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- **Preliminary Evaluation of the Significance of Health and Water Quality Related Problems Associated with Waste Water Discharges to the Chattahoochee River**

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### RESTRICTIONS

- **See Attached N/A Supplemental Information Sheet for Additional Requirements.**

### Travel

- **Foreign travel must have prior approval — Contact OCA in each case.**

### Equipment

- **Title vests with none proposed or anticipated**

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Project Director(s) Joseph P. Gould  GTRC / SAR

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Research Administrative Network
Research Property Management
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Procurement/GTRI Supply Services
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Angela Jones
Russ Embry

RM OCA 69.285
Final Report

Preliminary Evaluation of the Significance of Health and Water Quality Related Problems Associated with Wastewater Discharges and Other Man-made Actions to the Chattahoochee River in Metro Atlanta

by

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Submitted to
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June 1986
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EXECUTIVE SUMMARY

The Chattahoochee River from Buford Dam to Peachtree Creek plays an important, multipurpose role in the Atlanta Metropolitan Area. It is a National Recreation Area, a source of drinking water and a recipient of treated wastewater. Because the last use impacts negatively upon the first two and because the impacts will increase in magnitude with continued growth and development of the area it is important that action be taken to minimize them. Consequently a literature study was conducted to determine whether health or water quality related problems are likely to be associated with the expected increases in the quantity of treated wastewater discharged to the river and to recommend experimental studies which will expedite development of an action plan for mitigating such problems.

Current or proposed effluent limitations for the wastewater treatment plants discharging to the Chattahoochee River between Buford Dam and Peachtree Creek are adequate to protect water quality for recreational use. Consequently the major emphasis of the literature study was upon the impacts of the discharges upon the river as a water supply; specifically, the study addressed the effects of: pathogenic organisms; metals; other inorganic constituents; and organic contaminants.

The impact of pathogenic organisms is likely to be minimal. This follows from these facts. First, the treated wastewaters must be disinfected adequately to protect recreational users of the river. Second, the types of organisms entering the river with the disinfected wastewaters are of the same type as those that will enter the river from nonpoint sources and from the recreational users. Third, the water treatment plants must be designed to protect the users from those organisms regardless of their source. Thus, as long as the numbers of organisms discharged from the wastewater treatment plants are not large relative to the numbers entering from other sources, the fact that they came from treated wastewater is irrelevant. Thus, increases in the discharge of treated and disinfected wastewater are not likely to increase problems associated with pathogenic organisms.

Metals do not currently constitute a problem in the treated wastewaters discharging to the river and because the wastewater treatment plants receive domestic wastewater almost exclusively it is unlikely that they will in the near future. Even if metals were to enter the river in concentrations above the maximum contaminant levels (MCLs) specified in drinking water standards, typical unit operations as practiced at the water treatment plants would be effective in reducing their concentrations to acceptable levels. It should be noted, however, that the best way to protect against excessive metal levels is through a stringent pretreatment program for any parties discharging metals to the POTWs.

Other inorganic constituents of concern are those listed in the primary and secondary drinking water standards. Among them, the ones that are most likely to be affected by wastewater discharges are sodium, nitrate, nitrite, chloride, and sulfate. Given the levels of sodium, chloride and sulfate normally present in treated wastewaters and the low inorganic content of the Chattahoochee River, it is unlikely that these constituents will be a problem in the foreseeable future. On the other hand, nitrate and nitrite should be
given special consideration. As documented in the report, it is likely that
the current MCL for nitrate is too high and that lower limits should be con-
sidered to protect public health. Effluent nitrogen concentrations from the
wastewater treatment plants could be on the order of 40 mg/L. If the volumes
of the wastewater treatment plant effluents increase to the point where they
contribute 10% of the river dry weather flow they could increase the nitrate-N
content by as much as 3-4 mg/L, which could be a significant amount. Conse-
quently, the river should be monitored for all forms of nitrogen, existing
records from the POTWs should be examined to document nitrogen discharges and
computations should be performed to determine likely maximum nitrate and
nitrite levels in the river. If the data suggest that nitrate and nitrite
levels are likely to rise sufficiently to be a problem, economic methods for
controlling nitrogen discharges should then be investigated.

The major uncertainty associated with the provision of safe drinking
water stems from the presence of organic materials. These materials can enter
the Chattahoochee River from a number of sources, including urban and agricul-
tural runoff, rainfall which has absorbed organics from the urban atmosphere,
landfill leachate, natural decay processes, and wastewater discharges. This
multitude of sources suggests that consideration of the wastewater discharges
must be placed in proper perspective. Because of the multiple potential
sources of organic contamination it would still be necessary to monitor and
treat the drinking water in a way which ensures its chemical purity even if
the wastewater discharges were diverted to a point below the water treatment
plant intakes. Consequently, if study were to show that additional treatment
of the wastewater was necessary to remove trace concentrations of health-
endangering organic contaminants it might be preferable to install that treat-
ment at the water treatment plants rather than to divert the effluents or to
install the additional treatment at the wastewater treatment plants. Installa-
tion at the water treatment plants would also protect the consumer from uncon-
trollable (i.e., nonpoint) inputs of those contaminants and use the natural
processes acting in the river to reduce the concentrations of the micro-
contaminants, thereby minimizing the operating costs associated with the treat-
ment required to remove them. The above argument does not suggest that the
wastewater discharges pose no potential problems for water quality in the
river. Indeed, it assumes that the POTWs are operated in a manner which pro-
vides maximum removal of all pollutants and that nothing is done in them which
increases the hazard associated with the discharged organics.

Organics of concern reaching the water intakes can be divided into seve-
ral categories: those which have been classified as potentially hazardous
chemicals through inclusion in primary or secondary drinking water standards
or in lists such as the priority pollutant list; those which have not been
specifically identified but which are known to belong to classes of compounds
which are hazardous (e.g. chlorinated organics); those which have not been
identified but which are toxic, mutagenic and/or carcinogenic, particularly in
complex mixtures; and those which are likely to react with chemicals used
during water treatment to form compounds which may pose a long-term threat to
human health.

When compounds are known to pose a threat to human health it is necessary
that their concentrations be controlled and that is the purpose of the MCLs
and recommended MCLs (RMCL) in the primary and secondary drinking water stan-
dards. Statutory measurement frequencies have been established for those
contaminants covered in the primary drinking water standards. Although such requirements do not yet exist for the organics which have recently been added as secondary standards it is recommended that a routine sampling program be instituted at several points along the Chattahoochee River to establish a data base concerning the presence of those chemicals and their fate in the river. The finished drinking waters should also be analyzed to establish the efficacy of current water treatment practices in removing such compounds.

The danger with publishing lists of organic compounds in drinking water standards is that they focus attention on only a small fraction of the potential contaminants rather than on the much larger, but unidentified, number of organics which are present. This can lead to a false sense of security. Furthermore, it should be recognized that our drinking water standards were developed for "first use" rather than reuse. Nevertheless, like many large cities in the world, Metropolitan Atlanta is practicing indirect water reuse and the current drinking water standards do little to address that situation. This suggests that monitoring for organic contaminants must go past the requirements of drinking water standards. Unfortunately, at this time there is no widely accepted surrogate parameter which can be utilized to monitor the organic quality of a water supply. It has been suggested, however, that much can be learned through analysis for groups of compounds such as halogenated organics and through screening for toxicity and carcinogenicity.

Halogenated organics as measured by the total organic halide (TOX) analysis have been suggested as a group surrogate parameter for evaluating water quality because so many organic compounds in that class are xenobiotic, thereby causing problems with aquatic organisms as well as with animals consuming water containing them. Although little treated wastewater of industrial origin reaches the river, halogenated organics may still be particularly significant in the Chattahoochee River because they are formed during disinfection of wastewater by chlorine, a practice that is employed at all of the POTWs discharging to the river. Thus a pertinent question is whether significant amounts are formed in this case. Furthermore, it is important to know whether they persist in the river, thereby reaching the water intakes in significant concentration, or whether they are destroyed or removed by natural processes. Consequently, it would be informative to sample the POTW effluents on a routine basis both before and after disinfection and to analyze them for TOX. It would also be useful to sample the river for TOX in order to determine their fate there. Such information would be useful in establishing whether alternative disinfection practices should be evaluated.

Because so little is known about the nature and effects of organic matter in water, many think that direct measurement of health effects through screening studies is the most effective way of determining whether unidentified organic compounds constitute a problem. As discussed in the report, where health effects are a serious concern because of their likely significance, a multifaceted approach to health-effects screening has been recommended. Consideration of the apparently high water quality in the Chattahoochee River suggests that such comprehensive and expensive screening studies are not justified at this time. It would be prudent, however, to begin a screening program based upon bacterial assays for toxicity and mutagenicity. The latter is important not only because it can be correlated with carcinogenicity but because it is also suggestive of future increased incidences of genetic diseases as well as other diseases including atherosclerosis, senile cataracts and various metaplasias. Such a screening study could provide an early warning for a developing problem and would suggest ways of alleviating or eliminating it.
Toxic or mutagenic chemicals can enter the river from the POTWs, from nonpoint sources or from natural processes in Lake Lanier or in the river itself. Furthermore, their production by natural processes may be seasonal. To establish the current quality of the water in the Chattahoochee River from a health-effects perspective and to assess the impact of both point and non-point discharges on it, it is recommended that an appropriate number of sampling stations be established along the river from Buford Dam to Peachtree Creek and that samples from those stations be tested on a monthly basis for one year for toxicity and mutagenicity using appropriate bacterial assays. Samples should be collected under both wet and dry weather conditions. Such a program is especially important to a realistic evaluation of the impact of the wastewater treatment plant effluents relative to other organics entering the river from other sources.

It is recommended that toxicity and mutagenicity screening also be used to evaluate the impact of the disinfection techniques used in the POTWs on the quality of the effluent being discharged. It is not logical to employ a unit operation during wastewater treatment which has a detrimental impact upon water quality if alternative operations are available which do not have the negative impact. The report shows clearly that disinfection by chlorination can form halogenated organics and can increase the mutagenicity and toxicity of organics in waters or wastewaters. The report also shows, however, that the circumstances under which such increases occur are very site specific and are influenced by factors which are not well understood. This suggests that the POTW effluents should be tested both before and after disinfection to determine whether existing disinfection techniques increase the quantity of problem organics discharged to the river. Because the magnitude of any effect is likely to change seasonally it is recommended that this screening study be conducted concurrently with the river study.

Should the screening study at the POTWs reveal that existing disinfection practices cause a deterioration in water quality, the data from the river study will provide preliminary evidence concerning the fate of the deleterious chemicals in the environment. If they are removed by natural processes and if their concentrations remain low enough to be of minimal concern, then it may be acceptable to continue disinfecting in the same manner. On the other hand, should they impact the river water negatively, or if mass balance computations suggest that they will have a negative impact in the future, then experimental studies should be initiated to investigate alternative disinfection techniques. One facet of those studies, of course, should be the production of toxic or mutagenic materials.

Organics existing in the river from natural decay processes as well as those entering from the various point and nonpoint sources are likely to react with chemicals used to disinfect the drinking water. Current standards focus on the trihalomethanes (THMs) but they are only a small fraction of the chlorinated organics formed during disinfection with chlorine. Furthermore, it is now recognized that disinfection with chlorine, chlorine dioxide or ozone can result in oxidation products which are toxic or mutagenic in bacterial assays. Although the waters produced by the water treatment processes are currently meeting the THM standard it is recommended that a screening program be instituted to evaluate the TOX concentration of the finished water as well as its toxicity and mutagenicity in bacterial tests. Because the reactivity of the organics in the river is likely to vary seasonally, it is recommended that this study be done for one year with at least monthly samples. It should also
be done under both wet and dry weather conditions. Technology currently exists for minimizing the formation of THMs. Should the screening study reveal problems with TOX, toxicity or mutagenicity it is likely that the same technology would be effective in reducing their formation. If the screening study reveals a problem then it would be appropriate to investigate the efficacy at that technology for eliminating the problem.

In closing, a review of the literature concerning the health and water quality related problems associated with the discharge of treated wastewater in proximity to the water intakes on the Chattahoochee River has resulted in the following recommendations.

1. Establish sampling stations along the river from Buford Dam to Peachtree Creek, collect at least one sample a month for one year, including both wet and dry weather conditions, and analyze those samples for all forms of nitrogen, all organic compounds listed in the primary and secondary drinking water standards, TOX, and toxicity and mutagenicity in bacterial tests.

2. Sample the effluents from the POTWs before and after disinfection at least once a month for a year and analyze them for TOX and for toxicity and mutagenicity using a bacterial test.

3. Sample the finished drinking water produced by the water treatment plants once a month for at least a year and analyze the samples for the organic compounds listed in the primary and secondary drinking water standards, TOX, and toxicity and mutagenicity in bacterial tests.

Evaluation of the results of such a study will allow rational evaluation of the significance of any potential problems associated with an increase in the quantity of treated wastewater discharged.
II. INTRODUCTION

A. Problem Statement

The Chattahoochee River between Buford Dam and Peachtree Creek, plays an important role in the Metropolitan Atlanta Area. It is the source of drinking water for approximately one-third of Georgia's population, with four existing water intakes and a fifth to be built soon. It is a popular recreational resource with as many as 25,000 people using it on almost any summer weekend to engage in water sports activities. Finally, it serves as the recipient of flows from four major wastewater treatment plants.

Because of the river's use as a drinking water supply and as a recreational resource it is important that its quality be maintained at high levels. This has not been a problem in the past because the treated wastewater discharges were diluted sufficiently by the river to reduce any residual contaminants to insignificant levels. However, this situation may change because of the high growth rate being experienced in the Metropolitan Atlanta Area. For example, during the first nine months of 1985 the average total wastewater discharge rate to the river was 13.9 MGD but the total projected flow for the year 2010 is in excess of 43 MGD, or more than triple the current rate (63). This suggests that the wastewater discharges could begin to have a significant impact upon the river quality, particularly with respect to its use as a water supply.

Concerns about the impact of increases in the discharge rate from the wastewater treatment plants led the Cobb County-Marietta Water Authority and the Atlanta Bureau of Water to contract with Clemson University and Georgia Institute of Technology to conduct a literature study concerning it. The goal of the study was to answer two questions:

1. Are there likely to be health or water quality related problems associated with the projected increase in the percentage contribution of treated wastewater to the river?

2. What other investigations and experimental studies should be conducted to develop an action plan for better defining and/or mitigating any problems, should they exist now or in the future?

This document presents the results of that study.

B. Significant Problems of the Water Treatment Industry

Water treatment practice in the United States is in a period of flux. Throughout most of its history the major concern of the water industry was on the microbiological purity of their product. During the 1970's however, it was discovered that chemical contamination was also a problem in certain supplies. Study of the problem revealed that there were two major types of contaminants: synthetic organic chemicals (SOC) and reaction products resulting from disinfection with chlorine.
The United States was not alone in the first problem because SOC's were entering water supplies of industrialized countries worldwide from a multitude of sources as a result of modern lifestyles and industrial development. Bedding et al. (8,9,10) published an extensive review of SOC's, their origin, fate, and effects and it is recommended as an excellent source of background information. A significant conclusion from their review was that "The significance of trace concentrations of organic contaminants in drinking water to public health is largely inconclusive and controversial, since there is a general paucity of information concerning human health effects from which to draw conclusions" (8). Similarly, Kool et al. (112) concluded that because so little is known about the identity of the majority of the organic substances present in drinking water, reliable estimates of the possible health risks associated with lifetime consumption of them cannot yet be made. Although considerable additional research has been conducted since these conclusions were reached, no information was found in the literature to change them. Thus, no clear-cut answers are available to guide those in authority who must make decisions about the health significance of SOCs in drinking water.

