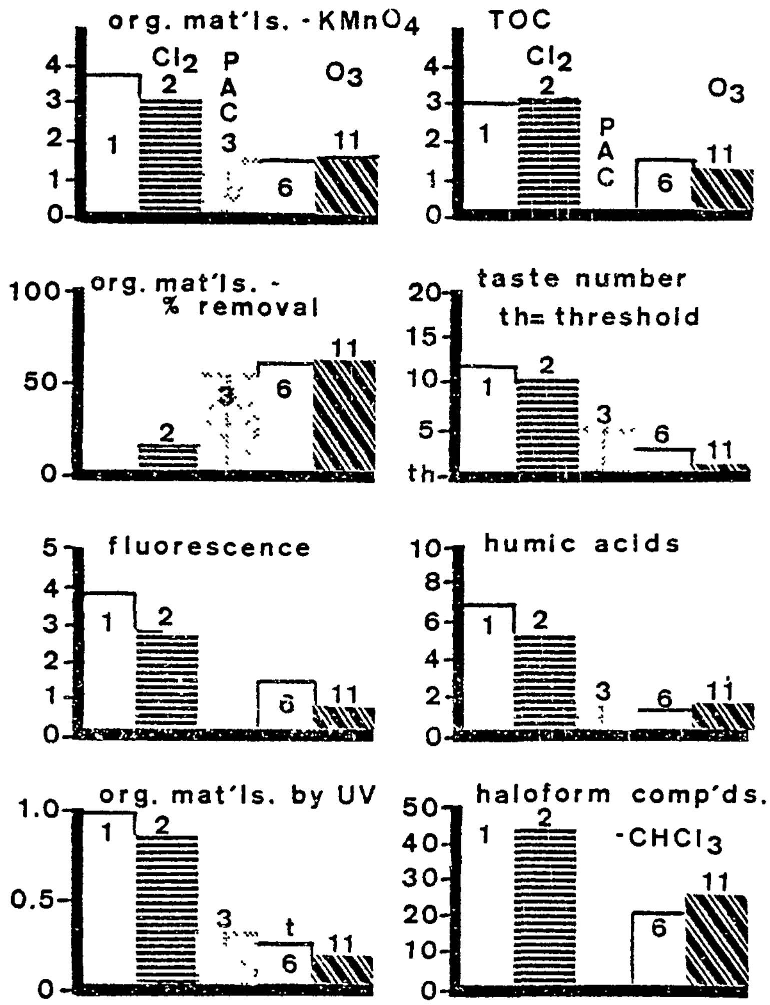
PILOT PLANT STUDIES WITHCUT PRECHLORINATION

In Process #4, the prechlorination step has been eliminated. Raw Seine River water is clarified with alum and lime (no powdered activated carbon), decanted, sand filtered, ozonized, passed through GAC adsorbers and post-chlorinated. Chemviron F-400 granular activated carbon is used in Process #4 and the bed depth is 1.4 m. Dissolved oxygen levels in the raw Seine River water at Morsang are 3 to 5 mg/l. Prior to the GAC adsorption step in Process #4 the DO is 10.4 mg/l and drops to 8.8 mg/l after GAC adsorption. Ammonia levels in the Seine River raw water are 0.1 to 0.2, but 0.1 mg/l in the product water. Therefore, nitrification is insignificant in Process #4.

For all four processes, data on organic materials content (by the $KMnO_4$ and UV absorbance methods), percent reduction of organic materials content, TOC, taste threshold, fluorescence, humic acids content and chloroform content at various points in the different treatment processes are presented in Figures 91 through 94 (for Processes #1, #2, #3 and #4, respectively). Figure 95 is an overview diagram of the four treatment processes showing the points where samples for the analyses given in Figures 91 through 94 were taken. Data presented in Figures 91 through 94 are averages of 5 samples taken from side-by-side process operation.

For comparison, data for all four processes are summarized in Table 87. The quality of water produced by Process #4 appears to be the highest of all processes, but comparison is difficult to make since the GAC used in Process #4 was placed in use about 2 years after that used in Processes #2 and #3.

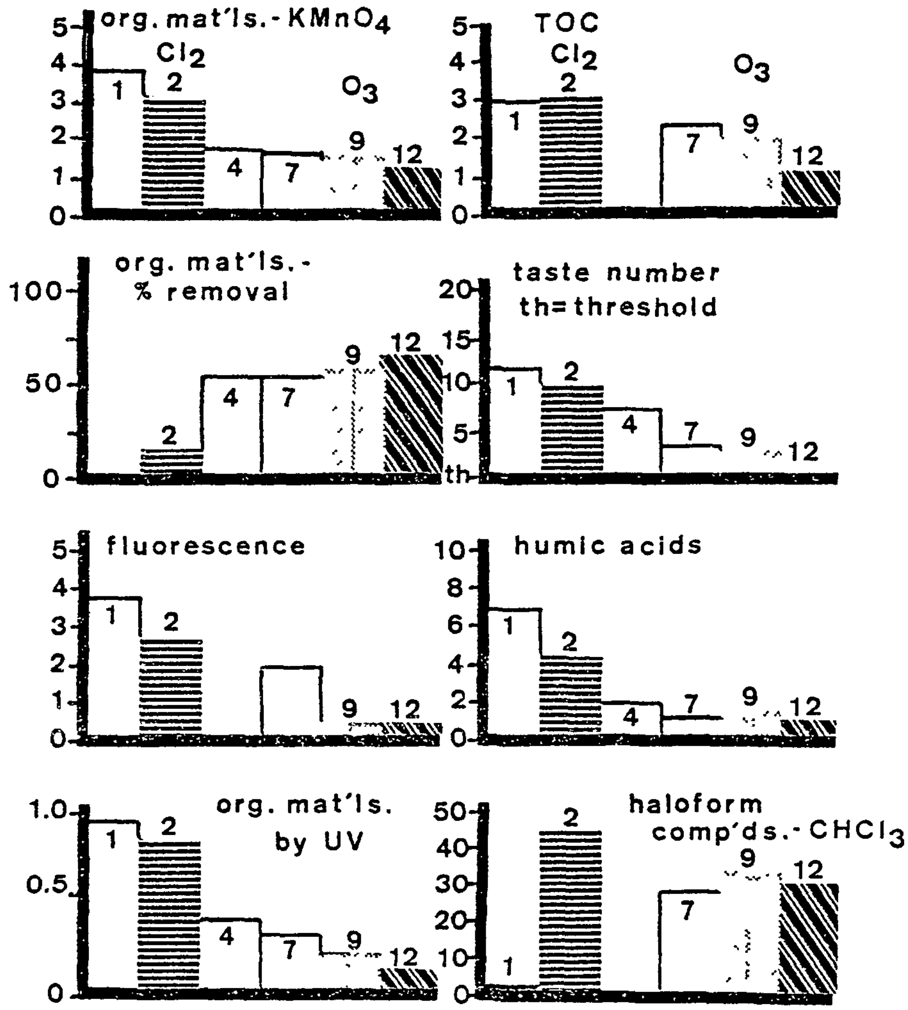
Therefore, the advantages of not prechlorinating at Morsang remain debatable. It is still too early to predict the final process that will be installed in the third stage of the first star (Richard, 1979).



1 - raw water; 2 - after prechlorination; 3 - after clarification; 6 - after sand filtration; 11 - after ozonation

Figure 91. Process 1 performance parameters at Morsang plant.

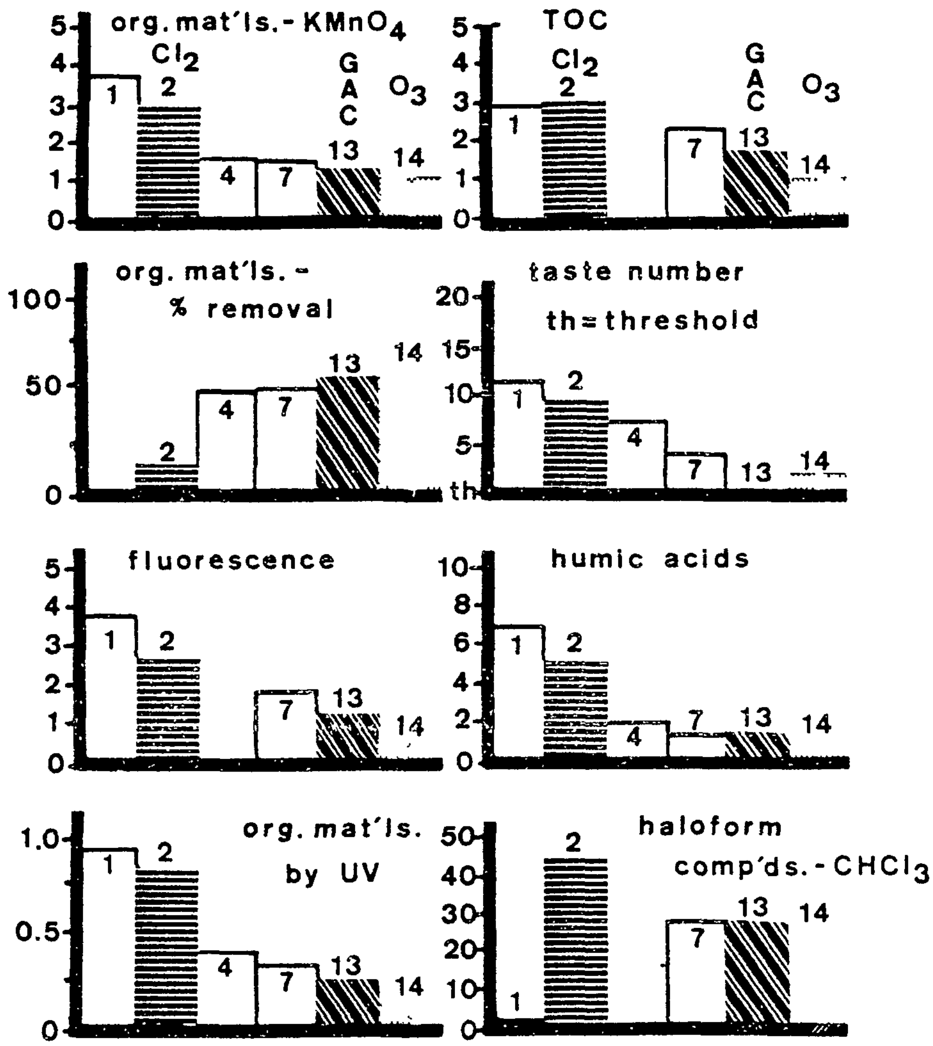
(Richard, 1978)



7 - after sand filtration; 9 - after ozonation;
12 - after GAC adsorption

Figure 92. Process 2 performance parameters at Morsang plant.

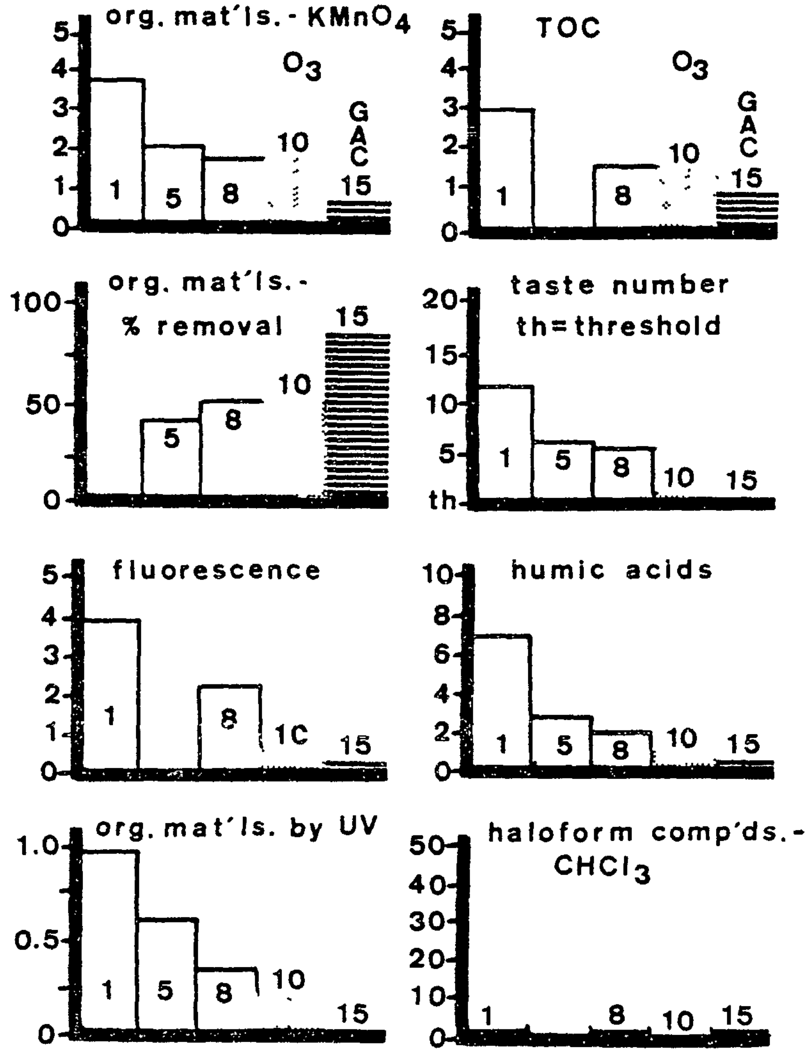
(Richard, 1978)



13 - after GAC adsorption; 14 - after ozonation

Figure 93. Process 3 performance parameters at Morsang plant.

(Richard, 1978)



5 - after clarification; 8 - after sand filtration;
10 - after ozonation; 15 - after GAC adsorption

Figure 94. Process 4 performance parameters at Morsang plant.

(Richard, 1978)

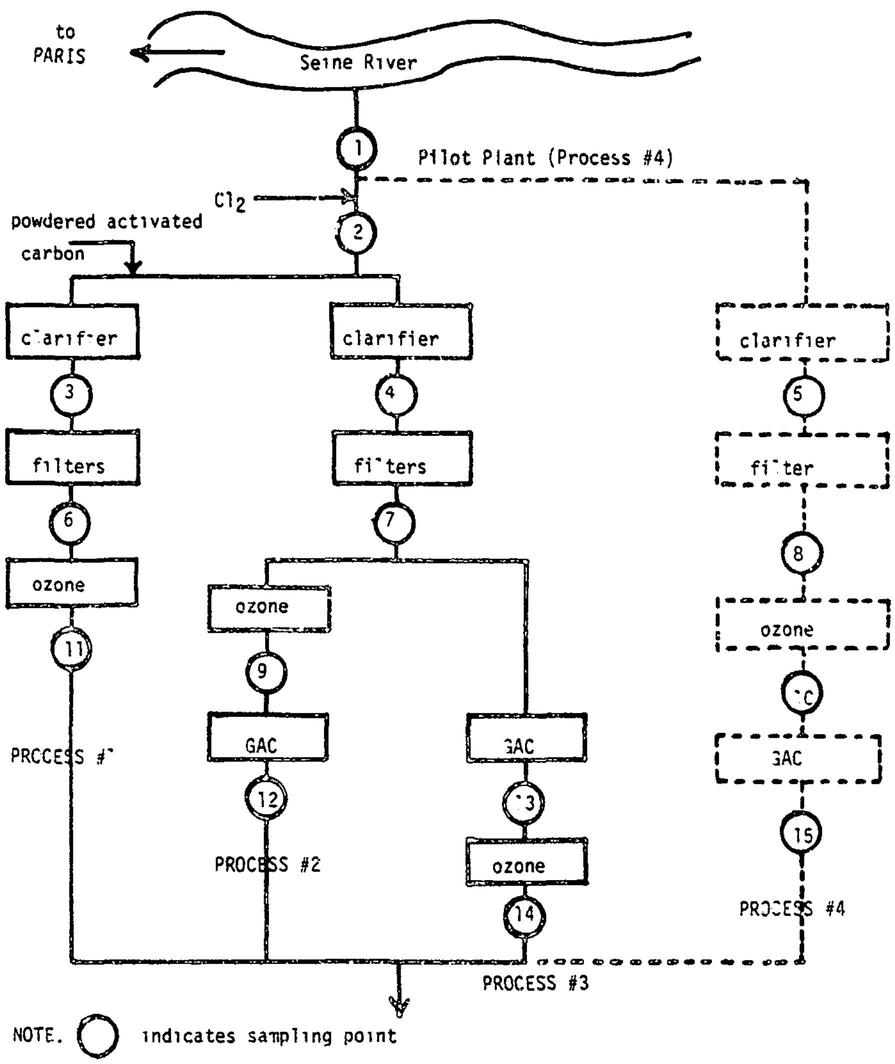


Figure 95. Analytical sampling points for the 4 water treatment processes at Morsang-sur Seine plant, France

TABLE 87 COMPARISON OF PROCESSES 1, 2, 3 AND 4 AT MORSANG SUR SEINE DATA AVERAGED OVER 5 MONTHS OF SIDE BY SIDE OPERATION.

Parameter	Raw Water	Finished Water Parameter by Process			
		Process #1	Process #2	Process #3	Process #4
Organic Materials (by $KMnO_4$)	3.8 mg/l	1.6 mg/l	1.4 mg/l	1.3 mg/l	0.8 mg/l
TOC	3.0 mg/l	1.2 mg/l	1.2 mg/l	1.1 mg/l	0.9 mg/l
Taste Threshold	12	1	none perceptable	2	none perceptable
Fluorescence	3.9	0.8	0.4	0.5	0.2
Organic Materials (by UV)	0.9	0.2	0.2	0.2	0.05
Humic Acids	7 mg/l	1.8 mg/l	1.0 mg/l	1.2	0.5 mg/l
$CHCl_3$	1 microg/l	26 microg/l	30 microg/l	26 microg/l	1 microg/l

Note: Post-chlorination (0.5 0.6 mg/l dosage) follows all treatment processes for distribution systems

Process #1. chlorination, coagulation, flocculation, clarification (powdered activated carbon), sand filtration, ozonation

Process #2: chlorination, coagulation, flocculation, clarification(without powdered activated carbon), sand filtration, ozonation, GAC filtration

Process #3: chlorination, coagulation, flocculation, clarification (without powdered activated carbon), sand filtration, GAC filtration, ozonation

Process #4: coagulation, flocculation, clarification (without powdered activated carbon, sand filtration, ozonation, GAC filtration

FUTURE PLANS AT MORSANG

The pilot plant study of the process without prechlorination was to have been continued through 1979, then a decision was to have been made as to the process to be installed in the third stage of the first star. A recent presentation (Fiessinger & Montiel, 1980) implies that the decision will be to install Process #4.

Granular activated carbon adsorption has been proven to be an efficient process step and is being retrofitted into the first stage of the star (Process #1) following ozonation.

When GAC adsorption in Process #1 becomes operational in 1979, powdered activated carbon was to be eliminated as a permanent treatment step, but will be maintained in the ready state for discontinuous addition in the event of incidents of pollutional surges.

After the first stage at Morsang has been retrofitted with GAC adsorption, there will be sufficient GAC installed in the South Paris region plants of Société Lyonnaise des Eaux et de l'Eclairage (in the Viry, Vigneux and Morsang plants) to warrant a central GAC regeneration facility. Plans for constructing such a facility were being considered during 1978.

The Degrémont water treatment plant at Orly (in Paris), which currently uses ozone treatment, also is being retrofitted with GAC adsorption to follow after ozonation.

