Chlorine and the Chesapeake Bay

A Review of Research Literature

Linda L. Breisch, David A. Wright and Delois M. Powell

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Editor's Preface

Each year an expanding population leaves behind thousands of pounds of chemicals and metals that inadvertently find their way into rivers feeding the Chesapeake Bay. Fertilizers arrive in sediments that wash off farmlands; hydrocarbons seep into streams from urban streets; metals leach steadily into sewer systems from piping in our homes or from the hulls of boats newly painted with metal-based paints. Still, many of these inputs to the Bay pale in comparison to the daily tonnage of sewage water intentionally dumped into Maryland's rivers and streams.

The Back River Waste Treatment Plant near Baltimore, for example, treats some 180 million gallons each day--that includes the wastes of more than a score of heavy industries. Washington, D.C.'s Blue Plains Waste Treatment Plant receives an average of 580 million gallons daily.

It is not so long ago that wastewater flowed directly into public waterways. Near the turn of the century, a sewerage commission in Baltimore recommended that waste from the city's population of 350,000 be discharged directly into the Bay. The commission was confident that the Bay's natural processes would purify the untreated wastewater by dilution, but strenuous objections by the oyster industry led to rejection of the commission's report. By 1912, when a waste treatment facility was built at Back River, the plant was one of the first of its size and capacity in the country.

Today the cleansing of waste requires a series of processes that includes preliminary treatment (the screening of large objects and granular particles), primary treatment (the settling of suspended solids through sedimentation and their removal as sludge), secondary treatment (a biological process that consumes oxygen-hungry organic compounds), and then chlorine disinfection. Without secondary treatment, those large numbers of compounds--if released directly into the water--could consume enough oxygen to make a river uninhabitable for marine life.

Until the Federal Water Pollution Control Act Amendment of 1972 and the Clean Water Act of 1977, which established national standards for controlling water pollution, many waste treatment plants in the United States did not perform secondary treatment. This is no longer the case: now all sewage water discharged into public waterways must receive secondary treatment and meet standards for maximum bacterial levels.

Primary and secondary treatments, in removing suspended solids, also remove the microbes which adhere to those solids. But at best only an esti-

mated 50-60 percent of the pathogens, or disease-causing bacteria, are removed, a number that public health officials have long argued is not adequate. While there is evidence that pathogens die off naturally, they may not die before the water is reused. Those microbes, it is argued, could pose a serious threat to recreational users of rivers that receive treated wastewater or to shellfish beds--each case potentially leading to human health problems. It is for this reason that for more than fifty years, sewage waters throughout the United States have been disinfected after they have been through primary and, where available, secondary treatment. And the most common disinfectant has been chlorine.

Why chlorine? Because it is relatively inexpensive, has low maintenance needs and is simple to use. It is also so effective that many electrical power plants use it during the warmer months to kill microorganisms that flourish in heat exchangers and condenser systems.

And--until recent years--chlorine was generally thought to be an innocuous chemical. Its use gained such widespread acceptance, in fact, that few records of it were kept in waste treatment plants. But some ten years ago, chemists discovered that chlorine, on mixing with water, formed very small amounts of halocarbons, complex compounds that in large doses were known to be carcinogenic and mutagenic. Moreover, researchers were finding some disturbing results in their laboratories: in examining the effects of chlorine on larger marine organisms, they discovered that extremely low concentrations of chlorine compounds were either disabling or lethal.

For Maryland, these laboratory findings seemed to coincide with declines in harvests of important species in the Chesapeake Bay, first shad and then striped bass. With large increases in population throughout the watershed had come increases in the number of waste treatment plants in Maryland (in 1950, there were some 190; by 1980, there were 442) and a growing use of chlorine in those plants. It seemed evident to many that chlorine was the cause of the decline in harvests. Laboratory results suggested confirmation of this when they showed that organisms at their earliest stages of development were particularly vulnerable to chlorine compounds. A Department of Natural Resources news release cited a four-fold increase in chlorine use between 1974 and 1980 in six spawning rivers as evidence of how chlorination was directly implicated in the mortality of commercial species.

Chlorine--used extensively for the protection of human health and shellfish beds--appeared to be a detriment to estuarine and public health.

A controversy arose between those who were concerned with protecting the public health and those who managed and protected aquatic species. Each could draw upon the enormous volume of research for evidence to support its contention: to eliminate chlorination on the one hand, and, on the other, to assert its necessity for the public health.

To sort through the thickets of research literature and data bases, this volume identifies and reviews the effects of chlorination from waste treatment plants and electrical power plants. The objectives of this study have

been two-fold: to provide an overview of the effects of chlorination on aquatic microorganisms and macroorganisms and to identify important research questions that would be of significance for the Chesapeake Bay.

Toward these ends, Chlorine and the Chesapeake Bay provides brief chapters on the background and history of chlorine use, on chlorine chemistry and analytical techniques for measuring chlorine residuals, and on available alternatives to chlorine for disinfection. The chapter on the effects of chlorine on microorganisms focuses on bacteria and viruses, while the chapter on the effects of chlorine on aquatic macroorganisms summarizes a vast array of laboratory data covering chlorine's toxicity for vertebrates and invertebrates. A final chapter assesses potential application of chlorine models for correlating laboratory and field waterflow conditions.

The effects of chlorine on such a complex estuarine system as the Chesapeake Bay admit for no easy generalizations. For example, while laboratory data are important for giving some measures of chlorine toxicity to different species and for demonstrating the vulnerability of early stages to low concentrations of chlorine residuals, it is difficult to assess the significance of these data, generally taken under static environmental conditions, for actual field situations.

In addition, there are complex interactive effects about which there is limited research. Because chlorine is an oxidizing agent, its use in power plant condensers, for example, could alter the binding capacity of copper, thus releasing copper that might otherwise remain chemically bound.

Furthermore, the indirect effects of chlorine in the environment—on aquatic vegetation, to take another example, which may in turn affect species survival--have seen limited exploration. Recent laboratory evidence indicates that concentrations of chlorine so low that they are barely detectable could still cause significant harm to plant life.

As this report indicates, there are so many unanswered questions about the effects of chlorine that it is hazardous to make reductive generalizations. What the controversy over chlorine use in waste treatment and power plants has led to is the formulation of a more reasonable agenda by state authorities for minimizing its potentially detrimental effects. First, the state has aimed at reducing the use of chlorine in waste treatment plants through more efficient primary and secondary treatment operations. At the same time, agencies require special precautions at plants in the vicinity of spawning grounds. And, most recently, new rules require dechlorination so as to impede the formation of complex organic compounds that could cause long-term damage to the estuary.

--Merrill Leffler

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I

Introduction

BACKGROUND

Chesapeake Bay, one of the world's most fertile estuaries, provides the drinking water, recreation and livelihood for thousands of people, businesses and industries in both Maryland and Virigina. As fish harvests have decreased, public concern over chemical pollution and its effects on the Bay and its inhabitants has increased. Biocides, such as chlorine, and their degradation by-products are chemical pollutants which are eliciting intense interest and conroversy.

Chlorine has been widely used since World War II for the disinfection of municipal wastewater and for the control of biofouling organisms in power plant cooling systems. Chlorine's ease of application, adequate persistence in water, fairly short contact time, efficiency and, above all, low cost has made it the preferred disinfectant (Sugam 1977). Twenty-seven million pounds of chlorine in sewage treatment plants and 2.2 million pounds in power plant cooling systems have been used annually in Maryland's portion of the Bay (Davis and Middaugh 1978). The potential for harm by the release of vast amounts of biocide is staggering. In northern Chesapeake Bay, once-through power plant cooling systems (those that draw water from streams, pass it through condensers and release it immediately back to the stream) require for cooling purposes a volume of water equivalent to ten percent of the natural water (Stewart et al. 1979). The large numbers of eggs, larval organisms and small fish entrained (carried along) with this huge stream of cooling water are exposed to mechanical, thermal and chemical damage.

