The work upon which this document is based was supported in part by the Office of Water Research and Technology, U. S. Department of the Interior, under the provisions of Public Law 88-379, as amended.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
</tr>
<tr>
<td>DIRECTOR'S STATEMENT</td>
</tr>
<tr>
<td>EXAMPLES OF RESEARCH FINDINGS AND THEIR ACTUAL OR POTENTIAL APPLICATION TO WATER RESOURCE PROBLEMS</td>
</tr>
</tbody>
</table>

## ANNUAL ALLOTMENT PROJECTS

<table>
<thead>
<tr>
<th>A-002-DC</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-002-DC</td>
<td>9</td>
</tr>
</tbody>
</table>

## MATCHING GRANT PROJECTS

<table>
<thead>
<tr>
<th>B-004-DC</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-006-DC</td>
<td>16</td>
</tr>
<tr>
<td>B-007-DC</td>
<td>20</td>
</tr>
<tr>
<td>B-008-DC</td>
<td>23</td>
</tr>
</tbody>
</table>
LIST OF TABLES

1. Amphoteric Materials ................................................................. 21

LIST OF FIGURES

1. Automatic storm runoff-combined sewer sampler of D. C. Environmental Services ................................................................. 4
2. Research assistant from American University sampling combined sewer line at the RFK Stadium and National Guard Armory Station ............................. 8
3. Absorbance at 630 nm vs. concentration ........................................ 11
4. Dark field photomicrograph of the suctoriant ciliate protozoan Lernaeophrya capitata showing the tentacles used to capture their ciliate prey ......................... 17
5. Several Leterotrich ciliates, Spirostomum intermedium swimming among some smaller ciliate protozoons ................................................................. 18
6. Point of rocks on the Potomac flow diff vs. critical period - RHO Least Square ....................................................................................... 26
7. Point of rocks on the Potomac flow diff vs. critical period - RHO Historic ......................................................................................... 27
8. Fredericksburg on the Rappahannock - RHO Least Square .............. 28
9. Fredericksburg on the Rappahannock - RHO Historic ....................... 29
10. Unity on the Patuxent - RHO Least Square .................................... 30
11. Unity on the Patuxent - RHO Historic ............................................ 31
DIRECTOR'S STATEMENT

The Northeastern United States Water Supply (NEWS) Study identified the Metropolitan Washington Area (MWA) as one of the areas with an uncertain water supply.

In addition to the problem of potentially insufficient water supplies, the task of ensuring water availability for drinking, recreational and industrial purposes is compounded by the pollution of existing water resources.

Point and non-point sources of pollution in the District of Columbia, such as urban land and sewer runoffs are problems for which solutions are needed. Water entering streams is a problem because it encourages aquatic growth, increases the biological oxygen demand (BOD) and has a deleterious effect on the growth of aquatic biota.

Because of the magnitude of these problems, recent research emphasis has been on rational disposal of wastewater and sludge, the recovery of usable waste and the characteristics of estuarine ecosystems. The District of Columbia has projected daily production of sludge of the order of 710 tons per day though December 1977. This date is expected to reach a peak of more than 2000 tons per day after the completion of advanced waste treatment facilities at the Blue Plains Waste Water Treatment Plant.

Also, water quality problems have been exacerbated by the recent discovery of organic compounds having potential carcinogenic activity in the water supplies. It was postulated that these compounds resulted from the chlorination of trace organic substances, which were not removed by the water treatment procedure.

A recent report released to the White House by the Council of Environmental Quality notes that whereas air pollution can be reduced substantially, given the present state of the arts, problems relating to water pollution still remain intractable. The report notes that the 1962 Public Health drinking water standards had to be relaxed because of a paucity of information on health effects and the absence of adequate techniques for detecting and removing organics from water resources.
Specific Thrust of Center's FY 1976 Research Program

The thrust of the Center's FY 1976 research program has been on the following problem areas:

(1) *Urban Land Development Impacts*

(2) *Predictive Water Availability Models*

(3) *Diffuse Sources of Contaminants Organic Residues*

(4) *Estuarine Ecosystems.*

Matching Grant Project B-004-DC relates to the problem area, Urban Land Development Impacts. The objectives of this project are to study the runoff coefficients as used in the rational method, particularly its variability with rainfall frequencies and to establish an objective method for determining this factor so that it is representative of actual watershed-rainfall conditions.

Matching Grant B-008-DC is concerned with predictive water availability models. In this study, the frequency and occurrence of drought are investigated using a Markov persistence model. The results obtained from this study will have potential for use in the design of reservoirs.

