INTRODUCTORY SECTIONS

WATER TREATMENT PROCESS MODIFICATIONS FOR TRIHALOMETHANE CONTROL AND ORGANIC SUBSTANCES IN THE OHIO RIVER

OHIO RIVER VALLEY WATER SANITATION COMMISSION

prepared in cooperation with

Beaver Falls Authority
Cincinnati Water Works
Evansville Water Works
Fox Chapel Authority
Huntington Water Corporation
Louisville Water Company
Municipal Authority of the Borough of West View
Pittsburgh Department of Water
Western Pennsylvania Water Company
Wheeling Water Department
Wilkinsburg-Penn Joint Water Authority

and U. S. Environmental Protection Agency

Guidance in the startup phase of the project was provided by the *Steering Committee:*

F. T. Bess, Union Carbide, ORSANCO Chemical Industry Committee
Don T. Duke, Louisville Water Company, ORSANCO Water Users Committee
James Erb, Pennsylvania Department of Environmental Resources, Public Water Supply Agencies of Commission member states
Michael J. Taras, American Water Works Association Research Foundation
James Finger, USEPA Region IV
Edward C. Kispert, Cincinnati Water Works, ORSANCO Water Users Committee
Dr. Pasquale Scarpino, University of Cincinnati
Jack DeMarco, USEPA Water Supply Research Division

The Commission's *Water Users Committee* provided essential support, expertise, and commitment from the project's planning stages through its realization:

Charles Andrews, Beaver Falls Municipal Authority
Clifford Angelo, U. S. Geological Survey
Albert Campbell, Wheeling Water Treatment Plant
Lloyd N. Clausing, Portsmouth Water Treatment Plant
Don Close, Cincinnati River Forecast Center
Joseph Dinkel, West View Water Authority
Don Duke, Louisville Water Company
Victor Fender, Covington Water Works
Robert Hagy, American Cyanamid Company
Mahlon Henderson, Evansville Water Works
Thomas W. Holbrook, Huntington Water Corporation
A. C. Huston, E. I. Dupont deNemours
C. R. Johnson, American Electric Power Service Corporation
James King, Procter & Gamble Company
Edward C. Kispert, Cincinnati Water Works
Harry McFarland, Wilkinsburg-Penn Joint Water Authority
W. T. McKenna, American Cyanamid Company
William Mayberry, Indiana-Kentucky Electric Corporation
John C. Miller, City of Pittsburgh Water Department
William Neuman, Western Pennsylvania Water Company

Project Staff:

Robert J. Boes, Project Director
Richard J. Miltner, Principal Investigator (November 1977 through April 1979), Project Engineer (November 1976 through October 1977)
Bill G. Razor, Principal Investigator (November 1976 through October 1977)
Bonnie Barger Cummins, Project Scientist
Sarah B. Dirr, Project Secretary
Robert C. Kroner, Consultant

Walter A. Feige, Dr. Harry D. Nash and Jack DeMarco, USEPA Project Officers

WATER TREATMENT PROCESS MODIFICATIONS FOR TRIHALOMETHANE CONTROL AND ORGANIC SUBSTANCES IN THE OHIO RIVER

INTRODUCTORY SECTIONS

August, 1979

Ohio River Valley Water Sanitation Commission
414 Walnut Street Cincinnati, Ohio

ABSTRACT

Plant-scale studies at seven water utilities using the Ohio, Allegheny, Beaver, and Monongahela Rivers as their source of supply evaluated various water treatment process modifications for both the control of trihalomethane levels and the modifications' impact on bacteriological quality of the finished water. Process modifications studied, based on comprehensive organic analysis, included relocation of the chlorine application point, chlorination/ammoniation, partial or complete substitution of chlorine dioxide for chlorine, and placement of four different types of virgin granular activated carbons in filter beds. Supplemental studies included organic analysis of monthly raw and finished water samples collected for a one-year period at each of 11 participating water utilities. In addition to providing plant facilities and personnel, the 11 utilities joined USEPA in funding this project, which was conducted by the Ohio River Valley Water Sanitation Commission.