It was formerly thought that chlorine, diluted in the receiving waters, had little or no effect on the health and vitality of desirable aquatic organisms. In fact, in 1909, the oyster industry of Baltimore encouraged the chlorination of sewage effluents to protect nearby oyster beds from bacterial pollution (Kinnicutt et al. 1919). Bacterial pollution, or high densities of fecal coliforms, were blamed in a 1972 EPA report for the closure of several beaches and shellfish areas in Chesapeake Bay and its tributaries (Pheiffer et al. 1972); oyster bars are closed regularly because of bacterial pollution. In the upper Potomac Estuary, the continuous chlorination of wastewater effluents has reduced the previously high fecal coliform densities (recorded before 1969) although bacterial pollution from sanitary and combined sewer overflows has continued to be a problem (Pheiffer et al. 1972).

Many public health officials believe chlorination to be necessary to prevent disease outbreaks. A positive correlation has been proved between the disinfection of drinking water and decline in typhoid caused by Salmonella bacteria (Buxton and Ross 1979). While there also seems to be an inverse relationship between the number of sewage treatment plants over time and the incidence of typhoid (Levin et al. 1980 from Dugan 1970), there is no valid epidemiological data to document the effectiveness of wastewater disinfection.

The purpose of chlorinating wastewater effluents is to prevent the discharge of pathogenic organisms to the environment; the objective, since drinking water is further disinfected before it reaches the distribution system, is to protect swimming areas and fishing areas from unacceptable levels of water-borne disease organisms. There is, however, disagreement as to the connection between fecal coliform levels and the resultant level of disease in a bathing population (Buxton and Ross 1979).

The current attitude of public health officials in the United States is that the control of disease organisms is best controlled with a series of "multiple barriers" in which wastewater treatment (whether chlorine or another disinfectant) at the source of effluent is one barrier between pathogens and human contact. Among other barriers are the dilution of pathogens, their dispersion in the waterflow and dissolution over time. Wastewater disinfection is a significant barrier and health officials consider its abandonment a compromise of public health principles (Kawata et al. 1980). They point to a 1974 study linking an outbreak of Shigellosis in Iowa to the act of swimming in the Mississippi River, downstream of Dubuque's sewage treatment plant; however, other possibly polluting agents were not eliminated from the study (Buxton and Ross 1979).

Some researchers and resource managers have been questioning both the innocuous image of chlorine and its disinfection efficiency (Durham and Wolf 1973; Jolley et al. 1978; Kopperman et al. 1978; Coulter 1982). Sepp (1981), comparing the effluent toxicities from both full- and pilot-scale sewage treatment plants, found chlorine to be the most toxic constituent of the sewage effluents. Improvements in the chlorination process design and operation in pilot plants have made it possible to save up to 50% in chlorine use; this has led to lower chlorine discharges and, subsequently, a much lower toxicity to organisms in 96-h bioassay tests (Sepp 1981).

While 2-4 mg/L (2-4 ppm, White 1978a) and 0.18-0.53 mg/L (0.18-0.53 ppm, Snow and Sladek 1978) are the residual concentrations (or the concentration of chlorine remaining after reactions have taken place during a specified contact period) from a municipal wastewater treatment plant and a freshwater power plant cooling water system, respectively, laboratory studies have shown that even lower residual chlorine levels can adversely affect some organisms, particularly the young or less mobile life history stages. Roberts et al. (1975) found total residual chlorine levels as low as 0.05 ppm to be lethal to Acartia tonsa (a copepod important in food webs) after 48 h. Morgan and Prince (1977) found the eggs and larvae of white perch Morone americana to be fatally affected by 0.27 and 0.31 ppm, respectively. In addition, only slight

differences in a residual's concentration (such as a difference of 0.14 ppm) can mean either 100% mortality or zero mortality of an organism (Brooks and Seegert 1978b).

Levels of total residual chlorine, while not necessarily lethal, may have important sublethal effects on organisms. In laboratory studies, the eggs of both M. americana and striped bass M. saxatilis exposed to 0.35 and 0.15 ppm total residual chlorine, respectively, resulted in larval fish with a length shorter than the average (Morgan and Prince 1978).

Applying these laboratory results directly to field situations, however, can be misleading. The lack of field experiments makes extrapolations of laboratory conclusions difficult. Total residual chlorine (TRC) is neither hypochlorous acid nor chlorine bleach but rather the chlorine compounds that are formed after the acid or bleach dissociates (White 1972; Sugam and Helz 1977; Morris 1978; Opresko 1980), and the resulting chlorine compounds differ in their toxicity to different organisms (White 1972; Opresko 1980). Entrained organisms in power plant cooling streams may be exposed to a much higher concentration of chlorine than is reflected in the residual concentration (Goldman et al. 1978). To further complicate matters, environmental factors alter chlorine form and toxicity. For example, the total residual chlorine concentrations reported at sewage treatment plants or power plants usually are measured before the chlorine is actually released into the receiving water: hydrological conditions of the receiving water body can increase the dilution rate or alter the exposure time, both of which affect toxicity of the chlorine residual (White 1972; Opresko 1980). Meanwhile, the ambient water temperature affects an organism's physiological response and tolerance to chlorine residuals, sometimes lowering tolerances, sometimes raising it, depending on the organism. Reducing agents in the receiving water (e.g., sulfides, iron, manganese) exert a chlorine demand (or the difference between the amount of chlorine added to the effluent and the amount remaining after a specified contact period) and can alter the chlorine compounds and influence the toxicity.

During the past decade, concern over the possible effects of chlorine on aquatic organisms has led to numerous studies on the chemistry of chlorine, analytical techniques for measuring chlorine residuals, alternatives to chlorination, effects of chlorine on specific microorganisms and macroorganisms, and applications of chlorine modelling to field conditions. The chapters that follow give a critical review of the extensive research literature that has resulted from these studies. To provide a context, the remainder of this chapter briefly surveys the history of chlorine use for disinfection purposes, and describes chlorine use in modern sewage treatment and power plants, the manner in which some foreign contries view chlorination, and the indicators of pollution levels.

HISTORY OF CHLORINE USE

The use of chlorine for disinfection purposes dates back almost 200 years. Discovered by the Swedish chemist Scheele in 1774, chlorine, in the form of

chloride (sodium or calcium), was first employed as a disinfectant in 1800 by de Morveau in France and by Cruikshank in England (White 1972). While employed as a disinfecting agent, chlorine was not at first known to destroy pathogenic bacteria; rather, it was widely used (in the form of chloride of lime) by the English Royal Sewage Commission in 1854 to deodorize sewage. Since disease at that time was thought to be transmitted by foul odors, the strong deodorizing properties of chlorine implied a disinfection function (White 1972). The first known use of chlorine to disinfect effluents containing microorganisms (the typhoid bacteria) was by William Soper in 1879 in England and later in 1893 in Hamburg, Germany.

With the advent of the water closet in 1833 in the United States, wastewater was disposed of in the waterways. Thus, the problem of pollution was transferred from the immediate locale to downstream communities. The negative health aspects were then dealt with by disinfecting drinking water. Sewage treatment dealt mainly with preventing a nuisance rather than protecting drinking water. In 1930, 66% of America's urbanites drank filtered and/or chlorinated water; only 26% had their sewage treated.