To further complicate the decision process concerning the significance of SOCs and other contaminants, there is a wide diversity of opinion among professionals. At one extreme there are those who point out that exposure to toxic organics via drinking water represents only a small percentage of the total exposure to such chemicals. As an example, Bedding et al., (8) cited a survey of pesticide levels in the United Kingdom (34) which revealed that even in the worst case human intake of organochlorine insecticides from drinking water would not exceed 0.5% of the total dietary intake of such substances. From such data, some professionals would conclude that there is little cause to be concerned about SOC at microcontaminant levels. At the other extreme are those who argue that there is no known "safe" dose for some types of carcinogens, i.e., that threshold concentrations do not exist. Furthermore, they argue that the latency periods for cancer are so long and the exposures to xenobiotic compounds so recent that it may be years before we know the effects of long-term exposure to microcontaminants. Under that circumstance they think that the prudent action is to take every realistic measure to minimize risk.

Given the uncertainty regarding the question of the significance of SOCs in water supplies, and recognizing the cost of "eliminating" them, water treatment professionals are turning to experts in risk analysis (19,33) for assistance. Unfortunately, studies are only now beginning to apply those techniques to this question and it is doubtful whether clearer answers will be available for several years. This suggests that the most reasonable course of action to take with regard to the Chattahoochee River, which is relatively unpolluted compared to many water supplies in the United States, is to determine exactly what the situation is. By the time more is known about the presence of micropollutants, their concentration, etc., it is likely that the application of risk analysis to this problem will be more advanced, thereby making it possible to make rational decisions from which to develop an action plan. This concept was an underlying principle of this report.

The existence of reaction products from disinfection of water by chlorine was discovered in Holland in 1974 by Rook (164). Since then the problem has been studied so extensively that five symposia have been held on the subject in the United States alone (96-98,101,102). In water treatment practice most
attention has been focused on the formation of volatile, halogenated organics which are generally grouped together under the heading trihalomethanes (THMs), but considerable quantities of nonvolatile halogenated organics may be formed as well, particularly during disinfection of treated wastewater (95,95). While this subject will be treated in detail later, it is worth noting here that THMs are regulated through the primary drinking water standards (52). Although an initial effort was made to require a particular mode of treatment (186), it has since been learned that THM formation may be minimized through removal or control of the organic materials from which they are formed as well as through proper manipulation of the process train.

Concern about the impact of the discharge of treated wastewater to the Chattahoochee River on the quality of drinking water extracted from it is centered in large part on the presence of SOCs and the formation of THMs and consequently, these subjects constitute the bulk of this review. At the same time, however, there are other concerns which must also be addressed. For example, even though a number of SOCs have been included in the new proposed secondary drinking water standards (45,46,51,52), they represent less than 5% of the compounds which have been identified in water supplies (112). Furthermore, those that have been identified are only a minute percentage of the total number of organic compounds that might be present (9), suggesting that a compound-by-compound evaluation of chemicals in drinking water is beyond the scope of any reasonable effort (122). All of this leads to the conclusion that other techniques must be relied upon in the attempt to assess the health effects of organic contaminants which reach the water intakes either from point or nonpoint discharges. Consequently, methods for directly assessing those effects must also be reviewed.

Finally, it is appropriate to comment briefly on the significance of the fact that treated wastewater is discharged to the Chattahoochee River in the Metropolitan Atlanta area. Because of the proximity of the treated wastewater outfalls to the water intakes along the river, de facto wastewater reuse is being practiced. This is not an unusual situation in the United States since a recent study of 540 water utilities drawing from surface supplies revealed that the contribution of municipal wastewaters to their supplies was as high as 24 percent of low stream flow and one to three percent of average flow (185). Furthermore, 20 cities have surface supplies containing 3.5 to 16 percent wastewater during average flow conditions (150). It does suggest, however, that something can be learned from health effects studies which have been conducted in areas practicing direct water reuse.

There are three important problems associated with indirect reuse of wastewater which must be guarded against. One stems from the fact that the public is consistently opposed to the use of reclaimed water for potable water use (150). This suggests that care must be exercised in the handling of this subject so that realistic alternative actions are not eliminated through unwarranted public concern. The second involves the reliability of the wastewater treatment facilities. Van Rensberg et al., (195) have argued that direct wastewater reuse is preferable to indirect reuse because of the safeguards that are built into a direct reuse system. Because the responsible water authorities in the Atlanta area are in different governmental jurisdictions from those responsible for the wastewater treatment facilities, they can do little to ensure the reliability of the wastewater treatment systems. Consequently, the water treatment processes must be conservatively designed and operated to provide the extra degree of removal that will be needed to protect...
consumers during periods of less than adequate treatment of the wastewater (35). Ironically, the high recreational use of the Chattahoochee River may provide a major means of protecting it as a water supply because there will be strong public pressure to provide reliable wastewater treatment in order to protect water quality for recreational purposes. The third problem concerns the perception of those in authority of the appropriateness of the drinking water standards. Even though more organic compounds are addressed in the new standards than ever before, the general assumption in the development of such standards is that the source water is protected from gross contamination (150). As pointed out earlier, however, the total number of compounds included in the standards is only a minute quantity of those which might be discharged to the river with the treated wastewater. Furthermore, the health effects associated with long-term consumption of micropollutants are largely unknown. Consequently, it would be inappropriate to assume that those standards totally define a safe water in this context. Rather, attention must be focused on water quality parameters which go beyond those listed.

C. Potential Health and Water-Quality Related Concerns

Before enumerating the potential health and water-quality effects associated with the discharge of treated wastewater to the Chattahoochee River it would be beneficial to review briefly situations in which reuse is deliberately practiced. The results of such studies would reveal potential problems and might help place the Chattahoochee River situation in proper perspective. Although several papers have been published which draw together information on the topic of water reuse (5, 35, 145, 150) relatively few studies have attempted to measure directly the health effects associated with the practice. This is primarily because there is so little recognized water reuse, although there is considerable, unrecognized, indirect reuse. Currently, the major application of water reuse occurs in South Africa where both direct and indirect reuse are practiced (195). The water is extensively treated and no papers were found which documented any adverse health effects associated with its use. Capetown is initiating direct wastewater reuse, with up to ten percent of the total potable water being reclaimed wastewater (18). Epidemiological studies were planned and the importance of collecting baseline data prior to the initialization of reuse was stressed (18), but no results have been published because reuse has been practiced for only a short time. Within the U.S., although extensive pilot studies have been conducted in Denver, CO (118) in preparation for direct wastewater reuse, full-scale implementation has not yet been accomplished. Nevertheless, these projects will be sources of valuable information in the future.

The most extensive study of the health effects associated with water reuse was done in association with the Whittier Narrows groundwater replenishment project in Los Angeles (146). In this case, groundwater, rather than surface water, received the treated wastewater and was the source of drinking water. Their experience is important to the Atlanta situation, however, because the percent of treated wastewater in the groundwater supply is of the same magnitude as that expected in the Atlanta area. From 1962 to 1977 the reclaimed water was disinfected secondary effluent but dual-media filtration was then added to enhance virus inactivation during final disinfection. After 20 years of replenishment practice an ecological epidemiological study was performed (59, 60). Although such studies are generally quite difficult to
control and interpret (27), the pattern of water distribution and the available health information made it possible to conduct a well-controlled study on 21 health outcomes. None indicated a contribution of the use of reclaimed wastewater to disease (59). Although the authors state the usual disclaimers regarding the interpretation of epidemiological studies, the results are significant to the current study because they demonstrate that it is possible to practice indirect reuse to a slightly greater degree than that anticipated in Atlanta without any apparent adverse effects on human health. This suggests that as long as orderly planning is done and proper safeguards are provided, it should be possible to provide healthful water in spite of the wastewater discharges.

What are the constituents of major concern in the Chattahoochee River and their most important sources? Basically, they can be grouped into four categories and this report will consider each separately. They are pathogenic organisms, metals, non-metal inorganic constituents, and organic contaminants. Pathogenic organisms would enter the river primarily with the treated wastewater and would be of concern to those using the river for recreation or as a water supply. Metals, in the concentration likely to be discharged from the wastewater treatment plant, are not likely to impact negatively upon the aquatic life in the river or on the river's recreational use. Their effects are more likely to be associated with use as a water supply. It is possible, however, that more significant concentrations of metals could enter the river from uncontrolled sources such as landfill leachate. Non-metal inorganic contaminants fall into several categories and each might impact the river in a different way. Ammonia nitrogen, for example, could adversely affect sensitive aquatic life or could lower the dissolved oxygen level through its oxidation. The resulting nitrate nitrogen would have less impact upon aquatic life but may have a larger impact upon consumers of the water. Generally, the mineral composition of wastewater discharges will be the same as that of the water supply, but with slightly higher concentration. The levels entering in the treated wastewater are not likely to be a problem but the amounts that may enter from uncontrolled sources are unknown.

Organic contaminants can be subdivided into several categories and all can enter the river from many sources. For example, SOCs can enter with treated wastewaters, rural and urban runoff, rainfall, and other uncontrolled discharges such as leachates. Furthermore, some SOCs such as polynuclear aromatic hydrocarbons (PAHs), which are often associated with anthropogenic sources of contamination, are actually ubiquitous in water, being produced by plants and microorganisms as well as by human activity (9). Thus, it would be inappropriate to focus on the wastewaters as the primary source of SOCs. In addition, there are natural organic constituents, such as humic substances, which enter the river from many sources and which may react negatively with certain disinfectants during water treatment. Although about 60% of the organic matter in wastewater effluents is of this type (9), humic substances will be generated in Lake Lanier and in the river itself as part of the natural biological cycle. Thus, again, it would be inappropriate to focus on the wastewater discharges as their primary source. Finally, we must consider those problem organics which are formed during water or wastewater treatment, particularly chlorination. A major question to be considered is whether their formation during wastewater treatment is likely to have a negative impact on the river from either a water quality or a health perspective. Finally, it
will be necessary to determine the importance of the formation of such compounds during water treatment.
III. PATHOGENIC ORGANISMS

Microbiological water quality was not considered in detail during the review because it was considered to be of less significance than the chemical water quality. This follows from several facts.

1. The treated wastewaters must be disinfected sufficiently to protect recreational users of the river. Existing permit limits for the wastewater treatment facilities require them to discharge no more than 200 fecal coliforms per 100 ml of effluent (63). Since the recommended limit on fecal coliforms in primary contact water is 200/100 ml (168) the dilution in the river should provide adequate protection for recreational users. This also suggests that disinfection at the water treatment plants is not adversely affected by the wastewater discharges. Conventional water treatment can effectively remove up to 5000 coliforms per 100 ml (13) and that value is well above the number likely to be present when the fecal coliforms are reduced to less than 20/100 ml by disinfection and dilution in the river.

2. The types of organisms entering the river with the disinfected wastewaters are of the same type as those that will enter the river from non-point sources and from the recreational users. Shertzer (174) has presented a table originally prepared by C. Sawyer which lists the predominant types of pathogenic organisms present in the wastewaters from U.S. communities. Many of those organisms will be eliminated by disinfection of the effluents and the remainder will be greatly reduced in number. Because many of the organisms have mammalian reservoirs other than man they will enter the stream from many sources.

3. The water treatment plants must be designed to remove pathogenic organisms regardless of their source. Since the wastewaters have already been disinfected for recreational purposes the number of organisms entering the river will be relatively low. Furthermore, some die-off will occur in the river, although the retention time in the reach of stream involved is likely to be shorter than the survival time of some pathogenic organisms (35). All of this suggests that the impact of the treated wastewaters on the microbiological purity of the water produced by the water treatment plants is likely to be minimal.

In spite of the above arguments, one should not be complacent about the discharge of pathogens to the river. As pointed out earlier, one potential problem with indirect water reuse is that the system is not built with the same reliability as a direct water reuse system. Studies at Denver have shown that through the use of multiple barrier techniques it is possible to produce a water with microbiological quality better than first-use mountain runoff (163). The key then is a reliably operated, multiple barrier system. Such concepts can be applied to design and operation of the plants which are interconnected through the river, thereby achieving the same result.
IV. METALS

Current primary drinking water standards contain MCLs for five metals (cadmium, chromium, lead, mercury and silver) and proposed secondary standards contain RMCLs for one more (copper) as well as reductions in MCL values for four others (52). The Georgia EPD also has in-stream standards for lead, mercury, chromium and zinc which are close in magnitude to the MCL values (63). All of the metals listed by EPA are known to have some adverse health effect and those effects are documented in the proposed rules (52).

Surveys done at three of the water supplies drawing from the Chattahoochee River showed that the treated water met all of the MCLs (63). Because the RMCLs are below the lower detectable limits of the analytical techniques used in the survey it is difficult to state with certainty whether the concentrations would meet the new RMCLs. The generally unpolluted nature of the river suggests that they would, however. In addition, metal data from the Gwinnett Crooked Creek Wastewater Treatment Plant (63) showed that chromium, cadmium and copper concentrations in the influent were below the MCLs (RMCL for copper). Consequently any removal through the wastewater treatment plant would provide added protection, as would dilution and removal in the river.

Metals can be removed to a limited degree in wastewater treatment plants through adsorption onto biomass and through precipitation if any precipitation steps are employed. Given the concentrations contained in the wastewaters discharging to the river, natural water chemistry will remove many of them from the soluble state, although they may become a part of the bottom sediment (167). The values specified by the Georgia EPD for in-stream concentrations and the generally low levels for metals in NPDES permits for POTWs suggests that these natural removal mechanisms will be able to effectively handle any anticipated inputs. Should metal levels in the river exceed the MCLs in the drinking water standards they will probably be reduced to allowable levels in the water treatment processes, although some alteration of process chemistry might be required. For example, metals are generally removed best at high pH with solution conditions appropriate for their precipitation (41). Such conditions may not be required, however, because metals tend to be complexed by humic substances, which are then removed to a reasonable degree during alum coagulation (41). Truitt and Weber (191), for example, found that low concentrations of naturally occurring organic matter increased the removal of trace metals at neutral pH.

In conclusion, metals are not currently a problem in the Chattahoochee River nor are they likely to be in the near future. This is primarily because their input to the wastewater treatment plants is minimal. It is important, however, that as growth occurs in the area that tight control be maintained over metals discharges through stringent pretreatment requirements on inputs to the wastewater treatment plants. The major uncertainty with respect to metals lies in the potential entry of landfill leachate into the river. Since such leachate would also increase the concentration of other constituents receiving routine monitoring it is likely that its presence would be rapidly detected, thereby providing opportunity for corrective action. Considering all of the above arguments no recommendations concerning metal removal are considered necessary at this time.
V. NON-METAL INORGANIC CONSTITUENTS

Current primary and secondary drinking water standards contain a number of inorganic constituents and the new proposed secondary standards add three more (52). Among the listed constituents, the ones that are most likely to be impacted by the discharge of treated wastewater are sodium, chloride, sulfate, nitrate and nitrite. Of these, sulfate and sodium are no longer listed in the proposed standards (52).