This report was prepared in fulfillment of USEPA Grant R-804615 for project activities for the period October 1976 to August 1979.

DISCLAIMER

CONTENTS

CONTENTS

ACKNOWLEDGMENTS

The Commission is especially appreciative of the efforts of the superintendents, directors and managers of the participating water utilities, who assisted in development, financing and conduct of the project. Special thanks is accorded the water utility personnel, who devoted many hours to the operation of the project.

- Fox Chapel Authority
  - Melvin Hook; Reginald Adams and Thomas Stehle (Reginald Adams Laboratory, Pittsburgh, Pennsylvania)
- Wilkinsburg-Penn Joint Water Authority
  - Harold McFarland, Dennis Beck
- Pittsburgh Department of Water
  - John Miller, John Beck and staff
- Western Pennsylvania Water Company
  - William Neuman, Michael Burns and staff
- West View Water Authority
  - Joseph Dinkel
- Beaver Falls Authority
  - Frank Richter and staff
- Wheeling Water Department
  - Albert Campbell and staff
- Huntington Water Corporation
  - Thomas Holbrook and staff
- Cincinnati Water Works
  - Richard Miller, Edward Kispert and staff
- Louisville Water Company
  - Frank Campbell, Don Duke and staff
- Evansville Water Works
  - Mahlon Henderson and Matthew Rexing

The cooperation of Radian Corporation of Austin, Texas, contributed to the success of the project. Individuals who merit special acknowledgment are Dr. Donald Rosebrook and Dr. Lawrence Keith; Dr. Kenneth Lee, David Present and the gas chromatography staff; and Dr. Robert Spraggins and the mass spectrometry staff.

The comprehensive task of preparing the initial draft report was carried out by Richard J. Miltner, Principal Investigator, and Bonnie Barger Cummins, Project Scientist, under the general direction of the Project Director, Robert J. Boes.

SECTION 1

INTRODUCTION

BACKGROUND

In 1974 and 1975, surveys and studies reported the identification of trihalomethanes and other organic compounds in the public drinking water supplies in the Ohio River Valley and nationwide.[1-3] Some compounds were present in rivers that were the water sources for water utilities, and trihalomethanes and other compounds were formed during the water treatment process.

Because of increasing concern about these organic compounds, the Ohio River Valley Water Sanitation Commission (ORSANCO) and its Water Users Committee, representatives of public and industrial water supply systems using the Ohio River and major tributaries as their source, developed a cooperative project to evaluate treatment process modifications for the control of trihalomethanes and analyze the utilities' raw and finished waters for organic substances. The project established a program to be operated by the Commission with the assistance of eleven water utilities, who pledged both financial support and use of their water treatment facilities and personnel. The U. S. Environmental Protection Agency (USEPA) awarded the Commission a research grant for the project in October 1976.

PARTICIPATING UTILITIES

The project utilities (Figure 1) were:

Evansville Water Department, Indiana
Louisville Water Company, Kentucky
Cincinnati Water Works, Ohio
Huntington Water Corporation, West Virginia
Wheeling Water Department, West Virginia
Beaver Falls Authority, Pennsylvania
Municipal Authority of the Borough of West View, Pennsylvania
Western Pennsylvania Water Company, Pennsylvania
Pittsburgh Department of Water, Pennsylvania
Wilkinsburg-Penn Joint Water Authority, Pennsylvania
Fox Chapel Authority, Pennsylvania

OBJECTIVES

The first of two major objectives was the investigation and evaluation of modifications of water treatment practices for the control of trihalomethanes.