The first recorded use of chlorine disinfection of sewage in the U.S. was at Brewster, New York, in 1875. But up until 1910, chlorination of sewage was generally considered too expensive for routine, non-emergency systems (Kinnicutt et al. 1919; Enslow 1938). In 1905, Rideal in England proved that small amounts of chlorine (<30 ppm) coupled with some level of treatment (primary, secondary or tertiary) could reduce B. coli bacteria from several millions to less than one per milliliter (Kinnicutt et al. 1919).

The first systematic study of the use of chlorine as a disinfectant in sewage treatment in the U.S. was done by Phelps and Carpenter at MIT in 1906 (Winslow 1938). The effluents from trickling filters treated with 5 ppm available chlorine (applied as hypochlorite of lime) resulted in the removal of 99.96% of bacteria and of 99.993% of B. coli (Kinnicutt 1919).

Concern over the bacterial pollution of shellfish beds led to a series of experiments by Daniels and Phelps between 1906 and 1907 to determine the practicability of treating septic effluent from the town of Red Bank, New Jersey (approx. pop. 6,500), with hypochlorite of lime (Kinnicutt 1919). In 1908, the New Jersey Sewerage Commission recommended an application of 12-15 ppm available chlorine at Red Bank (Kinnicutt 1919).

By 1914, there were 24 operating disinfection plants in New Jersey maritime communities (Kinnicutt 1919).

The oyster industry in Maryland, alarmed at the prospect that sewage discharge from Baltimore (approx. pop. 500,000) would be released at a single point, encouraged studies of sewage disinfection by Phelps and Whitman in 1909. Chlorine was applied at a concentration of approximately 2 ppm available chlorine from bleaching powder to trickling filter effluent at Walbrook Testing Station and was determined to be more cost-effective than supplementary sand treatments (Kinnicutt 1919).

Developments in chemical manufacture during World War I led to significant decreases in the cost of producing liquid chlorine, which previously had been used successfully in various communities throughout the U.S (Enslow 1938), leading to widespread adoption of chlorine in sewage treatment.

In 1918, Eddy, like Rideal before him, obtained a higher degree of disinfection when suspended matter was removed before chlorination (Enslow 1938). In 1927, Tiedeman experimented on the relation between contact time and bacterial kill with varying chlorine residuals (Enslow 1938). A contact time of 60 min. at a very low chlorine residual (zero as measured by the orthotolidine test, slight residue by acid starch-iodide) resulted in 99.92% mortality of bacteria (99.94% of B. coli) while a chlorine residual of 0.2-0.6 resulted in 99.995% mortality of bacteria (99.999% of B. coli) at 37°C.

In 1930-1931, the Back River Sewage Treatment Plant in Maryland was the first plant designed incorporating a chlorination process (M. J. Garreis, Maryland Department of Health and Mental Hygiene, personal communication). By 1938, chlorine disinfection of sewage was routinely practiced at Hagerstown, Westminster and Baltimore.

Extreme and continuous fouling of a popular beach south of Los Angeles, California, led in 1943 to a landmark state court decision which established a statistical coliform concentration to define polluted and non-polluted waters (White 1978b), thus setting the first guidelines in the nation for proof of disinfection in receiving waters. After 1945, there was active interest in wastewater disinfection. During World War II, it had been military policy that sewage effluents at army bases had to be chlorinated (White 1972). From 1926 to 1970, the amount of chlorine used in water treatment (including treatment of drinking water) grew from 19,000 net tons to 377,000 net tons (Schultze 1974).

The state of Maryland passed the Maryland Water Pollution Control Law in 1947 (Silbermann 1976), thus demonstrating its early commitment to the control of pollution. The water pollution control program in Maryland is currently administered by the Department of Health and Mental Hygiene, which monitors the bacterial level in oysters and opens and closes shellfish beds to fishing when high levels deem it necessary; in addition, the Department of Health and Mental Hygiene monitors water quality, determines allowable discharge levels, issues discharge permits to wastewater dischargers and enforces compliance to the given levels. Present law prohibits discharge of chlorinated effluents into trout waters. Permitted residuals in other effluents are determined by receiving water characteristics and size of discharge.

There is a lack of documentation of the history of chlorine use in the Chesapeake Bay area. Though widely after World War II, chlorine was not considered to be a hazardous, thus records were not adequately maintained (M.J. Garreis, Dept. Health Mental Hygiene, personal communication).

In 1972, the Federal Water Pollution Control Amendments (FWPA), or Public Law 92-500, was passed, based on the philosophy "that no one has the right to pollute . . . and that pollution continues because of technological limits, not because of any inherent right to use the Nation's waterways for the purpose of disposing of waste." In 1977, the Clean Water Act set limits on the

discharge of pollutants from sewage treatment plants and established requirements for secondary treatment of municipal wastes. To meet permit requirements of reduced pollution, the FWPCA established the Construction Grants Program to assist states in the building of new or existing treatment plants (EPA 1978).

Chlorine Use in Sewage Treatment and Power Plants

Sewage Treatment Plants

More detailed descriptions are provided in EPA (1980) and Arora (1980). What follows is a simplified description of the basic sewage treatment process.

Basic sewage treatment consists of two stages: primary and secondary. In primary treatment, incoming sewage passes through a grit chamber where it is screened to remove large particles and debris (sand, cinders, small stones); the effluent then goes through a sedimentation tank to remove suspended solids. If there is no further treatment, chlorine is added to the effluent to kill pathogenic bacteria and to control odors before release to the environment.

Since the FWPCA was enacted in 1972, secondary treatment has been required for all discharges into the environment (Arora 1980). In secondary treatment, the effluent from the sedimentation tank is pumped through either a trickling filter or an activated sludge chamber where the biological breakdown of soluble organic compounds takes place. In the trickling filter process, the effluent is sprayed out upon a bed of stones or sheets of plastic upon which a film of bacteria has been allowed to grow. The bacteria consume most of the organic material from the effluent. The effluent then passes out through the bottom of the filter and through a sedimentation tank in which the bacteria settle out from the water column. In the activated sludge process, the effluent from the primary sedimentation tanks passes through an aeration tank containing large amounts of bacteria and is mixed with air. The bacteria, after consuming organic material, settle out of the water column when the effluent is passed through a sedimentation tank. They are then recycled through the aeration tank, continuously seeding a new bacterial population.

The final step in both of these methods is the addition of chlorine to disinfect the effluent. Chlorine is added in solid, liquid or gaseous form, and the effluents held in a contact chamber for 15 - 30 min. before discharge into receiving waters. There is some concern that this typical disinfection system does not provide efficient use of chlorine because of design and operational deficiencies (Sepp 1981).

Further advanced, or tertiary, treatment can vary, removing any of a number of compounds, from nitrogen and phosphorus to organics and salts. Industrial waste treatment processes are similar with additional specialized tertiary treatments. Figure 1 depicts schematically the typical sewage treatment processes. Chlorine may be added at any point in the process to help in the control of odors and unwanted biofouling.