BIOLOGICAL REMOVAL OF ORGANIC MATERIALS BY GRANULAR ACTIVATED CARBON --

RESULTS OF A MODELING STUDY AT MORSANG-SUR-SEINE

In 1977, Benedek reported a study conducted at the Morsang-sur-Seine treatment plant using data obtained from Processes #1, #2 and #3 of the full-scale plant. The objective of this study was to try to establish the mechanism(s) of organics removal in the biologically active activated carbon adsorbers and, thereby, to attempt to develop application and design principles for the ozonation/granular activated carbon treatment combination. This study will be reviewed during this discussion because it presents further insights into the 15-month study previously conducted by Richard & Fiessinger (1977).

A mathematical model for describing activated carbon particles with biological activity has been developed by Maqsood and Benedek (1977) and by Peel and Benedek (1977). The basis of this model involves mass transfer in a differential GAC column segment containing percolating water, a bacterial "film" and activated carbon. The concept of a uniform bacterial "film" was presented to allow simplification of the mathematical expressions derived.

The major required inputs for the model were based on batch tests for (a) adsorbable isotherms for the carbon surface equilibrium reaction (with adsorbable solutes) and (b) batch adsorption kinetics of solutes. In addition, an estimate was made of the bacterial degradation rates of solutes, and these are expressed as zero order, carbon surface-based reactions in either batch or continuous column tests. Adsorbability and biodegradability were assumed to be operative on the same organic fractions. Finally, the presence of refractory organics, possibly produced by the bacteria, was considered to be negligible.

Respiration measurements were made in a Hach BOD apparatus on pulverized activated carbon samples, to determine the amounts and rates of biodegradation of organic materials.

Isotherms were determined on ozonated and non-ozonated water and pulverized activated carbon in terms of TOC, COD (determined by $KMnO_4$ oxidation) and optical density at 254 nm (10 cm cells). By all three parameters, ozonation appeared to decrease carbon adsorption capabilities. The apparent particle diffusivities were not affected significantly by ozonation.

The activated carbon adsorbers used in the Morsang plant treatment Processes #2 and #3 removed similar quantities of organic materials, although ozonized organics appeared to be slightly better removed (Figure 96).

After 0.24 g of TOC had been applied per gram of GAC (4,522,499 cu m -- 1.2 billion gallons), activated carbon samples were withdrawn from the GAC adsorbers and isotherms were redetermined by measuring UV absorption. By this technique, it was shown that the GAC was exhausted.

The rate of biological reaction, R_f, was calculated to be approximately 1.8×10^{-11} g of TOC/sq cm/sec for non-ozonated water and 2.1×10^{-11} for ozonated water. This difference is not considered to be significant, since it is within the experimental error of the COD (by $KMnO_4$ oxidation) and TOC determinations.

For comparison, the biological reaction rate for Rhine River water was calculated by Benedek (1977) from the work of Eberhardt, Madsen & Sontheimer (1975) to be on the order of 10^{-10} g/sq cm/sec. On the other hand, for municipal wastewaters, the rate is on the order of 10^{-9} g/sq cm/sec (Peel & Benedek, 1977).

The low biological degradation rate found at Morsang probably is caused by the relatively stable nature of the organic materials in the Seine. This "stability" might also be a result of the formation of chlorinated organic materials during the prechlorination steps involved with Processes #1, #2 and #3 during this modeling study.

Samples of GAC withdrawn from the adsorbers at various depths were analyzed for viable cell counts and respiration rates. In general, more viable cells were found in the adsorber through which ozonized water was passed. The highest bacterial levels (10^7/ml) were found at the top of the activated carbon columns (with and without treatment with ozonized water) which decreased to 10^5 to 10^6/ml at 40 to 80 cm depths.

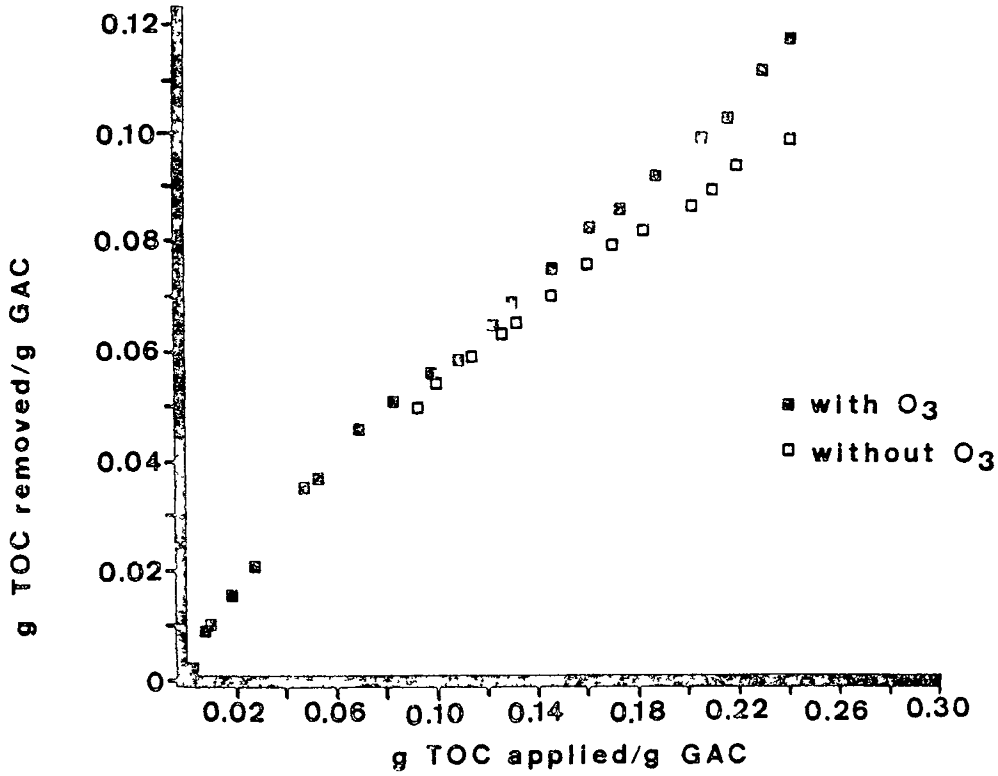


Figure 96. Effect of ozone on GAC adsorption at Morsang plant.

(Benedek, 1977)

Bacterial respiration rates also were similar, although more activity was observed at the top of the adsorber receiving ozonized water. Respiration rates corresponded to the degradation rates of the organic materials.

In these modeling studies, Benedek (1977) used the isotherms and kinetic constants determined at Morsang to predict breakthrough curves, as well as cumulative adsorption curves. Figure 97 is a plot of C/C_0 versus the throughput parameter, Z, which represents the ratio of substrate fed to the adsorptive capacity of the GAC.

The non-adsorbable component of the feed immediately broke through (Figure 97). Thereafter, the concentration of solute in the effluent remained unchanged until a value of $Z = 0.7$ was reached (27 days for the ozonized feedwater). Subsequently, complete breakthrough occurred in an additional 27 days.

On a cumulative plot (Figure 98) using a GAC adsorber containing no biological activity, the adsorption curves rise rapidly and thereafter level off as no more adsorption occurs. The lower capacity of the activated carbon for TOC in the ozonized water may be caused by ozonation rendering the TOC more polar and less readily adsorbed.

With biological activity present in the GAC adsorber, cumulative plots showed a non-zero slope after adsorptive exhaustion. Figure 99 shows that TOC removals are very sensitive to the assumed values of R_f, the biological reaction rate. Moving from the observed value of $R_f = 2.0 \times 10^{-11}$ g/sq cm/sec to 5.0×10^{-11} would result in virtually complete elimination of adsorbable and biodegradable organic materials in the feed waters.

The cumulative removals expected on the basis of Benedek's modeling studies for the Morsang GAC adsorbers used with preozonized versus non-ozonized water are shown in Figure 100. Up to an applied TOC loading of 0.23 g/g of GAC, the GAC adsorber which followed non-ozonized water would have adsorbed more organic materials (both biodegradable and non-biodegradable). After 0.23 g/g of GAC applied TOC loading, however, the GAC adsorber which followed ozonized water would be superior in all respects (because of biodegradation occurring in the GAC adsorber), although under the conditions of Process #3 at Morsang, only slightly more so.

Ozonized water data (Figure 96) and prediction (Figure 100) are compared in Figure 101. The apparent agreement is acceptable, although the data should match reasonably well since R_f was obtained from the data of Figure 96. This agreement shows that the model is capable of matching operational data.

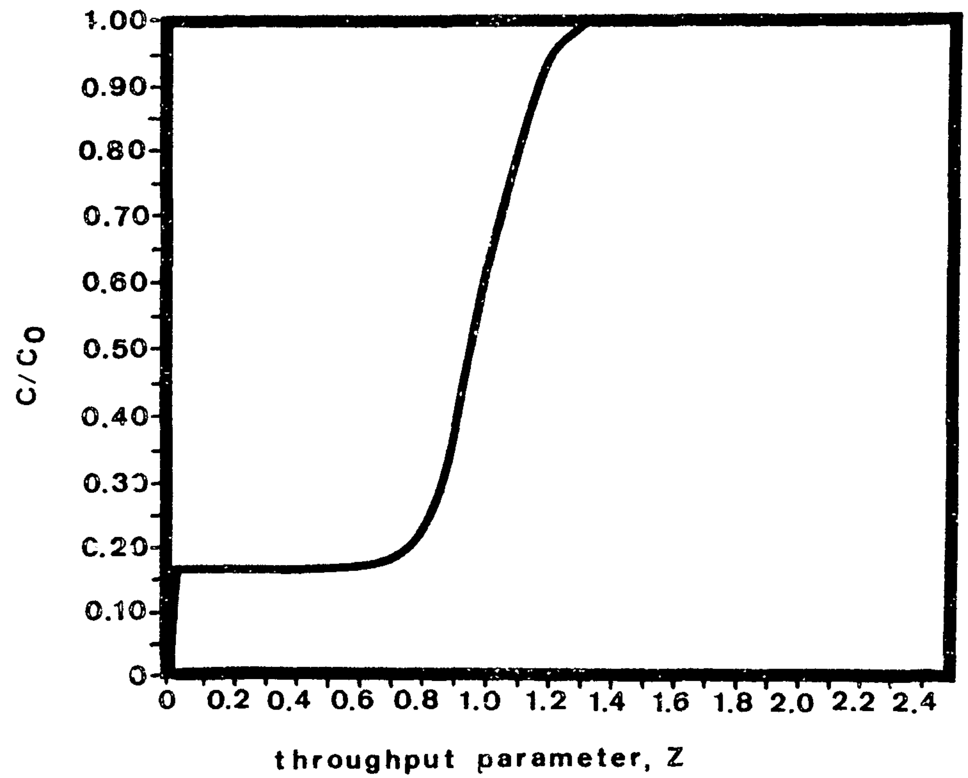


Figure 97. Breakthrough curve for the ozonated GAC adsorber without biological activity (D_0=2.8 x10^{-9}cm^2/sec).

(Benedek, 1977)

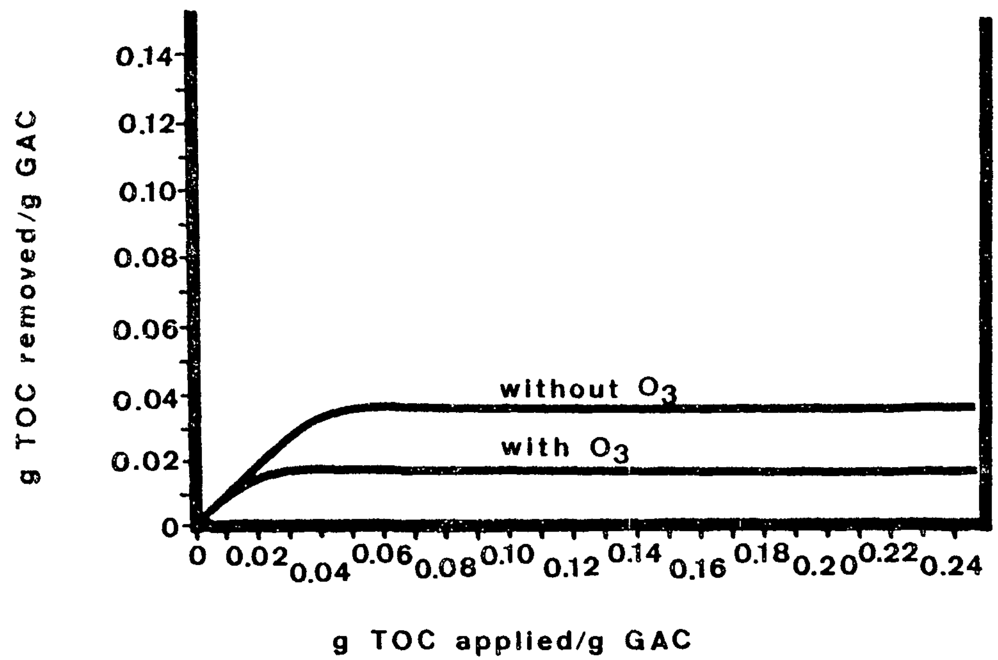


Figure 98. Cumulative plots: GAC adsorption vs. loading; with and without ozone ($D_O = 2.8 \times 10^8 \, cm^2/sec$; $R_F = 0.0$)

(Benedek, 1977)

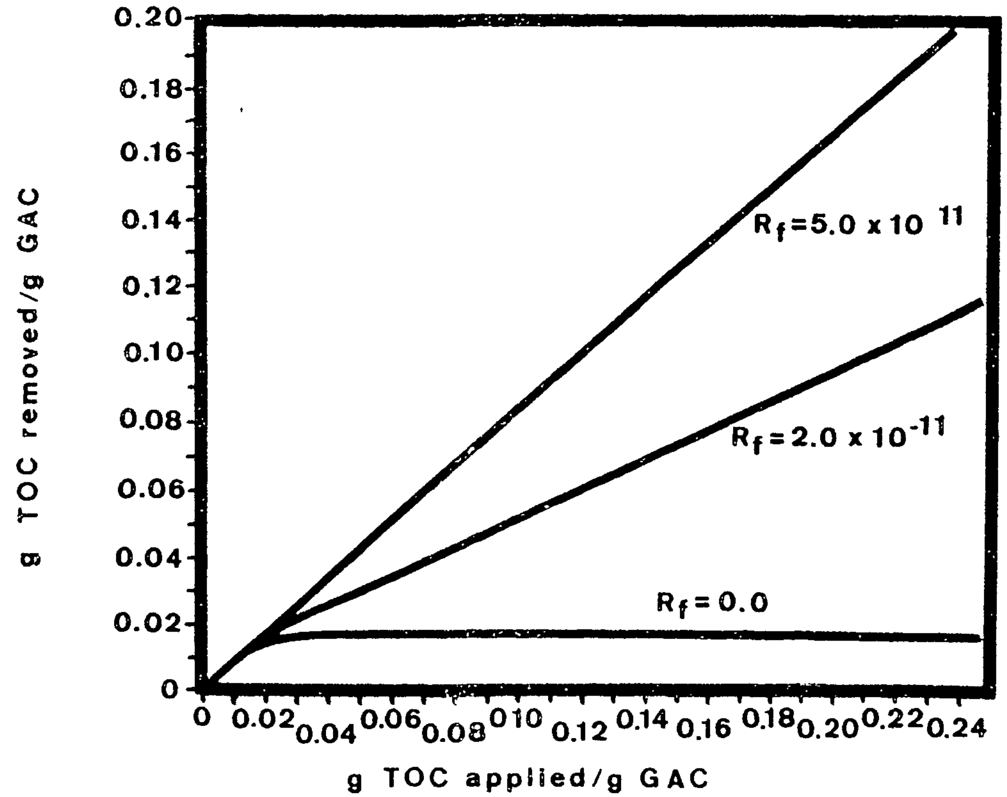


Figure 99. Effect of biological activity on the cumulative TOC removal of a GAC adsorber.

(Benedek, 1977)

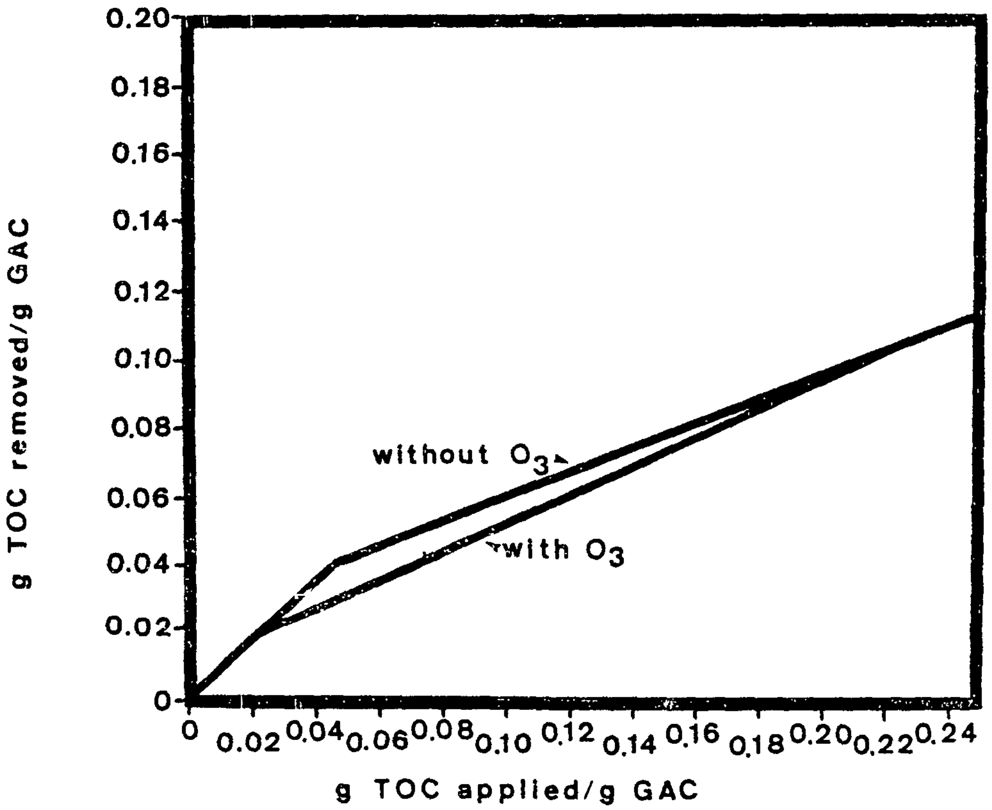


Figure 100. Comparison of ozonated* and non-ozonated** GAC adsorbers (*$R_f = 2.1 \times 10^{-11}$; **$R_f = 1.8 \times 10^{-11}$).