The health effects associated with elevated sulfate levels are minimal and in many parts of the country the drinking water contains sulfate levels well in excess of those experienced in the Atlanta area. In the proposed standards the EPA presents 250 mg/L as a guidance level based on aesthetic considerations. Finished water from the Atlanta system had a concentration of only 7.5 mg/L (63) and given the normal sulfate additions through wastewater discharge it is apparent that sulfate levels pose no potential problems.

Although sodium intake is linked to hypertension in susceptible people, the EPA concluded that there is insufficient data showing an association between sodium in drinking water and hypertension in the general population to warrant an RMCL (52). They are, however, supporting the American Heart Association's recommended level of 20 mg/L in drinking water and are adopting that as a guidance level since drinking water meeting that goal would not present a sodium-related hazard to those segments of the population thought to be at high risk. Finished water from the Atlanta system had a concentration of 3.2 mg/L (63) and thus it is unlikely that the discharge of treated wastewater will impact significantly upon the sodium level in the river in the near future.

The primary reason that chloride has an RMCL of 250 mg/L is to prevent an objectionable salty taste in water (141). Atlanta water currently contains 5 mg/L and thus it is unlikely that the wastewater discharges will have any significant effect.

Nitrate ion is listed in existing primary drinking water standards with an MCL of 10 mg/L (as N) whereas nitrite ion is a recent addition to the proposed standards with an RMCL of 1 mg/L (as N). These levels have been set to prevent acute toxicity to infants through methemoglobinemia (52). Although the potential carcinogenicity of nitrate/nitrite was discussed in the proposed standards (52) the data were considered to be inadequate for classification of them as potential carcinogens. It should be noted, however, that one question posed by EPA for comment by interested parties was whether their carcinogenic potential should be considered in setting RMCLs. Evidence for their carcinogenic potential comes from studies which have shown that nitrate/nitrite administered with nitrosatable compounds are carcinogenic in animals (52). Presumably this results from the formation of nitrosamines (65,178), which are among the most potent carcinogens. Evidence for the existence of problems from drinking water comes from ecological epidemiological studies which relate nitrate in drinking water to cancer (178). One recent study of a region in Italy with elevated nitrate levels showed a strong correlation between the ingestion of nitrate levels in excess of 4.5 mg/L (as N) and gastric carcinomas (65). Although all of this evidence is not definitive, it suggests that
nitrate/nitrite may be a problem and this potential should be considered in future planning.

A medium strength wastewater can contain 40 mg/L of nitrogen of various forms (136). Although a portion of this nitrogen will be incorporated into the microbial cell material formed during wastewater treatment, the bulk of it will be discharged to the river as either ammonia or nitrate nitrogen, depending on the nature of the wastewater treatment process. Even if predominantly ammonia is discharged, nitrification is likely to occur in the aerobic environments of the river, particularly in the summer when water temperatures are higher. This suggests that for planning purposes all nitrogen discharges to the Chattahoochee River should be considered to be as nitrate. Although nitrate concentrations in the water supplies are not currently a problem they could well be in the future. It is conceivable that wastewater discharges will equal ten percent of dry weather flow by the year 2010. Since dry weather flow is most likely to occur in summer when the nitrogen will be fully nitrified, this means that nitrate/nitrite could be as high as 3-4 mg/L as N in the river. This is approaching the level at which a correlation between nitrate and gastric carcinomas was detected in Italy (65).

The evidence that nitrate concentrations in the Chattahoochee River could reach levels of concern is sketchy, at best. Limited data (63) indicate that total nitrogen concentrations in the river are currently well below values which should cause concern. Nevertheless, it is important that those in authority be aware of the situation and prepare for the eventuality that further epidemiological and experimental data will confirm the health-related problems associated with nitrate. In that way they can plan for nitrogen removal from the wastewater, which can be accomplished easily through biological denitrification. Because of the highly aerobic conditions which are maintained in the river it is doubtful that much nitrate would be lost through denitrification in the bulk liquid, although some may be lost from biological activity in the bottom sediments. If data are not already available, it is recommended that samples be collected at various points along the river and from the discharged wastewaters at various times during the year to determine the fate of the nitrogen. Once the general characteristics of the river regarding nitrogen are known, they can be coupled with data taken from the routine reports prepared by the wastewater treatment plants to compute mass balances indicating likely nitrate levels in the river for various dry weather flow conditions. Such computations will give a good indication of likely maximum nitrite and nitrate levels. Should they indicate future problems, then studies should be initiated to select methods of nitrogen removal for the wastewater treatment plants.
VI. ORGANIC CONTAMINANTS

A. Categories of Organic Contaminants

In November 1985 the EPA published three documents in the Federal Register which concern organic contaminants in drinking water. One (50) promulgated RMCLs for the eight volatile SOCs listed in Table 1. Another (51) proposed MCLs for those same eight compounds and presented proposed monitoring and reporting requirements for 51 other volatile SOCs (Table 2). The third (52) proposed RMCLs for 24 SOCs or combinations of the SOCs and their metabolites. Those compounds are listed in Table 3.

The 9 compounds in Table 1 (including tetrachloroethylene) are known to be present in some water supplies and are considered to be harmful to human health. The 51 compounds in Table 2 are there primarily because they can be detected and quantified at the same time as the 9 in Table 1 with only minor additional expense. In addition, they are there because they have some other significance to public water supplies: four are trihalomethanes; some are being considered for RMCLs at a later date; some have been detected in groundwaters; others have the potential for being in water supplies because of their detection in wastewaters, etc. The 24 SOCs in Table 3 are either known to be present in drinking water supplies or have the potential to be present. In addition, all have significant potential health effects. The reasons for including each chemical are given in detail in the proposed rulemaking document (52).

The 84 SOCs listed in Tables 1, 2, and 3 could enter the water supplies from a number of sources: wastewater discharges; nonpoint sources such as

Table 1
Volatile Synthetic Organic Chemicals for which RMCLs Have Been Promulgated (50) and MCLs Have Been Proposed (51)

<table>
<thead>
<tr>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
</tr>
<tr>
<td>p-Dichlorobenzene</td>
</tr>
<tr>
<td>1,2-Dichlorobenzene</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
</tr>
<tr>
<td>1,1-Dichloroethylene</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
</tr>
<tr>
<td>Trichloroethylene</td>
</tr>
<tr>
<td>Vinyl chloride</td>
</tr>
</tbody>
</table>

In addition, the comment period on the RMCL for tetrachloroethylene was extended.
urban and agricultural runoff; rainfall which has absorbed organics from the urban atmosphere; and landfill leachate. Indeed, some may even be formed during disinfection with chlorine. Consequently, it would be a mistake to focus on the wastewater discharges as their primary source. Rather, the focus should be on their occurrence and fate throughout the entire river corridor and any planning documents should be based on that focus. In order to begin to understand the importance of such chemicals in the Chattahoochee River it is recommended that a sampling and analysis program be developed which includes the entire reach of river from Buford Dam to the last wastewater outfall at Peachtree Creek. The sampling program should include the river at several points, the wastewater discharges and the water intakes. The exact number of samples and the locations from which they are taken will have to be carefully chosen to maximize the information obtained while keeping the analytical costs to a reasonable level. Similarly, the frequency of sampling throughout a one year period should be sufficient to establish a reasonable understanding of seasonal changes without excessive expenditure. Initiation of this program prior to any statutory requirement for monitoring will provide baseline data on the river quality and will allow rational planning for handling the impact of increased wastewater discharges.
Table 3
Synthetic Organic Compounds for Which RMCLs Have Been Proposed (52)

<table>
<thead>
<tr>
<th>Acrylamide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alachlor</td>
</tr>
<tr>
<td>Aldicarb, Aldicarb sulfoxide and Aldicarb sulfone</td>
</tr>
<tr>
<td>Carbofuran</td>
</tr>
<tr>
<td>Chlordane</td>
</tr>
<tr>
<td>Dibromochloropropane</td>
</tr>
<tr>
<td>o-,m-Dichloropropane</td>
</tr>
<tr>
<td>2,4-D</td>
</tr>
<tr>
<td>Epichlorohydrin</td>
</tr>
<tr>
<td>Ethylbenzene</td>
</tr>
<tr>
<td>Ethylene dibromide</td>
</tr>
<tr>
<td>Heptachlor and heptachlor expoxide</td>
</tr>
<tr>
<td>Lindane</td>
</tr>
<tr>
<td>Methoxychlor</td>
</tr>
<tr>
<td>Monochlorobenzene</td>
</tr>
<tr>
<td>Polychlorinated biphenyls</td>
</tr>
<tr>
<td>Pentachlorrophenol</td>
</tr>
<tr>
<td>Sturene</td>
</tr>
<tr>
<td>Toluene</td>
</tr>
<tr>
<td>Toxaphene</td>
</tr>
<tr>
<td>2,4,5-TP</td>
</tr>
<tr>
<td>Xylene</td>
</tr>
</tbody>
</table>

While it is thought that analysis for the specific organics will provide valuable information about the quality of Chattahoochee River water, especially in light of the regulations proposed by EPA, it should be recognized that those 84 SOCs represent only a minute fraction of the compounds that have been identified in water, to say nothing of the total number of synthetic organic chemicals which might be present. For example, as of 1983 over 2200 organic compounds had been identified in the aquatic environments and over 750 of them had been found in drinking water (8). However, more than 80% of the identified organic compounds were volatile, nonpolar compounds whereas that classification contributed less than 10 percent of the dissolved organic carbon (DOC) present (112). This has led some authors to estimate that virtually every known organic compound would be found in treated drinking water from highly urbanized areas if the detection limits were only low enough (44). Furthermore, epidemiological studies indicate that the risk of cancer associated with drinking water consumption is higher than that extrapolated from animal data on the carcinogenicity of individual chemicals which have been identified as being present (36). This suggests that additional risk is associated with the unidentified organic fraction in water. Consequently, any study of water quality and potential health impacts must go beyond the lists of compounds published by EPA. Given the uncertainty concerning the health effects associated with organic chemicals, it would be both unwise and uneconomic to look only for the presence of some arbitrary list of organic constituents during studies to establish water quality. Rather, some form of surrogate parameter must be used in any analysis of water quality and health effects.
The choice of surrogate parameters is rather limited because little work has been done concerning the health effects associated with organic contaminants. In other words, although a number of organic groups could be proposed as surrogate parameters, it would be difficult to provide concrete evidence that they could be related directly to potential health effects. It appears possible, however, to choose two or three parameters for which there is strong indirect evidence.

A number of workers have addressed the question of whether any general chemical parameters could be used to assess the impact of organic constituents on water quality (109,132,166). Dissolved organic carbon (DOC) is a widely used general parameter and it should be measured to provide evidence of the total amount of organic matter present. A large amount of the DOC, however, will be due to humic and other natural substances and thus changes in DOC level generally will not correlate well with the removal of many specific organic compounds (132,166). Nevertheless, its concentration should be followed during studies on water quality because it can be used in combination with other analyses to indicate how effectively particular unit operations are performing with respect to both specific and general pollutants.

Chlorinated organic compounds constitute an important class of organics, not only because many are toxic but because they are widely distributed in the environment. Examination of Tables 1, 2, and 3 shows that a large number of the compounds that EPA is proposing to regulate in drinking water contain halogens. Furthermore, many of the organic compounds on the priority pollutant list are halogenated compounds (105). Finally, halogenated organics can be formed during disinfection of waters and wastewaters. This suggests that the total concentration of halogenated organics would be a useful parameter to use in assessing water quality. Dohrmann instruments has developed a test for total organic halide (TOX) (47) and it is finding increased usage as a surrogate parameter (132). Other procedures also exist which do not require the specialized instrumentation (31). Actually, total organic halide may be a misnomer because the Dohrmann test relies upon activated carbon for removal of the organics from the aqueous phase and concentration for analysis. Thus it might more accurately be called "adsorbable organic halide" or "TOX adsorbable on activated carbon" (109,166). At any rate, the TOX procedure is relatively simple and rapid, is consistent with the requirements of a screening program which might generate a large number of samples, and provides information on a large class of compounds of environmental significance.

The main reason for being concerned with organics in water is because of the effects that they may have on humans and other life. Thus, it would be advantageous to simply measure these effects rather than trying to measure the presence of organic compounds which might cause them. Consequently, there has been broad interest in the use of bioassays in water pollution monitoring. Two types of bioassays have received the most attention: those dealing with toxicity and those measuring mutagenicity.

Kool et al. (112) have summarized the various types of toxicity tests and their summary is shown in Table 4. The merits of the various assays are presented in their review; the important point to recognize here is that there are many potential assays. During this review distinction will not be made between types; rather, their results will simply be referred to as toxicity results.
### Table 4
Types of Toxicity Assays (112)

<table>
<thead>
<tr>
<th>Type of Assay</th>
<th>Biological Parameter(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>In vivo assays</strong></td>
<td></td>
</tr>
<tr>
<td>(plants, animals)</td>
<td></td>
</tr>
<tr>
<td>Acute toxicity</td>
<td>Survival (mortality)</td>
</tr>
<tr>
<td>Subchronic toxicity</td>
<td>Survival, growth, reproduction physiology, biochemistry etc.</td>
</tr>
<tr>
<td>Chronic toxicity</td>
<td>See subchronic toxicity, cancer induction, genetic effects (heritable disease)</td>
</tr>
<tr>
<td>Specific effects</td>
<td>Behavior, immunology</td>
</tr>
<tr>
<td><strong>In vitro assays</strong></td>
<td></td>
</tr>
<tr>
<td>(eukaryotic and prokaryotic cells)</td>
<td></td>
</tr>
<tr>
<td>Cytotoxicity</td>
<td>Survival, growth, morphology</td>
</tr>
<tr>
<td>Biochemical effects</td>
<td>Growth- and energy-related metabolism, ATP, nucleic acids, protein synthesis, other enzyme functions</td>
</tr>
<tr>
<td>Cytogenetic effects</td>
<td>Mutation, cell transformation (short term tests)</td>
</tr>
</tbody>
</table>

Mutagenicity assays have been reviewed by Hoffmann (84), who covers all types, including both long-term and short-term. The mutagenicity of chemicals is important for a number of reasons. First, if a chemical were to cause an increase in the mutation rate of human germ cells it might cause an increased incidence of genetic disease in future generations (84). Second, chemicals which cause mutations in somatic cells may lead to increased cancer incidence in the present generation (84). Indeed, there is a high degree of correlation between mutagenicity and carcinogenicity for chemicals that have been tested for both (4, 84). Finally, the exposure to mutagenic agents may play a role in the etiology of other human diseases, including atherosclerosis, senile cataracts and various metaplasias (82). Like toxicity testing, there are many systems within which mutagenicity testing can be done (84). However, because the activity is against DNA and DNA is the hereditary material in all organisms, extrapolation between species is generally possible. Consequently, in this review distinction will not be made between the types of tests employed.

Since valid tests are available for measuring toxicity and mutagenicity the assays can be used as surrogate parameters for the organic matter that causes the response even when the specific compounds have not been identified. For example, mutagenicity has been associated with increases in adsorbable TOX in water (111). Although techniques are available whereby the responsible compounds can be isolated and identified (2, 146, 187), we will not be concerned
with their use herein. Rather, we shall simply use the assays as another class of important organic matter. It should be recognized, that when a reduction in toxicity or mutagenicity occurs during treatment that it could be a net effect due to the elimination of one organic constituent and the addition of another of lower concentration or less potency.