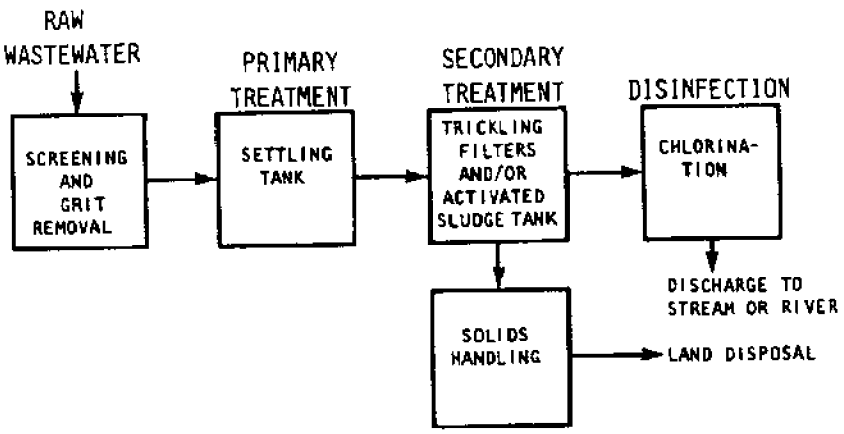

Figure 1. Schematic of sewage treatment process.

Power Plants

Power plants for generating electricity use massive amounts of water to cool the condensers. In 1974 (Water Supply 1977), all but three steam power plants in the Chesapeake Bay region used once-through cooling systems, in which water is drawn from a natural body of water, directed through the condensers to absorb heat, and discharged directly into a receiving body of water. The cooling water drawn from natural bodies of water carries entrained micro- and macrobiological organisms--algae, bacteria, fungi and larvae of benthic sessile organisms as well as young fish (Opresko 1980). Some of these organisms settle out and adhere to the condenser surface, forming slimes and sessile communities. This "biofouling" decreases the heat exchange efficiency between the condenser and its cooling water.

Concern about the effects of thermal pollution on the receiving body of water--the temperature of the cooling water effluent is many degrees higher in temperature than the ambient receiving water--has led to an increasing number of "closed cycle" cooling systems. Cooling water may be drawn from and discharged into cooling ponds or cooling towers. While this eliminates the danger of biofouling from benthic organisms, bacterial and fungal slimes continue to be a problem.

Several methods of biofouling control exist, among them intermittent and continuous chlorination of the cooling water. Chlorine is applied to the incoming stream of cooling water; the necessary dose is dependent on ambient water quality--a cooling water high in organic content requires a high chlorine dose. Opresko (1980), after reviewing the literature, reports that a chlorine dose of 1-2 mg/L applied between 5-60 min. and up to 4 times a day is effective in relatively unpolluted waters. This intermittent application of chlorine results in pulses of chlorine products downstream (Snow and Sladek 1978).

Chlorination in Foreign Countries

European wastewater disinfection practices differ markedly from North American practices (Buxton and Ross 1979). Many countries do not routinely disinfect their sewage at all, relying instead on thorough disinfection of drinking water to prevent outbreaks of water-borne disease (Barrow 1977; WPCD 1978). Despite the fact that some 60% of the drinking water in England is drawn (or recycled) from sewage polluted surface waters, there is no epidemiological evidence of water-borne disease transmission in routinely processed drinking water in this century (Barrow 1977). Chlorination of sewage effluents in England, Italy, Germany, France, Switzerland and Norway is practiced only in areas where swimming beaches or drinking water intakes may be located and affected. Some of these countries consider chlorination to be an ineffective disinfection method which may be potentially harmful or have unknown consequences to the environment (WPCD 1978).

The disinfection of sewage and use of chlorination in Canada varies widely from province to province, much as it varies from state to state in the United States. While the Yukon and Northwest Territories do not disinfect sewage, New Brunswick requires year-round disinfection of effluents. North Americans endorse wastewater disinfection as a method of safeguarding recreational areas and industrial (i.e., food processing) water supplies (Buxton and Ross 1979). Comparisons between European and North American wastewater treatment practices must take into account several variables: differing population densities, hydrographic features, physiography, climate and even aesthetics. The use of chlorine as an effective biofouling control agent appears to be similar in Europe as in the United States. Høstgaard-Jensen et al. (1977) state that other means of control are not equal to chlorination efficiency.

Pollution Indicators

Whether or not to use chlorine may be less of an issue than whether or not it is being used properly. Buxton and Ross (1979) argued that disinfection of wastewater produces few if any documentable public health benefits. They discourage blanket disinfection, recommending instead properly operated and designed treatment plants with relocation of outfall pipes where effluents may interfere with recreation. In some cases, they note, stormwater runoff and sewer overflows are not subjected to any treatment whatsoever, yet are usually overlooked in discussions of sewage bacterial water quality.

There is some concern that the method for determining the amount of chlorination needed for adequate disinfection, that is, the coliform or fecal coliform test, may not accurately reflect the efficiency of chlorine disinfection against viruses (White 1972; Durham and Wolf 1973). The indicator organisms and the tests used to isolate them (the coliforms and fecal streptococci) may not accurately reflect the presence or absence of pathogenic organisms (Clausen et al. 1977; Farmer and Brenner 1977; Kraus 1977; Berg et al. 1978; Fluegge et al. 1981). The natural relationships between indicators and pathogens in freshwater have yet to be determined (Smith et al. 1973) and may not be constant (Hunt 1977). The concentrations of indicator organisms

can be affected by collection sampling design (Breniman et al. 1981) and by such environmental variables as sunlight (Fujioka et al. 1981), bird population (Hussong et al. 1979), non-point pollution sources (Erkenbrecher 1981), water temperature (Hussong et al. 1980), predacious microorganism populations (McCambridge and McMeekin 1980) and perhaps sediment populations of enteric organisms (Matson et al. 1978; Liew and Gerba 1980). The regrowth of indicator organism populations after chlorination has also been recorded (Hulka et al. 1973; Clausen et al. 1977; Kinney et al. 1978).

Kott (1977) lists a number of criteria that a given indicator organism must meet: it must be (1) prevalent in sewage, (2) excreted by humans, (3) greater in abundance than pathogenic bacteria, (4) incapable of proliferation, (5) more resistant to various disinfectants than pathogens and (6) quantifiable by simple and rapid laboratory procedures.

There are a number of organisms excreted by humans that are prevalent in sewage. In fact, the large variety of pathogenic bacteria and viruses potentially present in sewage is one of the drawbacks in using pathogens themselves as indicators: monitoring for each would be an impossibly large task (Cabelli 1977b). In addition, there is some evidence that at least one pathogen, Vibrio cholorae, may survive and multiply in the natural seawater environment (Colwell et al. 1981; Spira et al. 1981).

Standard laboratory techniques for measuring indicator levels (membrane-filter, standard most-probable-number, modified most-probable-number) may be heavily biased, each selecting for a specific group of coliforms (Evans et al. 1981a), or may be sensitive to interference from water temperature (Hussong et al. 1980) or bacterial populations antagonistic to coliforms (Evans et al. 1981a). Efforts are underway to improve techniques of coliform enumeration and to reduce the errors in false-positive and false-negative tests (LeClerc et al. 1977; Olson 1978; LeChevallier et al. 1980; Tobin et al. 1980; Dufour et al. 1981; Evans et al. 1981b; Hussong et al. 1981).

The two requirements which cause the most dispute in the use of coliforms as an indicator are their incapacity to proliferate and their higher resistance to disinfectants. Berg et al. (1980) found a slightly higher recovery rate in the population growth of Streptococcus from disinfected samples than was found in untreated samples. Kinney et al. (1978), similarly, had speculated that indicator populations in chlorinated effluents may be little different than those in non-chlorinated effluents. Earlier, Hulka et al. (1973) had found regrowth of total and fecal coliforms in chlorinated water. Matson et al. (1978) suggest that the rapid die-off of enteric organisms from the water column may mean that they are settling out and forming sediment populations which, when resuspended, pose potential threats to water users.