(Benedek, 1977)

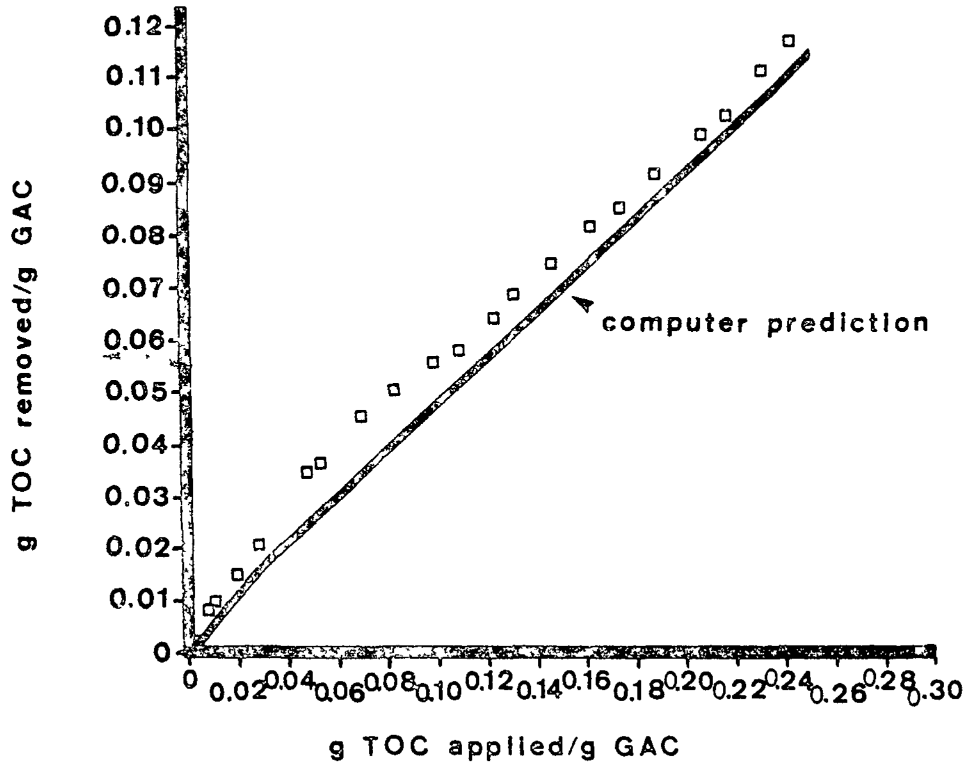


Figure 101. Comparison of actual vs. computer-predicted data for ozonized water/GAC adsorber.

(Benedek, 1977)

APPENDIX E

THE DOHNE PLANT AT MÜLHEIM, FEDERAL REPUBLIC OF GERMANY

BACKGROUND

From 1962 until April, 1977, the Dohne plant at Mülheim processed Ruhr River water directly (without sand bank filtration) by the following sequence: breakpoint chlorination (for the removal of ammonia), chemical coagulation, flocculation, clarification, filtration, dechlorination (by passage through GAC columns), ground passage and chlorination for residual before introduction into the three Mülheim distribution systems. Prior to 1962, the Ruhr at Mülheim was treated simply by slow sand filtration followed by chlorination.

German law prohibits discharges of industrial wastes into the Ruhr because the Ruhr is used as a drinking water supply by a number of cities, but allows the discharge of sewage (which is biodegradable). Local industrial wastes are transported 60 to 80 km north of Mülheim to the Emscher River for discharge. Treatment of the Emscher for potable water applications is prohibited by German law because of the allowed industrial discharges.

Ammonia levels frequently rise to as high as 4 to 6 mg/l because of the prevalence of sewage in the Ruhr. This results in prechlorination dosages as high as 50 mg/l for conversion of ammonia-nitrogen to elemental nitrogen. German law allows a maximum level of 0.6 mg/l of ammonia in finished drinking water. Higher levels will require addition of more than 0.6 mg/l of chlorine to produce a stable chlorine residual. A maximum dosage of 0.3 mg/l of chlorine is allowed by German drinking water laws, but this can be raised to 0.6 mg/l dosage in exceptional circumstances, with prior approval of health authorities.

THE DOHNE TREATMENT PROCESS, 1970 to 1977

High prechlorination dosages were employed (10 to 50 mg/l) to remove ammonia. These chlorination levels produced high levels of chlorinated organic materials (above 200 microg/l) which were not easily removed by GAC "dechlorination" or by subsequent ground passage. Table 88 shows the old Dohne water treatment process and the median levels of Dissolved Organic Chlorine (DOCl), Dissolved Non-polar Organic Chlorine (DOClN), total haloforms and amounts of chloroform produced over the last two years that the old process was employed (1975 and 1976) (Sontheimer et al., 1978). Maximum DOCl values as high as 0.5 mg/l (500 microg/l) have been observed at Dohne under extreme conditions.

During the period 1969 through 1972, detailed pilot plant studies had been conducted at the Bremen, Germany water works on the biological activated carbon process (Eberhardt, Madsen & Sontheimer, 1974; Eberhardt, 1975). The BAC studies at Bremen showed that ammonia can be "removed" biologically (converted to nitrate) rather than by employing breakpoint chlorination with its attendant production of chlorinated organics. German drinking water regulations allow a maximum of 50 mg/l of nitrate in finished water.

TABLE 88. OLD TREATMENT PROCESS AT THE DOHNE PLANT, MULHEIM, GERMANY, AND MEDIAN VALUES OF CHLORINATED ORGANICS PRODUCED DURING 1976 AND 1977

Process Stage	Treatment	DOCl* microg/l	DOClN* microg/l	Sum of haloforms microg/l	$CHCl_3$ microg/l
Raw water (10 mg/l SS, mostly organics	-	17	5	9	below 1
Chemical addition	10 50 mg/l Cl_2 4 6 mg/l Al^{+3} 0.1 kw/cu m Ret. time: 0.5 min				
Flocculation & sedimentation	5 15 mg/l $Ca(OH)_2$ Ret. time 1.5 hr		-	15	6
Sand filtration	10.7 m/hr	203	30	23	7
Granular activated carbon	2 m high 22 m/hr EBCT = 5.5 min	151	17	21	7
Ground passage	Ret time: 12-50 hr	- -	-	--	
Safety chlorination	0.4-0.8 mg/l	92	18	23	9

* DOCl = Dissolved Organic Chlorine, determined by the pyrohydrolysis method of Köhn & Sontheimer (1974)

DOClN = Non polar Dissolved Organic Carbon, extractable from GAC by dioxane

Source: Sontheimer, et al., 1978

As a result of the successful BAC studies at Bremen, a detailed pilot plant study was initiated at the Dohne plant in Mülheim, beginning in September, 1976 to adapt the BAC process to this plant. The pilot plant program was successful immediately and the full scale plant was converted to the BAC process and began initial operations in mid-April, 1977. After 3 months of operation, several modifications were made to the plant, and the new BAC process began operating continuously in its present mode in November, 1977.

The pilot plant testing program was continued until mid-1978, to check the full scale plant operations. At all times, the performances of the full scale plant have paralleled those of the pilot plant. Through 1979, the GAC columns have not had to be regenerated and, based on the length of time that the pilot plant GAC columns functioned without regeneration, it is predicted (Sontheimer, 1978) that the full scale plant GAC columns should operate up to at least two years before regeneration will be required.

The Dohne plant can process 48,000 cu m/day (12.7 mgd) of Ruhr River water (without sand bank filtration), and is located in the center of a residential neighborhood; in fact, 4 residential back yards butt against the plant property. Breakpoint chlorination had been employed as a pretreatment step since 1962, and because of the residential location, special attention had been paid to guard against chlorine leaks or spills.

THE DOHNE PILOT PLANT PROGRAM (Jekel, 1977)

This pilot plant facility began operating at the Dohne plant in September, 1976, under the direction of Prof. Dr. H. Sontheimer. Dr. Martin Jekel of the Engler-Bunte Institut der Universität Karlsruhe carried out the pilot plant investigations at the Dohne water treatment plant. The BAC process currently being used on full-scale by the Dohne plant is based upon the work performed by Dr. Jekel in this pilot plant.

A schematic diagram of the Dohne pilot plant is shown in Figure 102. Ruhr River water (without being treated by river sand bank filtration) was saturated by air using an injector, then treated with poly(aluminum chloride), clarified in a Pulsator, and the Pulsator effluent ozonized in a bubble column using ozone generated in air.

The major portion of the ozonized water was filtered directly through a two-stage sand filter then passed through GAC column adsorbers. The pilot plant filters consisted of two groups of two sand filters each and the adsorbers consisted of three single GAC contactors, each filled with 2.5 m of GAC.

A minor portion of the ozonized water was mixed with a small amount of aluminum sulfate (2.5 mg/l = 0.2 mg/l Al^{+3}), filtered through a double layer sand filter, then passed through two GAC adsorbers.

A parallel pilot plant process was operated in which full-scale plant water which had been treated by breakpoint chlorination and flocculation then was treated by ozonation, sand filtration and GAC adsorption.

All GAC adsorber/contactors were operated at flow rates of 10 cu m/sq m/hr, which was equivalent to an empty bed contact time of 15 minutes. Five different commercial grades of GAC were tested in the Dohne pilot plant.

In addition to the two parallel pilot plants described above, two fluidized bed reactors were set up for studying the biological oxidation of ammonia to nitrate. One of these reactors was supplied with air-saturated Ruhr River water, the other with ozonized effluent from the flocculator.

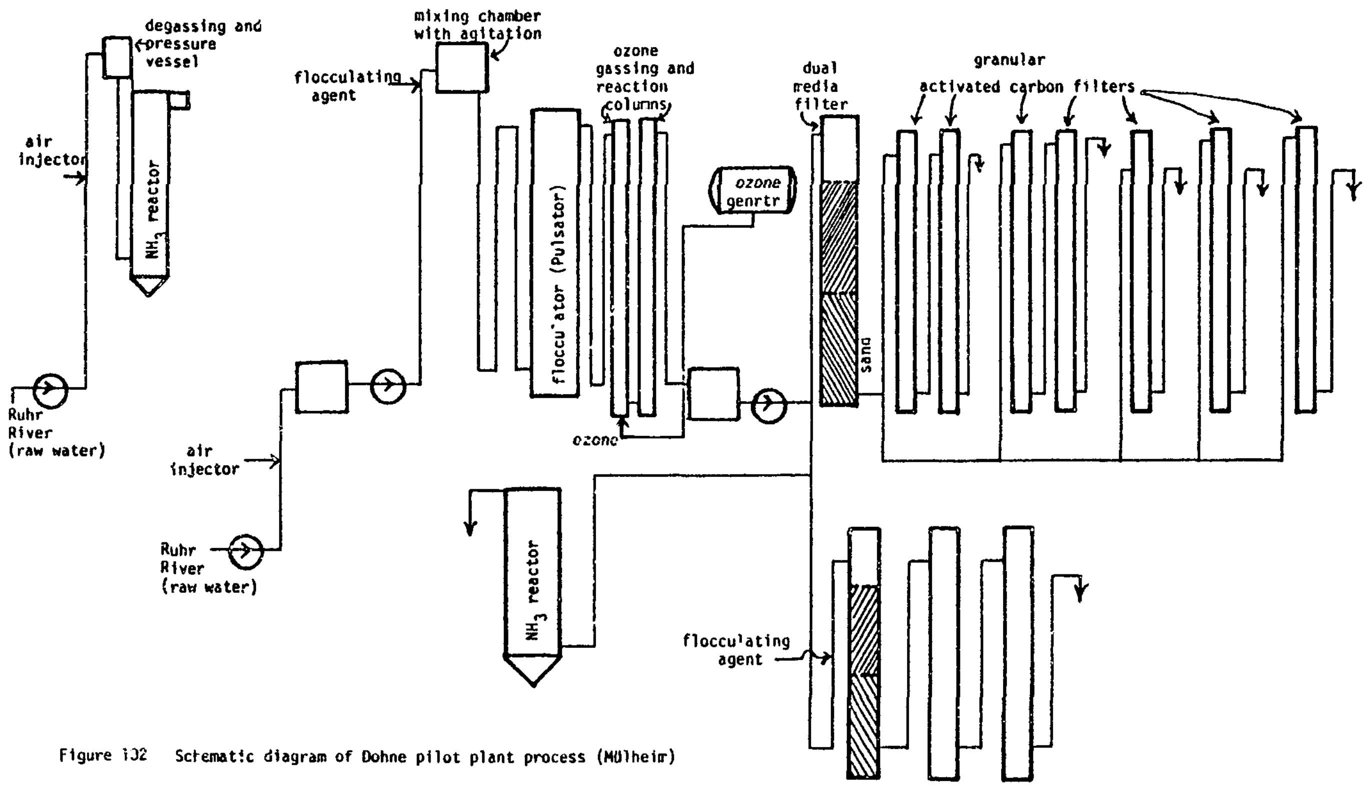


Figure 132 Schematic diagram of Dohne pilot plant process (Mülheim)

Source Jekel, 1977.

The purpose of these studies was to obtain information concerning collapses or poisonings of the biomass which had been noted during the preceeding year.

Comparison of Treatment With & Without Breakpoint Chlorination

Table 89 compares the performance of the two pilot plants with and without breakpoint chlorination. These plants were operated side by side under the same processing conditions. Data shown in Table 89 are the mean values of DOC (Dissolved Organic Carbon) obtained during October and November, 1976. Prechlorination led to almost no reduction in the initial 5.3 mg/l DOC content after flocculation, whereas without prechlorination, a 1.4 mg/l reduction in DOC level was obtained after flocculation. In later treatment steps (ozonation, filtration, GAC adsorption), the pilot plant without prechlorination produced better DOC removals than did the pilot plant with prechlorination.

TABLE 89. COMPARISON OF TREATMENT WITH & WITHOUT BREAKPOINT CHLORINATION

Treatment Step	DOC, mg/l With Cl_2	DOC, mg/l Without Cl_2
Ruhr River water	5.3	5.3
After flocculation	5.3	3.9
After O_3 & sand filtration	4.7	3.7
After GAC adsorption	3.4	2.4

Mean values of pilot plant data obtained during Oct. & Nov., 1977

Source: Jekel, 1977

The higher DOC concentration in the prechlorinated water caused an early breakthrough of the GAC adsorber, as shown in Figure 103. This figure shows the percent reduction in concentration of organic materials (as measured by UV absorption at 254 nm) versus the amount of water passed through the GAC for the two process waters. The upper curve (with biological treatment in the GAC) was extended at least up to a flow of 40 cu m/l of GAC, without any significant decrease in DOC removal efficiency. This amount of flow corresponded to a GAC column operating time of more than 1 year.

GAC Adsorption Versus Biological Activity

Table 90 compares the mean DOC concentrations in GAC column effluents obtained during the first three months of use (during which time DOC removal was primarily by adsorption) with the DOC concentrations obtained during the next 8 months of operation (during which time DOC removal was primarily by biodegradation). Significant differences were observed for the five activated carbons during the initial adsorptive period. On the other hand, during the biological period which followed, few differences in DOC removals were observed. Only the F-400 GAC, which has a smaller grain diameter, performed better than the other four carbons. This indicates that biological activity does not depend upon adsorptive capacity, but may depend upon grain size of the GAC.

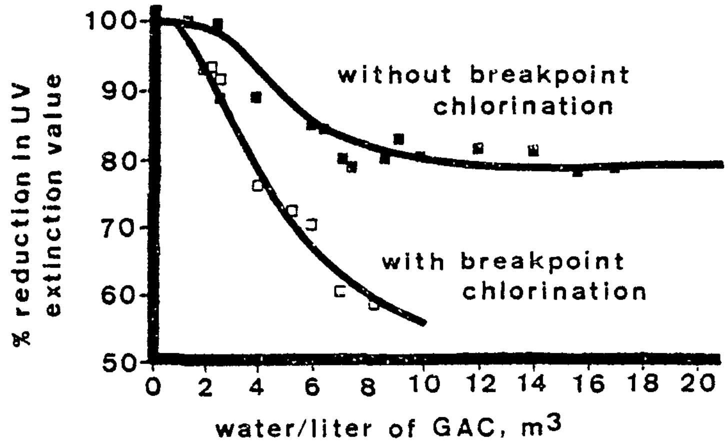


Figure 103. Influence of prechlorination on the effectiveness of a process consisting of flocculation, sedimentation, ozonation, filtration and GAC treatment.

(Sontheimer et al., 1978)

Figure 104 shows the removal performances of the pilot plant GAC adsorbers in g of DOC/cu m of GAC/day and the total organic loadings of the various types of GAC tested during the first 18 months of operation (Jekel, 1979). These data were interpreted by Jekel (1979) as indicating that the breakthrough behavior of biologically active GAC adsorbers is influenced, among other factors, by the adsorbed biologically resistant organic substances.

Figure 104 also shows that an average of about 75% of the total organic materials removed is biologically oxidized, while the remainder, primarily biologically-resistant materials, is removed by adsorption. Due to the enrichment of these compounds on the GAC surfaces, recognizable by the increased GAC loading values in the lower section of Figure 104, the total removal performance of the GAC adsorbers clearly falls off, particularly during the third half-year period of operation.

During this third half-year period, a clear improvement in the quality of the raw water occurred in the Ruhr river, the influent DOC decreasing from about 2.5 to 1.8 mg/l. This intensified the observed decrease in GAC performance. Nevertheless, Jekel (1979) concluded that the operating time of biologically active GAC adsorbers for the treatment of Ruhr river water

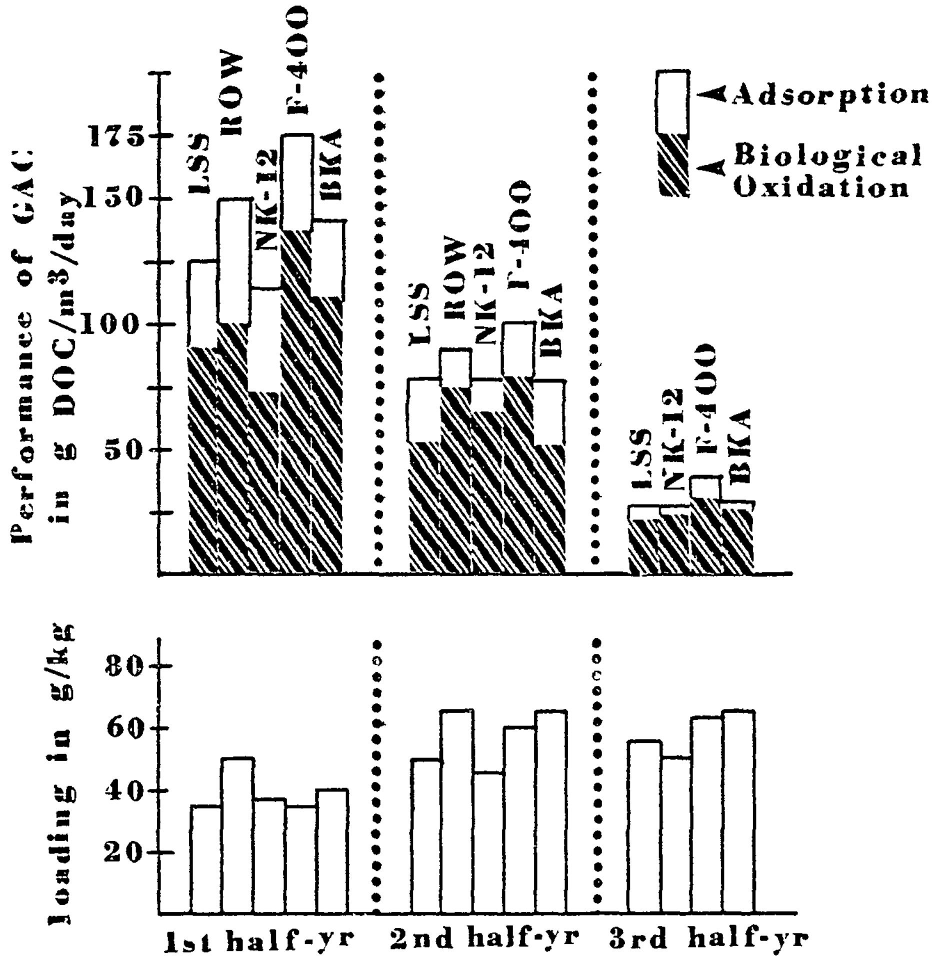


Figure 104. Performance & loading of BAC adsorbers.
(Jekel, 1979)

at the Cohne pilot plant was prolonged by a factor of approximately 4 in comparison with GAC columns operating purely by adsorption.