Finally, when considering classes of organic matter that are important to water quality considerations it should be recognized that some unit operations can interact with organics in a negative way. For example, chlorination of water or wastewater for the purpose of disinfection may result in the formation of chlorinated organics. However, such deleterious reactions are not limited to chlorination or the formation of halogenated organics. Thus, an important class of organics are those which react with chemicals during water or wastewater treatment to form compounds which may pose a long-term threat to health and the environment. By their very nature the presence of these compounds can only be measured by their effects. An important class of halogenated organics formed during disinfection with chlorine is trihalomethanes (THM). Consequently, a parameter which may be used to characterize the amount of organics prone to reactions resulting in their formation is the trihalomethane formation potential (THMFP) (132), measured by observing the increase in THMs following chlorination under certain specified conditions. Similarly, one could use total organic halide formation potential (TOXFP) as well. For other reactions the nature of the products is unknown and thus their presence must be detected by toxicity and mutagenicity testing. Consequently, there is a body of literature which uses changes in those parameters as indicators of reactions occurring during treatment.

B. Removal of Organic Contaminants during Wastewater Treatment

A major reason for this study was to determine whether there are likely to be health or water quality related problems associated with the projected increase in the percentage contribution of treated wastewater to the Chattahoochee River. The answer to that question, of course, will depend in part upon how effectively the wastewater treatment plants have removed organic contaminants of particular concern which may have been present in their influents. Are compounds like the priority pollutants or those in Tables 1-3 removed effectively by conventional biological treatment systems when they are present in only low concentration in the wastewater? Grady (76) addressed that question in late 1984 in a report prepared for the EPA-funded Center for Environmental Management at Tufts University. In the closure to his report he stated "The literature review established that while a great deal of work has been done on the removal of toxic pollutants by conventional biological treatment systems, few generalities can be made. The main reason for this is that the capabilities of any given system are influenced strongly by its physical configuration, i.e., they are conditional. ... In spite of that, the available results indicate that most biological treatment systems are remarkably robust and have a large capacity for degrading toxic and hazardous material." In other words, given the fact that the wastewaters being treated and discharged to the Chattahoochee River are predominantly domestic sewage and that the treatment facilities utilize secondary treatment, it is highly likely that any specific problem pollutants which happen to be present will be removed to below detectable limits, but there is no guarantee. Others (10) have reached
similar conclusions about the fate of micropollutants in wastewater treatment systems.

One of the most comprehensive studies on the effects of conventional wastewater treatment practice on micropollutants was done by the EPA in Cincinnati (88,151,152). Two parallel pilot-scale activated sludge systems were operated on domestic sewage, with one also receiving μg/L quantities of 22 priority pollutants. Although the overall removals of the pollutants were excellent, several problem compounds were only removed to a small degree, thereby releasing them to the environment in concentrations of environmental concern. This led to the conclusion that a POTW is not a totally effective system for controlling discharge of some compounds to the environment. This, together with the statement in the preceding paragraph, suggests that the best way to protect the Chattahoochee River from micropollutants is to prevent their discharge to the treatment plants. Like metals, micropollutants are presumably at low levels in the wastewater now and could be kept that way through proper application of pretreatment requirements. Given the potential importance of micropollutants in the Chattahoochee River and the fact that they may enter from nonpoint sources, it seems prudent to limit their discharge by point sources.

An important aspect of the EPA study is that it also looked at toxicity of the wastewaters (88,152). The influent to the control reactor (without priority pollutants) was toxic but the effluent was not. However, the test effluent (with priority pollutants) was still acutely toxic to three different test animals. This demonstrates that even though good removal of conventional and priority pollutants is achieved in a wastewater treatment system, toxicity can still exist. Furthermore, this suggests that the only way to determine whether problems exist as a result of wastewater discharges is to measure directly any toxicity associated with them.

The same EPA pilot facility was used to study the mutagenicity of a mixed industrial/municipal wastewater (135). The untreated wastewater was mutagenic and the removal of mutagenic activity varied from essentially none to as much as two-thirds of that originally present in the raw wastewater. This indicates that the majority of the mutagenic activity was associated with a small fraction of the total organics present. Their results also suggest that an appreciable portion of the responsible mutagens are relatively refractory to removal by conventional primary and secondary treatment. Parallel tests on a totally domestic wastewater revealed that the level of mutagenicity was substantially lower. This supports the assertion that a good way to protect the water quality in this critical reach of the Chattahoochee River is to severely limit the introduction of problem organics through stringent pretreatment regulations.

The data base on toxicity and mutagenicity of domestic wastewaters is limited and is clouded by the presence of industrial wastes. Rappaport et al. (155) conducted one of the first tests on mutagenicity in wastewaters when they investigated plants treating domestic or mixed industrial/domestic wastewaters. All positive samples were obtained from plants treating mixed industrial/domestic wastewater while samples from plants treating strictly domestic wastes were always negative or marginal. Ellis et al. (48) surveyed 10 municipal and industrial secondary effluents and found significant mutagenicity in all of them whereas Cumming et al. (37) found only three of nine
wastewaters (seven were primarily residential wastewater) to be either mutagenic or mildly mutagenic. Surprisingly, the most mutagenic effluent was entirely domestic in origin. Consequently, questions like the one under consideration here reinforce the need for studies advocated by some (135) to establish whether a normal or baseline level of mutagenic activity exists in domestic wastewaters.

C. Alteration of Organics during Wastewater Treatment

The fate of toxic and hazardous organics in wastewaters undergoing treatment is only one aspect of the questions associated with the discharge of treated wastewater to the Chattahoochee River. Because of the recreational use of the river, the treated wastewaters must be disinfected. With the exception of UV light, all currently used disinfectants are strong oxidants which have the potential for reacting with organics in a manner which can increase their toxicity and/or mutagenicity (27). Consequently, that problem must be considered.

Effects of Chlorine

Although the earliest indications of the hazard posed by the chlorination of waters and wastewaters was the observation of THMs and other volatile haloorganic compounds in drinking water (164,165), similar findings have been reported for such diverse systems as wastewater effluents (23,62,66,68,69,117,175,209) industrial wastes, and leachates. In studies relating to the halogenation of humic acids and low molecular weight organic compounds the inescapable conclusion is reached that the chlorination of wastewaters containing any of a wide array of natural organic compounds results in the formation of volatile haloorganic compounds. Thus, both direct evidence and the body of theoretical data necessarily compel us to believe that these compounds will be produced in significant levels as a consequence of wastewater chlorination.

As an indication of the range and complexity of the volatile haloorganic compounds produced by the chlorination of wastewaters, a summary of several of the more significant research findings relating to this area is presented in Table 5.

The formation of halogenated organics is not limited to volatile compounds. In fact, they are thought to be only a small part of the total, with nonvolatile haloorganics constituting the bulk. This extremely broad category includes those compounds which do not have a significant vapor pressure in equilibrium with their aqueous solutions. They will include such substances as halophenols and haloaromatic acids and other high boiling and/or highly polar compounds. These compounds, while of low volatility are not entirely impossible to analyze by gas chromatographic methods. However, in many cases liquid chromatography has been the method of choice in research on the formation and level of these materials. Another class to be treated separately is the class of N-halo compounds or haloamines.

The scope of research into this area is so extensive as to preclude a comprehensive treatment here. Rather, an effort will be made to highlight areas of significance to the subject at hand.
Table 5
Summary of Volatile Haloorganic Compounds
Identified in Chlorinated Wastewaters

<table>
<thead>
<tr>
<th>Compound</th>
<th>References</th>
<th>Volatility*</th>
<th>Sorbability*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>62,66,68,69</td>
<td>H</td>
<td>L</td>
</tr>
<tr>
<td>Dichlorobromomethane</td>
<td>66,68,69</td>
<td>H</td>
<td>L</td>
</tr>
<tr>
<td>Dibromochloromethane</td>
<td>66,68,69</td>
<td>H</td>
<td>L</td>
</tr>
<tr>
<td>Dichlorobutane</td>
<td>66,68,69</td>
<td>H</td>
<td>L</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>175</td>
<td>H</td>
<td>L</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>175</td>
<td>H</td>
<td>L</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>175</td>
<td>H</td>
<td>L</td>
</tr>
<tr>
<td>2 Chloro-3-methyl-1-butene</td>
<td>117</td>
<td>H</td>
<td>L</td>
</tr>
<tr>
<td>Chlorocyclohexane</td>
<td>62,66,68,69</td>
<td>H</td>
<td>M</td>
</tr>
<tr>
<td>Dichlorobenzenes</td>
<td>23,66,68,69,117,209</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Trichlorobenzenes</td>
<td>23,66,68,209</td>
<td>M</td>
<td>H</td>
</tr>
<tr>
<td>Tetrachlorobenzenes</td>
<td>23,109</td>
<td>L</td>
<td>H</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>23,209</td>
<td>L</td>
<td>H</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>23,209</td>
<td>L</td>
<td>H</td>
</tr>
<tr>
<td>Chlorotoluences</td>
<td>69</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>62</td>
<td>H</td>
<td>L</td>
</tr>
<tr>
<td>Tetrachloroethanes</td>
<td>62</td>
<td>H</td>
<td>L</td>
</tr>
<tr>
<td>Pentachloroethane</td>
<td>62</td>
<td>H</td>
<td>M</td>
</tr>
<tr>
<td>Hexachloroethane</td>
<td>62</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Chloroethylbenzenes</td>
<td>69</td>
<td>M</td>
<td>H</td>
</tr>
<tr>
<td>Chlorocumene</td>
<td>69</td>
<td>M</td>
<td>H</td>
</tr>
<tr>
<td>Chloroanisoles</td>
<td>23,117</td>
<td>L</td>
<td>H</td>
</tr>
<tr>
<td>Chlorostyrenes</td>
<td>66,68,69</td>
<td>M</td>
<td>H</td>
</tr>
</tbody>
</table>

*These are subjective estimates based on properties of the compounds. 
L=Low, M=Moderate, H=High

In a pioneering series of studies, Jolley and coworkers applied High Performance Liquid Chromatography (HPLC) to chlorinated sewage effluents (94, 95,99,100). They found 17 chlorinated organic compounds of low volatility in chlorinated sewage effluents as listed in Table 6. Garrison and coworkers (62) identified pentachlorophenol in wastewater effluents. Glaze and coworkers (69) identified a wide array of chlorinated aromatic compounds in a chlorinated sewage effluent by GC/MS methods (Table 7). They also observed large increases in levels of effluent total organic chlorine (TOCl) as a result of chlorination, as have other investigators (7,108,176). Kopperman and associates (117) found chlorophenols and chloranisoles bioconcentrated in fish exposed to chlorinated waste treatment effluents. Although these compounds are measured at very low levels in chlorinated wastewater effluents (0.5-10 μg/L), it is not easy to dismiss them. It is worth noting that very little of the TOCl produced by wastewater chlorination has, in fact, been characterized since Glaze and associates (69) have observed the production of organic chlorine levels on the order of several hundred μg/L during wastewater chlorination. Furthermore, even at levels as low as 12 μg/L one pound per day of haloorganic compound will be discharged by a 10 MGD treatment plant. In the con-
### Table 6
Non-Volatile Haloorganic Compounds Identified by Jolley and Coworkers (94,95,99,100) in Chlorinated Sewage Effluents

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-chlorouridine</td>
<td>1.7</td>
</tr>
<tr>
<td>8-chlorocaffeine</td>
<td>1.7</td>
</tr>
<tr>
<td>6-chloro-2-aminopurine</td>
<td>0.9</td>
</tr>
<tr>
<td>8-chloroxanthine</td>
<td>1.5</td>
</tr>
<tr>
<td>5-chlorouracil</td>
<td>4.0</td>
</tr>
<tr>
<td>chlorobenzoic acids (3)</td>
<td>2.0</td>
</tr>
<tr>
<td>3-chloro-4-hydroxygenzoic acid</td>
<td>1.3</td>
</tr>
<tr>
<td>4-chloromandelic acid</td>
<td>1.1</td>
</tr>
<tr>
<td>4-chlorophenylacetic acid</td>
<td>0.4</td>
</tr>
<tr>
<td>5-chlorosalicylic acid</td>
<td>0.2</td>
</tr>
<tr>
<td>4-chloro-3-methylphenol</td>
<td>1.5</td>
</tr>
<tr>
<td>chlorophenols (3)</td>
<td>2.9</td>
</tr>
<tr>
<td>4-chlororesorcinol</td>
<td>1.2</td>
</tr>
</tbody>
</table>

### Table 7
Non-Volatile Haloorganic Compounds Identified by Glaze and Coworkers (69) in Chlorinated Sewage Effluents

- N-methyltrichloroaniline
- Trichlorodimethoxybenzene
- Chloro-α-methylbenzyl alcohol
- Dichloro-α-methylbenzyl alcohol
- Trichlorophenols
- Telrachlorophenols
- Tetrachlorodimethoxybenzene
- Trichlorophthalic acid ester
- Tetrachlorophthalic acid ester
  - Tetrachloroacetone
  - Pentachloroacetone
  - Hexachloroacetone

Text of current concern over the health effects of trace levels of haloorganic compounds, this is not an insignificant quantity.

Organic chloramines are a special case of the nonvolatile compounds distinguished by their relatively high reactivity as oxidants. While there is present no direct unambiguous identification of any specific organic chloramine in a wastewater effluent documented in the literature, much indirect evidence is available. Morris and coworkers (142) and Jolley and associates (94,95,99,100), among many others have identified a wide array of nitrogenous organic compounds in natural and wastewaters. These include aromatic and aliphatic amines, amino acids and purine and pyrimidine bases. There is every
likelihood that chlorination of waters containing these species will generate the corresponding chloramines. Indeed, Gould and Richards (71–74), Scully and Bempong (11,170) and others (54,180) have demonstrated in pure systems that many of these compounds readily form organic chloramines characterized by very high stability. The failure to detect these species in natural waters derives almost certainly from their labile nature and consequent destruction by existing analytical methods. There is little reason to doubt that these compounds are formed or that they will persist for a considerable distance downstream of a sewage outfall.

In addition to the studies cited above in which specific compounds were identified, a number of studies on the impacts of wastewater chlorination have been conducted in which more general parameters were measured. For example, it has been shown that chlorination can reduce the molecular size, biodegradability, and adsorbability of the residual organics (190), which could cause the compounds to persist longer in the receiving water. In addition, it has been shown that the bulk of the incorporated chlorine resides in the small molecular weight organics (77). Chlorination can also increase the toxicity of treated wastewaters, although the effects can be quite complex (58). When eight effluents from lab-scale activated sludge reactors receiving synthetic wastewater were tested for toxicity, four were found to be toxic and four nontoxic. Chlorination made all four of the nontoxic effluents very toxic, whereas it had a mixed effect on the four toxic effluents: two became less toxic while two became more toxic. This emphasizes the impact of the nature of the organic matter in the wastewater on the outcome of chlorination. This mixed response has also been observed with mutagenicity tests. When the eight effluents discussed above were tested for mutagenicity it was found that chlorination developed mutagenicity in five effluents that had been nonmutagenic while reducing mutagenicity in three which had been mutagenic (58). Similarly, when five effluents from full-scale wastewater treatment plants were tested before and after chlorination it was found that chlorination eliminated mutagenicity in one effluent, increased it in two, had no effect on a fourth, and both increased it and decreased it in another (two samples) (37). Other similar results could be cited (131,135), but the point is the examples can be found in the literature for almost any result. This suggests that the only way to determine how chlorination is impacting on the effluents discharging into the Chattahoochee River is to conduct toxicity and mutagenicity assays.