Estuarine ecosystem problems were addressed by Matching Grant Project B-006-DC. This project represents the first comprehensive quantitative and qualitative study of the aufwuchs community of a metropolitan river system.

Matching Grant Project B-007-DC and Annual Allotment Projects A-002-DC and A-003-DC are related to diffuse sources of contaminants-organic residue. Project A-002-DC investigates the distribution, transport and seasonal cycling of organic carbon. The results of these studies will give an indication of the amount of organic residues from point sources such as sewage treatment plants and diffuse sources such as urban and terrestrial runoff and combined sewer overflows.

Annual Allotment Project A-003-DC developed a quantitative colorimetric assay for submicrogram quantities of ammonia and primary amines found in natural as well as treated freshwater sources. The results of this study will provide a measure of the magnitude of nitrogenous pollutants emanating from diffuse and point sources.
Center's Program for the Next Five Years

The Center's research program in the next five years will continue to focus on research methods for identification and control of diffuse and point sources of pollution. In addition, the program will be expanded to include the following areas of study:

A. Analysis of diurnal peaks and troughs in the demand for and supply of water

B. Sedimentation and chemical biocide pollution

C. Assessment of waste treatment technologies

D. Institutional and legal instruments in water resources management.

EXAMPLES OF RESEARCH FINDINGS AND THEIR ACTUAL OR POTENTIAL APPLICATION TO WATER RESOURCE PROBLEMS


The goals of this study were to determine the degree of organic concentration in both point and non-point urban runoff and flooded river waters of the Potomac Basin. The results will be used by the following municipality and Federal agencies: (1) District of Columbia Environmental Services in determining which particular storm sewers and combined sewers will be allowed to overflow the Potomac River or routed to the Blue Plains Sewage Treatment Plant; (2) Interstate Commission on the Potomac River Basin to evaluate water quality; (3) National Park Service to indicate sources of organic carbon contamination; (4) U. S. Environmental Protection Agency to add to the stock of knowledge about natural loading of organic carbon in rivers and river self-purification processes.
Figure 1: Automatic storm runoff-combined sewer sampler of D. C. Environmental Services.

This is a four year project which seeks to identify to species and quantitatively study the microbiota of the Upper Potomac Estuary prior to the introduction of improved waste treatment plants envisaged for 1977. Laboratory methods will be used to count and identify monthly, samples of aufwuchs, microfauna and microflora taken from four sites of the Potomac River. These biota data will be compared to the monthly abiotic data collected from the same sites by the EPA Annapolis Field Office. In addition, links in the food webs will be constructed using direct observation, predator-prey numerical studies, microcompression of digestion chambers and radiotope tracer methods. The major goals here will be the differentiation of the biotic and abiotic controls on population numbers and species diversity, the determination of seasonal changes in species diversity and species dominance.

The results of Phase II of this project indicate some evidence that aquatic populations are adversely affected by toxin in the sewage and not by heat or other toxin in the river.

Persistence Modeling for the Potomac River. (B-008-DC)

This study is concerned with the development of a model for analyzing drought duration and probabilities in the Potomac, Patuxent and Rappahanock Rivers near Washington, D.C. The model is usually used as a screening device in reservoir design and water resource planning. This is achieved by using synthetic data to estimate statistical confidence levels associated with critical periods of drought. However, in practice, historic data shows that critical periods are usually greater in severity than can be apprehended by statistical models. This problem can be alleviated by assuming that the data are Markovian, i.e. we have a rapidly decaying function (geometric) autocovariance function-- a condition described as being of "short memory". Better still, we may assume that the data are self-similar, i.e. we have a slowly decaying, autocovariance function of "infinite memory". However, the former model does not provide a sufficient description of persistence based upon empiric observation. The latter model is expensive to implement and is still in its developmental stages. More persistence (is) built into the Markovian assumption by calculating empiric autocorrelations for 20 to 30 lags from historic data and fitting one parameter theoretic autocovariance function to the empiric autocorrelation by the method of least squares.

The results of this study could be applied nationally to quantify drought and yield probabilities more accurately.
RESEARCH PERIOD: March 1, 1975 - February 28, 1976

PRINCIPAL INVESTIGATOR
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Limnology

STUDENT ASSISTANTS Bruce M. Bortz, M. S., Biology
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Washington, D. C.