TABLE 90. CCMPARISON OF DOC REMOVED DURING FIRST 3 AND SECOND 8 MONTHS OF USE OF GRANULAR ACTIVATED CARBON FOR 5 ACTIVATED CARBONS

Treatment Step		DOC, mg/l 10-12, 1976 (adsorption)	DOC, mg/l 1-8, 1977 (biological)
After sand filtration		3.5	2.6
After GAC contacting			
LSS	2.5 m	2.2	1.7
LSS	5.0 m	1.2	1.1
ROW	2.5 m	1.9	1.8
ROW	5.0 m	1.0	1.3
NK-12	2.5 m	2.4	1.8
F-400	2.5 m	1.6	1.5
BKA	2.5 m	1.9	1.8

Source: Jekel, 1977

Ozonized clarifier effluent treated with 2.5 mg/l of aluminum sulfate then passed through LSS GAC during the adsorption period (October to December, 1977) resulted in further reduction in DOC levels, due to precipitation of insoluble alum salts of (probably) organic acids, formed by oxidation during ozone treatment. Pertinent data are compared in Table 91, which also show that a deeper GAC column removed more DOC.

Chemical Balancing of Biological Activity

It was concluded that biological activity in an aerobic, filter - adsorber system leads to:

1) biological degradation of dissolved organic compounds (DOC)
2) the formation of CO_2 (from which the amount of inorganic carbon formed was calculated) from the DOC,
3) oxidation of ammonia to nitrate and
4) consumption of dissolved oxygen by both processes.

Measurement of these three parameters yielded information as to the rate of biological activity occurring during passage through GAC adsorbers. Each mg/l of DOC removed biologically consumed 1 mg/l of dissolved oxygen and produced 1 mg/l of inorganic carbon (calculated from the amount of CO_2

measured). Each mg/l of ammonia oxidized used 3.6 mg/l of DO (based upon the equation $NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O$) and produced 3.4 mg/l of nitrate ion.

TABLE 91. REMOVAL OF DOC AFTER TREATING OZONIZED WATER WITH Al^{+3}

Treatment Step	DOC, mg/l 10-12, 1977 (adsorption)
After flocculation + O_3 + alum + sand filtration	3.2
After GAC adsorption	
LSS 2.5 m	1.8
LSS 5.0 m	0.9

Mean values of data obtained during the period of study

Source: Jekel, 1977

Table 92 shows the mean values for reduction in levels of DOC, NH_4^+ and DO and mean values for increases in inorganic carbon found over the period January to March, 1977. During this time the mean water temperature was 6.8°C. Nearly all DOC removed in the first 2.5 m of GAC columns was found as inorganic carbon in the effluent. The ratio, $-\Delta DOC/+\Delta$(inorganic carbon) was unity or slightly higher for all GACs tested, except for the NK-12, for which the ratio was 0.83. A ratio of less than 1 indicates that nearly all of the DOC being removed was being degraded biologically. A ratio of about 1 indicates that the BAC system was in biological equilibrium.

However, in the next 2.5 m of activated carbon (see data for 5 m GAC columns), the ratio $-\Delta DOC/+\Delta$(inorganic carbon) was significantly greater than 1. Therefore, more DOC was being removed from solution than was being degraded biologically. Since the data for 2.5 m GAC column heights show that biological equilibrium had been attained (rate of DOC removal was equal to the rate of inorganic carbon production), the additional DOC being removed by the 5 m high columns must have been a result of adsorption in the lower half of the columns, in which biological equilibrium had not yet been attained.

Data in Table 92 also show that the ammonia levels were reduced to near zero in the first 2.5 m of GAC depth without showing any significant performance differences between GAC types. Increasing the GAC depth to 5 m did not increase the amount of ammonia converted to nitrate significantly. This means that nearly all of the ammonium ion was oxidized in the first 2.5 m depth of GAC.

TABLE 92. BIOLOGICAL ACTIVITY IN PILOT PLANT GAC COLUMNS, JAN.-MAR., 1977

Treatment Step	ΔDOC mg/l	Δ(inorganic carbon) mg/l	ΔDOC/Δ(inorg C)	ΔNH_4^+ mg/l	ΔO_2 mg/l
After GAC adsorption					
LSS 2.5 m	1.1	1.0	1.1	1.43	7.2
ROW 2.5 m	1.2	1.1	1.09	1.41	7.2
NK-12 2.5 m	1.0	1.2	0.83	1.45	7.1
F-400 2.5 m	1.3	1.2	1.08	1.43	7.1
BKA 2.5	1.2	0.9	1.33	1.44	7.1
LSS 5.0 m	1.6	1.2	1.33	1.46	7.7
ROW 5.0 m	1.7	1.3	1.31	1.47	7.7

Sand filtrate contained 2.6 mg/l DOC and 1.53 mg/l NH_4^+

Mean water temperature: 6.8°C

Mean values of data obtained over the 3 month period

Source: Jekel, 1977

Table 93 shows similar data obtained during the summer period of June to August, 1977 when the mean water temperature was 19.5°C. The feed to the GAC adsorbers was ozonized water from the full-scale plant after flocculation and sand filtration. As a result, the ammonia concentration was zero and the pilot plant GAC columns thus showed no nitrification activity. Comparison of the amount of DOC removed with the amount of inorganic carbon produced at 19.8° (Table 93) or at 6.8°C (Table 92) showed no significant differences because of water temperature.

However, it is significant that during the June to August, 1977 period, the ratio of ΔDOC/Δ(inorganic carbon) was slightly less than 1 for the activated carbons NK-12, F-400 and BKA (at 2.5 m bed depths) and for LSS and ROW activated carbons at 5.0 m depths. This indicates that more DOC was being converted to inorganic carbon than was being removed from the influent solution, which implies that biological regeneration of the GAC was occurring. The biological reactivation of GAC is believed to have been demonstrated unequivocally later in the full-scale plant (see Figure 108, later in this Appendix).

TABLE 93. BIOLOGICAL ACTIVITY IN PILOT GAC COLUMNS, JUNE-AUG., 1977

Treatment Step	ΔDOC mg/l	Δ(inorganic carbon) mg/l	ΔDOC/Δ (inorg C)	ΔNH_4^+ mg/l	ΔO_2 mg/l
After GAC Adsorption					
LSS 2.5 m	0.9	0.8	1.13	0	2.8
ROW 2.5 m	0.9	0.8	1.13	0	2.7
NK-12 2.5 m	1.0	1.1	0.91	0	2.4
F-400 2.5 m	1.2	1.3	0.92	0	3.0
BKA 2.5 m	1.0	1.2	0.83	0	2.0
LSS 5.0 m	1.3	1.4	0.93	0	3.5
ROW 5.0 m	1.3	1.4	0.93	0	3.5

Sand filtrate contained 2.8 mg/l DOC and less than 0.05 mg/l NH_4^+

Mean water temperature: 19.5°C

Mean values of data obtained over the 3 month period

Source: Jekel, 1977

Table 94 presents data obtained over the 6-month period (January to June, 1977) after a 3-month starting period. The ratios of ΔDOC/Δ(inorganic carbon) were always greater than 1, except for NK-12 activated carbon (at 2.5 m bed depth). These data, gathered over double the length of time than those of either Table 92 or Table 93, indicate that slightly more DOC was being removed than was being converted into inorganic carbon. Therefore, slightly more adsorption of DOC was occurring than was biological degradation.

Bacterial Counts in the GAC Adsorber Effluents

Table 95 shows total bacteria counts in the effluents of a 2.5 and 5.0 m high GAC column with pilot plant process water involving no prechlorination. The data indicate that as biodegradable DOC was removed in the GAC columns, the number of bacteria in the effluents decreased. This shows that it is possible to convert DOC into biodegradable organic materials which then can be biodegraded in the water treatment plant (in the GAC contactors). The greater the amount of biodegradable DOC that can be removed in the treatment plant, the less will be the amount of biological aftergrowth which can occur after safety chlorination and after the chlorinated water is sent to the distribution system. Such treatment practice also can be expected to lower the amount of chlorine required to provide a measureable chlorine residual in the distribution system.

TABLE 94. BIOLOGICAL ACTIVITY IN PILOT GAC COLUMNS. MEAN VALUES FOR A 6-MONTH PERIOD (JAN-JUNE, 1977) AFTER A 3-MONTH STARTING PERIOD

After GAC	Bed Depth	ΔDOC mg/l	Δ(in-org C) mg/l	ΔDOC/Δ(in-org C)	ΔNH_4^+ mg/l	ΔO_2 mg/l
LSS	2.5 m	0.92	0.83	1.11	1.31	6.32
LSS	5.0 m	1.69	0.96	1.76	1.34	6.67
ROW	2.5 m	1.09	0.97	1.12	1.31	6.49
ROW	5.0 m	1.59	1.05	1.51	1.34	6.71
NK-12	2.5 m	0.99	1.36	0.73	1.28	6.03
F-400	2.5 m	1.26	1.11	1.14	1.32	6.95
BKA	2.5 m	1.00	0.97	1.03	1.28	5.99

Source: Sontheimer *et al.*, 1978

TABLE 95. TOTAL BACTERIAL COUNTS IN BIOLOGICALLY ACTIVE GAC ADSORBERS

Treatment Step	No. of Bacteria/ml M_g	σ_g
After sand filtration	6,040	4.9
After GAC Adsorption, 2.5 m	747	8.1
After GAC Adsorption, 5.0 m	253	4.8

M_g = geometric mean value

σ_g = geometric standard deviation

Source: Sontheimer *et al.*, 1978

Fluidized Bed Reactors For Ammonia Oxidation

During the summer of 1976, pilot plant studies were conducted at the Dohne plant using air-saturated Ruhr River water passed upflow through fluidized sand beds for biological removal of ammonia rather than breakpoint chlorination. Aeration provided sufficient dissolved oxygen to allow nitrification of all ammonia originally present at the time. This technique has been developed at the Water Research Center at Medmenham, England. The biological activity was very effective during the first month, but then two collapses of the biomass occurred. High concentrations of heavy metals were found in the fluidized solids, adsorbed or incorporated from the river water, and these were suspected of having poisoned the nitrifying biomass.

A new fluidized bed pilot plant reactor was set up and was fed with ozonized effluent from the full-scale plant (no breakpoint chlorination). Heavy metals were removed effectively during the flocculation step. The fluidized bed reactor was operated during the June to August, 1977 period at the rate of 10 m/hr and the mean water temperature was 19.5°C.

Mean data obtained during this period are shown in Table 96, which also shows data obtained from aerated Ruhr River water without flocculation and ozonation. The level of ammonia decreased with no collapses or poisoning of the biomass using the flocculated and ozonized water over a period of 1 year. In addition, about 1 mg/l of DOC was removed biologically in each reactor. The amount of dissolved oxygen utilized corresponded to that expected from the biological oxidation reactions observed.

TABLE 96. BIOLOGICAL OXIDATION IN FLUIDIZED BED REACTORS

Treatment Step	NH_4^+ mg/l	DOC mg/l	DO mg/l
Ruhr River water + aeration	0.91	4.5	8.5
After ammonia reactor	0.09	3.5	2.6
Decreases in levels	0.82	1.0	5.9
After clarification + O_3	0.39	3.1	9.1
After ammonia reactor	0.05	2.2	4.6
Decreases in levels	0.34	0.9	4.5

Flow velocity: 10 m/hr

Mean water temperature: 19.5°C

Mean data values obtained over the 3 month period

Source: Jekel, 1977

THE BAC PROCESS AS INSTALLED, APRIL 1977

Based on the successful early pilot plant results with the new ozonation process, the breakpoint chlorination step at the full-scale Dohne plant was eliminated in April, 1977 and ozonation of the clarifier effluent was begun. Dohne's treatment process as it was instituted in mid-April, 1977 is shown in Figure 105 (Sontheimer et al., 1978). Ruhr River water, which contains about 10 mg/l of suspended solids (mostly organics) is pumped into a flash mixing tank (1.8 x 1.8 x 5.2 m) which contains a high speed aspirating turbine which uses 2.5 kw of power per cu m of tank volume. Water is dosed with 4 to 6 mg/l of poly(aluminum chloride) and an average of 1 mg/l of ozone. Most of the ozone used in this preozonation step is obtained from the off-gases from the second (major) ozonation step. In fact, all of the off-gases from the second ozonation step are drawn into the flash mixing tank by the suction action of the aspirating turbine. Additional quantities of fresh ozone, as required, are added to these off-gases. Additional ozone is required whenever the manganese content of the raw water is high (see below) or when algae levels rise in the river (Spring and Fall).

Residence time in the flash mixing chamber is about 0.5 minute. During this time, nearly all of the ozone added in this chamber is utilized in performing various oxidation functions. Only 3% of the ozone originally generated is present in the off-gases from the flash mixing chamber. The combination of ozone plus high speed mixing results in improved flocculation of suspended solids in the presence of the hydrolyzed aluminum chloride.

After flash mixing, the water is pumped to a Degrémont Pulsator for clarification where 5 to 15 mg/l of $Ca(OH)_2$ could be added, if needed. The Pulsator consists of 2 basins, each 27.7 x 13.2 x 4.2 meters in dimension. Distribution of water in the Pulsator is achieved by means of perforated asbestos cement pipes, which allows for good final flocculation within the floc blanket. Clarification time is 1.5 hrs. By this treatment, turbidity of the water is lowered to 0.4 to 0.8 FTU.

The ozonation system is supplied by Trailigaz, and consists of 2 ozone generators, each containing 220 water-cooled dielectric tubes and each capable of generating 4 kg of ozone/hr at a concentration of 20 to 25 g of ozone/cu m of air (8 kg/hr total ozone generating capacity).

The ozone dosage at this point in the process averages 2 mg/l, the contact time is 5 minutes, and this step is controlled by monitoring 0.3 mg/l of dissolved ozone residual at the exit of the contact chamber. Ozone contacting efficiency in this single diffuser chamber is 90%. A further reduction of turbidity level usually is achieved at this point by the formation of larger flocs, caused by agglomeration of residual solids. In addition, organics are oxidized to more polar compounds which are capable of being flocculated by aluminum cations and also become more biodegradable.

Off-gases from this primary ozonation step (containing 10% of the originally generated ozone) are drawn back into the flash mixing tank by the high speed aspirating turbine and are injected into the raw water. If the manganese content of the water after the Pulsator clarification step is

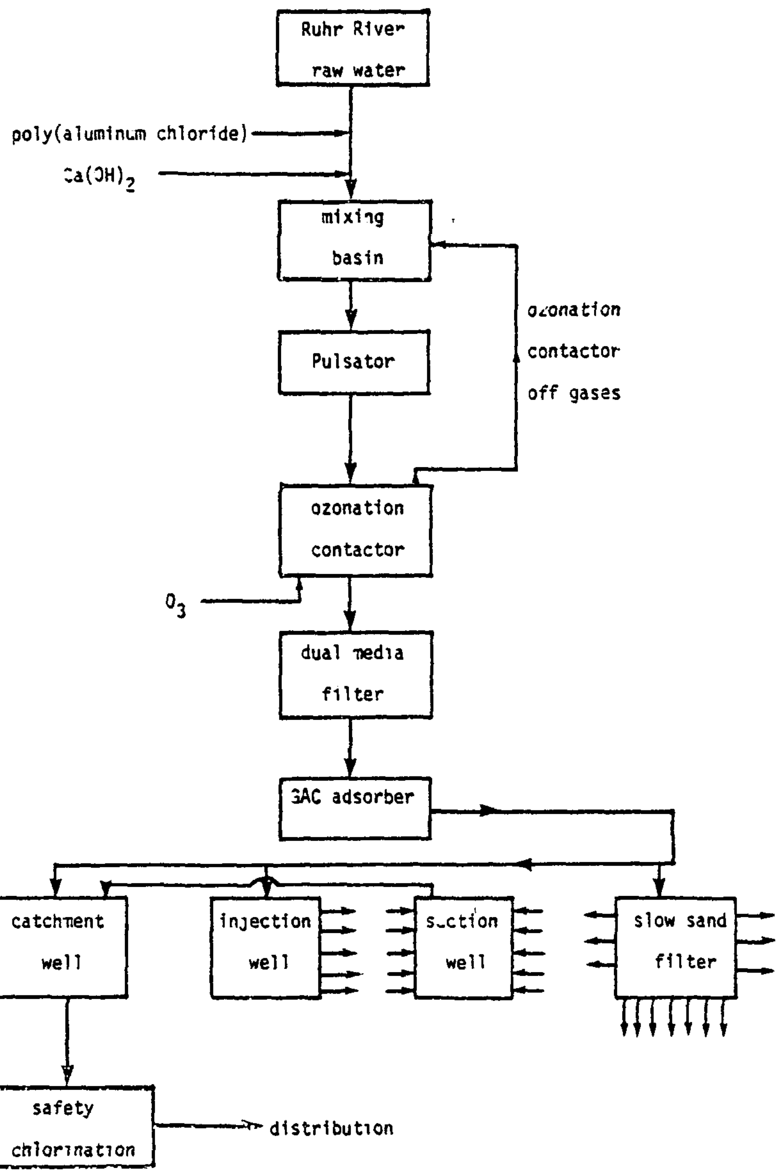


Figure 105. Process scheme for surface water treatment at the Dohne water utility in Mülheim after introduction of combined chemical and biological oxidation.

(Sontheimer et al., 1978)

greater than 0.05 mg/l, then additional fresh ozone is added to the flash mix chamber. Manganese content is monitored at this point in the process. Additional ozone also is required when the algae content of the raw water rises (in the Spring and Fall). During such periods, simply doubling the preozonation dosage from 1 mg/l to 2 mg/l overcomes any tendencies of the algae to clog the filters; the treatment process is otherwise unaffected (Nolte, 1978).

The use of off-gases from the primary ozonation step in the flash mixing chamber allows 97% of the generated ozone to be utilized in performing useful work. The flash mixer off-gases contain only 3% of the ozone generated, and this is destroyed by passage through a Degussa catalytic destruction unit (palladium on alumina) at 60°C before the gases are discharged to the atmosphere.

Ozone is monitored (1) in solution after the primary contact chamber, (2) in the primary contactor off-gases (by a Hartman & Braun monitor, Metz, France) and (3) in the ozoneur room atmosphere (by a Wallace & Tiernan KI monitor). This last monitor will cause an alarm to be signalled at the control panel if the ozone concentration in the room atmosphere exceeds 0.05 ppm. In addition, the plant provides Dräger tubes for plant personnel to determine the ozone concentration manually at various places in the plant, if desired.

After ozonation, the water is pumped to 4 horizontal pressure sand filters (1.6 m high -- see Figure 106), for filtration at the rate of 11 cu m/sq m/hr (11 m/hr). It had been planned to dose 0.2 mg/l of poly(aluminum chloride) and 0.1 mg/l of polyelectrolyte after installation of new dual media filters in December, 1978, if necessary for further turbidity removal.