Effects of Chlorine Dioxide

Chlorine dioxide (ClO₂) has been proposed as an alternative to chlorine as a disinfectant for water and wastewater. Studies by Roberts and coworkers (162) have demonstrated that chlorine dioxide is between two and 70 times more effective as a disinfectant than is chlorine as measured by coliform kill and poliovirus inactivation on both a bench scale and in pilot plant studies. Very early research by Ridenour and associates (158–161) using an array of bacteria and viruses demonstrated its high efficiency and relatively low sensitivity to pH by contrast with chlorine. These studies were further confirmed by Bernarde and coworkers (14–16) who also indicated that the mechanism of disinfection was associated with inhibition of protein synthesis.

In addition to being an excellent disinfectant, chlorine dioxide is substantially less likely than chlorine to form haloorganic compounds (162).
Gall (61) and Masschelein (130) have demonstrated that chlorine dioxide reacts with many classes or organic compounds as an oxidant rather than a halogenating agent. For example, vanillin, a facile trihalomethane precursor with chlorine, undergoes mainly ring cleavage and other oxidation processes on reaction with chlorine dioxide. For example, the reaction of chlorine dioxide with phenols is more likely to lead to the formation of oxidation products—quinones and cleavage products—than halogenation products although small quantities of the latter are formed (70). Lin and Carlson (120) examined the reactions of eighteen nitrogen and sulfur heterocycles with chlorine and chlorine dioxide. They found that the major reaction pathway for ClO₂ was one of oxygenation with virtually no chlorination observed. Similarly, on reaction with a broad range of aromatic organic compounds, the main reaction pathways entail formation of quinones and ring cleavage with only a minor degree of chlorination occurring (12). The primary thrust of these results is uniformly to indicate that, in reaction with organic compounds in water, ClO₂ is far less likely to lead to the formation of haloorganic compounds than is chlorine.

While ClO₂ forms fewer haloorganic compounds than chlorine one should not assume that it is without environmental consequences. Although no literature was found which addressed the problem of the mutagenicity or toxicity of wastewater effluents treated with chlorine dioxide, the fact that it is a strong oxidizing agent suggests that problem organics will be formed. Furthermore, as will be documented later, mutagenicity and toxicity of drinking water have been increased as a result of disinfection with chlorine dioxide. This, plus the fact that treated wastewater contains more organic matter than drinking water, suggests that disinfection of wastewater with chlorine dioxide may cause almost as many environmental problems as does disinfection with chlorine. Thus, any urge to grasp chlorine dioxide as a panacea for the problems associated with wastewater disinfection should be avoided and its use should not be adopted until many studies have been done on the nature of the products formed.

Effects of Ozone

Ozone is another chemical that has been proposed as an effective wastewater disinfectant, although it is generally more expensive than the alternatives (198). Overall, ozone is considered to be at least as effective as chlorine as a disinfectant (198) and is superior in many regards (26). Although it can act to form haloorganics, particularly when the water contains bromide ion (81), its main impact upon organics is through oxidation reactions (10). It is particularly adept at oxidizing carbon-carbon double-bonds, aromatic compounds, and most nitrogen and sulfur containing compounds in which the elements are in a low oxidation state (10). Some of the reactants are likely to be toxic or mutagenic because ozonation reactions tend to form peroxides, epoxides, and other highly oxidized intermediates such as glyoxal and methoxyglyoxal from aromatic precursors (10). The products from ozonation have not been studied as extensively as those from chlorination, in part because of inadequacies in the most commonly used separation and identification techniques for handling ozonation products (144).

Several studies have been done which looked at ozonation products in a general way, however. For example, ozonation of eight effluents from lab-
scale activated sludge reactors revealed an increase in low molecular weight material at the expense of high molecular weight organics without any appreciable change in the concentration of DOC present (77). The ability of ozone to cleave organic molecules has led some to speculate that ozonation will increase the biodegradability of organic compounds. Studies have revealed that while this is true in some cases, it is not always true (64,182,202). For example, low doses (1 g O$_3$/g DOC) had little impact on biodegradability of five different organics whereas higher doses did (64). While increased biodegradability may be advantageous in some circumstances, increasing the biodegradability of the final effluent from a wastewater treatment plant could have a deleterious effect on stream quality. It would tend to increase the oxygen sag in the river, but more importantly, it may allow rapid regrowth of pathogens or nuisance organisms whose concentration had been reduced by disinfection (169). Those desiring detailed data on the reactivity of various organics with ozone in aqueous solution should consult the excellent series of papers by Hoigne and associates (81,85-87).

Most studies on the impact of ozone upon the toxicity and mutagenicity of organics in water have been performed with drinking water and will be reviewed later. However a few studies relative to wastewater disinfection were found. In Marlborough, MA (183) highly nitrified effluent from a wastewater treatment plant treating sewage of primarily municipal origin was disinfected with both ozone and chlorine. On one occasion when the wastewater was mutagenic, disinfection with either chemical reduced the mutagenicity. On another occasion when higher disinfectant doses were required, ozone reduced the mutagenicity whereas chlorine increased it. In a study of the effects of ozone on the mutagenicity of effluents from lab-scale activated sludge reactors it was found that ozonation tended to destroy base-pair mutagens while producing frameshift mutagens (58). Likewise, ozonation reduced the toxicity of the effluents to base-pair sensitive organisms while increasing the toxicity to frameshift sensitive ones. Finally, studies with pure organic compounds confirm that the impacts of ozone are very chemical specific. When 36 organics were studied it was found that ozonation increased the mutagenicity of polynuclear aromatic hydrocarbons and aromatic amines; had no effect on alkylating agents, nitro aromatics, and nitroso compounds; and increased the mutagenicity of hydrozines (110).

All of this suggests that while ozone appears to have less effect on the environment than chlorine, it is not without its bad side. Moreover, the effects appear to be very specific for given situations. Given the cost of ozone disinfection and the fact that problems may exist, very careful study would be required before any decision to require the wastewater treatment plants to shift to this technology.

**Effects of UV Light**

Because of the recognized problems associated with disinfection with chlorine and the expense of the other techniques, there has been an increased interest in disinfection of wastewaters using UV light. A number of recent articles (198,205,206) have discussed UV disinfection in detail and have compared it to other systems for wastewaters. The main problems associated with UV disinfection are not with the technology itself, but with the electrical,
mechanical and hydraulic systems associated with it (206). This is characteristic of a new technology and thus problems of this type will tend to be solved as more experience is gained. One of the striking things about UV disinfection is that in spite of the "teething" problems, almost without exception, plant operations personnel preferred UV over other methods of disinfection (206). Combined with the fact that the costs of UV are quite competitive with chlorine for small to moderately-sized plants (205), this suggests that UV would be an excellent alternative should it be necessary to stop chlorinating the effluents discharging to the Chattahoochee River.

A recent study showed that *Yersinia* and *Giardia* were both more resistant to UV than was *E. coli* (25). This suggests that it may be necessary to adopt another indicator organism for monitoring the effluents in order to adequately protect recreational users of the river. Another potential problem with respect to the recreational users is photoreactivation which occurs when light at a wavelength of 310 to 500 nm cleaves the pyrimidine dimers formed by the UV light, thereby restoring the original base sequence in the DNA and allowing the cell to function normally (198). This can be minimized by proper control of dose or by sequential use of disinfectants. For example, UV followed by ozone is more cost effective than either technology alone for plants in excess of 10 MGD (199). Although no data were given, one would presume that the greatly reduced ozone dose (=20% of ozone alone) would reduce the concentration of problem organics.

Relatively few studies have been performed to assess the effect of UV on organic matter and its toxicity or mutagenicity. While it is possible to oxidize organic matter through the action of UV light (17) the intensity must be much greater than one would ever encounter in wastewater disinfection. Consequently, one would expect UV to have little effect and this is what the limited literature suggests. For example, several studies indicate that UV does not alter the toxicity of an effluent to fish (24,149,205). Furthermore, Jolley et al. (103) showed that UV irradiation of nonvolatile organics in secondary effluent produced only slight chemical changes in them and even eliminated mutagenic constituents in one effluent.

In summary, considering all impacts upon the river and its users, it is likely that benefits could be realized by changes to UV disinfection at the wastewater treatment plants. However, before such expenditures are suggested, it would be wise to investigate the current situation with regard to TOX, toxicity and mutagenicity to determine whether the existing situation constitutes a problem, and if so, whether that problem is likely to grow worse as more development occurs in the Atlanta area.

D. Fate of Organic Contaminants in the Environment

The preceding sections have shown that conventional wastewater treatment plants provide a reasonable degree of protection to the river and its users from toxic organic chemicals which may be discharged with wastewater. Although definitive conclusions cannot be reached about the exact degree of treatment to be expected, it is possible to conclude that the wastewater treatment plants will remove a portion of the compounds entering them. Off-setting that reduction, however, is the potential for formation of toxic and mutagenic
organics during disinfection with chlorine. Thus it is likely that some noxious materials will reach the river. While it is doubtful that their concentrations will be high enough to affect the people using the river for rafting, swimming, etc., it is possible that they could influence aquatic life. A more important question from the standpoint of public health, however, is whether those compounds will persist in the river and reach the water intakes or whether they will be reduced in concentration by various mechanisms in the river.

Bedding et al. (10) have reviewed in detail the mechanisms of pollutant transport and removal. Photolysis, both direct and indirect, can act to degrade SOCs into simpler compounds, thereby increasing their susceptibility to biodegradation. The importance of photolysis will depend upon the light transmitting properties of the water, which may vary seasonally. It is likely that photolysis will be more important in the Chattahoochee River than in many others because of its shallow, rapid nature which would cause a rapid surface renewal rate, thereby frequently exposing all of the water to sunlight. Volatilization is likely to be an important mechanism for removing any volatile SOCs formed during disinfection of the wastewaters because those compounds are relatively resistant to adsorption (which would retard loss by volatilization) and because the nature of the river encourages gas transfer. Hydrolysis can be an important mechanism for destruction of nonvolatile SOCs, especially organic esters such as those found in many pesticides. Thus, it is likely to play a role in removing those SOCs which enter via urban or agricultural runoff. A very important mechanism for removal of SOCs in the natural environment is adsorption because of the hydrophobic character and very low aqueous solubility associated with many of them. Humic and fulvic acids will adsorb low solubility hydrophobic compounds whereas clay particles tend to adsorb polar compounds and compounds containing ionic functional groups. Since the river is likely to contain naturally occurring organic material as well as clays, a broad range of organic contaminants from many sources will tend to be removed. Countering this somewhat, is the fact that incorporation of low solubility micropollutants into humic substances may make them appear to be more soluble than they actually are.

Association of trace organics with clays and humic substances will facilitate their removal in the water treatment plants (41). Because normal water treatment operations are quite effective in removing clays and humic substances the associated organics will also be removed to some degree. Consequently, discharge to a river actually provides a degree of protection which would not be available during direct reuse of a wastewater.

Evidence for the removal of micropollutants in a river environment has been provided by studies done in South Africa (75,106,107). In one study (106,107) the toxicity and mutagenicity of river water were monitored over a 15 mile river run. The mutagenicity was unchanged but the toxicity was reduced. In the other study, (75) mutagenicity was destroyed over a 25 mile stretch of river.

Storage can also have a beneficial effect. When the water from the river with the 15 mile run was stored in an impoundment the mutagenicity was reduced but there was little change in toxicity, perhaps because it had already been reduced in the river. In another study (166), long term storage of a contaminated water led to a shift in organic matter to 90% humic and fulvic acids.
Although it is possible that organic micropollutants are entering the Chattahoochee River with the treated wastewater it should be recognized that they also enter from many other sources. One important source in an urban area like Metropolitan Atlanta is rainfall. Although several studies have been done, two in particular illustrate the importance of this source. Unfiltered rainwater (thereby containing particulates) from the Los Angeles area was either solvent-extracted or treated by purge-and-trap (104). The resulting materials were analyzed with capillary GC-MS revealing over 600 peaks, of which about 300 have been tentatively identified. Typical compounds, all in the µg/L range, included aliphatic and aromatic hydrocarbons, phthalates, benzaldehydes, phenols, aliphatic and aromatic ketones, mono- and di-carboxylic acids, amines, azaarenes, etc. In other words, a broad spectrum. In Portland, OR (119) an important study demonstrated that gas scavenging in the atmosphere can dissolve pollutants directly without the intermediary action of particulates. In this case, phenolics in ng/L and µg/L quantities were found to be at concentrations which were close to equilibrium with the concentrations in the atmosphere. Both of these studies demonstrate that even water from a protected watershed can contain xenobiotic compounds in low concentration if the rainfall on the watershed comes from urban areas.

Urban runoff is another source of micropollutant contamination. In a survey of 19 cities, 71 priority pollutants were detected (14 inorganic and 57 organic) (30). Eleven of the organic micropollutants were detected with a frequency of greater than 10 percent.

It should be recognized that many toxins and carcinogens are produced naturally in the environment (1,177,204). Thus, it is quite possible for an otherwise unpolluted water source to contain mutagenic or toxic materials. As an example, the bottom sediment of a reservoir in Missouri as well as water from it, was found to be mutagenic even though there was no evident source of external pollution (124). Furthermore, Lake Michigan water from two miles off-shore showed seasonal mutagenic activity (56), indicating that it might be of natural origin although pollutants have obviously entered the lake. Seasonal variations in mutagenic activity may be common because they have been observed both in the United States (79) and in South Africa (75). This suggests that any sampling program to test the river water for toxicity or mutagenicity must cover at least one calendar year.

As shown in Table 8, many untreated surface waters have been shown to be mutagenic. Some obviously receive industrial and other xenobiotic contaminants while others do not. As shown above, although many purification mechanisms are probably active in the Chattahoochee River, contaminants can enter from many sources and cases have been observed where rivers and lakes more protected than it have contained mutagens and toxins. The only way to determine if the river water contains problem organics is to test it on a routine basis for at least one year. Furthermore, since the impact of urban runoff and other nonpoint discharges will likely vary with the amount of rainfall, studies should include both wet and dry weather conditions. Tests would also have to be made of the treated wastewaters to determine their contribution to any observed mutagenicity or toxicity and to allow evaluation of the self-purification in the river. Because toxins and mutagens are produced in nature and enter rivers from nonpoint sources it would be a mistake to focus on the wastewater and to assume that piping it to a point below the water intakes would solve any potential problems. Rather, one should first investigate the
Table 8
Untreated Surface Waters and Groundwaters Giving Mutagenic Responses in the Ames Salmonella Assay

<table>
<thead>
<tr>
<th>Source of Water</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td>111</td>
</tr>
<tr>
<td>Groundwater</td>
<td>111</td>
</tr>
<tr>
<td>Groundwater</td>
<td>187</td>
</tr>
<tr>
<td>Nishitaka River in Japan</td>
<td>129</td>
</tr>
<tr>
<td>Four interconnected Japanese rivers</td>
<td>128</td>
</tr>
<tr>
<td>Rhine River</td>
<td>3, 38, 192, 210</td>
</tr>
<tr>
<td>Meuse River</td>
<td>3, 109, 210</td>
</tr>
<tr>
<td>Mississippi River</td>
<td>3</td>
</tr>
<tr>
<td>Sheep River</td>
<td>3</td>
</tr>
<tr>
<td>Sava River</td>
<td>3</td>
</tr>
<tr>
<td>Calumet River</td>
<td>3, 56</td>
</tr>
<tr>
<td>Fox River</td>
<td>3, 56</td>
</tr>
<tr>
<td>Vaal River</td>
<td>3</td>
</tr>
<tr>
<td>Unnamed river in Iowa</td>
<td>79</td>
</tr>
<tr>
<td>Unnamed river</td>
<td>109</td>
</tr>
<tr>
<td>Four surface waters</td>
<td>111</td>
</tr>
<tr>
<td>Surface water</td>
<td>6</td>
</tr>
<tr>
<td>Lake Michigan</td>
<td>56</td>
</tr>
<tr>
<td>Belgian reservoir</td>
<td>121</td>
</tr>
</tbody>
</table>

conditions in the river and in the effluents to determine whether a problem exists, its magnitude, the contribution of the river to both self-pollution and self-purification, etc. Only then can rational decisions be made which will protect human health over the long term.