RESEARCH PROJECT ACCOMPLISHMENTS

The project sampled the Potomac and Anacostia Rivers at main channel stations on 41 dates from March 1, 1975 to February 28, 1976. Special storm runoff studies were conducted by sampling storm sewers, combined sewers, sanitary sewers, street runoff, parking lot runoff, National Parks (Rock Creek Park and the Zoo) and golf courses at very short time intervals following the onset of rainfall. Special studies were conducted to see if runoff from residential, industrial, apartments and shopping centers in different locations of the Greater Washington, D. C. area influenced organic carbon concentrations. Also, special studies were conducted investigating organic carbon concentrations during river flooding to and from crest.

PUBLICATIONS
None to date.

PROJECT STATUS

Phase I completed and final report written. The Principal Investigator has had a difficult time reducing the large quantity of field data taken into an easily readable report. Several of the Principal Investigator's colleagues have been consulted in the interpretation of the data. One section of the report, which correlates tidal influence on the concentration of organic carbon has been deleted from the report due to lack of strong statistical support,
APPLICATION OF RESEARCH RESULTS

Basically, there are five main users of the findings of this study.

1. D. C. Department of Environmental Services – The findings will be used to decide which particular storm sewers and combined sewers should not be allowed to overflow in the Potomac River and should be routed to Blue Plains Sewage Treatment Plant.

2. The Interstate Commission on the Potomac River Basin – The Commission is responsible for evaluating water quality data for the Potomac River and this data will be very helpful interpreting previous sporadic nonseasonal data.

3. The National Park Service – They will use the data from Rock Creek to pinpoint undesirable sources of organic carbon contamination.

4. U. S. Environmental Protection Agency – This data from the Potomac River greatly increases the knowledge about the natural loadings of organic carbon in Eastern U. S. rivers and of particular value is the data from the study which compares different land use practices to runoff data.

5. Academic Community – Basically, this data is very important in designing river sampling studies, because several projects were conducted to determine the capacity of the Potomac River to be able to accept high Blue Plains Sewage Plant discharges (approximately 300 million gallons/day) and to determine the number of days required (and river mile) for natural self-purification to reduce this loading of organic carbon to river background levels.

WORK REMAINING AND PROGRESS CONTEMPLATED

During next year. Fiscal Year I project completed. Final report to follow.

Fiscal Year II will begin mid-October and the project will focus on storm runoff from selected land uses. Stations have been selected to compose 14 different land use types (i.e., golf courses, parks, terrestrial areas, grass areas, shopping centers, low and high density residential areas, high rise housing, etc.).
Figure 2. Research assistants from American University sampling combined sewer line at the RFK Stadium and National Guard Armory Station.
ANALYSIS OF AMMONIA AND PRIMARY AMINES IN WATER
OWRT PROTECT NO. A-003-DC AGREEMENT NO. 14-31-0001-5052

RESEARCH PERIOD: March 1, 1976 - March 30, 1976

PRINCIPAL INVESTIGATOR
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STUDENT ASSISTANTS
Rosalind L. Gross, M. S., Chemistry
Richard D. Huhn, Chemistry
Patricia L. Thane

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Washington, D.C.

RESEARCH PROJECT ACCOMPLISHMENTS

1. Chemical Assay of Ammonia

There is a need for an inexpensive, reliable and accurate method for the analysis of ammonia as a pollutant of water since it is a primary product of biological decomposition and serves as a nutrient for undesirable organisms.

Several methods have been developed to meet this need. Most involve a direct quantification of ammonia or conversion of the ammonium ion to ammonia gas. A number of these methods suffer from being time-consuming, lacking precision, having side reactions or displaying interference from other sample components. Hence, the objective of this study was to develop a cheap, simple, reliable, specific, sensitive, and fast method of analysis of ammonia in water.

A colorimetric method was chosen for its low cost. Moaly has demonstrated that (S)-(+-)-amphetamine may be quantitatively converted to a pyrrole derivative using an excess of 2,5-dimethoxyoxoiane. The product forms a complex with p-dimethylaminocinnamaldehyde (p-DACA) having intense absorption in the visible spectral region since the dimethylamino group acts as an auxochrome, causing a bathochromic hyperchromic shift. The visible absorption of the product serves as the basis for a quantitative colorimetric assay.
A similar strategy for the analysis of ammonia was tested. The reactions are shown in Schemes 1 and 2.

Compound I is suggested as a reasonable but unproven structure for the blue complex.