After sand filtration, the water is passed through 4 GAC adsorbers, each containing media which is 2 m high and 5 m in diameter, at the rate of 22.5 cu m/sq m/hr. During the period April to July, 1977, these carbon contactors contained the same GAC as had been used for dechlorination in the old process. Because of this, the GAC was "fully loaded" with chlorinated organics. Empty bed contact times of these 2 m high GAC contactors is 5.5 minutes.

Following passage through the GAC columns, the water then passes into 15 injection wells for storage in the ground where it remains 12 to 50 hours. When removed for distribution (from wells within 50 m of the infiltration points), 0.4 to 0.8 mg/l of chlorine is added. This low dosage provides a stable, measureable 0.1 mg/l chlorine residual in the Mülheim distribution system. The measureable 0.1 mg/l chlorine residual is required by German drinking water regulations. However, even the 0.4 to 0.8 mg/l safety chlorination dosage is above that normally authorized under German drinking water regulations (0.3 mg/l, maximum), and an exception had to be applied for and granted to allow this high a dosage to be used at the Dohne plant.

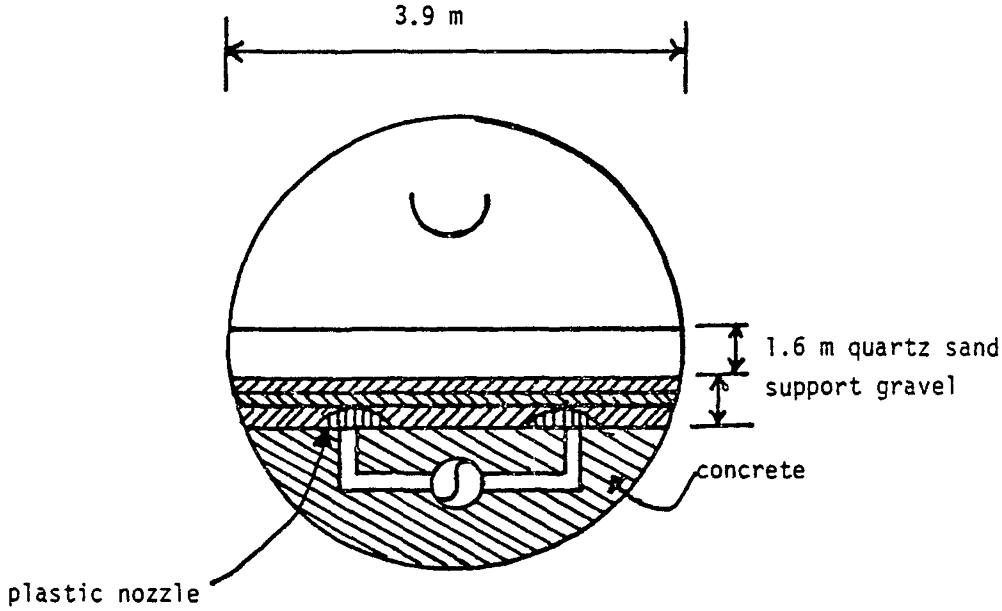
30 meters long, 3.9 meters diameter

Sand media: 1.6 meters deep, 1.2 to 1.8 mm particle size

Support Gravel: Three layers 2 to 3 mm particle size

3 to 7 mm

7 to 15 mm



Filter hydraulic loading rate: 18 cu m/sq m/hr

backwashing rate : 20 cu m/sq m/hr

Chemical filter aid: 0.2 mg/l Al^{+3}

0.1 mg/l polyelectrolyte

In December, 1978, convert media to:

bottom layer 0.6 to 1.2 mm particle size hydroanthracite

top layer 2 to 3 mm particle size low density GAC

Figure 106. Pressure filters at the Dohne (Mülheim) plant.

PROCESS PERFORMANCE, APRIL-JULY, 1977

In Table 97 are listed the Dissolved Organic Carbon (DOC), ultraviolet absorbances and ratios of UV/DOC measured at various process points for 1975 (old process), 1976 (old process) and April to July, 1977 (new process using old GAC). DOC is determined after passing the sample through a 0.45 micron filter by oxidizing all dissolved carbonaceous materials with ultraviolet radiation and measuring the amount of CO_2 formed (Wölfel & Sontheimer, 1974).

Ultraviolet absorbance of process waters is measured at 254 nm in 1 or 5 cm cells, but then is calculated for cell lengths of 1 meter. This measurement relates to the amount of carbon-carbon unsaturation contained in the molecular structures of the dissolved organic materials. Unsaturation can consist of individual carbon-carbon double bonds, aromatic nuclei (multiple and conjugated C=C bonds) or carbon-oxygen (C=O, carbonyl) functions. Ozonation destroys many isolated carbon-carbon bonds and most aromatic moieties, converting them to CO_2 or to carbonyl groups, thus lowering (but not totally eliminating) the total UV absorbance value.

The UV/DOC ratio by itself is not as meaningful as is the change of this ratio in comparison with changes in both components. If DOC values remain constant while the UV absorbance decreases, this indicates that unsaturated organics are being converted to saturated, dissolved, oxidized organic products (which may contain more carbonyl functions), but not to CO_2 and water. If both UV absorption and DOC decrease, this indicates that unsaturated organics are being destroyed and that DOC is being converted to CO_2 and water.

Table 98 compares the mean DOC values obtained by the old process during 1975 with the mean values obtained during May to August, 1977. During this later period, the GAC adsorbers were operated with the exhausted carbon used in the old treatment process. It is apparent that ozoration enhanced the biodegradation of DOC during ground passage. In addition, it is also clear that chlorinated organics were not being synthesized since the prechlorination step had been eliminated. Ammonia levels were reduced from an average of 1.07 mg/l in the influent to zero after ground passage. Some ammonia (0.25 mg/l) was removed biologically during flocculation and most of it (0.60 mg/l) during sand filtration.

PROCESS MODIFICATIONS, NOVEMBER, 1977

After the initial testing period of April to July, 1977, the following plant modifications were made during August to October, 1977, the plant was restarted in November, 1977 and has been operating continuously since:

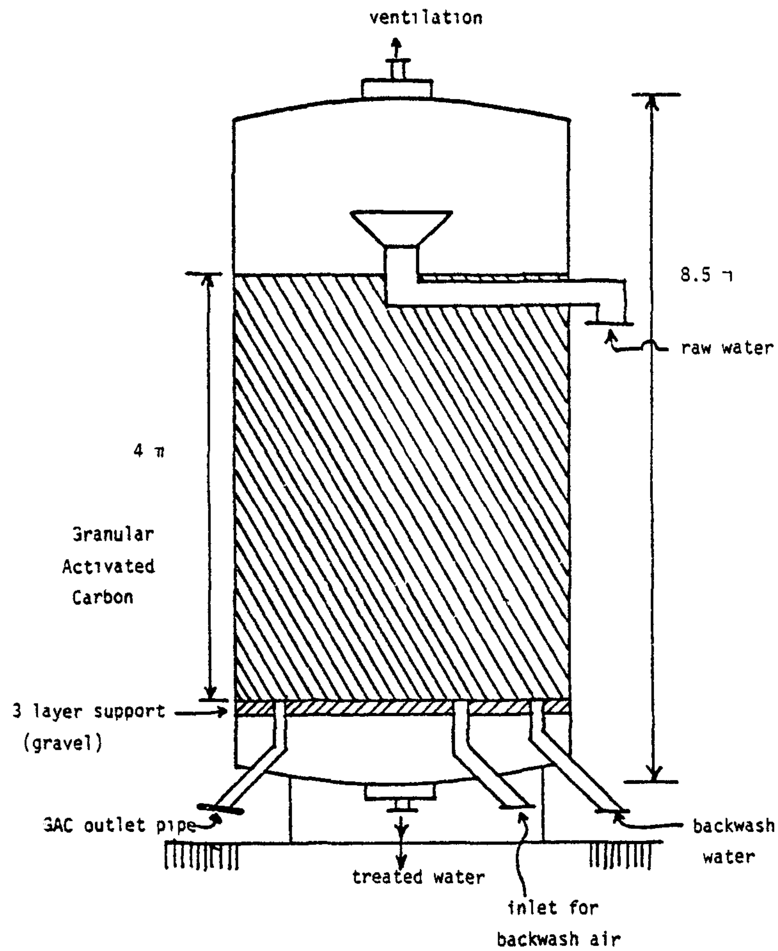
1) The granular activated carbon depths were doubled from 2 meters to 4 meters (see Figure 107). This increased the empty bed contact time in each filter from 5.5 to 11 minutes. At the same time, each of the four GAC columns was charged with a different fresh granular activated carbon (NK-12, F-300, LSS and AG-1). Three of these four activated carbons had been studied in the pilot plant. The intent of the Dohne

TABLE 97. MEAN DOC AND UV-EXTINCTION VALUES FOR THE DIFFERENT TREATMENT STEPS AT THE DOHNE PLANT

Sampling Point	1975			1976			April-July 1977*			Nov. 1977-June, 1978**
	DOC mg/l	UV 254 nm m^{-1}	UV/DOC ratio	DOC mg/l	UV 254 nm m^{-1}	UV/DOC ratio	DOC mg/l	UV 254 nm m^{-1}	UV/DOC ratio	DOC, mg/l
Raw water (Ruhr)	3.9	6.8	1.8	5.0	9.1	1.8	3.6	6.1	1.7	2.4 - 3.7
After flocculation & sedimentation	3.2	4.5	1.4	4.0	5.5	1.4	2.9	3.2	1.0	1.8 - 3.0
After filtration	3.2	4.4	1.4	3.8	5.6	1.4	2.6	1.8	1.0	1.7 - 3.1
After GAC adsorption	3.0	4.0	1.3	3.7	5.3	1.4	2.3	1.6	0.7	1.0 - 2.6
After ground passage	1.8	3.1	1.8	2.1	4.0	1.9	0.9	1.4	1.6	---

* GAC adsorbers filled with fully loaded GAC, used during old process

** Source: Jekel, 1978, otherwise Sontheimer *et al.*, 1978



GAC backwash rate: 27 to 30 m/hr; air then water;
backwash each 10 to 14 days

Figure 107. GAC adsorbers at Dohne plant, Mülheim, Federal Republic of Germany.

plant management is to test all four activated carbons in the full scale plant, side by side, to select the best performing type at some future date. One-fourth of the sand filtered water is passed through each GAC contactor. Thus the water is in contact with only one of the four activated carbons being tested. After GAC contacting, the effluents from the four GAC contactors are blended in the slow sand filters, in the injection wells and in the underground reservoir.

TABLE 98. COMPARISON OF OLD & NEW PLANT PROCESSES FOR REMOVAL OF DOC & NH_4^+

Treatment Step	old process 1975 DOC mg/l	new process May-August, 1977 DOC mg/l	new process May-August, 1977 NH_4^+ mg/l
Ruhr River water	3.9	4.0	1.07
After flocculation	3.2	3.1	0.82
After O_3 + sand filtration	---	2.8	0.22
After GAC contacting	3.0	--	--
After ground passage	1.8	0.9	0

Source: Jekel, 1977

2) Pure oxygen is added after ozonation, at the pumps which send ozonized water to the sand filters. Some 80% of the nitrification has been found to occur in the sand filters and the remainder occurs in the GAC contactors. During the summer, all of the nitrification occurs in the sand filters.

Since each mg of ammonia-nitrogen requires 3.6 mg of dissolved oxygen for conversion to nitrate (assuming the equation: $NH_4^+ + 2O_2 \quad NO_3^- + 2H^+ + H_2O$), it is apparent that a raw water ammonia level of 5 to 6 mg/l will require 18 to 22 mg/l for nitrification alone. In addition, biological conversion of dissolved organic carbon to CO_2 and water also requires dissolved oxygen (2 mg of DO for each mg of DOC converted to CO_2). Such levels of dissolved oxygen cannot be supplied solely from air, which saturates the water during ozonation. Aeration produces maximum DO levels of only 8 to 11 mg/l, depending upon the water temperature. Addition of pure oxygen, however, can provide DO levels up to 45 mg/l.

Liquid oxygen (LOX) is stored in a 3 cu m tank in the room which used to house the chlorine cylinders. This is vaporized (2 LOX evaporators are installed, one for backup) and the gaseous oxygen is introduced to the ozonized water at the pumps which send the water to the sand filters. This pump provides considerable mixing action for water and gas. No special corrosion problems have been encountered during the first seven months of operation and no changes in the materials of construction of the pumps have been required.

The DO is monitored at the outlet of the GAC contactors. Addition of gaseous oxygen is controlled by maintaining a level of 7 mg/l at the GAC column outlets. Average oxygen dosage to attain this 7 mg/l residual DO level usually is around 10 mg/l. As a rule, excess dissolved oxygen can cause outgassing, which can cause mechanical problems during filtration. However, since the oxygenated water at the Dohne plant is under 1.6 bar pressure, no outgassing problems have been observed during the first 7 months of operation.

3) The second poly(aluminum chloride) + polyelectrolyte addition step (after the primary ozonation step) has not yet been found to be necessary. This is because the flash mixing step utilizing poly(aluminum chloride), 1 mg/l of ozone and high speed agitation has been so effective in lowering turbidity (to 0.1 FTU after sand filtration). Sigrist turbidity meters have been installed after sand filtration to monitor turbidities at this point (see later discussion on head loss vs turbidity breakthrough of the sand filters).

As of June, 1978, the Dohne plant had a total of 41 monitoring points in the plant.

PERFORMANCE OF MODIFIED BAC PLANT PROCESS

Plant performance data obtained over the period November 1977 through May, 1978 are listed on the far right hand side of Table 97. It is clear that the DOC of water exiting the GAC contactors was lower than that obtained at the same point during the April to July, 1977 study. This difference may be due to one or more of several factors:

1) the increased EBCT of the 4 m GAC columns (11 minutes vs 5.5)

2) the use of virgin GAC in November 1977 vs "fully loaded" GAC used earlier

3) higher levels of dissolved oxygen (pure oxygen was not added during the April to July, 1977 tests). This effect would be expected to be minor compared with the first two.

When the four new GAC columns were started up in November 1977, DOC values in their effluents were very low, on the order of 1.2 to 1.6 mg/l. However, these effluent levels increased over the next few months, reaching 2.1 to 2.6 mg/l during the May to June, 1978 period. These increases were attributed to the Spring algae bloom. Pertinent data in this regard are listed in Table 99.

TABLE 99. DOHNE PLANT PERFORMANCE DATA SINCE NOV. 1977. DOC DATA, mg/l

Sample Point	11-12/77	1-2/78	3-4/78	5-6/78
Raw water	3.0	3.0	2.4	3.7*
After O_3 + floccln	2.5	2.7	1.8	3.0
After sand filtrn	2.5	2.6	1.7	3.1
After GAC				
-Lurgi NK-12	1.3	1.7	1.5	2.5
-Calgon F-300	1.2	1.0	1.2	2.1
-Lurgi LSS	1.6	1.9	1.6	2.6
-Essen Rsch AG-1	1.4	1.5	1.5	2.6

* higher DOC levels during this period are attributed to the Spring algae bloom

Data of Table 99 are interpreted by Dr. M. Jekel of the Engler-Bunte Institute of the University of Karlsruhe as indicating adsorptive removal of DOC during the initial 6 month period of carbon use. During this time, biological activity was building up to equilibrium very slowly (because of the low water temperatures) and the ratio -ΔDOC/+Δ(inorganic carbon) was greater than 1. The May to June 1978 data indicate that biological activity had increased. The ratio of -ΔDOC/+Δ(inorganic carbon) passed through unity and became slightly less than 1.

The values for ΔDOC and Δ(inorganic carbon) are plotted in Figure 108 for the period November, 1977 through July, 1978. During July, the rate of formation of inorganic carbon increased significantly, and the ratio -ΔDOC/+Δ(inorganic carbon) decreased to 0.55.

This behavior confirms the data obtained during the Bremen pilot plant studies. During the initial 3 to 4 months, the removal of dissolved organics by virgin GAC took place primarily by adsorption. The maximum removal of organics by adsorption took place for about 6 weeks, after which the degree of removal of organics decreased to 25 to 33% over the next 3 to 4 months. As the biological activity in the GAC media increased, however, the amount of dissolved organic carbon removed from solution by adsorption plus biological activity increased (at the Dohne plant) to just over 50% of the amount removed by virgin GAC. This 50+% removal remained constant over the last two months for which data are reported (the 6th and 7th months after virgin GAC startup).

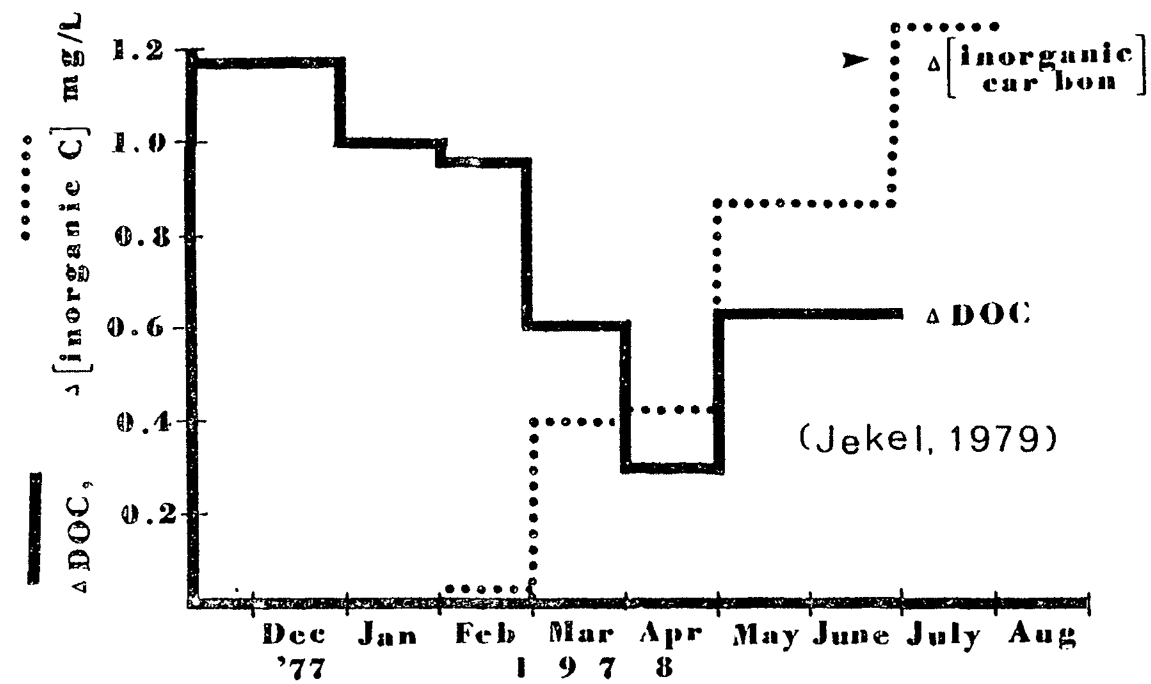


Figure 108. Initial performance of BAC adsorbers in the Dohne water works

Based upon the more than two year long pilot plant program which he conducted at the Dohne plant, Dr. Jekel anticipates that this 50+% dissolved organics removal will continue for up to 2 years before reactivation of the GAC may be required. Dohne's plant management has budgeted for regeneration on this basis (see later section in this Appendix on Costs).

Dr. Jekel also believes that had the new GAC columns at Dohne been started up during the summer period of higher water temperatures, high levels of biological activity would have been established in a much shorter time, say 2 to 3 months.