While hypochlorous acid rapidly kills some viruses, the chlorination of wastewater results not in persistent hypochlorous acid, but in chloramines and a variety of other compounds, some of which are less toxic to marine organisms including perhaps bacteria and viruses (White 1978b; Opresko 1980). Some pathogens, primarily viruses, have been found to be more resistant to chlorination than are the coliforms or enteric bacteria (Durham and Wolf

1973; Kott 1977). The absence of fecal coliforms in chlorinated effluent cannot be construed as an indication that no pathogens of enteric origin are present. Some beneficial heterotrophic organisms were found to be very susceptible to chlorination while fecal coliforms, non-fecal coliforms and fecal streptococci were less susceptible, in that order (Silvey et al. 1974). This is not a recent concern: over ten years ago the reliability of coliform bacteria reduction as a sufficient indication of adequate disinfection was questioned (Morris 1971).

Chlorine may deactivate viruses (i.e., stop their growth) but not actually kill them (Olivieri et al. 1975; Davis 1982). In fact, over-chlorination may lead to the development of immune or resistant pathogens (Bates et al. 1978; Buxton and Ross 1979; Davis 1982). On the other hand, conventional chlorination practice does inactivate some viruses, such as the virus causing polio, and does prevent some disease (Ludovici et al. 1975; Buxton and Ross 1979; Olivieri 1981).

Even if coliform levels accurately measure pathogen level, there is very little dose-response information tying the numbers together (Cabelli et al. 1974). Risk assessment is an extremely difficult task--it entails more than determining a simple disease-risk, chemical-risk curve with a minimum chlorine dosage (Schneiderman 1978). While the smallest number of detectable viruses may be sufficient to produce disease in the susceptible individuals who ingest them (Katz and Plotkin 1967; Plotkin and Katz 1967; deWind and Leeuwen 1980), there are few epidemiological studies correlating disease symptom rates with coliform density (Cabelli 1977b). Those studies which have been conducted show barely detectable differences in illness rate between high and low coliform density (Levin et al. 1980).

There is no real scientific justification for maintaining that recreational waters with less than a total coliform count of 1000 with 20% fecal coliforms are safe for bathing (Brenniman et al. 1981). The current standard of the fecal coliform level of 200/100 ml has been translated to mean that a detectable health effect might occur in waters having a fecal coliform density of 400/100 mL of water sample, and has been altered to 200/100 ml for aesthetic reasons (Levin et al. 1980). International standards vary widely from this level (Brenniman et al. 1981).

It may be that, instead of a universal microbial indicator, there are many possible indicators, the choice depending on the particular water use (e.g., recreational or drinking water) and how the information is to be applied (e.g., regulation vs. elucidation: Muller 1977; Bisson and Cabelli 1980). Possible indicators and the cases in which they may be used include (1) drinking water--E. coli (Dufour 1977; Muller 1977), Clostridium perfringens (Cabelli 1977a); (2) unchlorinated sewage effluents--bifidobacteria (Resnick and Levin 1981), C. perfringens (Bisson and Cabelli 1980), coliform or fecal coliform (Hunt 1977); (3) chlorinated sewage effluents--coliphage (Kraus 1977), fecal streptococci (Clausen et al. 1977); (4) swimming waters--Pseudomonas aeruginosa (Muller 1977), enterococci (Levin et al. 1980).

II

Chlorine Chemistry

INTRODUCTION

Chlorine is a highly aggressive and reactive element; its use in wastewater disinfection carries the potential for both benefit or danger (Davis 1982). Chlorination of freshwater, estuarine and marine systems produces an expanding cascade of products (Helz 1981), some toxic, some non-toxic. Over 50 chloro-organic constituents have been analyzed in primary and secondary effluents which had been chlorinated in the laboratory (Jolley et al. 1978). While a few basic reactions appear to be understood, the majority of reaction pathways and products have only recently been studied in detail. The products at the lower reaches of this cascade, their stability and their effects on the aquatic environment, remain to be understood.

This section begins with a brief description of the chemistry of chlorine in freshwater and marine systems. For more detailed discussions, the following papers should be consulted.

1. Helz, G. R. 1981. Chlorine Chemistry. In: L.W. Hall, Jr., G.R. Helz and D.T. Burton (eds.), Power plant chlorination: a biological and chemical assessment. Ann Arbor Science. Reviews 196 papers; deals with reaction rates and pathways, oxidant analysis, oxidation products.

2. Opresko, D. M. 1980. Review of open literature on effects of chlorine on aquatic organisms. EPRI Report EA-1491. Summarizes 86 papers; deals with basic chlorine chemistry in freshwater and marine systems.

3. White, G. C. 1972. Handbook of chlorination. Van Nostrand Reinhold Co. A civil engineer's view of chlorine chemistry.

The section continues with a description of the complex influences that site-specific environmental variables such as salinity, temperature and pH have on the products and results of chlorination, and that make it difficult to generalize about the consequences of chlorination. The section concludes with a summary and identification of areas requiring further research.

FRESHWATER CHEMISTRY

Conventional chlorination practices in domestic sewage treatment plants or power plant cooling systems add chlorine in the form of liquid sodium hypo-

chlorite (NaOCl), powdered or tablet calcium hypochlorite ($Ca(OCl)_2$) or chlorine gas (Cl_2). The chlorine dosage required for adequate sewage disinfection depends upon the level of treatment to which the effluent has previously been exposed (Pressley et al. 1972; White 1974). For example, primary treatment (the screening and removal of particulate matter) requires a chlorine dose of 10-13 mg/L, while secondary treatment (removal of organic material) and tertiary treatment (removal of excess nutrients or other compounds) require 5-6 mg/L. Power plants typically use a chlorine dose of 1-2 mg/L (Sugam and Helz 1977).

Sodium or calcium hypochlorite reacts with water to form hypochlorous acid (HOCl), hydroxide ions and calcium or sodium ions (eq. 1 and 2; White 1978b). Chlorine gas dissolves rapidly and almost completely in water (hydrolysis reaction) to form hypochlorous acid, hydrogen ions and essentially innocuous chloride ions (eq. 3; Sugam and Helz 1977; Morris 1978). Thus, the half of the applied chlorine which becomes chloride ions is not available for biocide purposes (WPCD 1978). Hypochlorous acid dissociates rapidly to hypochlorite ions and hydrogen ions (eq. 4; Sugam and Helz 1977; White 1978b). This reaction occurs quickly, in about a quarter of a second (50 msec = 1/20 sec, Helz 1981). The three species Cl_2, HOCl and OCl^- co-exist, their relative proportions determined by pH and temperature (Palin 1975). They are difficult to distinguish by analysis at the trace level (Sugam 1977), so they have usually been grouped together under the heading of free residual chlorine (Sugam and Helz 1977).

$$NaOCl + H_2O \longrightarrow HOCl + Na^+ + OH^- \quad (1)$$

$$Ca(OCl)_2 + 2H_2O \longrightarrow 2HOCl + Ca^{++} + (OH)^{=} \quad (2)$$

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^- \quad (3)$$

$$HOCL \longrightarrow OCl^- + H^+ \quad (4)$$

Haas (1981), after analyzing data from published studies, suggested that yet another reaction may occur which produces sodium hypochlorite (NaOCl), a potentially virucidal and bactericidal species.