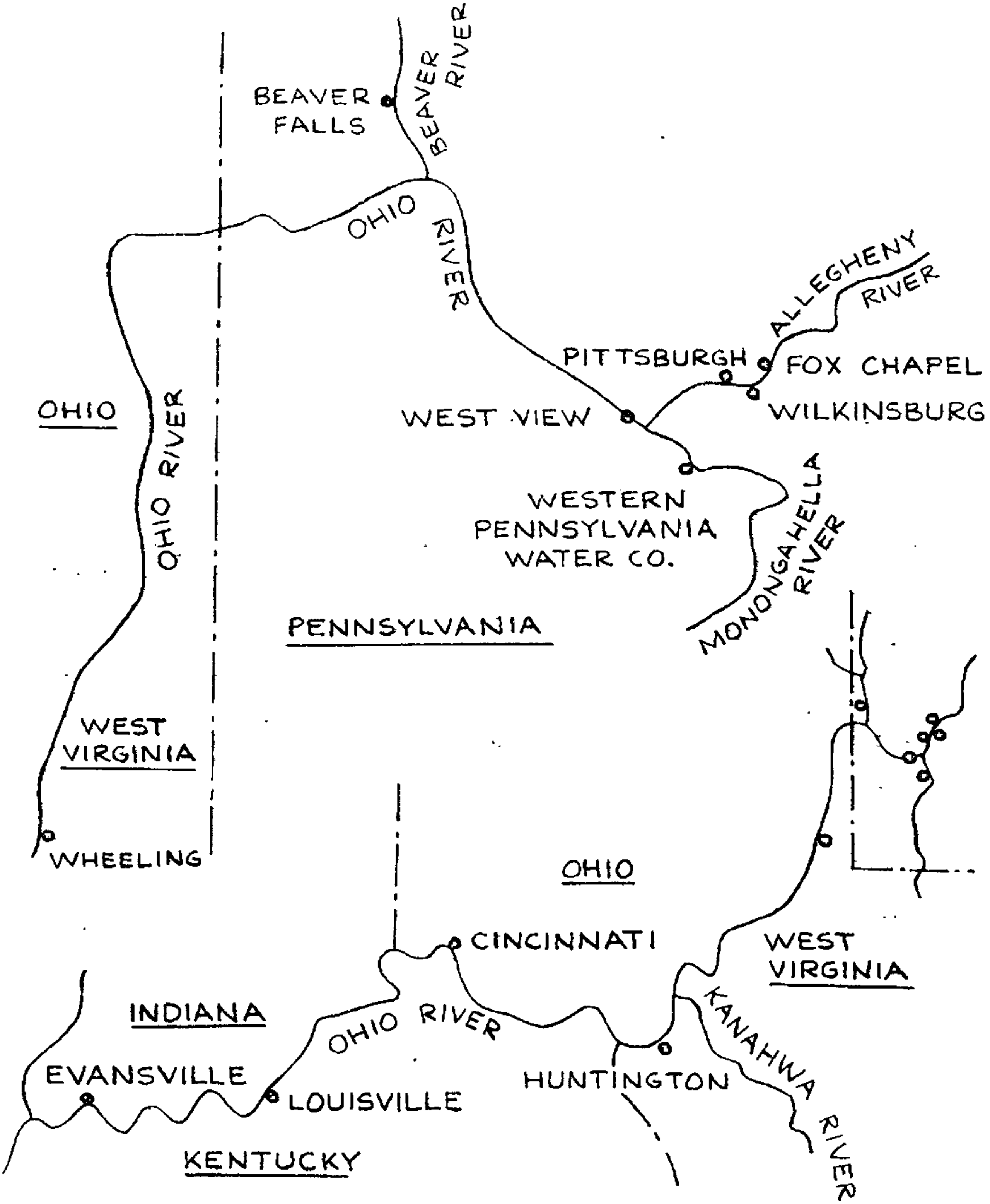

Figure 1. Utility locations.

These control studies were based on bench scale and pilot plant studies done by USEPA to investigate, sample for and control trihalomethanes.[4-7] This objective also included an investigation of bacteriological levels to ensure that treatment modifications designed to lower trihalomethane concentrations were not compromising finished water quality.

The second major objective was the determination of the levels of trihalomethanes and other selected organic compounds in raw and finished waters at all project utilities for one year. Other compounds for investigation were selected from a list designated by USEPA as organic Priority Pollutants for which an analytical protocol was available.[8]

CONTRACT LABORATORY

A laboratory service contract was awarded to the Radian Corporation, Austin, Texas, after a review of proposals from several private laboratories detailing analytical costs and capabilities for performing gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) analyses for selected organic Priority Pollutants.