Substantiation of the increasing biological activity in the GAC columns is shown in Table 100, which lists the increase in inorganic carbon concentrations obtained during passage through the GAC contactors for the periods January to April, 1978, and May to June, 1978. During the May to June period, production of CO_2 more than doubled in all 4 GAC columns. These data should be coupled with those of Table 99, which show that the DOC in the GAC column effluents was about 67% higher during the same period than during March to April, 1978.

TABLE 100. DOHNE PLANT PERFORMANCE DATA, JAN.-JUNE, 1978. BIOLOGICAL PRODUCTION OF INORGANIC CARBON IN GAC CONTACTORS

	Inorganic Carbon Produced (CO_2 as C), mg/l	
GAC Contactor Contg*	Jan-April, 1978	May-June, 1978
NK-12	0.2	0.5
F-300	0.2	0.6
LSS	0.3	0.6
AG-1	0.3	0.8

* During these studies there was no ammonia in the GAC influent. Therefore, no nitrification was occurring.

When the water temperature rose in the Spring of 1978, the biological activity in the activated carbon columns increased significantly, and the amount of CO_2 produced more than doubled. The amount of CO_2 produced during the May to June, 1978 period with the carbons LSS and AG-1 actually was greater than the amount of DOC being removed from the GAC influent (Table 101). This indicates that some biological regeneration of the GAC must have been occurring. Since the only sources of dissolved organic carbon to produce CO_2 were the influent water and what had been adsorbed by the GAC during the winter period, the excess CO_2 produced over that present in the influent water must have arisen from the biodegradation of adsorbed DOC.

TABLE 101. DOHNE PLANT PERFORMANCE DATA. COMPARISON OF DOC REMOVED VERSUS INORGANIC CARBON PRODUCED IN BIOLOGICALLY ACTIVE GAC CONTACTORS DURING MAY - JUNE, 1978

GAC Type	DOC removed, mg/l	inorg C produced, mg/l
LSS	0.5	0.6
AG-1	0.5	0.8
BUT		
NK-12	0.6	0.5
F-300	1.0	0.6

Source: Jekel, 1978. Private Communication

A significant benefit of the new BAC process to the Rheinisch Westfälischen Wasserwerksgesellschaft mbH, is that the amount of chlorine dosage required to produce the 0.1 mg/l of chlorine residual has been lowered from 0.4-0.8 mg/l to 0.2-0.4 mg/l, halving the amount of chlorine formerly used for this purpose and bringing Dohne's chlorine dosage down to levels used with less polluted and treated surface waters, such as lakes, reservoirs and some groundwaters.

During the pilot plant testing program at Dohne, pronounced slowing down of biological activity was noticed in the GAC adsorbers whenever the DOC in the influent to the adsorber dropped below 2 mg/l and approached 1 mg/l. This slowing down of biological activity is believed to have been caused by a shortage of biodegradable substances over a longer period.

RELATIONSHIP OF EPA'S PROPOSED ORGANICS REGULATIONS REGARDING GAC TO DOHNE PLANT PERFORMANCE

EPA's proposed regulations for the use of GAC to remove synthetic organic chemicals (SOCs) from U.S. waters would require that the GAC be regenerated when the TOC in the GAC effluent becomes 0.5 mg/l higher than that obtained with virgin GAC. The proposed regulations also would require that the TOC removed by virgin GAC be at least 50% of that in the water influent to the GAC column.

It can be seen from the data of Table 99 that if EPA's proposed regulations were to have been applied to the modified Dohne treatment process (4 m GAC columns; 11 minute EBCT) that 50% TOC removal was obtained by only one of the four activated carbons being used. Only the F-300 carbon removed 50% or more of the influent (to the GAC column) TOC and continued to provide this amount of TOC removal through April, 1978 (5 months). However, it is probable that longer empty bed contact times with the other three activated carbons would have produced the desired initial 50% removal of TOC.

On the other hand, continued removal of TOC by all four activated carbons at Dohne would have met the proposed EPA requirement of no more than a 0.5 mg/l maximum increase in effluent TOC concentration through April, 1978 (5 months).

On the basis of these considerations alone, one would conclude that only the F-300 GAC would meet the proposed EPA requirements at Dohne, with an 11 minute EBCT, and that this carbon would have to be regenerated after 5 months of use.

However, when biological equilibrium had been obtained in April, 1978 (after 5 months of use), the F-300 activated carbon now allowed 0.9 mg/l of DOC more in the GAC column effluent than did the virgin activated carbon. At this time, only about 33% of the DOC in the GAC influent was being removed. After an additional 2 months of use, however, the degree of DOC removal had risen to about 50% (see Figure 1C8). This performance was expected to remain essentially constant (33 to 50% DOC removal) for at least the next 18 months (through 1979). At this 11 minute empty bed contact time, F-300 GAC would not, however, meet the proposed EPA regulation which would limit the effluent TOC level to only 0.5 mg/l above that obtained with virgin GAC.

On the other hand, performances of all four of the biologically active GAC columns at Dohne during the period May to June, 1978 are considered to be satisfactory by the RWW, and no plans are being made to reactivate the GAC until after two years of use. Even though only 33 to 50% of the influent DOC is being removed, the GAC is not saturated with the very strongly adsorbed, more refractory, halogenated organic materials which are present in the Ruhr River only in very low concentrations. GAC column performances at Dohne are being followed closely, not only by DOC, UV and UV/DOC ratios, but also by TOCl and TOClN analyses. As long as the rate of DOC removal remains constant at 33 to 50% and there is no indication of TOCl, TOClN or bacterial breakthroughs, Dohne plant management does not plan to regenerate the GAC, at least during the first two years of use.

SAND FILTER OPERATIONS

Dohne's 4 sand filters (before the GAC contactors) are 3.9 m diameter, 30 m long cylinders, with sand 1.6 m deep and fed with ozonized then oxygenated water at the rate of 11 m/hr (9 to 10 minutes EBCT). Before ozonation was incorporated into the process, the running time of these filters was 2 days, then backwashing was required because of increased head loss. Since ozonation has been installed, however, the running times have increased to 7 days. Furthermore, the indicator of backwashing need during 1978 no longer was head loss, but rather breakthrough of turbidity (0.4 to 0.8 FTU before sand filtration -- 0.1 FTU after). When the turbidity of the filtered water rises above 0.2 FTU, the filters are backwashed. Breakthrough of turbidity rather than head loss is the reason that Dohne has installed turbidity monitors after sand filtration (Jekel, 1978b).

In December, 1978, however, Dohne plant management planned to change the sand filters, because it wants to control this sand filtration step by head loss, not by turbidity breakthrough. The new filters will be composed of dual carbon media. The lower layer will be hydroanthracite and the upper layer will be a light density granular activated carbon. This light density GAC is a filtration medium, and has very poor adsorption qualities.

During the summer of 1978, "a population explosion of nematodes" was observed to have developed both in the rapid sand filters and in the following GAC adsorbers at the Dohne plant. These growths were shown to have been caused by the extended intervals between backwashes, during which the nematodes developed. When the backwashing cycles were reduced to 3 days (just below the time of reproduction of these microorganisms), the nematode problem disappeared (Heilker, 1979).

GAC COLUMN BACKWASHING

Dohne's GAC contactor columns are backwashed first with air to loosen the biomass which tends to cause GAC particles to stick together at times. After loosening the mass with air, water alone is pumped through the columns at the rate of 27 to 30 m/hr. The time between backwashings is controlled by head loss through the columns. Because of the fact that there are four different granular activated carbons being tested in the Dohne plant, backwashing frequencies of the four GAC contactors are not the same. Each GAC has a different grain size, and head loss buildup occurs at a different rate for each of the four contactors. On the average, however, backwashing was being performed every 10 to 14 days during early 1978. However, because of the development of nematodes (see above), the backwashing time subsequently has been lowered to 3 days (Heilker, 1979).

Turbidity of the water after the GAC contactors ranges from 0.1 to 0.2 FTU, and averages 0.14 FTU.

The four activated carbons being studied in the Dohne plant have different adsorption capacities, which were determined during the pilot plant testing program. The full-scale plant 4 meter virgin GAC columns were started up during the winter of 1977, when water temperatures were below 8°C for the first 3 to 4 months of operation. As a result, bacterial growth buildup was very slow in the GAC media. This was confirmed by the data of Table 100, which show low levels of CO_2 being produced during this period.

During backwashing, only small amounts of carbon fines are removed. These had not been sufficient to require the addition of any makeup GAC during the first 7 months of plant operation.

No buildup of slimes has been observed at the Dohne plant in either the sand filters or in the GAC contactors during the first 7 months of operation. Neither were slimes observed during the 2 year pilot plant study. Therefore, it can be concluded that the pretreatment steps, including ozonation, prevent the buildup of such detrimental materials.

BACTERIAL TESTING

Table 102 shows bacterial count data obtained at various points in the Dohne plant process. It is clear from these data that the GAC effluents from the old GAC columns contained considerable biological activity. After 5 months of use, effluents from virgin GAC columns showed much lower bacterial counts. However, it is equally clear that E. coli are not present in the effluents from columns containing old or new GAC. Two groups of European microbiologists (KIWA -- The Netherlands and Univ. of Saarlands -- Federal Republic of Germany) agree that E. coli cannot survive in the GAC columns in the presence of the other strains of water and soil bacteria which are present.

TABLE 102. BACTERIAL COUNT DATA AT DOHNE PLANT WITH BAC TREATMENT PROCESS

Sampling Point	With Old GAC* Total Counts/ml		E. coli/100 ml		April, 1978 (new GAC)** counts/ml	E. coli/100 ml
	M_g	σ_g	M_g	σ_g		
Raw water	14,490	2.0	1,620	1.7	20,000	---
After flocln + sediment.	2,340	4.2	6.7	3.2	20,000	---
After sand filt.	6,010	4.9	<< 1	---	90	0
After GAC	3,700	4.0	<< 1	---	57	0
After ground passage	27	2.3	<< 1	---	22	2.2***

M_g = geometric mean σ_g = geometric standard deviation

* Source: Sontheimer et al., 1978

** Source: Heilker, 1978, Private Communication

*** About 20% of the water present after ground passage comes from infiltration from the Ruhr River. This infiltrated water is the source of the E. colis found.

The Dohne plant waters are analyzed routinely for total bacterial counts, E. coli and algae in the raw water, filtered water, after ozonation, after GAC and after ground passage. Raw water from the Ruhr River is analyzed once each day and groundwater stations are analyzed once each week.

COSTS

Substantial cost data were obtained during visitation to the Dohne plant in June, 1978. These will be presented in three sections: (a) Costs For Enlarging GAC Contactors And For GAC, (b) Costs For Ozonation Equipment and (c) General Cost Data, which include Costs For Plant Operations and rates charged to water customers.

Costs for Enlarging GAC Contactors and for GAC

The originally installed GAC contactors (which provided a 2 m depth of GAC) were enlarged in late 1977. Plant management had planned for this eventuality when the original GAC contactors were installed, and had designed the building and associated appurtenances to be able to accomodate the enlarged GAC depths. Currently, the four GAC contactors are 5 m in diameter and 8.5 m high. The current depth of GAC contained in each contactor is 4 meters.

Enlargement of the four GAC contactors was completed at a cost of 300,000 Deutsch marks (DM) ($150,000 at an exchange rate of 2 DM/$), including necessary modifications to the building. On the other hand, four new GAC contactors of the current size at the Dohne plant would have cost an estimated 600,000 DM ($300,000). A single new GAC contactor would have cost approximately 250,000 DM ($125,000) on a turnkey basis.

In addition, 450,000 DM ($225,000) were expended for the purchase of 320 cubic meters (about 100 metric tons) of GAC to charge these contactors with virgin GAC in November, 1977. The GAC cost represents an average of about 75¢/lb, but it should be remembered that four different granular activated carbons have been installed at Dohne, and the price for any one of these four may differ slightly from the others.

The RWW utility managers expect to reactivate spent GAC on a two year cycle, based upon pilot plant results obtained using the new ozonation process. This compares with a conservatively estimated maximum bed life of 6 months, were the 4 m deep GAC columns to have been used with the plant being operated by the old treatment process. The 2 meter deep GAC columns actually used in the old process had to be regenerated every 6 to 8 weeks.

In 1978, the Dohne plant was using double the amount of GAC than it did with the old process. However, because of the extended GAC reactivation cycle, the RWW management was not considering the purchase of a furnace for on-site reactivation. The cost for reactivating the entire plant stock of GAC is about 180,000 DM ($90,000), or slightly less than 1,000 DM ($500) per ton of GAC reactivated. Transportation to the reactivation site is the largest fraction of this cost. The firm which provides the reactivation service also supplies the truck, but Dohne plant labor is used to unload GAC from the columns and load it onto the truck. The beds of GAC are fluidized with water for removal, then the carbon is pumped as a slurry to the truck. When the 2 m deep GAC columns were reactivated, unloading the columns and transferring the truck was accomplished by 2 men in 2 hours. The RWW manager hopes that the labor required to unload and transfer GAC from the 4 m deep columns will be less than double this figure.

The Dohne GAC contactors have only required backwashing every two weeks since the 4 meter depths of activated carbon were installed in November, 1977. With the old treatment process, the 2 meter deep GAC columns required backwashing every week and the sand filters were backwashed every 24 to 48 hours. Backwashing of the sand filters since switching to the new process (same sand filter sizes as when used in the old process) now is required only on a weekly basis. These extended backwashing cycles are attributed largely to the new ozonation process. It had been hoped that extended backwashing times would have provided substantial cost savings both in pumping costs and in wastewater treatment charges. However, the nematode problem arose, which necessitated lowering the backwashing times to every 3 days, in order to avoid their development.

Ozonation System Costs

The capital cost of the total ozonation system for the Dohne plant was 2,200,000 DM in 1976. This figure includes air compressors and driers, ozone generators, associated piping and control instrumentation and construction of the ozone contact chambers. The ozone generation capacity is 8 kg/hr (422 lbs/day), which provides for ozone dosages of 3.5 to 5 mg/l, depending upon the rate of water flow through the plant.

The energy demand of the ozone generation system at Dohne is 20 kwhr/kg of ozone generated, or 9.1 kwhr/lb. It was not clear whether this figure includes electricity used by the air preparation unit. If not, an additional 21% (1.9 kwhr/lb)* should be added. This would result in a total energy demand of 11 kwhr/lb for air preparation and ozone generation. An additional 1.8 kwhr/lb* of energy is required by the ozone contact system (diffusers plus off-gas recycling to the preozonation step). This makes a grand total of 12.8 kwhrs/lb of ozone generated and applied. [The figures of 1.9 and 1.8 kwhr/lb required for air preparation and ozone contacting, respectively, were obtained from a questionnaire completed by The RWW during 1977 (see Miller et al., 1978)].

Although the addition of ozonation to the Dohne water treatment process involved a capital cost of 2,200,000 DM ($1,100,000) and an increase in purchased electricity, 5,086 kwhrs/day (523 to 755 DM; $262 to $378 at 0.09 to 0.13 DM/kwhr local power cost), these increased costs have been offset by several operating cost savings:

1) Much less chlorine is used in the new process than in the old process. A minimum of 96% of the chlorine formerly required (1,059 to 5,295 lbs/day) has been eliminated.

2) A reduction in labor force by 7 or 8 persons for an estimated total annual savings of 300,000 DM ($150,000).

3) The GAC reactivation cycle has been extended from a conservatively estimated hypothetical 6 months to a projected minimum of two years -- an annualized savings of just over 600,000 DM ($300,000)/year in GAC reactivation costs alone.

Although individual items of cost savings can be deduced by comparing the old and new treatment processes, other modifications of the process required increases in costs. Heilker (1979) summarized the cost comparisons for water treatment at the Dohne plant by the old and by the new processes and made the following ststement:

"The treatment plants in the Dohne waterworks have been operating for more than 1.5 years using the revised process. The drinking water quality has been significantly improved without increasing treatment costs. The Dohne plant is less susceptible to disturbance and as a result can be operated with 50% of the former staff size. The activated carbon filter runs are 3 to 5 times longer than before."

In addition to the Dohne plant, the Rheinisch-Westfälischen Wasserwerksgesellschaft mbH also owns and operates several other plants near Mülheim. Based upon the performance and cost benefits obtained using the ozone/GAC process at the Dohne plant, two other plants have been redesigned and are being modified to use the ozone/GAC process for both plants. Completion and startup of these plants is expected during 1979.

Bids were received in early 1978 for the ozonation equipment for both new plants. The larger of the two plants requires a 36 kg/hr (1,900 lbs/day) ozone generation system which cost 2.9 million DM ($1.45 MM). This price included all related hardware, such as the air preparation equipment, ozone generators, turbines (for first stage ozonation), contacting (for second stage ozonation), associated instrumentation and controls and contactor off-gas destruction equipment. On the other hand, this price does not include the second stage ozone contact chambers or buildings.

The ozonation system at the smaller plant will generate 14 kg/hr (739 lbs/day) and has been purchased for 1.6 million DM ($800,000). This price included and excluded the same items as the larger plant, but was described as a more complicated installation requiring more piping at several points in the water treatment system.

In Table 103 cost figures and ozone generation capacities are compared for the three RWW ozone installations discussed above. It is evident that economies of scale result in lower costs per unit of ozone generation at the larger installation. However, site-specific factors (such as the need for relatively more piping at the smaller plant) also affect the cost/lb of ozone generation capacity/day.

General Cost Data

Residential customers of the RWW in Mülheim were charged 0.89 DM/cu m of water supplied during 1978. This is somewhat lower than the rate charged by other major German municipalities. At the exchange rate prevailing during June, 1978 (slightly under 2 DM/$), this rate converts to about $1.65/1,000 gallons.

Costs of treatment plant operation at Dohne were described by RWW management as falling into three catagories -- treatment, distribution and pumping (for both treatment and distribution). These categories account for, respectively, 21%, 46% and 33% of total operating costs. A breakdown of the costs within each of these categories is included in Table 104. Several interesting conclusions can be drawn from these data in comparing German treatment practice at the Dohne plant of Mülheim with typical United States practices. Treatment costs of 21% are a relatively low percentage of

TABLE 103. COSTS FOR OZONATION SYSTEMS* IN MÜLHEIM, FEDERAL REPUBLIC OF GERMANY

Plant	Ozone Generation Capacity			Capital Cost	Cap Cost of Ozone Generation	
	kg/hr	kg/day	lbs/day	MM of DM	DM/kg/day	$/lb/day*
Dohne	8	192	423	2.2 (1976)***	11,458	2,600
"A"	14	336	741	1.6 (1978)	4,762	1,080
"B"	36	854	1,905	2.9 (1978)	3,356	761

* includes cost of air preparation, ozone generation, turbine contacting, contactor off-gas treatment, controls, but no contact chambers.

** at an exchange rate of 2 DM/$

*** includes building costs

total costs. Labor also represents a smaller part of the total. On the other hand, costs related to capital (interest and depreciation) are high. Taken together, these three observations show that a more capital-intensive system is used at Dohne, which relies less on labor than is typical in United States plants.