Chlorine in the form of HOCl is a strong oxidizing agent and reacts rapidly in electrophilic and displacement reactions (Morris 1978) with many substances in both freshwater and seawater (White 1972). These substances in the receiving water exert a "chlorine demand," or the difference between the amount of chlorine added to the effluent and the amount of oxidative by-products remaining after a specified contact period (Sugam and Helz 1977). Wong and Davidson (1977) could observe no limit on chlorine demand in seawater. Instead, chlorine demand increased with increasing dose and increasing contact time. Demand reactions remove free chlorine from the effluent, result in substitution reactions and, in the presence of ammonia and amino-nitrogen, the formation of inorganic chloramines or combined chlorine residuals: rapidly formed monochloramine (NH_2Cl) (eq. 5; White 1974; Sugam and Helz 1977); slowly formed dichloramine ($NHCl_2$) (eq. 6; White 1972); and even more slowly formed nitrogen trichloride or trichloramine (NCl_3) (eq. 7; Saquinsin and Morris 1975). The chloramines retain some oxidative power and are referred

to as combined residual chlorine. The formation of monochloramine is so fast, completed in a fraction of a second (Sugam and Helz 1977), that it precedes reactions with microorganisms (White 1974).

$$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O \quad (5)$$

$$NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O \quad (6)$$

$$NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O \quad (7)$$

(Sugam and Helz 1977)

After satisfying rapid demand reactions, the remaining hypochlorous acid (or free available chlorine) is available for disinfection purposes. Each chemical form of chloramine differs in its toxicity to aquatic organisms.

SEAWATER CHEMISTRY

The increased presence of bromine in seawater complicates reactions. Davis and Middaugh (1978) refer to the results of chlorination as "a cascade of chemical transformations, favoring bromination in increasing salinities in an estuary." While the reaction mechanisms involved in the chlorination of seawater aren't completely understood (Carpenter and Macalady 1978), the process results in the formation of the bromine analogs of freshwater products. The bromide ion is oxidized by free chlorine (Eq. 8,9 and 10):

$$Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2 \quad (8)$$

$$HOCl + Br^- \longrightarrow HOBr + Cl^- \quad (9)$$

(Sugam and Helz 1977)

$$OCl^- + Br^- \longrightarrow OBr^- + Cl^- \quad (10)$$

(Wong and Davidson 1977)

Wong and Davidson (1977) found the formation of hypobromite (OBr^-) from hypochlorite and bromide (Br^-) (eq. 10) to be fast, requiring only 2.5 min. to reach completion. Chloramines can also react to some extent with Br^- (Sugam and Helz 1977).

The conversion of HOCl to HOBr depends on the salinity and the pH of the receiving water. The products from seawater chlorination are HOBr, OBr^-, monobromamine (NH_2Br), dibromamine ($NHBR_2$), tribromamine (NBr_3) and probably chlorobromo compounds (Sugam and Helz 1977). Trofe et al. (1980), using spectral and kinetic evidence, found the principal reaction product from seawater chlorination to be bromochloramine (NHBrCl). They expect that this species is unstable and, consequently, less toxic to organisms than the more stable monochloramine.

Free residual bromine (HOBr and OBr^-) is chemically more reactive than is free residual chlorine (HOCl and OCl^-) (Morris 1978). After approximately 20 sec, oxidative chlorine disappears and disinfection capabilities are maintained by bromine. Where the bromide concentration exceeds the concentration of chlorine applied and where the ammonia and organic nitrogen concentrations are not excessive, the predominant oxidant species will be free and combined bromine in the natural pH range 6-8 (Sugam and Helz 1977). According to their thermodynamic equilibrium model, Sugam and Helz (1977) predict that with a dose of 1.0 mg/L Cl in marine and estuarine waters within a salinity range from 3.5-35 ppt, the bromine species completely dominate their chlorine analogs. These bromine species may be of significance only in the chlorination of coastal power plant cooling waters, where the chlorine is added directly to the seawater or estuarine water. In sewage treatment plants, the chlorine is added to the predominantly freshwater sewage effluent which is heavily laden with ammonia and amino-nitrogen, forming chloramines. Chloramines in the discharged effluent are then very slowly converted to bromamines in the estuarine receiving waters, but this reaction is probably not important (Helz personal communication) Figure 2 shows the principal reaction pathway of chlorine in saline waters.

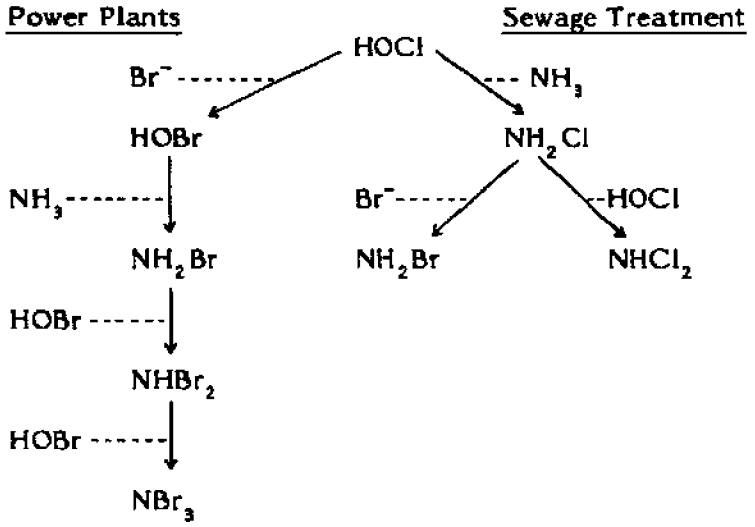

Figure 2. Principal inorganic reaction pathways of chlorine in saline waters (from Trofe et al. 1980).

TOXICITY AND CHEMICAL FORM

The initial chlorine dose interacts with a number of environmental factors to influence the chemical form of chlorination products and their toxicity. Earlier studies which reported chlorinated residuals only as total residual chlorine or "chlorine" disregarded this difference in the relative toxicities of the components comprising total residual chlorine (Cherry et al. 1979). Because the gross categories of free residual chlorine and combined residual chlorine appear to obscure real toxicological differences, Mattice et al. (1981)

recommend discarding the two terms and relying on measurements of the individual components (e.g., HOCl, OCl^-, NH_2Cl, $NHCl_2$) of total residual chlorine. Table 1 shows the relative toxicity of a number of free and combined chlorine and bromine residuals (Sugam and Helz 1977, from Johnson and Overby 1971).

While Brungs (1973) provides a detailed review of toxicities of the several forms of chlorination products, he does give a thorough discussion of bromine analogs. The free halogen forms (hypochlorous acid, hypochlorite ion, hypobromous acid, hypobromite ion) are generally stronger oxidizing agents and more toxic in freshwater than are the combined forms (Tsai and Tompkins 1974; Palin 1975; Johnson 1978; Snead et al. 1980). Of the free halogen forms, free bromine, particularly hypobromous acid, although slightly weaker as an oxidizing agent (Johnson 1978), is chemically more reactive than is free chlorine (Opresko 1980). However, bromine lacks a stable residual making it a less efficient disinfectant than chlorine (Sugam and Helz 1977), 5-6 times less efficient in freshwater (White 1972). High pH values can further reduce disinfection properties. Since hypochlorous acid is about 4 times as toxic as hypochlorite ion, Mattice et al. (1981) suggest that free residual chlorine is more toxic at low pH where the acid predominates, and less toxic at high pH where the hypochlorite predominates.

Table 1. Oxidant Toxicity Data[1]

Species	10 Min Residual (moles/L x 10^5)	Toxicity Index (relative to Br_2)
Br_2	0.626	1.00
$NHBr_2$	0.572-2.86	0.66
Cl_2	1.43	0.44
HOBr	1.03-5.15	0.37
OBr^-	1.04-5.20	0.36
HOCL	1.9-9.5	0.20
NH_2Br	5.2-10.4	0.09
$NHCl_2$	5.8-11.6	0.08
NH_2Cl	19.4-29.1	0.03
OCl^-	38.8	0.02

[1]Sugam and Helz (1977), from Johnson and Overby (1971).