The sample is treated with a minimum one hundredfold excess of 2,5-dimethoxyoxolane at 80°C in 1,2-dichloroethane containing acetic acid for 30 minutes and then the reaction mixture is allowed to cool to room temperature for 2 hours (pyrrole, the product of reaction 1 is present at this point). The resultant solution is then mixed with a minimum fifty-fold excess of g-DACA in absolute ethanol containing 60% perchloric acid and is allowed to stand at room temperature for 15 minutes (the product of reaction 2 is present at this point).

The resultant product is an intensely blue complex, $\lambda_{\text{max}}$630 nm, $\epsilon$ - 45,200 at $\sim$ 2 x 10^{-5} M concentration, which forms in a minimum of 6 minutes and has a half-life of at least 7.8 hours (approximated as a first order rate constant). Absorbance at 630 nm vs. ammonia concentration results are shown in Figure 3. Controls using authentic pyrrole in place of ammonia are also shown. The identical results within experimental error indicate that reaction 1 must be quantitative. The results were analyzed using an orthogonal polynomial least squares curve fitting program. The
Figure 3. Absorbance at 630 nm vs. concentration.

The final concentration of pyrrole (c), a measure of the original ammonia concentration after correction for dilution, is given by the equation:

\[ c = 29.44 \times 10^{-6} A^2 - 6.42 \times 10^{-8} A + 2.18 \times 10^{-8} \]

where A is the absorbance at 630 nm.

This method has a lower limit of $10^{-4}$ M total free ammonia. It is inexpensive, rapid (3 minutes per analysis), precise (2.8% standard error), and accurate. This assay is suitable for automation and the lower limit may be extended one hundredfold to $10^{-8}$ M ammonia by using a 10 cm path-length.
cell and a spectrophotometer with an expanded scale of 0 - 0.1 absorbance units.

2. **Biochemical Assay of Ammonia**

A simple colorimetric assay specific for aqueous ammonia over a broad concentration range is being developed. The method employs the measurement of nicotinamide adenine dinucleotide concentration by enzymatic cycling with a color-producing reagent which will show visible range absorption dependent on the original NAD⁺ concentration. The oxidized dinucleotide will be produced by the enzymatic reductive amination of α-ketoglutaric acid to glutamic acid with the ammonia present in the samples to be assayed for ammonia content, producing one mole of NAD⁺ for every mole of NH₃ present. The cycling reaction consists of the oxidation of ethanol to acetaldehyde by NAD⁺, catalyzed by alcohol dehydrogenase. The reduced dinucleotide is then reoxidized by phenazine methosulfate (PMS), which in turn reduces the redox reagent, 2-iodophenyl-3-nitrophenyl-5-phenyl-tetrazolium chloride (INT). The rate of absorbance increase at 503 nm (λ_max for INT formazan) is the measure of the NAD⁺ concentration. The overall process is shown schematically:

```
NH₃ → α-KG → glutamate
NADH⁺ → NAD⁺ → ethanol → ADH → acetaldehyde → NAD⁺ → NADH⁺
PMS (red) → INT (formazan, λ_max 503 nm)
```

The absorbance is measured on a Coleman-Hitachi difference spectrophotometer with reference to a sample containing no NAD⁺ (a blank reaction consisting of slow reduction of INT has been observed). A standardization curve will be prepared comparing the NAD⁺ concentration to the absorbance increase rate. Results have shown linear reaction rates on all but the smallest NAD⁺ concentrations (1.0 µg/ml) which approximate linearity. Adjustments in procedure are being investigated to accommodate even lower concentrations.
The procedure is simple and utilizes stable reagents. It shows potential for high sensitivity and good accuracy.

**PUBLICATIONS**


**PROJECT STATUS**

This project has been completed.

**APPLICATION OF RESEARCH RESULTS**

The methods being developed in this project were employed to test samples supplied by Mr. Douglas A. Hornbeck (NSF) Student Oriented Studies Program-Wallops Island salt marsh samples) and by Mr. Howard M. Kingston and Dr. Michael A. Champ (OWRT Grant Potomac River water samples above and below the Blue Plains Sewage Treatment Facility).
RESEARCH PROJECT ACCOMPLISHMENTS

The research was undertaken to study how the runoff coefficient used in the rational formula varies with rainfall frequencies. Practicing engineers have been estimating runoff as a percentage of storm rainfall, via the rational formula since its introduction and the rational formula is the basis of design required by many city and county codes. Although the experienced engineer may be reasonably successful in selecting the proper runoff coefficient required for application of the rational formula, it is extremely subjective and its use cannot be advocated without further elucidation of how the runoff coefficient varies as a function of rainfall frequency.