TABLE 104. BREAKDOWN OF COSTS AT DOHNE PLANT, MÜLHEIM, FRG

Category of Cost	Treatment (21% of Total)	Distribution (46% of Total)	Pumping (33% of Total)
Labor	10%	10%	32%
Energy	15%	1%	36%
Materials	17%	2%	1%
Taxes	2%	7%(a) 16%(b)	1%
Depreciation (c)	17%	29%	17%
Interest (d)	39%	35%	13%
	100%	100%	100%

Notes:

(a) Property taxes to local communities
(b) Taxes to authorities providing raw water supply
(c) Includes capital set aside for future building
(d) Interest costs estimated to be 5 to 6%

Cost of water to Mülheim's residential customers averaged 89 pfennigs/-cu m (1.68¢/1,000 gallons) in 1978. Power costs are 9 to 13 pf/kwhr (4.5 to 6.5¢/kwhr) at Dohne, but are lower at other Mülheim plants where power is generated on-site. The RWW did not raise the price of water to their customers when the BAC process went on-stream in 1977.

Labor costs at Dohne are 2,800 DM ($1,400)/month. Dohne currently employs 10 machine operators (2/shift) + 1 plumber.

FUTURE PLANS AT MÜLHEIM

Based upon the successful incorporation of the BAC process into the Dohne plant, the RWW management is incorporating the process into two additional plants which also draw Ruhr River water. These plants will process 72,000 and 25,000 cu m/day of drinking water.

Both processes will be nearly identical to the current Dohne process, except that ground passage of treated water will be eliminated. Ground passage could be eliminated at Dohne now, from a treated water quality point of view, but will be retained to act as a storage reservoir. In addition, a Superpulsator will be used at the smaller plant instead of the Pulsator, because the newer equipment can be used at much higher upflow rates (12 m/hr).

Additionally, the sand filters at Dohne were scheduled to be replaced in December, 1978 with dual media filters. These were to be hydroanthracite (0.6 to 1.2 mm particle size) covered with a layer of light density (2 to 3 mm particle size) GAC (which has very little adsorption capability. The reason for this change is to allow backwashing of the filters to be controlled by headloss rather than by turbidity, which is the present control mechanism.

APPENDIX F

ROTTERDAM, THE NETHERLANDS -- KRALINGEN WATER TREATMENT PLANT

Background

The new Kralingen plant became operational in March, 1977. It was constructed to replace the older Honingerdijk plant which dated back to 1874. Raw water for the Kralingen plant is supplied by the River Maas through two Biesbosch storage reservoirs. An alternate water source is the Berenplaat storage reservoir and, under emergency conditions, River Rhine water may be drawn through the Nieuwe Maas emergency intake. Figure 109 shows the Kralingen plant water sources.

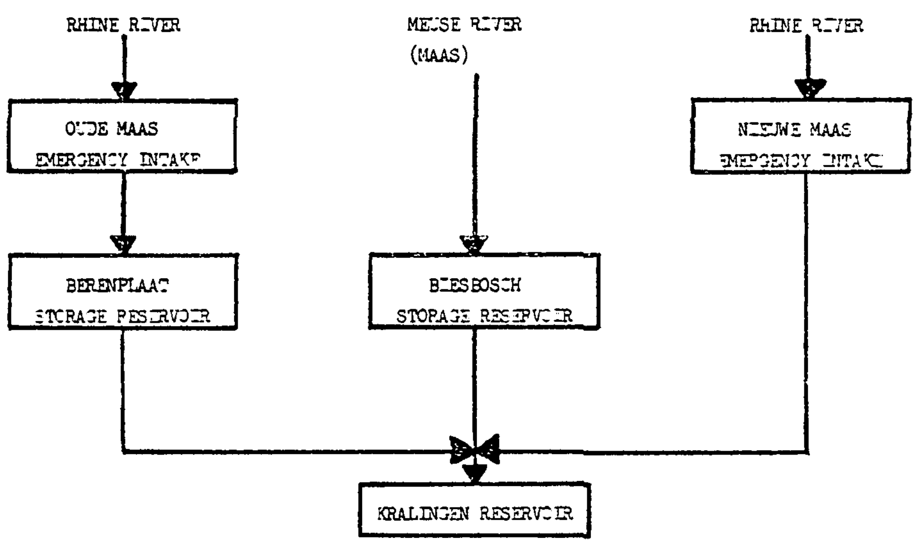


Figure 109. Kralingen (Rotterdam) plant water sources.

The Kralingen plant is of interest to students of European water treatment practices for a number of reasons, including the following:

1) Kralingen is a totally new plant which incorporates the latest knowledge of water treatment processes,

2) Being recently constructed, Kralingen provides contemporary cost information,

3) Kralingen incorporates a high level of process monitoring for organic chemicals, especially trihalomethanes, due to the interest in these problems by Dr. Johannes J. Rook, Chief Chemist. Dr. Rook is a pioneer in studying and identifying the mechanisms of formation of trihalomethanes in drinking water. Dr. Rook's basic objective is to minimize the amount of chlorine used in treating Rotterdam's surface water supplies, while producing high quality finished drinking water.

The Biesbosch Reservoirs

These two reservoirs store River Maas water, which flows sequentially through the first reservoir, then the second. Each reservoir is 20 meters deep and the two provide a combined retention time of three months. This storage time equalizes wide variations in River Maas flows, which are especially affected by the annual Spring thawing of snows.

The second reservoir has been fitted with aeration devices, primarily for the control of algae, to prevent stratification, to promote biological decomposition of dissolved organic materials and to promote conversion of ammonia to nitrate ion by nitrification. Ammonia levels in the reservoir influent from the Maas are as high as 4.5 mg/l during winter months, but this usually drops to less than 1 mg/l during the 90-day reservoir storage in winter and to zero during summer. Coliform levels drop to about 10% of their influent levels during the first 30 days of storage in these reservoirs.

Promotion of aerobic biological activity in the Biesbosch reservoirs incorporates biological pretreatment into the Kralingen plant treatment scheme.

The cost for installing these two reservoirs was equal to the cost for installing the Kralingen treatment plant itself (see cost section).

Water flows from the Biesbosch reservoirs to the Kralingen plant through a 20 kilometer long transmission line which requires 15 hours residence time. The Kralingen plant is designed to operate without prechlorination, however unacceptable head losses occur in the transmission line when water temperatures exceed 10°C during summer months. This is due to buildup of biological growths in the main. Therefore, up to 4 mg/l of chlorine is added at the reservoir to control biogrowths in the transmission line during summer periods. Prechlorination dosage is controlled by monitoring head loss in the transmission main. Nominal prechlorination dosage is set at 1 mg/l, but when head losses increase, more chlorine is added. Prechlorination at the reservoir for protecting the transmission line is referred to as "transport chlorination".

Prechlorination is not required during winter months when the water temperatures are below 10°C. Therefore, trihalomethanes are produced at Kralingen only during summer periods when transport chlorination must be practiced.

The Kralingen Treatment Plant

The site of the Kralingen plant is adjacent to that of the old Honingerdijk plant, as this is the focal point of the Rotterdam water supply system. Transmission mains and the Nieuwe Maas intake previously used by the Honingerdijk plant can be used by Kralingen.

Process selection was based on a lengthy (about 2 years) semi-industrial scale pilot plant study. Figure 110 shows details of the individual process steps and Table 105 summarizes the number of operational units and their capacities for each process step.

Low lift pumps draw water from the raw water storage reservoir at the end of the 20 km transmission line from the Biesbosch reservoirs. Iron sulfate coagulant is added in static mixers prior to discharge to flocculation, which is achieved in a 4-compartment unit utilizing horizontal shaft paddle mixers. The flocculated water is clarified in 55° lamella settlers (Parkson process).

Clarified water flows to a 5-minute retention time, aspirating turbine, ozone contacting chamber, and subsequently to an 11-minute retention time tank. A design dosage of 3 mg/l of ozone is added to produce a residual dissolved ozone level of approximately 0.4 mg/l in the water emerging from the contactor. However, the ozonation step is controlled by monitoring the level of ozone in the contactor off-gases at the level of 1 g of ozone/cu meter. This is done because Kralingen plant personnel have more confidence in being able to monitor ozone in the gaseous phase than in solution. Ozone is analyzed in both phases spectrophotometrically (with a Sigrist unit), but in solution a film of oxidized (by ozone) micropollutants gradually builds up which interferes with light transmission and results in inaccurate readings.

Ozone in the contactor off-gases is destroyed in heated catalytic units.

Ozonized water flows to multi-media filters (20 cm of anthracite on sand, supported on gravel) at a rate of 15 to 20 cu m/sq m/hr (m/hr). Filter backwashing is provided by air, then water backwash, when the headloss reaches a maximum of 1.5 meter.

Filtered water is pumped from the dual media compartment filter clearwell below the filters by medium lift pumps to the pressurized GAC columns. Filter and GAC column backwash water also is drawn from the filter clearwell. A depth of 4 meters of GAC is provided in the twelve, 8-meter high, 6-meter diameter, cylindical steel GAC contactors. These GAC contactors are constructed of carbon steel with a special proprietary coating on the inside surfaces. The GAC is supported by a coated steel plate with plastic nozzles inset in the plate for flow distribution. A 10-minute empty bed contact time is provided in the GAC contactors.

Backwashing of GAC columns is conducted about once/week by using the filter backwash pumps. The process is controlled by head loss of 5 m WC.

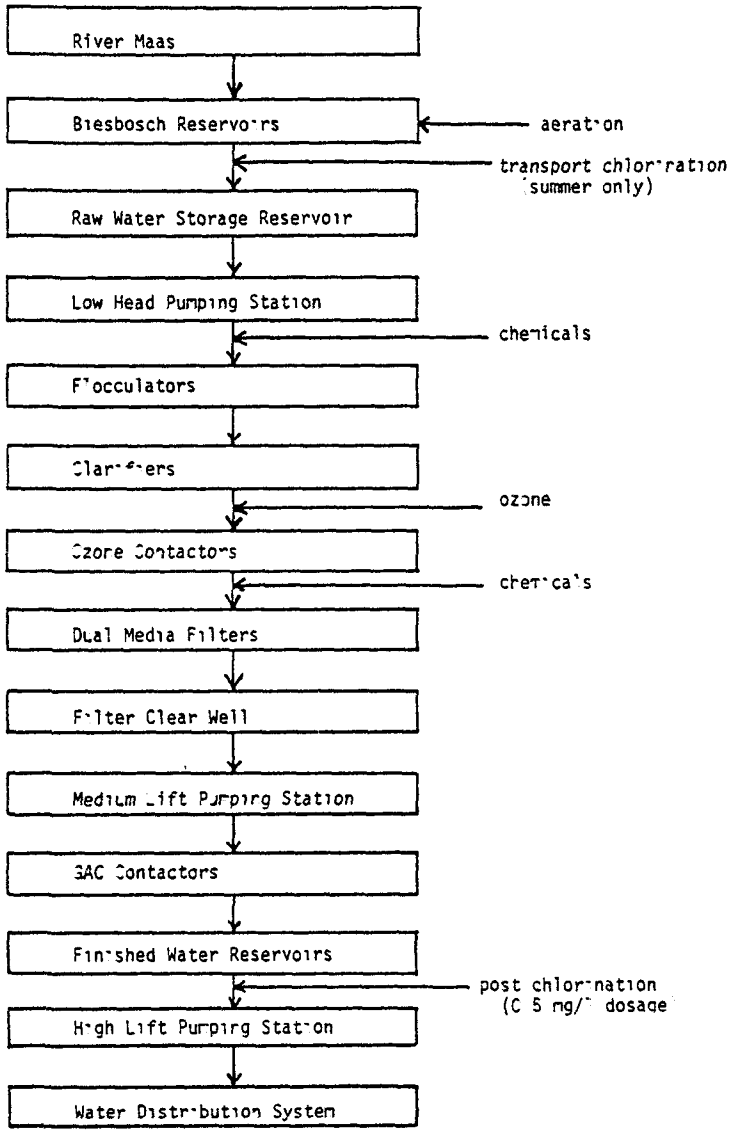


Figure 110. Process flow diagram of the Kralingen water treatment plant, Rotterdam, The Netherlands.

TABLE 105. DESCRIPTION OF TREATMENT PROCESS UNITS AT KRALINGEN PLANT

description of unit	capacity of unit	number of operational units	number of backup units
raw water storage basin:	87,984 m^3	1	--
low lift pumping station:			
constant speed	1.5 m^3/sec	1	--
variable speed	1.5 m^3/sec	1	2
coagulation: static mixer	1.94 m^3/sec	1	1
flocculation: four compartment, horizontal shaft, paddle flocculators	0.4 m^3/sec	5	1
clarifiers: lamella (Parkson process) separators	0.4 m^3/sec	5	1
ozonation: single stage, 5-minute retention time, aspirating turbine	0.4 m^3/sec	5	1
holding tank	0.4 m^3/sec	5	1
filtration: dual media (0.8 m sand, 0.8 m anthracite). Unit filter area -- 36 m^2		10	2
medium lift pumping station:			
medium lift pumps	1 m^3/sec	1	3
filter & GAC backwash pumps	1 m^3/sec	1	3
GAC contactors: 10 minute EBCT, 4 m GAC depth; unit filter area = 28.1 m^2	0.194 m^3/sec	10	2
finished water storage reservoirs	30,000 m^3	2	--
high lift pumping station: pumps	0.83 m^3/sec	6	2

The GAC in the columns is manufactured by Norit (currently Super, Normal and mixed Super/Normal) and leased from Norit. Spent GAC is returned to the Norit plant, some 20 miles distant, for reactivation. Any losses of the leased GAC during backwashing or transportation to Norit are charged to the Kralingen plant at the rate of 1,300 Dutch gilders/cu m.

During the plant visitation (June, 1978), only 8 of the GAC columns were being used. Of the eight, seven were scheduled to be on-line at any one time, with the GAC from the eighth column being regenerated at the Norit plant. Currently, GAC regeneration is expected to be required every one to two years, based on chemical laboratory analyses being developed by Dr. Rook (see later section).

Water flows from the GAC columns to above-ground, enclosed finished water reservoirs having a capacity of 30,000 cu m. High lift pumps draw from the reservoirs and discharge to the Rotterdam distribution system. Prior to storage, the processed water is treated with chlorine to attain a free residual of 0.1 to 0.2 mg/l, which normally requires chlorine dosages (total of 0.3 to 0.6 mg/l). During summer, a peak chlorine dosage of 1 mg/l is required to attain these chlorine residuals. At the extremities of the distribution system, total chlorine residual is zero to 0.1 mg/l.

Water Quality

Table 106 lists typical water analyses obtained during January, 1978. Biesbosch raw water analyses after entry into the plant but prior to treatment are shown as "raw water". Finished water analyses are made after residual chlorination. It should be noted that influent CCD and TOC levels of 8 and 4 mg/l were lowered to 4 and 2.8 mg/l, respectively, by the Kralingen treatment process. Dr. Rook believes COD to be a better parameter for monitoring effectiveness of GAC adsorption efficiency than is TOC.

Trihalomethane Production & Removal by GAC

Several well-known papers by Dr. Rook detail his pioneering studies on the formation of trihalomethanes in Rotterdam drinking water. These papers are cited in the bibliography section of this report. In addition, Dr. Rook provided the unpublished data of Table 107, which show that removal of THM precursors by the Kralingen water treatment process (ozonation followed by GAC adsorption) is efficient only with virgin (or freshly regenerated) activated carbon. From June through November, 1977 prechlorination of Biesbosch reservoir water was practiced at levels of 4 mg/l. Total THM levels over this period averaged 108 microg/l in the plant influent, 72 microg/l before ozonation and 71 microg/l after ozonation.

Without GAC adsorption and following 0.5 mg/l post-chlorination dosage, TTHM levels in ozonized water were 100 microg/l. With virgin GAC and post-chlorination, TTHM levels in ozonized water dropped to 17.5 microg/l, but with 4-month old GAC, TTHM levels in ozonized and post-chlorinated waters rose to 61 microg/l.

TABLE 106. ANALYSIS OF RAW AND FINISHED WATERS AT KRALINGEN, JANUARY 1978

parameter	raw water*			finished water		
	min.	avg.	max.	min.	avg.	max.
color, mg Pt/l	9	12	14	<1	<1	1
temperature, °C	5.5	6.0	7.5	5.5	6.0	7.5
turbidity, JTU	0.60	1.6	3.9	0.05	0.10	0.25
$KMnO_4$ demand, mg/l	10	11	12	3	4	5
nitrite, mg/l	0.019	0.050	0.070	--	0.000	--
nitrate, mg/l	18.5	18.8	19.0	19.5	19.9	20.0
sulfate, mg/l	78	83	90	113	116	119
NH_4^+ saline, mg/l	0.20	0.26	0.33	0.04	0.06	0.11
NH_4^+ albuminoid, mg/l	0.17	0.20	0.22	0.09	0.11	0.13
Fe, mg/l	0.02	0.03	0.05	0.01	0.02	0.04
Mn, µg/l	6	7	9	2	3	3
DO, mg/l	11.2	12.2	12.6	11.2	12.4	13.0
phenol, µg/l	1	1	2	<1	<1	<1
detergents, µg/l	45	50	55	10	11	15
COD, mg/l	8	8	9	2	4	5
TOC, mg/l	3.5	3.9	4.1	2.2	2.8	3.7
Br, µg/l	120	125	135	60	65	80
hexachlorobenzene, µg/l	--	<0.01	--	<0.01	<0.01	<0.01
- HcH, µg/l	<0.01	<0.01	<0.01	--	--	--
- HcH, µg/l	<0.01	<0.01	<0.01	0.01	0.01	0.01
- HcH, µg/l	0.01	0.01	0.01	0.01	0.01	0.01
cholinesterase inhibitors, in parathion equivalents, µg/l	0.04	0.07	0.08	0.02	0.03	0.04

* raw water = water influent to the plant

TABLE 107. HALOFORM PRODUCTION IN KRALINGEN PLANT, JUNE 1977 - MARCH 1978

sampling point	data taken	prechlorination at reservoir	haloforms produced (microg/l)				
			$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	total THMs
plant influent	average data, June-Nov. 1977	4 mg/l	55	34	17	2	108
after coagulation, lamella settling, sand filtration & evap'n.	average data, June-Nov. 1977	4 mg/l	35	23	12	1.6	72
after 5 min. ozonation	average data, June-Nov. 1977	4 mg/l	34	24	11.3	1.8	71
no GAC + 0.5 mg/l post-chlorination		0	51	34	14	1	100
after virgin GAC + 0.5 mg/l post-chlorination		0	3.3	3.6	4.6	6.0	17.5
after 4 month old GAC + 0.5 mg/l post-chlorination		0	22	15	13	11	61

Thus Dr. Rook concludes that GAC is effective in removing THMs from his waters only for short periods of time (less than 4 months). He also concludes that once his waters have been prechlorinated, ozonation is not effective either in reducing THM concentration levels or in preventing formation of more THMs upon subsequent post-chlorination.

From July to December 1977, the chloroform levels in Kralingen plant influent water and in one GAC column effluent followed the behavior pattern shown in Figure 111. Prior to July, 1977 the plant influent water was not chlorinated, therefore chloroform levels in the plant influent were zero. Starting in July, 1977, the amount of chloroform formed immediately increased to levels of 30 to 60 microg/l. Most of this was adsorbed quickly by the GAC, but the GAC effluent quickly began to show the presence of chloroform. During September/October, 1977 the chloroform level in the GAC effluent peaked at about 15 to 20 mg/l then began to fall. When prechlorination was ceased in December, 1977, however, chloroform still was measured in the GAC effluent for several months thereafter, falling to levels near zero by March/April, 1978. A second GAC column showed the same behavior over the same period, except that the chloroform concentration in the effluent levelled off more slowly after prechlorination was ceased.