SCOPE OF WORK

Early in the project, members of the staff visited each participating water utility to study its treatment practices and to determine the level of participation by each utility. Minimum participation included monthly sampling for organic analyses of raw and finished waters for one year, and measurement and reporting of several background water quality parameters. Participation in trihalomethane control studies included: sampling of raw, in-plant, and finished waters for organic analysis several times a week for periods ranging from four weeks to several months; determination of levels of routine physical, chemical, and bacteriological water quality parameters for each sampling location; and reporting of hydraulic, maintenance, and operation data during routine and modified treatment (Sections 5 and 6).

Monthly sampling began at all 11 utilities in July 1977 and continued through June 1978. Trihalomethane control studies at seven of the utilities began in July 1977 and concluded in November 1978. The project staff worked with each utility to coordinate sampling schedules and shipment to the contract laboratory and to follow the progress at those utilities involved in trihalomethane control studies.

The staff worked with Radian Corporation personnel to develop GC and GC/MS quality control programs, coordinate organic analyses and shipment of sample bottles to the utilities, and review the progress of organic analyses. This review led to changes in some analytical procedures and the implementation of a more rigorous quality assurance program. (Laboratory procedures and quality assurance programs are described in Section 5 and Appendices A, B, D, G and I.)

The project staff reviewed, interpreted and compiled all organic data received from the contract laboratory and all data received from the utility laboratories (Sections 6 and 7). Utility personnel collected a total of 3,446 samples for organic analyses of which 2,950 produced usable chromatograms or mass spectra. Data from about 500 samples were not available because of damage in shipment, damage at the contract laboratory, headspace development in volatile samples, samples not analyzed, and data not usable for reasons including occasional loss of GC sensitivity or deviation from routine GC operating conditions.

SECTION 2

CONCLUSIONS

The following conclusions are based on findings summarized in this section. They apply to raw and finished water in the treatment plant but not to the water in the distribution system.

1. Trihalomethanes are formed during the treatment of surface water when free chlorine is present for significant periods of time.

2. Modifications of the chlorination process which may be viable trihalomethane control methods include: relocation of the initial chlorine application to a location where treatment has reduced the precursor concentration; ammoniation to convert free to combined chlorine; and chlorine dioxide as an alternative to chlorine as the initial disinfectant.

3. Granular activated carbon (GAC) used in place of sand in the gravity filters (filtration/adsorption) may be an effective trihalomethane control process for approximately two months; however, periodic GAC reactivation is necessary if GAC is to be used for trihalomethane control for extended periods of time.

4. Evaluation of the effectiveness of treatment process modification for trihalomethane control should include determination of instantaneous and terminal trihalomethane concentrations and the trihalomethane formation potential (a measure of precursor concentration) to aid in defining changing precursor levels in the raw water and in determining the effects of treatment on precursor removal and trihalomethane formation.

5. Total coliform and standard plate count levels should be determined routinely on in-process and finished water samples to ensure that process modification for trihalomethane control has not adversely affected bacteriological levels in the treated water.

6. Process modification for trihalomethane control should extend over a period of time adequate to determine short-term, seasonal and other variations in raw water precursor concentrations, bacterial levels, and other water quality parameters, and to evaluate the effects of these variations on the quality of the treated water.

7. For the evaluation of raw, in-process, and finished water quality, a complete and continuing quality assurance program is necessary to ensure the accuracy and precision of the analytical procedures and the resulting data for trihalomethanes and other organic compounds.

8. Chloroform and other trihalomethanes were detected in many raw and all treated surface water samples. At most utilities, the reaction between precursor and free chlorine resulted in significant increases in trihalomethane concentrations. Other compounds occasionally present in raw and treated water samples included carbon tetrachloride, dichlorobenzene isomers, 1,2,4-trichlorobenzene, 1,2-dichloromethane and several polyaromatic hydrocarbons.