Of the combined forms, or halamines, monochloramine (NH_2Cl) is more stable but less toxic than either dichloramine ($NHCl_2$) or trichloramine (NCl_3) and much less toxic than free available chlorine (Heath 1978). It requires a much longer contact time (exposure to target organisms) to obtain the same kill with the same dose (Heath 1978). Dichloramine and trichloramine are unstable (as are their bromine analogs), although high initial chlorine concentrations would favor their formation. With equal or excess ammonia concentrations, such as the levels occurring in wastewater, monochloramine is the dominant residual (Palin 1975; Opresko 1980) and is the principal disinfectant (Johnson 1978). Residual chloramines may have been much more effective for bacterial kills than they were for viral kills under a conventional disinfection treatment at the Fort Meade Sewage Treatment Plant No. 2 (Longley 1978). Rapid mixing of the added chlorine with the effluent rather than increased contact time resulted in a higher viral kill. Since rapid mixing would expose more virus to the short-lived free chlorine species, this implies a greater viral sensitivity to free chlorine.

The toxicity of combined and free residuals differs with respect to larger organisms also. On four species of algae, monochloramine was the most inhibitory compound out of sixteen tested (Erickson and Freeman 1978); invertebrates as a group were more sensitive to chloramines than to free chlorine (Goldman et al. 1978). Erickson and Foulk (1980) found that continuous concentrations of chlorine even below a measurable residual resulted in the irreversible loss of biomass in algae. The relative toxicities of free chlorine and combined chlorine may depend on the concentrations tested: at concentrations greater than 0.5 mg/L, chloramines may be more toxic while at concentrations less than 0.5 mg/L, free chlorine may be more toxic (Tsai and Tompkins 1974).

Dibromamine ($NHBr_2$) becomes much more stable in seawater or estuarine waters which have high pH and ammonia levels, with a half life of nearly three days (Cromer et al. 1978). Tribromamine (NBr_3) is the principal species at concentrations just beyond the breakpoint (LaPointe et al. 1975). Bromide ion concentration, hydrogen ion concentration, tribromamine concentration and free residual bromine concentration all affect the decomposition rate to tribromamine (LaPointe et al. 1975). LaPointe et al. (1975) reported that bromamines, unlike chloramines, are potent virucides.

CHLORINE DOSE AND BREAKPOINT REACTIONS

Many treatment plants practice "breakpoint" chlorination, that is, enough chlorine is added so that free residuals are available for disinfection. The initial chlorine dose helps to determine the types and concentrations of the residual oxidants. The same residual chlorine concentrations are obtained for a given chlorine dose whether the chlorine is administered at a single point or at multiple points in the contact chamber (Kothandaraman and Beuscher 1974). In both freshwater and seawater containing ammonia-nitrogen, increasing the chlorine dose will result in increased amounts of combined residuals (mainly monochloramine (NH_2Cl) with equimolar or excess ammonia) up to a certain

point. At that dosage, or breakpoint chlorination, there is a sudden loss of chlorine residuals and a simultaneous disappearance of ammonia-nitrogen. This is due to the instability of dichloramine ($NHCl_2$) via oxidation to nitrogen gas and nitrate products (Pressley et al. 1972). After the breakpoint, increases in chlorine dose result in increasing amounts of free residual chlorine. The usual weight ratio for breakpoint is 10:1 chlorine to ammonia-nitrogen (Palin 1975). With an excess dose of chlorine, dichloramine and trichloramine (NCl_3), usually unstable species, are quite stable.

When organic nitrogen is present in addition to ammonia-nitrogen, the breakpoint phenomenon occurs, but it is less pronounced. While ammonia is oxidized within the first minute, amino acids are oxidized more slowly over an extended period of time (Pressley et al. 1972). The breakpoint reaction also occurs in bromination, but it is more rapid. The concentration of bromide may affect the rate or pattern of the breakpoint reaction (Morris 1978).

Figure 3 shows a typical breakpoint chlorination curve and the products formed at different segments of the curve. The chlorine dosage needed to achieve breakpoint chlorination decreases as the degree of wastewater treatment increases (Pressley et al. 1972).

Decay Rate

Dilution alone is not responsible for all the decreases in residual oxidant observed in discharged effluents in the field (Page and Wilson 1979) or in laboratory experiments (Sugam and Helz 1977).

The two-stage decay pattern of chlorine in water has been noted by several researchers (Eppley et al. 1976; Bender et al. 1977; Høstgaard-Jensen et al. 1977; Sugam and Helz 1977; Wong and Davidson 1977; Goldman et al. 1979; Helz 1981). Sugam and Helz (1977) noticed an initial rapid loss of about 90% of the oxidant added to power plant cooling water which they thought was due to any of the following:

- reaction of the oxidant with slime accumulation or metal ions
- volatilization
- oxidation of particulates
- auto-decomposition and disproportionation of the oxidant
- reaction with carbon and nitrogen on humic materials

The second stage is characterized by a continuous loss of oxidant at a much reduced rate. Kuo et al. (1977) noticed that free and combined chlorine decreased with storage time, indicating that chlorination still proceeded one week after chlorine dosage. Similarly, Goldman et al. (1979) found chlorine decay to occur over ten-day periods. Sugam and Helz (1977) explained the oxidant loss as the slow decomposition of organic chloramines and bromamines.

Figure 4 shows a typical decay curve, in this case at 25°C, pH about 8, salinity about 10 ppt. Waters with differing quality characteristics were found to have distinct decay curves (Sugam and Helz 1977). Among the variables affecting the shape of decay curves were salinity (and hence bromide

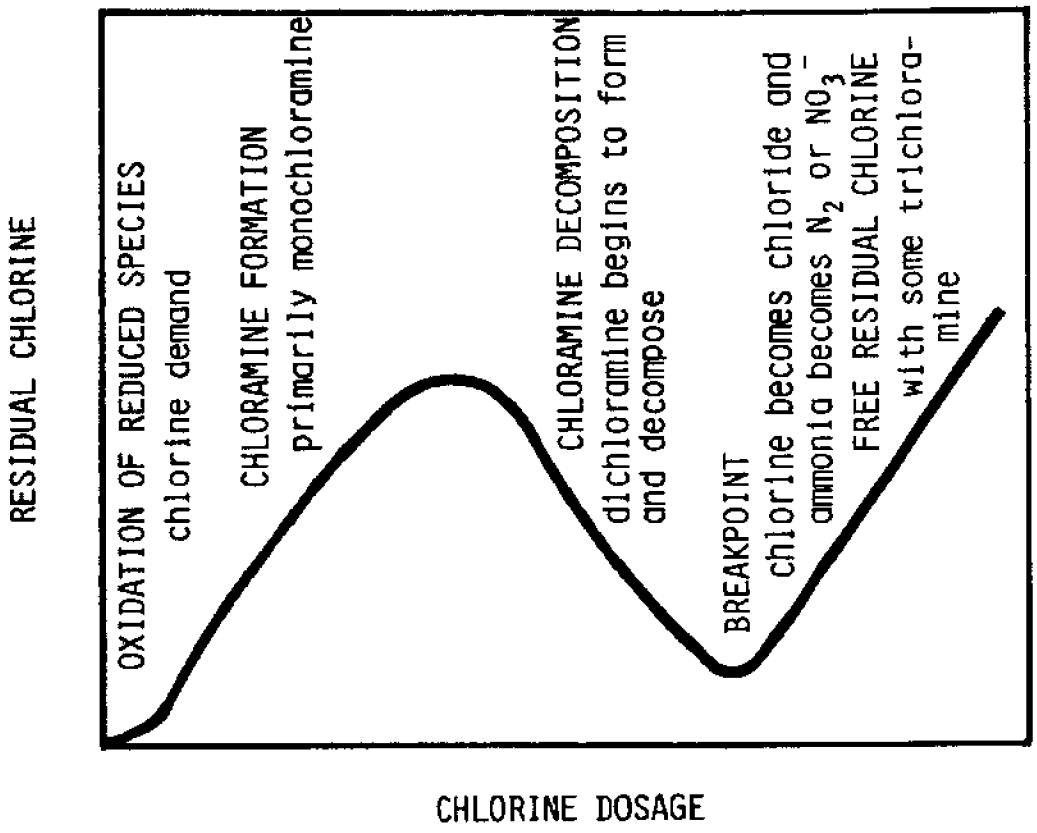

Figure 3. Relationship between chlorine dosage and residual chlorine for breakpoint chlorination. Neutral to alkaline pH range (Johnson 1978).