The research efforts to date have indicated that the runoff coefficient in the rational formula is not a constant, as is assumed by engineers, but is proportional to the rainfall frequencies. This correlation has been developed from data on watershed physical characteristics and rainfall and runoff quantities obtained from federal, state and local agencies in and around the Metropolitan Washington, D. C. area. The data management has included rainfall frequency analysis and base-flow separation in order to obtain information to define all parameters in the rational formula except the runoff coefficient.
PROJECT STATUS

Completion of final report.

APPLICATION OF RESEARCH RESULTS

Stormwater is a valuable resource which when mismanaged, may cause serious destruction. With the spread of urbanization, the difficulty in enforcing floodplain zoning, and with property values increasing at an unprecedented rate, floods of any kind are catastrophic. On the other hand, overdesign of stormwater detention facilities is an unnecessary burden on land developers and others who must bear the cost of material and labor. The results of the research project provide information, which enable design engineers in this area to size storm and combined sewers more economically and contain flood waters more effectively without the wastefulness of overdesign.
RESEARCH PROJECT ACCOMPLISHMENTS

Work on the definitive keys to the fauna of the Potomac River has been vigorously pursued. Drawings, photographs, and permanent slides were made of the Protozoa and Micrometazoa of the Potomac River. Several extensive and nearly complete literature searches, e.g., suctoria, peritrichs, Didinium, methoxychlor effects on fish, and cannibalism were completed. A new method for studying and counting activated sludge communities was discovered and applied. A radioactive tracer method for studying food chains was perfected. New designs for the microcompressor invented by the senior investigator were completed and patent procedures were pursued with the Department of the Interior. Extensive ecological and physiological studies were made on select suctorian and peritrich ciliates. The large culture collection of protozoa and micrometazoa were maintained and expanded. The major accomplishment of the year was the additional study using the two bench-scale experimental Potomac Rivers which were improved by addition of peristaltic pumps provided by the grant. The survey work, begun in February, 1976, when funding was confirmed, was plagued with continuous loss of floats. Fortunately, this situation has been corrected.

PUBLICATIONS

"Microbial Communities of the Upper Potomac Estuary: The Aufwuchs" by Donald M. Spoon. Published in April 1976 symposium volume edited by W. T. Mason and K. C. Flynn entitled "The Potomac Estuary, Biological Resources, Trends, and Options", 7 pg.


Figure 4. Dark field photomicrograph of the suctorian ciliate protozoan Lennaeophyra capitata showing the tentacles used to capture their ciliate prey.
PROJECT STATUS

This project is continuing into Phase III with allotment funds of a total of $14,300 for this current fiscal year. Phase III has in addition to aufwuchs microflora and microfauna, the study of the activated sludge community. A completion report from Phase II has been submitted to OWRT.

APPLICATION OF RESEARCH RESULTS

The research for Phase I as reported in the 117 page completion report has been presented at the Annual Meeting (1976) of the AERS and the Ecology Section (at which the senior investigator was the chairman) of the 1976 Annual Meeting of the Society of Protozoologists. There has been many inquiries about the work and numerous requests for copies of the report from individual researchers in basic and applied research.
WORK REMAINING AND PROGRESS CONTEMPLATED DURING NEXT YEAR

Phase III (1976-77) will add activated sludge survey at Blue Plains Sewage Plant and betich scale sewage treatment plants to the two experimental rivers. Phase IV (1977-78) will add zoo and phytoplankton to the ecology study and survey and lighting control to the experiment rivers. Phase V (1978-79) will add meiobenthos to the survey and ecology study and meiobenthos in sediments to the experimental rivers.
ORGANIC IDENTIFICATION IN PHYSICAL-CHEMICAL TREATMENT EFFLUENTS: CHARACTERIZATION OF THE TRACE ORGANICS IN D. C. RAW WASTE WATER
OWRT PROJECT NO. B-007-DC AGREEMENT NO. 14-34-0001-6066

RESEARCH PERIOD: July 1, 1975 - June 30, 1976

PRINCIPAL INVESTIGATOR
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STUDENT ASSISTANTS
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RESEARCH PROJECT ACCOMPLISHMENTS

This study was concerned with the nature and behavior of the nonvolatile organic material in the physical-chemical treatment of the raw wastewater at the Environmental Protection Agency - District of Columbia Advanced Waste Treatment Pilot Plant at Blue Plains in the District of Columbia.