9. Analytical procedures more sensitive than those employed for project samples (lower detection levels generally 0.1 to 0.2 ug/L) would be necessary to evaluate the removal of organic compounds, other than trihalomethanes, by normal or modified water treatment processes.

SUMMARY OF FINDINGS

The following summarizes the results of the treatment process modification studies and the analysis of raw and finished water monthly samples.

Trihalomethanes

Chloroform was present in the majority of untreated surface water samples at levels generally less than 1 ug/L; bromodichloromethane and dibromochloromethane were present less frequently, with most levels below 0.1 ug/L; bromoform and dichloroiodomethane were not present above 0.1 ug/L.

Trihalomethanes were formed during water treatment in the presence of free chlorine. Trihalomethane levels in treated water (clear well effluent) varied seasonally, with the lowest levels occurring during the winter and the highest levels during the summer. The levels also varied with each utility's treatment. Total trihalomethane (TTHM) levels for finished surface waters ranged from 2 ug/L at one utility in February to 240 ug/L at another utility in August. Finished water total trihalomethane levels at West View, a groundwater source, did not exceed 2 ug/L. For ten utilities treating surface water, trihalomethane levels in finished waters were:

	Concentration, ug/L	
	Mean Annual	Maximum
Chloroform	35	180
Bromodichloromethane	13	54
Dibromochloromethane	5.6	33
Bromoform	0.4	4.4
Dichloroiodomethane	0.1	1.0
Total trihalomethanes	54	--

Relatively higher concentrations of brominated trihalomethanes resulted in finished water when the in-plant reaction time with free chlorine was reduced.

All finished waters contained unreacted trihalomethane precursor as measured by trihalomethane formation potential (THMFP). Data averaged from ten utilities treating surface water indicated that 23% of raw water THMFP was converted to total trihalomethane during treatment, 37% of raw water THMFP was removed by treatment, and 40% of raw water THMFP was passed into the distribution system. Reduction in terminal TTHM concentrations generally coincided with reduction in turbidity levels.

Trihalomethane Treatability

Moving the point of initial chlorine application to a location where treatment had reduced precursor levels resulted in decreased instantaneous trihalomethane concentrations in the finished water, because a better quality water, in terms of reduced THMFP, was chlorinated. The reduction of precursor-chlorine reaction time was also a factor in the decreased trihalomethane formation.

In studies at Pittsburgh and Wheeling, significant reduction in bacterial densities occurred in unchlorinated waters when potassium permanganate was fed with other chemicals prior to flocculation and settling.

At Pittsburgh, Wheeling and Cincinnati, moving the initial chlorine application point caused a delay in reduction of bacterial densities, but the bacterial quality of the finished waters was maintained.

The Louisville study showed that when sufficient ammonia was applied to in-plant waters to convert free chlorine to combined chlorine, little or no further trihalomethane formation resulted. The bacterial quality of the finished water was satisfactory; ammoniation followed three hours of free chlorine contact time. At the Western Pennsylvania Water Company's Hays Mine Plant, only very low levels of trihalomethane were formed when raw water ammonia levels were such that no free chlorine resulted from raw water chlorination.

The study at the Western Pennsylvania Water Company also showed that little or no trihalomethanes were formed when chlorine dioxide was fed to the raw water in place of chlorine. Although 1.5 mg/L chlorine dioxide was not as effective as 2.6 mg/L chlorine in reducing raw water bacteria levels, clear well chlorination provided adequate disinfection. Chlorine dioxide was generated from sodium chlorite and hydrochloric acid at an 80% yield and with only limited formation (less than 5%) of free chlorine. Although 60 to 70% of the chlorine dioxide reacted with substances in the water forming chlorite ion, flocculation, settling and filtration through two-and-one-half year old GAC reduced the residual chlorite concentration in the treated water to less than 0.1 mg/L.

The effects of individual treatment materials, including powdered activated carbon (PAC), potassium permanganate or chlorine dioxide, on precursor levels could not be determined, because all of the chemicals are generally added at a single point prior to flocculation and settling.