E. Removal of Organic Contaminants during Water Treatment

From a health standpoint, the importance of SOCs, toxic organics, and mutagenic organics in the Chattahoochee River (regardless of source) will depend upon how effectively they are removed in the water treatment process. It is conceivable that water treatment processes could be designed which would protect the consumer against anticipated pollutant levels. In that case, the decision might be made to not alter the wastewater treatment processes but to concentrate any changes at the water treatment plants, thereby allowing maximum utilization of any natural purification processes occurring in the river. On the other hand, should future studies show that micropollutant levels in the river were sufficient to harm aquatic life, or if removal of those pollutants at the water treatment plants did not appear feasible, then it might be necessary to modify the wastewater treatment processes to eliminate or reduce their discharge. In either case, it is necessary to know something about the ability of the water treatment processes to remove problem organics.
Removal of Micropollutants

Awareness of the presence of micropollutants in drinking water is relatively recent and consequently the literature addressing the problem is not extensive. Nevertheless, the following is not an exhaustive literature search but rather is intended to give a reasonable picture of current knowledge. It should be recognized, however, that it is extremely difficult to generalize about the exact degree of micropollutant removal that will occur during drinking water treatment just as it was difficult to generalize about micropollutant removal during wastewater treatment. This is because micropollutants seldom occur singly; rather, they normally occur in complex mixtures of undefined character. If a change is made in the milieu in which a micropollutant is found, then a change will normally occur in the extent to which that constituent is removed by a given unit operation.

In spite of the aforementioned difficulties, Kool et al. (112) were able to group organic micropollutants into four categories and draw broad conclusions about the removals of each category. Group I contained volatile, nonpolar compounds, which are the most studied. Generally, conventional water treatment systems are not suited for their removal. Some compounds, like the alkylated benzenes, can be oxidized by ozone but the most universally applicable process for their removal are aeration and adsorption on activated carbon and this is reflected in EPA's recent review of available technology for removing volatile SOCs (51). Both techniques, however, have limited capability to remove the compounds completely. For example, lower chlorinted hydrocarbons rapidly break through beds of granular activated carbon (GAC). Group II contained volatile, polar compounds, which are the least studied. Although data are limited, they are thought to be removable by volatilization, activated carbon adsorption and biodegradation. Group III contained nonvolatile, nonpolar compounds. A useful characteristic of these compounds, particularly the high molecular weight ones, is that they tend to adsorb strongly to the particulates in the water. Consequently, operations which remove the particulates tend to remove them as well. Group IV contained nonvolatile polar compounds. It is currently receiving much attention because it contains many of the compounds contributing to TOX that are formed during water and wastewater chlorination. Little data are yet available on them.

Because coagulation is so widely used in the treatment of drinking water it has received attention by researchers seeking to know how micropollutants can be removed. Semmens and coworkers (171-173) investigated the removal of organics from Mississippi River water by coagulation with alum or with an iron/polymer mixture. When the removal of general organic matter was investigated it was found that acidic and neutral organic compounds were the main ones removed (172). Furthermore, hydrophobic compounds were slightly better removed than hydrophilic ones. Overall, alum removed 52 percent of the total organic carbon (TOC) whereas the iron/polymer mixture removed 47 percent. Other workers (93) have also observed appreciable removal of TOC from a variety of waters. In another part of Semmens' study, the removal of specific compounds was evaluated in the presence and absence of natural organic matter (171). Octanoic acid, salicylic acid and phenol were removed better in the absence of natural organic matter whereas benzoic acid was removed better in its presence. Overall, however, the removals ranged only from 3 to 20 percent. Removal was relatively insensitive to coagulant dose and appeared to be the result of complex formation and precipitation rather than of adsorption. This
result, together with their observation that organics with molecular weights below 1000 amu were not well removed by coagulation, suggests that individual micropollutants will not be removed to any great degree by coagulation and sedimentation. This inference is supported by the work of others who have studied the fate of specific micropollutants (39,143), although there is some question about the role that adsorption onto floc particules might play (188).

The removal of micropollutants by granular activated carbon (GAC) has received considerable attention in the last decade and a complete review of all work on that topic was considered to be beyond the scope of this project. Nevertheless, it should be recognized that in spite of the fact that the effectiveness of GAC depends upon the type of compounds involved and the organic milieu within which they are found, it is still generally considered to be the most satisfactory and cost effective technique available for the removal of the broad spectrum of SOCs present at low concentrations in raw waters (49,134,186,201,208). As a result over 50 treatment plants in the United States currently use it (186). GAC is certainly not a panacea for micropollutants, however. For one thing, it is not effective against halogenated C₁ and C₂-aliphatics such as trihalomethanes and chlorinated solvents (89). For another, the entire problem of chromatographic separation or displacement is unresolved (10). And finally, there is much controversy over the advantages and disadvantages associated with the presence of biological activity in the GAC bed (55). One technique that has been proposed for enhancing GAC performance is preozonation, presumably because it will increase the fraction of organics susceptible to biodegradation in the bed. However, if volatile halogenated organics are present the reduction in molecular size associated with ozonation (77) will increase competition for adsorption sites and reduce removal of the halogenated organics (125,147). As a consequence, when the criterion controlling GAC service life was removal of volatile halogenated organics, the cost of ozonation was not offset by lower GAC operating costs (147,148). When DOC removal controls service life, however, preozonation is a cost-effective measure, but other, more conventional treatment options may offer equal system performance at lower total cost (147,148).

Other oxidation systems have also been proposed for destroying SOCs during water treatment, but very little experience have been gained with them. Among them are ozone/UV (154) and ferrate oxidation (39,40). As might be expected, ferrate was very specific in its reactivity.

Finally, it should be noted that work has been done with water reclamation systems and that the projects have been very successful in reducing the concentrations of micropollutants to very low levels (118,133). The processes are much more complex than would be warranted in this situation, however.

Removal of Mutagenicity and/or Toxicity

Although we need information about the ability of various water treatment processes to remove micropollutants, there are so many of them in water that it would almost be an impossible task to investigate them all. Consequently, it is more efficient to concentrate on the ability of various unit operations or process trains to remove mutagenicity or toxicity, regardless of the compounds causing them. In this way we get a much broader picture.
The literature concerning positive or neutral impacts of various water treatment operations on mutagenicity in water is summarized in Tables 9-11. Ultraviolet (UV) irradiation appears in both Tables 9 and 10 but does not appear at all in Table 11. This is consistent with our earlier discussion of UV as a disinfectant of wastewaters in which it was seen that UV at doses normally employed had little impact on organic matter. Likewise, the discussion in the preceding section suggests that coagulation would have a mixed effect, depending upon the nature of the organic matter responsible for the mutagenicity. This is exactly what happens as coagulation appears in both Table 9 (does not destroy mutagenicity) and in Table 11 (reduces or eliminates mutagenicity). Furthermore, as might be anticipated, it does not form it (Table 10).

Table 9
Water Treatment Operations Having No Impact on the Mutagenicity of Mutagenic Waters

<table>
<thead>
<tr>
<th>Source of Water</th>
<th>Treatment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drinking Water from</td>
<td>Sand filtration and ozonation</td>
<td>153</td>
</tr>
<tr>
<td>a Polluted River</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhine River</td>
<td>UV irradiation</td>
<td>210</td>
</tr>
<tr>
<td>Lake Michigan</td>
<td>Coagulation and sedimentation</td>
<td>56</td>
</tr>
<tr>
<td>Lake Michigan</td>
<td>Coagulation, sedimentation and chlorination</td>
<td>56</td>
</tr>
</tbody>
</table>

Table 10
Water Treatment Operations Having No Impact on the Mutagenicity of Non-Mutagenic Waters

<table>
<thead>
<tr>
<th>Source of Water</th>
<th>Treatment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Water</td>
<td>UV irradiation</td>
<td>38, 210</td>
</tr>
<tr>
<td>Spring Water</td>
<td>Chlorination</td>
<td>139</td>
</tr>
<tr>
<td>Fox River</td>
<td>Chlorination</td>
<td>56</td>
</tr>
<tr>
<td>Fox River</td>
<td>Chlorination followed by coagulation</td>
<td>56</td>
</tr>
<tr>
<td>Fox River</td>
<td>Coagulation</td>
<td>56</td>
</tr>
<tr>
<td>Fox River</td>
<td>Coagulation followed by chlorination</td>
<td>56</td>
</tr>
</tbody>
</table>

The main information of interest is in Table 11 because those are the operations that reduce or eliminate mutagenicity. The predominant operations that appear there are ozonation and GAC adsorption. In this context the impact of ozonation would probably be through oxidation and cleavage of the responsible molecules whereas the effect of GAC would be through their removal from the water. In the lower part of the table are a number of miscellaneous
Table 11
Water Treatment Operations Reducing or Eliminating Mutagenicity in Water

<table>
<thead>
<tr>
<th>Source of Water</th>
<th>Treatment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Water</td>
<td>Ozonation</td>
<td>38, 210</td>
</tr>
<tr>
<td>Chlorinated drinking water</td>
<td>Ozonation</td>
<td>43</td>
</tr>
<tr>
<td>from the Arno River</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorinated drinking water</td>
<td>Ozonation</td>
<td>193</td>
</tr>
<tr>
<td>from the Meuse River</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drinking Water</td>
<td>Ozonation</td>
<td>113, 114</td>
</tr>
<tr>
<td>Meuse River</td>
<td>Ozonation</td>
<td>109</td>
</tr>
<tr>
<td>Rhine River</td>
<td>Ozonation</td>
<td>109</td>
</tr>
<tr>
<td>Rhine River</td>
<td>Ozonation</td>
<td>192</td>
</tr>
<tr>
<td>Rhine River</td>
<td>Ozonation</td>
<td>210</td>
</tr>
<tr>
<td>Treated Wastewater</td>
<td>Ozonation</td>
<td>183</td>
</tr>
<tr>
<td>Rhine River</td>
<td>UV plus Ozonation</td>
<td>210</td>
</tr>
<tr>
<td>Chlorinated drinking water</td>
<td>GAD Adsorption</td>
<td>113, 114</td>
</tr>
<tr>
<td>from Meuse River</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drinking Water from Meuse River</td>
<td>GAC Adsorption</td>
<td>109</td>
</tr>
<tr>
<td>Drinking Water from Rhine River</td>
<td>GAC Adsorption</td>
<td>109</td>
</tr>
<tr>
<td>Chlorinated drinking water</td>
<td>GAC + postchlorination</td>
<td>121</td>
</tr>
<tr>
<td>Calumet River</td>
<td>RO plus GAC</td>
<td>89</td>
</tr>
<tr>
<td>Lake Michigan</td>
<td>Coagulation</td>
<td>56</td>
</tr>
<tr>
<td>River Water</td>
<td>Coagulation and Sedimentation</td>
<td>56</td>
</tr>
<tr>
<td>Drinking Water from polluted river</td>
<td>Sand filtration, ozonation, GAC</td>
<td>153</td>
</tr>
<tr>
<td>and postozonation or postchlorination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coagulated and Settled Water from Lake Michigan</td>
<td>Chlorination</td>
<td>56</td>
</tr>
<tr>
<td>Rhine River</td>
<td>Chlorination</td>
<td>210</td>
</tr>
<tr>
<td>Rhine River</td>
<td>Chlorine dioxide</td>
<td>210</td>
</tr>
<tr>
<td>Chlorinated drinking water</td>
<td>Dechlorination with sodium sulfite</td>
<td>28</td>
</tr>
</tbody>
</table>

operations, demonstrating that almost any unit operation can destroy mutagenicity given the appropriate type of mutagenic organic matter. It is especially interesting to note that even chlorination can reduce mutagenicity, although as we will see later, it is much more likely to cause it.

The repetitive appearance of ozonation and GAC adsorption in Table 11 suggests that they are particularly well suited to the removal of mutagenic compounds. It should be remembered, however, that lab and pilot studies would be required to determine whether such operations would be effective on waters
removed from the Chattahoochee River, should they be mutagenic. As will be seen later, there are circumstances under which ozonation can increase mutagenicity, although the literature review revealed many more instances in which it eliminated it. Nevertheless, this observation illustrates the need for specific studies. One characteristic of GAC that may make its use on mutagenic waters more economical is that it continues to effectively remove mutagenicity even after it is exhausted with respect to DOC (123,137). In a study using Ohio River water, the bed reached exhaustion with respect to DOC by the end of 15 weeks but continued to remove mutagens for an additional 20 weeks. The bed was then taken off-line and the carbon at various points in the bed was extracted and the extracts were assayed for mutagenicity, thereby yielding some interesting findings. Frame-shift mutagens were found only in the top portion of the bed whereas base-pair mutagens were found throughout. Thus exhaustion was imminent with respect to base-pair mutagens but additional capacity remained for the other. This could be due to differences in adsorbability of the different types of compounds or to different quantities in the water. Furthermore, direct acting mutagens decreased in concentrations down the bed whereas promutagens were constant throughout. The authors are continuing to study this system because the results of their study will eventually provide better information on the design of GAC contactors to optimize the removal of mutagenic materials.

F. Formation of Problem Organics during Water Treatment

It would be counter productive to go to great lengths to remove micropol-lutants and other toxic and/or mutagenic compounds from the river water if action were taken during water treatment which resulted in the reintroduction of compounds of that type. Thus, it would be beneficial to investigate the circumstances under which such compounds might be formed. It must be recognized, however, that no disinfection technique is effective and also free of harmful by-products (27). The goal will be to choose a disinfectant and a disinfection technique which disinfects effectively while producing the least amount of hazardous by-products.

Formation of THMs and Other Chlorinated Organics

It is well known that chlorination of drinking waters can produce trihalomethanes and other chlorinated organics from reactions with humic and fulvic acids and other naturally occurring organic matter (164,165,175,189). Furthermore, as discussed earlier, chlorine dioxide and ozone produce far fewer halogenated products but still produce problem organics to a certain degree. Most attention in water supplies has been on the formation of THMs but recently it has been recognized that THMs represent only about 20 percent of the chlorinated organics formed (156). Consequently, now most research attention is being focused on the nonvolatile polar components, or Group IV presented earlier (112). Much of the information presented earlier under the heading of wastewater is pertinent to this subject but will not be repeated.
Formation or Increase in Mutagenicity

An extensive body of literature is now available concerning the formation or increase in mutagenicity associated with the disinfection of drinking water. Although the initial data on the formation of THMs was collected in Holland (164), interest in THM formation and mutagen production is worldwide. At this point, research is being conducted all over Europe and in South Africa, Japan and the United States.