Dr. Rook concludes from these and other data that GAC adsorbs chloroform, but that desorption of chloroform begins almost immediately. After cessation of prechlorination, all chloroform measured in the GAC filtrates is present because of desorption.

Biologically Active GAC

Dr. Rook has noticed biological activity in the Kralingen GAC adsorbers, but its buildup was slow during the first year of operation. Its current contribution to the overall efficiency of the treatment process is relatively small. At water temperatures above 10°C (summer) biological activity is operative in both the double layer filters and in the GAC adsorbers. Ammonia levels of 0.3 mg/l (winter) drop to 0.10 to 0.15 mg/l by nitrification in the dual media filters. There is no ammonia in the Kralingen plant influent during summer because it is all nitrified in the Biesbosch reservoirs.

The new Kralingen plant began operation in March, 1977 with virgin GAC. Reactivation of GAC did not begin until March, 1978. With virgin GAC, effluents from the adsorbers contained 0.9 mg/l of TOC and 1 to 2 mg/l of COD (from influent values of 4 and 8 mg/l, respectively). After the second month, the GAC effluent contained 2 mg/l TOC. By January, 1978, the TOC of the GAC effluent had risen to 2.8 mg/l (62% of that in the plant influent). At the same time, the average COD level in the GAC effluent was 50% of that in the plant influent. Therefore, in terms of EPA's proposed GAC regeneration criteria (remove 50% of the influent TOC), the effective life of the Kralingen activated carbon was less than 1 year. However, this GAC performance was considered to be satisfactory at Rotterdam.

Detergent levels in the Kralingen water averaged 50 microg/l during January, 1978 and were lowered to 11 microg/l during treatment. Dr. Rook noted that new GAC removed nearly all of the detergents originally present.

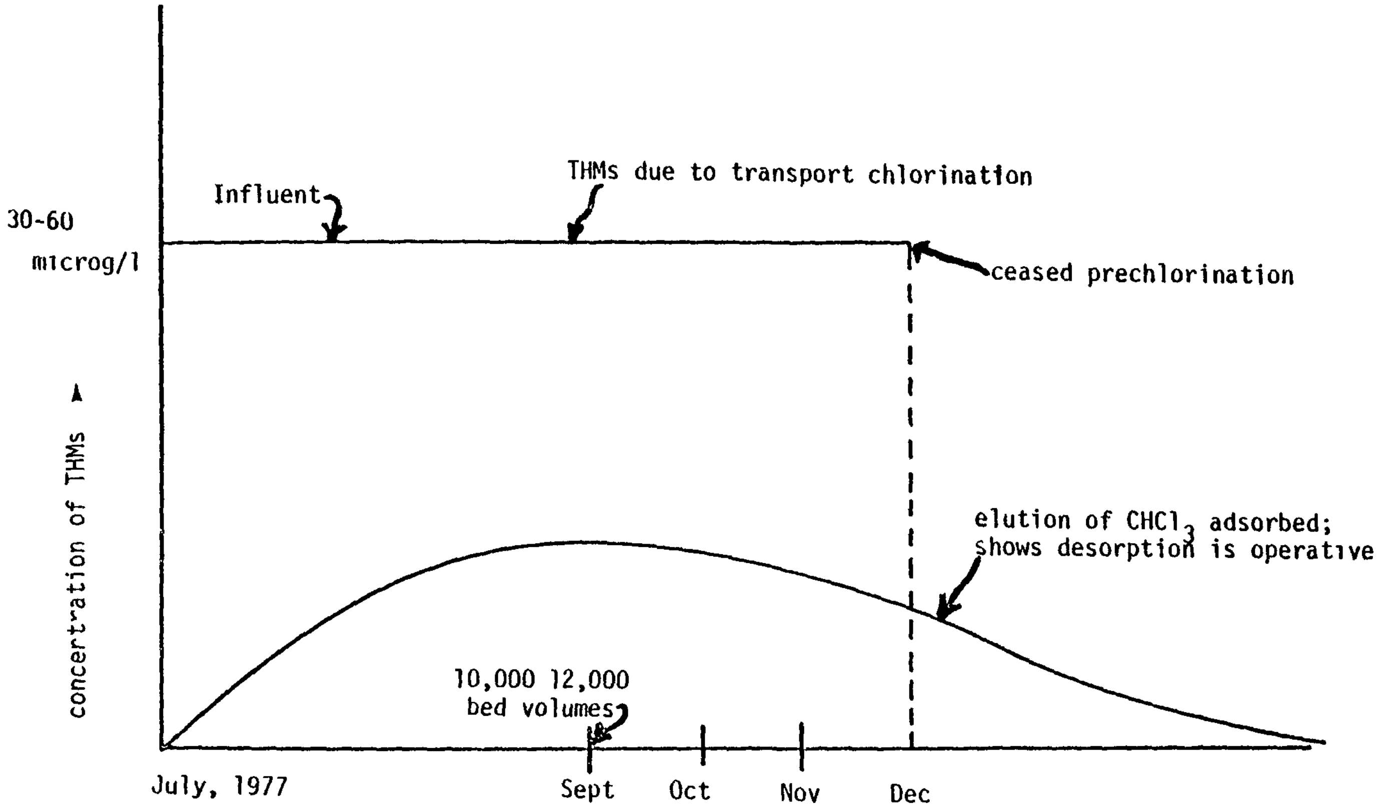


Figure 111. Desorption of trihalomethanes from GAC at Kralingen plant.

However, after some 6,0C0 bed volumes had passed through the GAC, hardly any detergent removal occurred. However, after continued passage of an additional 6,000 bed volumes of water through the same GAC, removal of detergents increased up to a level of about 50% (Figure 112). Dr. Rook believes that desorption of detergents may have been occurring during the period when no removal was apparent and that the biological activity had not yet reached a point at which biodegradation of detergents was significant. Upon continued use. however, biological degradation (and/or desorption) became responsible for the removal of about 50% of the influent detergent concentrations.

Biological activity in the Kralingen plant dual media filters and GAC adsorbers is present, but does not appear to be removing as much TOC and ammonia as at the Mülheim, Germany Dohne plant. This can be explained on the basis of the biological decomposition reactions which occur in the Biesbosch reservoirs during 90-day storage with constant aeration. During this storage period, most of the ammonia is nitrified and the readily degraded carbonaceous organic materials are decomposed in the reservoir. The balance of the TOC and COD which is removed in the Kralingen plant proper is a result of flocculation, clarification, ozonation, filtration, GAC adsorption and biological degradation in the filtration media and GAC adsorbers.

GAC Regeneration Parameters

Dr. Rook began sending the Kralingen GAC out for regeneration in March, 1978 (one or two columns at a time). However, he believes that even though the GAC may be passing relatively high levels of TOC through it in the form of dissolved organic materials which are not strongly adsorbed by GAC (or are easily desorbed), the less polar, more strongly adsorbed halogenated organic materials of concern still are being adsorbed. This belief is based upon work which had been conducted on Rhine River waters by the Engler-Bunte Institute of the University of Karlsruhe, Germany.

As a result, Dr. Rook has been developing analytical procedures for the measurement of chlorinated organic materials. TOCl and DOCl analyses are conducted following the Engler-Bunte Institute procedures. In addition, an "Ether-extractable Organic Chlorine" (EOCl) analysis has been developed by Dr. Rook. This extraction procedure employs petroleum ether (30°C boiling point) for extracting GAC effluent. As soon as the level of EOCl rises significantly, Dr. Rook plans to regenerate the particular GAC column(s) involved.

The March, 1978 GAC regeneration was based on TOC rise in the GAC effluent. However, as of June, 1978, regeneration now will be based on a maximum level of TOCl and/or EOCl. These parameters for GAC regeneration may be changed in the future by Dr. Rook as more data are gathered regarding the Kralingen plant performance.

Colony Counts

Table 1C8 lists representative colony counts/ml obtained during March, 1978 and May, 1978. There is little question that counts are low after the

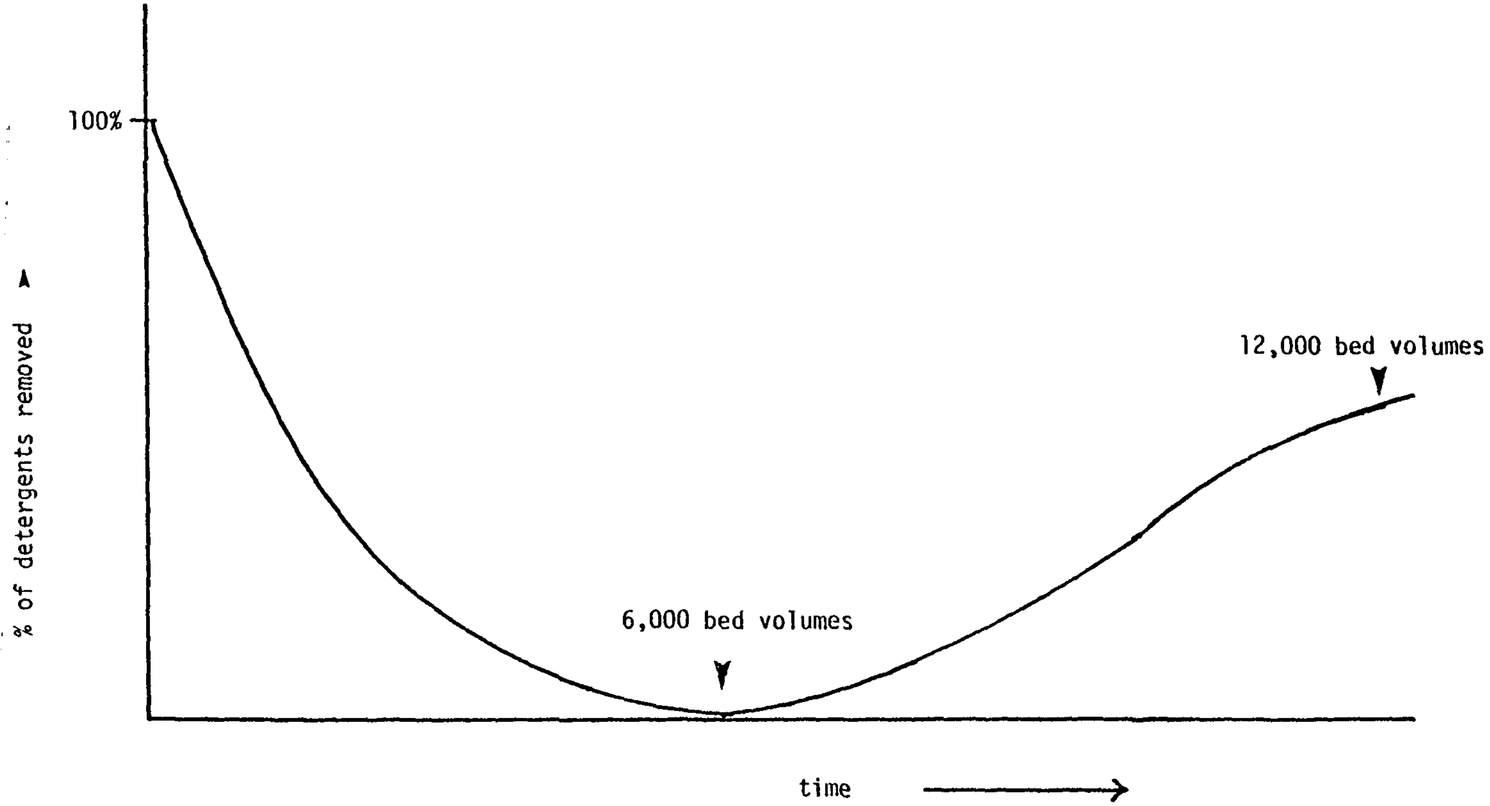


Figure 112. Removal of detergents by Kralingen plant GAC.

TABLE 108. REPRESENTATIVE COLONY COUNT DATA AT KRALINGEN PLANT

sampling point	data obtained during	no. of samples	colony counts/ml*	no. of samples having counts of			
				0/ml	1-10/ml	10-100/ml	100-1,000/ml
reservoir - before chlorination	March 1978	123	--	109	12	2	--
reservoir - after chlorination	March 1978	122	--	64	32	24	2 (av. 500)
plant influent	March 1978		19-20				
after lamella settling	March 1978		7				
after ozonation	March 1978		3				
after GAC	March 1978		10				
plant influent	May 1978		150				
after lamella settling	May 1978		2,000-5,000				
after ozonation	May 1978		70				
after sand filtration	May 1978		10,900				
after GAC	May 1978		5,800				

* incubated at 22°C; grown on agar

ozonation step but high after GAC adsorption. However, the post-chlorination step (0.5 mg/l chlorine dosage) lowers plate counts in the Kralingen product water to levels which meet the required public health standards.

Capital Costs And Financing

The Kralingen plant was completed in 1977 at a total capital cost of 170 million Dutch gilders, stated in April, 1978 values. Since the Rotterdam accounting procedure includes the statement of all assets in estimated current market values, figures were quoted to the site visitation team and are discussed below in April, 1978 values. The market exchange rate during June, 1978 was approximately 2.1 Dutch gilders per U.S. dollar. Hence, the Kralingen plant cost $81 million.

Table 109 breaks down the capital costs of the components of the plant; the figures are in millions of Dutch gilders and in U.S. dollars.

TABLE 109. CAPITAL COSTS OF KRALINGEN PLANT

Cost Categories	April 1978 values (millions of Dutch gilders)	millions of $ US
General items (land purchase, engineering, financing, overhead, architects, city planning fee, etc.)	40	19.05
Service building (offices, laboratory, mechanical workshop, pilot plant)	24	11.43
Streets, landscaping	12	5.71
Storage reservoir for raw water, pumping station	5	2.38
Emergency inlet pump station	2	0.95
Treatment plant (see separate breakdown of components)	46	21.90
Carbon facilities (excluding GAC)	7	3.33
Finished water storage tanks	9	4.29
High lift pumps	6	2.86
Shelter facilities for war emergencies	1	0.48
Items unaccounted for	18	8.57
TOTAL	170	80.95

Additional information was provided on the costs of each component of the treatment plant itself. The elements making up the total of 46 MM gilders are shown in Table 110.

TABLE 110. TREATMENT COMPONENTS AT THE KRALINGEN PLANT

Plant Component	April 1978 values (millions of Dutch gilders)	millions of $ US
Construction - concrete portions	13.5	6.43
Piping	1.8	0.86
Heating, cooling, ventilation	1.9	0.90
Electrical	2.2	1.05
Chemicals - initial stock	3.7	1.76
Electrical installations for chemical dosing and metering	2.1	1.00
Coagulation	1.2	0.57
Sedimentation	3.0	1.43
Sludge treatment & drying	0.1	0.05
Ozonation equipment*	4.3	2.05
Filtration	3.4	1.62
Medium lift pump station	2.2	1.05
Control system - automation	7.0	3.33
TOTAL	46.4	22.10

* includes air preparation, ozone generation, turbine contactors and off-gas destruction equipment

These costs were financed by the authority through funds drawn from general revenues rather than through issuance of new debt. Since it is a stock company owned by the city of Rotterdam, the water authority incorporates its capital needs with those of the city and acquires funds in this way. In return, the water company pays for the cost of this capital in the form of "interest" and depreciation payments to the city in future years. For the Kralingen plant, that annual payment is 7 MM gilders ($3.33 MM) annually, for a plant presently worth 170 MM gilders ($81 MM), about 4% per year for the current worth of the plant and a higher percentage of its original cost.

The total gross assets for the water company were 540 MM gilders ($257 MM) in April, 1978 values. Including the new plant less accumulated depreciation of 140 MM gilders ($66.67 MM), net assets totalled 400 MM gilders ($190.5 MM). Hence the new plant was a large portion -- about 75% -- of the net assets of the company existing before its construction. Such a large capital program would strain the capabilities of utilities lacking the resources and city ownership which Rotterdam enjoys.

Annual Operating Costs

In this section are discussed first the operating costs of the Kralingen plant and then a breakdown of the overall system operating costs. The plant costs are based only on general categories of expenses, while the system costs are based on the generalized steps in water supply from raw water procurement to treatment and distribution.

The operating costs of the plant total about 7 MM Dutch gilders ($3.33 MM) annually. Table 111 presents an approximate breakdown of these costs.

TABLE 111. ANNUAL OPERATING COSTS OF KRALINGEN PLANT

Cost Category	millions of Dutch gilders	millions of $ US
Wages - management & technical staff	0.9	0.43
Wages - operators	1.0	0.48
Maintenance	2.5	1.19
Utilities	1.2	0.57
Chemicals	0.5	0.24
Miscellaneous	0.9	0.23
TOTAL	7.0	3.34

In addition to the 7 MM gilders for operating the Kralingen plant, the water company pays 7 MM gilders to the City of Rotterdam to cover the cost of the capital funds provided for the construction of the plant. Hence, a total of 14 MM gilders ($6.67 MM) is required annually to cover the full plant costs. On a unit basis, assuming average annual production from the plant of about 120,000 cu m/day (32 mgd), these total treatment costs amount to 1.20 gilders/1,000 gallons, or 57¢(U.S.)/1,000 gallons.

Water treatment, however, is only one part of the total process of potable water supply. For the entire Rotterdam system, plant treatment costs about 30 MM gilders ($14.29 MM), or only about 26% of the total costs of potable water supply. The Kralingen plant costs of 14 MM gilders ($6.67 MM) represent 47% of this total, while the plant provides about 38% of the system production. Table 112 presents a breakdown of the Rotterdam system annual costs, excluding costs associated with a distilled water plant which offsets its own operating expenses with separate revenues.

TABLE 112. ANNUAL KRALINGEN WATER SYSTEM COSTS

cost category	costs in millions of Dutch gilders	% of total	millions of $ US
Raw water - procurement & reservoirs	41	35%	19.52
Treatment/production	30	26%	14.29
Distribution	32	27%	15.24
Administration & laboratory	5	4%	2.38
City use of water	6	5%	2.86
Other	4	3%	1.90
TOTALS	118	100%	56.19

Company Revenues And Rates

The Rotterdam City Council establishes the rates to be charged for water. The stated intent of this rate-setting authority is to cover fully all of the costs of providing water services.

The total revenues in 1977 were 112 MM gilders ($53.33 MM), which is slightly less than the operating expenses shown above due to the unbilled provision of water to the city itself. The total amount of water delivered during the year was 118 MM cu m (31,175.6 million gallons), at a calculated average rate of C.95 gilder/cu m ($1.20/1,000 gal). Table 113 shows these totals and a breakdown by class of service.

Since the water system serves 1.1 million people on a direct retail and a wholesale basis, the usage and revenues per person served can be calculated from these figures. The usage is 59 cu m/person/year, which converts to 42 gallons/capita/day. At the assumed rate of 1.16 gilders/cu m ($1.46/1,000 gal), this amounts to about 70 gilders ($33.33)/person/year, or about 23 gilders ($10.95)/month for a family of four.

TABLE 113. ROTTERDAM WATER SYSTEM REVENUES, WATER DELIVERIES AND RATES

use category	revenues - millions of Dutch gilders	deliveries - millions of cu m	calculated rates, gilders per cu m	US $ per 1,COO gal
Residential	49.7	42.8	1.16	1.46
Industrial	45.0	51.0	0.88	1.11
Wholesale	14.6	22.4	0.65	0.82
City use & unaccounted for	2.4	1.4	----	----
TOTAL	111.7	117.6	0.95	$1.195