Composite samples were taken after the following stages of treatment:
1) raw wastewater (influent)
2) lime clarification
3) breakpoint chlorination and carbon adsorption
4) alum coagulation and filtration

The nonvolatile organic material was characterized as total mass, carbon oxygen demand, and total nitrogen in terms of strong acids, weak acids, neutral materials, basic materials, and amphoteric materials. The amphoteric materials were further examined for carbohydrates, proteins and amino acids, and hydroxylated aromatic compounds. (See Table I)

PUBLICATIONS

None to date.
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<th>Carbohydrates (mg Glucose)</th>
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* Bovine Serum Albumin 53% Carbon (59).
PROJECT STATUS

Final report completed.

APPLICATION OF RESEARCH RESULTS

Environmental Protection Agency - District of Columbia Advanced Waste Treatment Pilot Plant at Blue Plains in the District of Columbia.
PERSISTENCE MODELING FOR THE POTOMAC AND ADJACENT RIVERS

OWRT PROJECT NO. B-008-DC
AGREEMENT NO. 14-34-0001-6067

RESEARCH PERIOD: January 1, 1975 - May 31, 1976

PRINCIPAL INVESTIGATOR
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Chemistry

STUDENT ASSISTANTS
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Washington, D. C.

RESEARCH PROJECT ACCOMPLISHMENTS

The purpose of this research is to analyze and test persistence modeling using stream flow data from the Potomac, Patuxent and Rappahanock Rivers.

The problem is related to how the statistical models incorporate the handling of persistence, i.e., critical period or drought analysis of stream flow and synthetic data generation are not compatible.

The simplest approach is to assume the data are Markovian; this implies a rapidly decaying (geometric) autocovariance function, as condition described as being of "short memory". A more recent, more complex approach is to assume the data are self-similar; this implies a slowly decaying, autocovariance function of "infinite memory".

Implication of past research is that the critical period of the historic record is a more severe hydrologic event than can be statistically reproduced with synthetic data generators. Normally, severity is defined for drought conditions and the critical period can be thought of as the worst drought occurring in a hydrologic record. The greater the drought the greater the storage required to buffer out its downstream effects.
This phenomenon, that the historic critical period, or drought, is of greater severity than can be captured by statistical models, has been observed by the investigators during the event of this research.

This study represents an initial attempt to strengthen the contention that parameter estimation for persistence models can be improved. Critical periods of the Potomac, Patuxent and Rappahanock determined. Monthly persistence models using the least squares fitting technique are developed. Synthetic stream flow traces are generated for each of the three rivers and synthetic critical periods determined. Success would be if each river’s historic critical period corresponds, more or less, to the average critical period of a set of synthetic critical periods, and improve the critical periods generated by the simple long-one Markov model.

To highlight least square persistence modeling and log-one autoregressive modeling, the flow difference between historic and synthetic critical period are shown for the Potomac in Figures 1 and 2, Rappahanock in Figures 3 and 4 and Patuxent in Figures 5 and 6.

It is apparent from the results that least square persistence modeling will improve the synthetic flow generation by decreasing the variability of the generating model for the Potomac (Figures 1 and 2) and Rappahanock (Figures 3 and 4). The Patuxent River is heavily regulated and no improvement is observable.

No improvement for drought duration can be detected, both models follow similar patterns in the critical return flow periods. Critical drought periods of more than three years cannot be captured correctly by synthetic models.

PUBLICATIONS


PROJECT STATUS

The study is completed.
APPLICATION OF RESEARCH RESULTS

Some variability of synthetic data could be removed by a least square estimator.

FUTURE WORK

Only limited success was met by the project. The marginal improvement of synthetic stream flow generation does not warrant an expanded effort.
POINT OF ROCKS ON THE POTOMAC
FLOW DIFF VS. CRITICAL PERIOD
Q(H)-HISTORIC FLOW  Q(S)-SYNTHETIC FLOW
RHO LEAST SQUARE

Figure 6
POINT OF ROCKS ON THE POTOMAC
FLOW DIFF VS. CRITICAL PERIOD
Q(H) - HISTORIC FLOW  Q(S) - SYNTHETIC FLOW
RHO HISTORIC

Figure 7
FREDERICKSBURG ON THE RAPPAHANNOCK
FLOW DIFF VS. CRITICAL PERIOD
Q(H)-HISTORIC FLOW  Q(S)-SYNTEHTIC FLOW
RHO HISTORIC

Figure 9