Table 12 summarizes the literature which documents that certain unit operations cause or increase the mutagenicity of finished drinking water. Perusal of that Table reveals that 36 of the cases involved chlorination in some form or other. Thus, it is abundantly clear the disinfection with chlorine can lead to the formation of mutagenic material in drinking water. Like THMs, this material is primarily the result of reactions of the chlorine with humic and fulvic acids as well as with other naturally occurring organic matter (22,127). There is evidence, however, that the mutagenicity is not due only to the THMs, but also to nonvolatile organics (122,187,196,210). In fact, some investigators (196) have been unable to obtain a correlation between mutagenicity and the concentration of volatile halogenated compounds. Consequently, low THM values do not necessarily mean the absence of mutagenicity (140). It should also be noted that while there is a very high likelihood that chlorination will form mutagens, their formation is not a certainty. Examination of Table 10 reveals two waters that did not yield mutagenicity upon chlorination; both were low in humic materials. Thus, the nature and quantity of organic material in the raw water at the point of chlorination is an important determinant of the amount of mutagenicity formed. As a consequence, it should not be assumed that the finished drinking waters produced from the Chattahoochee River are mutagenic. Rather, tests should be conducted to determine whether current practice produces mutagenic compounds. Because the formation of mutagens tends to vary seasonally (6,75,112,121,133) tests should be run for at least one calendar year to assess the significance of mutagen formation.

Only a few papers were found in which the impact of chlorine dioxide was studied. Whereas it is recognized that chlorine dioxide produces fewer halogenated organics as documented earlier, it is interesting to note that it has been shown to form mutagens in several instances. In fact, in one case disinfection doses of ClO2 had a greater affect on mutagenicity than did chlorination (38). With respect to mutagen formation, ClO2 evidently has no advantage over chlorine (210).

Similarly, only a few papers were found attributing the formation of mutagens to ozonation, whereas many were found in which it decreased mutagenicity (Table 11). There is some evidence that the action of ozone depends on its dose (194). When nonmutagenic water samples were treated with ozone, more of those receiving low doses developed mutagenicity than did those receiving high doses. This is consistent with other studies in which extremely high ozone doses applied to 28 different organic compounds did not produce mutagenicity (3). Ozonation is not without its problems, however. As discussed under wastewater, ozonation can increase the biodegradability of residual organic matter. If the water is then stored and distributed to consumers there is an increased potential for bacterial regrowth with that organic matter serving as growth substrate (166).
<table>
<thead>
<tr>
<th>Source of Water</th>
<th>Treatment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reclaimed Wastewater</td>
<td>Chlorination</td>
<td>146</td>
</tr>
<tr>
<td>Treated Wastewater</td>
<td>Chlorination</td>
<td>157</td>
</tr>
<tr>
<td>Treated Wastewater</td>
<td>Chlorination</td>
<td>183</td>
</tr>
<tr>
<td>Surface Water</td>
<td>Chlorination</td>
<td>127</td>
</tr>
<tr>
<td>Surface Water</td>
<td>Chlorination</td>
<td>53</td>
</tr>
<tr>
<td>Surface Water</td>
<td>Chlorination</td>
<td>38, 210</td>
</tr>
<tr>
<td>Surface Waters</td>
<td>Chlorination (in 8 of 11 tested)</td>
<td>111</td>
</tr>
<tr>
<td>Pristine River</td>
<td>Chlorination</td>
<td>187</td>
</tr>
<tr>
<td>River in Iowa</td>
<td>Chlorination</td>
<td>79</td>
</tr>
<tr>
<td>Meuse River</td>
<td>Chlorination</td>
<td>210</td>
</tr>
<tr>
<td>Rhine River</td>
<td>Chlorination</td>
<td>192</td>
</tr>
<tr>
<td>Rhine River</td>
<td>Chlorination</td>
<td>38</td>
</tr>
<tr>
<td>Calumet River</td>
<td>Chlorination</td>
<td>56</td>
</tr>
<tr>
<td>Norwegian Lake</td>
<td>Chlorination</td>
<td>140</td>
</tr>
<tr>
<td>Reservoir</td>
<td>Chlorination</td>
<td>121</td>
</tr>
<tr>
<td>Groundwater</td>
<td>Chlorination</td>
<td>187</td>
</tr>
<tr>
<td>Drinking Water</td>
<td>Chlorination</td>
<td>28</td>
</tr>
<tr>
<td>Arno River</td>
<td>Prechlorination</td>
<td>43</td>
</tr>
<tr>
<td>Meuse River</td>
<td>Postchlorination</td>
<td>109</td>
</tr>
<tr>
<td>Rhine River</td>
<td>Postchlorination</td>
<td>109</td>
</tr>
<tr>
<td>Meuse River</td>
<td>Breakpoint chlorination</td>
<td>109</td>
</tr>
<tr>
<td>Calumet River</td>
<td>Chlorination followed by coagulation</td>
<td>56</td>
</tr>
<tr>
<td>River</td>
<td>Prechlorination, flocculation, filtration and postchlorination</td>
<td>139</td>
</tr>
<tr>
<td>Lake</td>
<td>Prechlorination, flocculation, filtration and postchlorination</td>
<td>139</td>
</tr>
<tr>
<td>Meuse River</td>
<td>Breakpoint chlorination, coagulation, filtration, and partial dechlorination</td>
<td>193</td>
</tr>
<tr>
<td>Calumet River</td>
<td>Coagulation followed by chlorination</td>
<td>56</td>
</tr>
<tr>
<td>Norwegian River</td>
<td>Flocculation, filtration and chlorination</td>
<td>140</td>
</tr>
<tr>
<td>Norwegian River</td>
<td>Flocculation, filtration and chlorination</td>
<td>140</td>
</tr>
<tr>
<td>Two Norwegian Lakes</td>
<td>Flocculation, filtration and chlorination</td>
<td>140</td>
</tr>
<tr>
<td>Drinking Water</td>
<td>Flocculation, filtration and chlorination</td>
<td>196</td>
</tr>
<tr>
<td>Rhine River</td>
<td>Flocculation, filtration, GAC and chlorination</td>
<td>192</td>
</tr>
<tr>
<td>Source of Water</td>
<td>Treatment</td>
<td>Reference</td>
</tr>
<tr>
<td>------------------------</td>
<td>---------------------------------------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Industrial River</td>
<td>Flocculation, sedimentation, filtration and chlorination</td>
<td>187</td>
</tr>
<tr>
<td>Vaal River</td>
<td>Flocculation, sedimentation, filtration and chlorination</td>
<td>75</td>
</tr>
<tr>
<td>Ohio River</td>
<td>Flocculation, sedimentation and chlorination</td>
<td>123</td>
</tr>
<tr>
<td>Two Norwegian Lakes</td>
<td>Microstraining and chlorination</td>
<td>140</td>
</tr>
<tr>
<td>Norwegian Lake</td>
<td>Microstraining, ozonation, chlorination</td>
<td>140</td>
</tr>
<tr>
<td>Meuse River</td>
<td>Chlorine dioxide</td>
<td>140</td>
</tr>
<tr>
<td>Surface Water</td>
<td>Chlorine dioxide</td>
<td>38, 120</td>
</tr>
<tr>
<td>Rhine River</td>
<td>Chlorine dioxide</td>
<td>210</td>
</tr>
<tr>
<td>Rhine River</td>
<td>Chlorine dioxide</td>
<td>38</td>
</tr>
<tr>
<td>Treated Wastewater</td>
<td>Ozonation</td>
<td>80</td>
</tr>
<tr>
<td>Meuse River</td>
<td>Ozonation</td>
<td>194</td>
</tr>
<tr>
<td>Rhine River</td>
<td>Ozonation</td>
<td>192</td>
</tr>
<tr>
<td>Drinking Water</td>
<td>GAC</td>
<td>109</td>
</tr>
</tbody>
</table>
G. Alteration of Water Treatment Practice to Minimize Formation of Problem Organics

Since the discovery of THMs in drinking water there has been considerable discussion about the continued use of chlorine as a disinfectant (20,27). One must recognize, however, that there are risks associated with the use of all disinfectants and that the risks of the alternatives are often less well known than the risks associated with chlorination (21). Consequently, the primary response of the U.S. EPA and the water industry has been to examine ways in which the production of problem organics during drinking water treatment can be minimized.

Most work has been done on minimizing THM formation because recognition of the THM problem preceded recognition of the presence of mutagenicity due to the nonvolatile fraction. As a consequence, little work was found specifically addressing alteration of water treatment processes to minimize mutagen formation. Of course, the information reviewed earlier on the removal of organic contaminants is relevant to this topic. It should be noted that the formation of mutagens appears to be very site specific and that alterations in water treatment practice to minimize them will require experimental studies. This suggests that an important first step is to show that a problem exists. Consequently, one of the first things that should be done is to screen the treated water for mutagens. This will be discussed more later.

The main fact that surfaces from a review of the literature about the water treatment practice is that once THMs are formed they are hard to remove (10). Consequently, the emphasis has been on the prevention or minimization of their formation (179). This is generally accomplished by delaying chlorination until the humic and fulvic acid precursors of THMs have been reduced in concentration through coagulation, etc. (179). Alum has been shown to be reasonably effective in removing the precursors of THMs and TOX (156) although the overall removal is influenced more by the source of the water than by the particular water treatment process employed (32). This latter aspect is complicated by the fact that the potential for forming THMs and other chlorinated organics varies seasonally (83,197). Thus, any studies on how to control a problem must be conducted over a reasonably long time period. Investigators have also been interested in the use of activated carbon for the removal of THM precursors, but with mixed success (67,92). When ozone precedes GAC, relatively little benefit is seen when THM formation potential is the criterion (67). Others have stated that generalization can't be made about the impact of chemical pretreatment on the adsorption of humic substances and other THM precursors because of the importance of the overall chemical composition of the water (203).

With regard to mutagenicity, it appears that at least a portion of the mutagenic materials formed during chlorination can be destroyed by dechlorination (28,29). This is consistent with destruction of organochloramines. It should be noted, however, that more recent work (207) was not as successful as the original work, suggesting that destruction of mutagens once they are formed may not be a simple process. This suggests that, like THMs, the focus in water treatment should be on the prevention of mutagen formation.
H. Health Effects Associated with Organic Contaminants

Considerable information has been presented in this review which demonstrates that potentially toxic and hazardous materials are finding their way into our country's drinking water from a variety of sources. The critical question, however, is whether those materials are indeed having an impact on human health. In the Introduction, evidence was presented that groundwater replenishment with treated wastewater in Los Angeles has had no deleterious effect on human health (146). Are there other studies which suggest that the consumption of water containing SOCs, THMs, etc. will cause health problems? It is beyond the scope of this study and the expertise of the investigators to review all of the epidemiological studies that have been performed. However, two reviews of such studies made summary statements which are relevant to this question (8,36).

Crump and Guess (36) stated the following: "The case control studies completed to date (1982) have found rectal, bladder, and colon cancer risks associated with chlorinated water to be about 1.1 to 2.0 times higher than the risk for unchlorinated water. *** These risk ratios are large enough to be of concern, yet small enough to be difficult to separate confounding risks associated with other environmental factors such as smoking, diet, air pollution, occupation, and 'urban lifestyle'. By traditional epidemiological standards, risk ratios below 2.0 are generally subject to doubt no matter how large the study. *** Thus, all of the apparent increase in cancer risk associated with chlorinated water in these studies could be explained by confounding the variables that could not be taken into account within the limitations of present study designs and methodologies. *** Because of the methodological limitations of these studies and the generally small elevations in relative risk, it must be concluded that the association between chlorination and cancer found in these studies is weak by traditional epidemiological standards."

Bedding et al. (8) reached similar conclusions: "Toxicological studies and epidemiological surveys may provide indications of the potential hazards, but they cannot establish an incontrovertible cancer causality (13). Results from health studies to date have not produced firm evidence of a link between trace organic compounds in drinking water and cancer (14). Thus, precise conclusions cannot be drawn at this stage. Clearly, however, many drinking water supplies contain substances that would present an acute health risk if they were present at much higher concentrations (14). The risk associated with their presence in trace amounts in water may be estimated more accurately in the future when additional information has been accumulated."

Thus, the opinion of these experts is that the evidence is weak. There has recently been published, however, an ecological epidemiological study which avoided many of the problems associated with most (91). It was conducted in Iowa on towns with groundwater supplies and the purpose was to determine whether increased disease incidence could be correlated with contaminants in water supplies. The things which made this study unique were the fact that each town had its own water supply and the manner in which health records are maintained in Iowa. The results showed associations between 1,2-dichloroethane and cancers of the colon and rectum and between nickel and cancers of the bladder and lung. The investigators felt, however, that nickel and 1,2-dichloroethane were merely indicators of the groundwater supplies most susceptible to anthropogenic contamination. Thus, it does appear that trace
level contaminants in water supplies can lead to disease, although the association is admittedly weak.

I. Significance of the Problem and Recommendations

Are organic contaminants likely to be a problem as the contribution of wastewater to the Chattahoochee River is increased? No definitive answers are available to that question in spite of the large amount of literature reviewed. However, much more of the literature suggests that there may be a problem than suggests that there will be none. Priority pollutants and other xenobiotic pollutants which find their way into domestic wastewater are seldom removed completely by conventional wastewater treatment practice. Disinfection of wastewater with chlorine, chlorine dioxide and ozone can all lead to the production of toxic and/or mutagenic chemicals in trace concentrations. If micro-pollutants reach the water treatment plants, conventional treatment techniques as now practiced will do little to remove them. And finally, disinfection of the drinking water with chlorine may cause the production of mutagens and toxins in trace concentrations. The major impact of wastewater on that production would be to increase the concentration of humic materials and other organic matter upon which the chlorine could act. Mitigating all of these potential problems is the fact that the river is currently relatively clean and that natural removal mechanisms in it will act to reduce the concentrations of any materials discharged by the wastewater treatment plants. The extent of that reduction is unknown, however. The available evidence indicates that there is no cause for alarm; other water supplies within the United States are much more contaminated. At the same time prudence dictates that concrete data be gathered before an actue problem develops so that orderly planning can proceed.

The major need at this time is for specific information about the river and the treated wastewaters. Only then can decisions be made about whether a problem is likely to exist. Several types of data would be helpful.

First, it would be worthwhile to know whether the organic chemicals listed in the primary and secondary drinking water standards are entering the river through the treated wastewaters and if they are, what their fate is in the river. Consequently, it is recommended that the treated wastewaters be analyzed for those chemicals on sufficient occasions to establish whether they are routinely present. At the same time samples should be taken at various points along the river, starting at Buford Dam to monitor the fate of the contaminants in the river. Samples immediately above each wastewater outfall and at each water intake would be sufficient for this purpose. Finally, if the contaminants are found in the river at the water intakes, samples of raw and finished water should be collected at each treatment plant to establish the efficacy of the water treatment processes for their removal. The presence of these chemicals is not likely to be seasonal and thus a limited sampling program (i.e. 3 or 4 times) should be adequate.