During summer months at Huntington and Beaver Falls, virgin granular activated carbon (GAC) operated in the filtration/adsorption mode in beds designed for sand filtration was exhausted for the removal of chloroform at seven to 15 weeks of operation, for bromodichloromethane at eight to 15 weeks of operation, for dibromochloromethane at eight to 15 weeks of operation, for total trihalomethane at seven to 15 weeks of operation, and for THMFP at seven to 12 weeks of operation. Time to exhaustion was different for each utility and type of GAC used. GAC filter/adsorbers passed carbon tetrachloride at concentrations that could not be differentiated from influent concentrations after four to seven months of operation, and 1,4-dichlorobenzene at concentrations that could not be differentiated from influent concentrations after five to 12 weeks of operation.

At Huntington and the Western Pennsylvania Water Company, GAC filter/adsorbers which had been in service for one to two-and-one-half years were exhausted for the removal of chloroform, bromodichloromethane, dibromochloromethane, and instantaneous TTHM.

Desorption from GAC filter/adsorbers was observed. GAC in use for one to two-and-one-half years at Huntington desorbed carbon tetrachloride. When GAC influent trihalomethane concentrations were significantly reduced, two-and-one-half year old GAC desorbed trihalomethanes at the Western Pennsylvania Water Company, and GACs in service for five months desorbed trihalomethanes at Beaver Falls.

In three studies (Huntington, Beaver Falls and Western Pennsylvania Water Company) bacterial densities in GAC effluent waters exceeded densities in GAC influent waters when water temperatures exceeded 10°C. The bacterial quality of the finished waters was satisfactory with clear well chlorination.

Other Organic Compounds

Carbon tetrachloride was occasionally present at concentrations from 0.1 to 0.6 ug/L in raw water at and downstream from Huntington. Carbon tetrachloride was occasionally present at 0.1 to 6 ug/L concentrations in finished surface waters at all of the utilities. Its presence in finished waters was probably attributable to contamination of chlorine used for disinfection.

Chlorobenzene was occasionally present in Huntington's raw and treated water at concentrations up to 1 ug/L. It was not found in untreated or finished waters upstream from Huntington. It was frequently found in West View's untreated groundwater at concentrations reaching 3.9 ug/L. After a reported upstream spill, chlorobenzene was found at 8.5 ug/L in a finished surface water.

During the winter months, polyaromatic hydrocarbons (PAHs)--naphthalene, acenaphthylene, acenaphthene, fluorene, fluoranthene, pyrene, and phenanthrene and/or anthracene--were present in raw and finished waters at concentrations above 0.1 ug/L. Some GAC filter/adsorbers appeared to be effective in removal of the PAHs.

Dichlorobenzene isomers were occasionally present in raw and finished waters at levels above 0.2 ug/L. They were more frequently detected at and downstream from Huntington. During a reported upstream spill, 1,4-dichlorobenzene was found in a treated surface water at a concentration of approximately 11 ug/L.

1,2,4-Trichlorobenzene was occasionally present in raw and finished waters at levels greater than 0.2 ug/L. It was more frequently found at and downstream from Cincinnati.

Unidentified halocarbons were detected in chlorinated waters but these compounds were rarely found in raw waters. These may have been chlorination products or may have resulted from contamination of chlorine used for disinfection.

1,2-Dichloroethane, 1,2-dichloropropane, and 1,1-dichloroethane were occasionally present in raw and finished waters at concentrations of 0.1 to 1 ug/L.

Tetrachloroethylene was found in Allegheny River water at approximately 60 ug/L as a result of what appeared to be an upstream spill.

Other specific organic Priority Pollutants were not present or were rarely present at or above their lower detection levels in raw and finished waters.

SECTION 3

AREAS FOR FURTHER STUDY

During the winter months, several polyaromatic hydrocarbons were identified in raw and finished waters at most project utilities. Further research into the presence and concentration of these compounds and effective treatment methods for their removal is needed.

Several Priority Pollutant halocarbons were identified at and downstream from Huntington, West Virginia. Organic analyses of Kanawha River samples collected for another project indicated that these halocarbons in the Ohio River at Huntington originated from the Kanawha River. A comprehensive point source and river survey for these and other organic compounds in the industrialized section of the Kanawha River would provide information on specific organic compounds to be considered in renewal of NPDES permits.

Carbon tetrachloride and unidentified halocarbons may have been introduced to treated waters as a result of chlorine contamination. Chlorine manufacturing processes should be investigated and procedures for control of contamination by carbon tetrachloride and possibly by other halocarbons should be considered.

Unidentified halocarbons were found in chlorinated waters that were rarely found in raw waters and may be chlorination products. Continuing research to identify chlorination products other than trihalomethanes is needed.

When water temperatures exceeded 10°C, bacterial densities in GAC filter effluents were higher than in GAC influents at three utilities using GAC for filtration/adsorption. Comprehensive studies of the nature of this increase in bacterial densities and the development of methods to control bacterial levels in GAC effluent are suggested.

Project utilities typically feed powdered activated carbon and potassium permanganate during treatment. This project was not able to evaluate the full-scale effects of these chemicals on trihalomethane control but their effects at typical feed rates should be studied.

This project was not able to evaluate the full-scale effect of applied chlorine dioxide on precursor levels. Further study of the effect of reasonable feed rates of chlorine dioxide on the resulting chlorine species and the nature of resulting organic compounds is needed.

MEMBERS OF THE COMMISSION*

ILLINOIS
R. S. Engelbrecht, Ph. D., Professor of Environmental Engineering, University of Illinois
Daniel Malkovich, Editor and Publisher, *Outdoor Illinois*
Michael P. Mauzy, Director, Illinois Environmental Protection Agency

INDIANA
Robert A. Holt, Chairman, Stream Pollution Control Board
William T. Paynter, M. D., State Health Commissioner
Ralph C. Pickard, Assistant Commissioner for Environmental Health, Indiana State Board of Health

KENTUCKY
Frank C. Campbell, Vice President and Chief Engineer, Louisville Water Company
Eugene F. Mooney, Secretary, Department for Natural Resources and Environmental Protection
Frank L. Stanonis, Ph. D., Professor, Geology and Geography, Indiana State University

NEW YORK
Robert L. Barber, Assistant Professor of Government and Economics, Jamestown Community College
Robert F. Flacke, Commissioner, Department of Environmental Conservation
(Vacancy)

OHIO
Christine M. Carlson, League of Women Voters
Lloyd N. Clausing, Director of Utilities, City of Portsmouth
James F. McAvoy, Director, Ohio Environmental Protection Agency

PENNSYLVANIA
Wesley E. Gilbertson
Clifford L. Jones, Secretary, Department of Environmental Resources
Gail Rockwood, Vice Chairperson, Citizens Advisory Council to the Pennsylvania Department of Environmental Resources

VIRGINIA
Warren L. Braun, State Water Control Board
Millard B. Rice, State Water Control Board
Kenneth B. Rollins, State Water Control Board

WEST VIRGINIA
Edgar N. Henry, Director, West Virginia Water Development Authority
George E. Pickett, M. D., M. P. H., State Director of Health
(Vacancy)

UNITED STATES GOVERNMENT
Richard C. Armstrong, Chief, Engineering Division, U. S. Army Engineer Division, Ohio River
Norman H. Beamer
John C. White, Regional Administrator, Region IV, U. S. Environmental Protection Agency

OFFICERS
Warren L. Braun, Chairman
R. S. Engelbrecht, Ph. D., Vice Chairman
Eugene F. Mooney, Secretary
Albert J. Brooks, Treasurer
Leo Weaver, Executive Director and Chief Engineer

LEGAL COUNSEL
Leonard A. Weakley, Taft, Stettinius & Hollister

EXECUTIVE DIRECTOR AND CHIEF ENGINEER EMERITUS
Edward J. Cleary

---

* As of June, 1979