Knowledge is also needed about organic contaminants other than those in the primary and secondary drinking water standards because they represent only a small fraction of the organics which could be present in water. There are so many other organic chemicals, and so little is known about their health effects that it would make little sense to simply select an arbitrary list for
analysis. What is needed is a surrogate or general analysis which would represent a broad class of potentially toxic organics. Although there is no general consensus on such an analysis, the potential for formation of halogenated organics during wastewater disinfection suggests that some measure of them would be appropriate. Total organic halide (TOX) is a group parameter which includes many, but not all halogenated organics, as discussed earlier. Nevertheless, it appears to be a reasonable parameter to follow to determine the amount of potentially troublesome organics leaving the wastewater treatment plants. Furthermore, if it were measured on the wastewater effluents before and after disinfection it would give an indication as to the importance of that operation in the total amount being discharged. In addition, measurement of TOXD in the river would shed light on the fate of xenobiotics therein. This information will be very helpful in establishing whether alternative means of wastewater disinfection should be explored. Consequently, it is recommended that a routine sampling program be established in which the wastewater effluents before and after disinfection, and the Chattahoochee River at several points are analyzed for their TOX concentrations. Because the susceptibility of naturally occurring organics to chlorination reactions is likely to vary seasonally, and because the fate of the resulting chlorinated organics in the river is likely to depend on temperature and the general level of biological activity, the sampling program should extend through all seasons. In addition, to assess the impact of nonpoint discharges but high and low flow conditions should be included in the sampling program. A one year program with monthly samples would probably be adequate.

Another way to determine whether organic compounds of health significance are being discharged from the wastewater treatment plants is to measure the toxicity and mutagenicity of the effluents. Consequently, it is recommended that the samples collected for TOX analysis also be analyzed for their toxicity and mutagenicity. Although the report has shown that disinfection with chlorine can increase the toxicity and mutagenicity of wastewater effluents, it has also shown that the conditions under which toxins and mutagens are formed is extremely site specific. It is for this reason that each plant must be sampled over all seasons and during both dry and wet weather conditions.

Once data are available on the TOX, toxicity and mutagenicity of the treated wastewaters and the river, then it will be possible to determine whether a problem currently exists or is likely to exist in the future as the contribution of wastewater flow to the river increases. By measuring the effluents prior to discharge and the river at several points, it should be possible to obtain a rough estimate of the fate of the problem organics in the river. This information could then be used to estimate their impact when wastewater flows are higher. Furthermore, by measuring their levels in the wastewater both before and after disinfection it will be possible to make a rational decision about whether alternative means of disinfection should be explored. For example, limited data from the literature suggests that UV disinfection could protect the water-sports users of the river while minimizing any negative impact on water quality.

Data on TOX, toxicity and mutagenicity in the river will also allow evaluation of the impact of nonpoint sources on river quality. For example, it is possible that such nonpoint discharges might have a greater impact than the wastewater discharges. This would suggest that more effort should be expended on upgrading the water treatment plants to protect against those sources than
to alter the wastewater treatment plants. Only data on water quality in the river under both dry and wet weather flow conditions will allow these decisions to be made.

Finally, it must be recognized that organics existing in the river from natural decay processes as well as those entering from various point and non-point sources are likely to react with chemicals used to disinfect the drinking water. This review has shown clearly that the use of chlorine can increase the toxicity and mutagenicity of drinking water. However, it has also shown that the occurrence of such increases is seasonal and highly site specific. All of the water treatment plants under consideration are currently meeting the THM standard. However, THMs represent only a small fraction of the harmful organics which could be present. Thus, it is recommended that a sampling program be initiated to screen the finished water for TOX, toxicity and mutagenicity and that the program be continued for at least a year to establish whether seasonal effects are important. This program should be carried out in concert with the river sampling program to allow comparison of water quality after treatment to that before treatment. Technology currently exists for minimizing the formation of THMs. Should the screening program reveal a problem with TOX, toxicity or mutagenicity, it is likely that the same technology would be effective in reducing them as well. Knowledge of the existence of a problem would allow those alternatives to be investigated.

All of these recommendations are necessary because the literature has shown that the potential for problems exists. The literature has also shown that each situation is unique because the nature of the chemicals present in any given water or wastewater is unique. Thus, while it is likely that chlorination of the wastewaters or the drinking waters will increase the concentration of questionable compounds it is impossible to predict whether the quantity formed will be significant. That question must be answered by experimental data.
Techniques for analysis of the volatile organics listed in the primary and secondary drinking water standards are discussed in the EPA documents (51). TOX is also a standardized procedure (31,78). Thus, there is no problem deciding on a technique for them. The situation with the analysis of toxicity and mutagenicity is a different matter, however.

There has been extensive interest within the last decade in the various methods for testing water for toxicity and mutagenicity and this interest is reflected in the large number of reviews that have been published (2,8,84,112,116,122,145,187). For a detailed study assessing the hazards associated with potable reuse of wastewater, Bull et al. (22) recommended a complex, three-tier protocol involving organisms of different levels up to rats and involving study duration up to lifetime. With regard to short-term bacterial assays, they stated that although they were useful, they were inadequate as the sole biological testing method. Bedding et al. (8) agreed. Nevertheless, the vast majority of testing systems finding use world-wide are bacterial systems and of those the assay of Ames et al. (4) is by far the most popular. For example, water reuse in South Africa is being monitored for potential carcinogens using the Ames assay in conjunction with a mammalian cell bioassay (181). Therefore, based upon the trends in the literature and the fact that the recommended surveys are preliminary in nature to determine whether a problem is even likely to exist, a short-term bacterial test for mutagenicity and toxicity seems justified and is recommended.

Having decided to use a short-term bacterial test, these questions remain to be answered: the organisms to be used, the test system, and the method of concentrating the organics in the samples. The Salmonella tester strains TA98 and TA100 developed by Ames et al. (4) are by far the most commonly used bacteria for mutagenicity testing. TA98 is sensitive to frame-shift mutations and TA100 is sensitive to base-pair mutations. Both are often run both with and without microsomal activation although with many environmental samples activation is not required. Workers in Ames' lab have recently developed two new tester strains, TA97 and TA102 (126). TA97 is sensitive to compounds like benzo(a)pyrene and nitronaphthalene which could be important in an urban environment. TA102 is sensitive to a variety of oxidative mutagens and thus could be important to systems in which strong oxidizing agents have been used (e.g., chlorine and ozone). Maron and Ames (126) recommend that TA97, TA98, TA100 and TA102 be used routinely and that is what is recommended here as well. If initial experience reveals that one or more strains consistently give negative results when others are giving positive ones, then those strains which are not responding could be dropped from further testing (122).

Regardless of the test system employed it is important that close attention be paid to several details: follow the guidelines published by De Serves and Shelby (42) and by Maron and Ames (126); always employ dose/response curves and only report tests that give linear responses (122); measure the level of histidine in environmental samples and correct for its effect (122); and correct for toxicity (200). Toxicity correction is extremely important with environmental samples because toxicity effects can overshadow effects due to mutagenicity (2,58). Waleh et al. (200) have developed an ingenious technique for correcting toxicity in the Ames test and it is recommended that that
test be used. It can also serve as a general toxicity assay with which to test the various samples, thus serving a double purpose.

The original Salmonella/microsome assay system as proposed by Ames et al. (4) utilized spread plate techniques. Although it is the most widely used and accepted procedure it is time consuming and many replicates must be used to establish statistical validity. A more recent advancement is the fluctuation test (57,90) which is based on MPN techniques and is performed in microtiter plates. It is more rapid and allows better correction for toxicity than the original Ames procedure. Monarca and coworkers (137,138,140) have used the procedure in several environmental studies and advocate its use more broadly. An automated procedure of testing for mutagenesis has recently been developed in Finland (184). It is based on liquid culture like the fluctuation test but is supposed to be more rapid. Because the procedure is new, no references to its use were found. After reviewing the available procedures it is recommended that the fluctuation test be used. It would be wise, however, to investigate the cost of the automated procedure. If it was decided to continue mutagenicity screening on a routine basis after the one year survey, the later savings in lab time would probably justify the capital expenditure.

As originally designed, the fluctuation test was intended for use with unconcentrated samples but it is much more sensitive with concentrates. The Ames test, on the other hand requires sample concentration to detect most mutagens since even the most potent would have to be present at concentrations in excess of 2 μg/L to be detected (122). The beauty of microbial mutagenicity assays is that with only moderate concentration mutagens in environmental samples can be detected at concentrations well below those at which they can be easily identified. Hence, in this application, procedures should be employed for sample concentration. A number of techniques have been devised and they have been reviewed by Kopfler (115). Among the factors that should be considered when choosing a method are: type of selectivity; matrix effects; change in possible cumulative, antagonistic or synergistic effects; susceptibility to contamination; and propensity for chemical transformations leading to either loss or generation of toxicity (112). Because of all of these factors, concentration techniques have been extensively studied by EPA (116). Monarca and coworkers (138,140) have also compared concentration techniques and have concluded that for routine screening applications commercially available cartridges called Sep-Paks are superior to XAD resins, the most commonly used approach. Consequently, for the proposed screening tests it is recommended that concentration be performed with Sep-Paks.

In summary, the mutagenicity assay should be performed with the fluctuation test using samples concentrated on Sep-Paks. Initially, the assays should be run with Salmonella tester strains TA97, TA98, TA100, and TA 102. However, any strains consistently yielding negative results while others are giving positive responses will be dropped from the procedure. The tests should be run with and without microsomal activation. The same tester strains should be used for the toxicity assay since the results can serve a dual purpose: indication of toxicity and correction of the mutagenicity results.
A. Conclusions

1. Because of disinfection of the wastewater effluents their discharge is not likely to have a negative impact on microbiological water quality from either a recreational or water supply viewpoint.

2. Because of their low concentrations in the raw sewage, metals are not likely to be a problem in the Chattahoochee River in the foreseeable future.

3. It is highly unlikely that any non-metal in organics other than nitrogen will pose a problem in the Chattahoochee River in the foreseeable future.

4. Nitrate/nitrite nitrogen at a concentration of 4.5 mg/L as N has been correlated with gastric carcinomas. If no nitrogen removal is practiced, it is conceivable that levels in the Chattahoochee River could approach that concentration during dry weather flow by the year 2010.

5. The 84 organic compounds for which RMCLs have been proposed represent only a minute fraction of the organic compounds which could be present. Furthermore, they represent only a tiny fraction of those which have potential health effects. Thus they should not be focused on to the exclusion of other indicators of organic contamination.

6. Total organic halide (TOX) is relatively simple and rapid to measure and provides information on a large class of compounds of environmental significance.

7. Bioassays for toxicity and mutagenicity can be used as surrogate parameters for the organic matter that causes the response even when the specific compounds have not been identified.

8. Given the fact that the wastewaters being treated and discharged to the Chattahoochee River are predominantly domestic sewage and that the treatment facilities utilize secondary treatment, it is highly probable that any specific problem pollutants which happen to be present will be removed to below detectable limits, but there is no guarantee because a POTW is not a totally effective system for controlling discharge of some compounds to the environment.

9. Halogenated organics, as well as toxic and mutagenic organic compounds, are formed as a result of the disinfection of treated wastewaters with chlorine.

10. The only way to determine the impact of disinfection chemicals upon a particular treated wastewater is to measure it experimentally with toxicity and mutagenicity tests.
11. Disinfection with chlorine dioxide is far less likely to lead to the formation of haloorganic compounds than is chlorine. However, toxic and mutagenic materials are formed, although to a somewhat lesser degree than with chlorine.

12. The main impact of ozone upon organics in wastewaters is through oxidation reactions. These reactions may either increase or decrease the toxicity and mutagenicity of discharged organics.

13. Wastewater disinfection with UV light provides effective kill of pathogenic organisms with relatively little impact upon the organic matter present.

14. Mutagenic and toxic materials can enter the Chattahoochee River from a number of sources and can even be produced in it by microbial action. However, several mechanisms acting in the river can act to reduce the concentrations of such materials or place them in a state that will facilitate their removal during water treatment.

15. Coagulation and sedimentation can remove some micropollutants from solution, but in general it is not an effective means for their removal from drinking water. Granular activated carbon is generally considered to be the most satisfactory and cost effective technique available for removal of the broad spectrum of synthetic organic chemicals present at low concentrations in drinking water.

16. Ozonation and GAC adsorption can effectively destroy or remove mutagenicity and toxicity although ozonation can sometimes cause it.

17. Disinfection of drinking water with chlorine and chlorine dioxide can lead to the formation of mutagenic material in drinking water.

18. Low THM values do not necessarily mean the absence of mutagenicity.

19. Because the removal of THMs and mutagenicity is difficult once they are formed, the focus in water treatment should be on the prevention of their formation.

20. Epidemiological data linking disease to organic contamination of drinking water is very weak.

21. Although no definitive conclusion can be reached, the literature strongly suggests that increases in wastewater flows of the magnitude projected for the Chattahoochee River corridor between Buford Dam and Peachtree Creek will have a negative impact on the quality of drinking water extracted from that river. Prudence dictates that concrete data be gathered now so that orderly planning can proceed.

22. Ames Salmonella tester bacteria can be used in a fluctuation assay using samples concentrated with Sep-Paks as an effective and economical means of tracking the fate of mutagenicity in water supplies.
B. Recommendations

1. Because the water and wastewater treatment plants are interconnected through the Chattahoochee River they should be designed and operated with the same philosophy as is used in multiple barrier reuse systems.

2. To ensure that metals do not become a problem as wastewater discharges increase tight control should be maintained over metal inputs to sewers through stringent pretreatment requirements.

3. Samples should be collected at various points along the Chattahoochee River and from the discharged wastewater to estimate the fate of nitrate/nitrite nitrogen in the river. Knowledge of the fate should be combined with mass balance calculations to estimate likely concentrations under various flow and growth conditions, thereby allowing evaluation of the magnitude of any potential problems.

4. A program of sampling and analysis for the 84 compounds in Tables 1, 2 and 3 should be initiated to establish baseline data regarding the compounds for which RMCLs have been proposed. The sampling program should include the river at several points, the wastewater discharges and the water intakes.

5. Dissolved organic carbon, (DOC), total organic halide (TOX), and toxicity and mutagenicity to various strains of Salmonella should be used as surrogate parameters to evaluate the health-related quality of Chattahoochee River water.

6. Because of uncertainties associated with the ability of secondary treatment plants to remove organic micropollutants and given their potential importance in the Chattahoochee River, it is recommended that stringent pretreatment requirements be used to minimize their input to the wastewater treatment plants.

7. A survey of the wastewater treatment plants should be conducted to determine the impact of the existing disinfection systems upon the concentration of TOX and the toxicity and mutagenicity of the effluents. If the results indicate the existence of a problem, either now or in the future, then the installation of UV disinfection should be considered.

8. Because of seasonal effects on the production and removal of problem organics, a survey of at least one year's duration should be conducted to determine the fate of TOX and toxic and mutagenic materials in the Chattahoochee River. The survey should include the collection of samples under both wet and dry weather conditions.

9. Because it is difficult to generalize about the removal and formation of TOX, toxicity and mutagenicity during drinking water treatment, a year-long survey of the change in those characteristics during treatment of the drinking water should be conducted in parallel with the study of their fate in the Chattahoochee River.
10. A study of shorter duration should be conducted to establish the removal of the 84 compounds in Tables 1, 2 and 3 by the water treatment plants.

11. The data on the fate of organics in the river should be used to establish its natural treatment capacity. That information can then be used in mass balances to estimate the impact of future increases in wastewater flows.

12. Standardized procedures should be used for the analyses of TOX and the organics in Tables 1, 2 and 3. The fluctuation test procedure using Sep-Pak concentrated samples should be used with Ames' *Salmonella* tester strains to assay for mutagenicity. The same organisms can also be used to test for toxicity.
A. References Cited


B. Other Pertinent Articles