concentration, Goldman et al. 1979), humic acid, type of halide, temperature, organic concentration and total dose of chlorine (Sugam and Helz 1977).

Bourquin and Gibson (1978) suggest that marine as well as freshwater microorganisms may be able to dehalogenate organic compounds, thus aiding in chlorine decay.

Exposure Time

Organisms can tolerate higher concentrations of residual oxidants when exposure times are reduced and vice versa (Hom 1970; Tsai and Tompkins 1974; Brooks and Seegert 1978a; Burton et al. 1979). While sewage treatment plants release chlorinated effluents continuously into the environment, power plants discharge chlorinated effluents on a seasonal or intermittent basis. White (1978a) advocates a contact time of not less than 30 min. for adequate disinfection. However, while increasing the contact time may initially increase the efficiency of disinfection, there is a threshold after which additional disinfection is not possible at a given chlorine dose (Hom 1970). The Collins mathematical model (White 1978a) illustrates how contact time and chlorine dosage are related.

$$Y = Y_o (1 + 0.23\ ct)^{-3} \qquad (11)$$

where:

Y = MPN in chlorinated wastewater at the end of time t

Y_o = MPN in effluent prior to chlorination

c = total chlorine residual, mg/L, at end of contact time t

t = contact time, in min.

This model assumes there is rapid mixing and no shortcircuitings in the contact chamber. It can be seen that a lower MPN (most probable number of microorganisms) in the effluent due to more advanced treatment (say, secondary as opposed to primary) will require a lower dose of oxidant.

Circulation patterns, depth of stream and turbulence can determine the amount of time that an organism or community is exposed to chlorine residuals. Tidal forces in river systems like the James can create "pools" of elevated concentrations of oxidant which would not be predicted from dilution theory alone (Bender et al. 1977). Tidal patterns may result in the upstream intrusions of chlorination products (Sugam and Helz 1977). Thus the effects of chlorination may not be limited to downstream effluent plumes.

If there is no vertical mixing, chlorine residuals may be more concentrated in surface layers. Høstgaard-Jensen et al. (1977) found residual chlorine concentrations as well as temperature to decrease rapidly with depth. Turbulence of the water could allow the escape of some forms of the residual oxidant. Hypochlorous acid (HOCl) is more volatile than is hypochlorite (OCl^-) (Johnson 1978). In the more acid pH range where HOCl predominates, volatil-

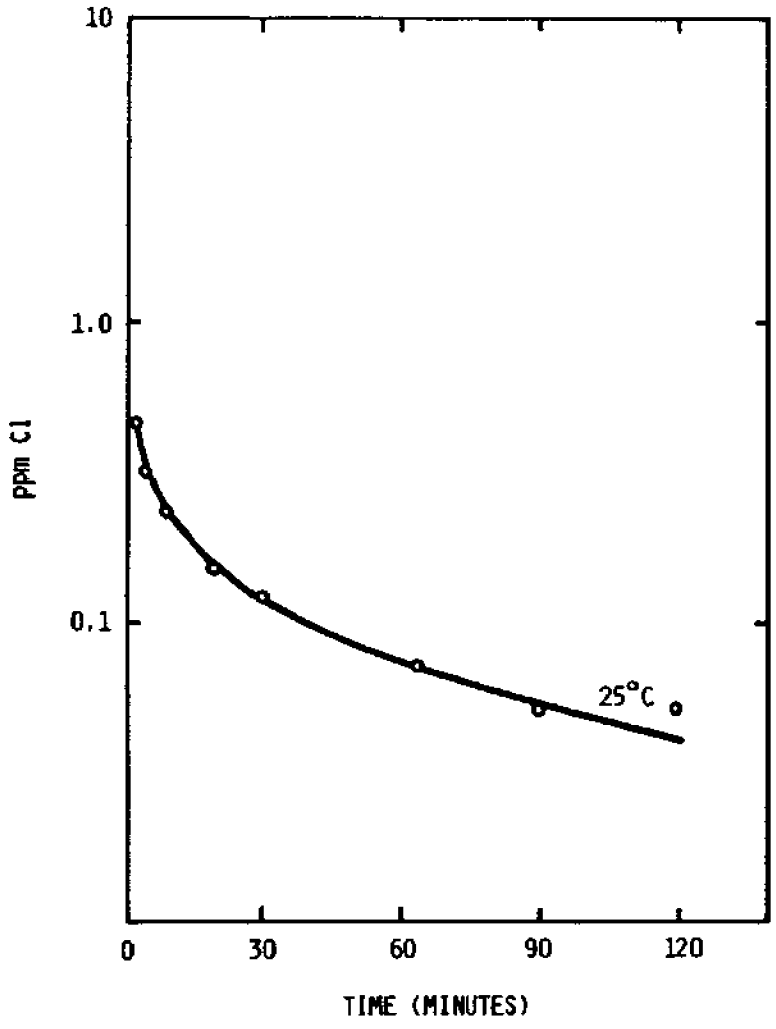

Figure 4. Temperature dependence of oxidant decay. pH approx. 8.4; salinity about 10.3; bromide concentration of 239 mM (Sugam and Helz 1977).

ity losses would be expected to be greater. Aeration removes the highly volatile trichloramine (NCl_3) followed by dichloramines ($NHCl_2$). Monochloramine (NH_2Cl) and free chlorine are much less volatile (Opresko 1980). Jense and Rosenberg (1975) found some chlorinated substances to be degraded more quickly in open rather than closed aquaria.

SALINITY

Bromide ion concentration in seawater increases with increasing salinity. The concentration of bromide ranges from 0.19 ppm in river and lake water to 65 ppm in full strength seawater (Data of Geochemistry 6th ed.). A rough estimation of bromide concentration in estuaries can be determined from the measured salinity.

With the salinity of full strength seawater at 35 ppt, the ratio of estuarine salinity to full strength seawater salinity is proportional to the ratio of the concentration of bromide in seawater to the estimated bromide concentration in estuaries (Helz personal communication):

$$\frac{\text{estuary salinity ppt (measured)}}{\text{seawater salinity in 35 ppt}} = \frac{\text{estuary } Br^- \text{ in ppm (estimated)}}{\text{seawater } Br^- \text{ in 65 ppm}} \qquad (12)$$

For normal seawater chlorination, the major residual oxidants would be either hypobromous acid (HOBr), hypobromite (OBr^-) and tribromamine (NBr_3) or monochloramine (NH_2Cl) and dibromamine ($NHBr_2$) depending on ammonia concentration and the ratio of halogen to nitrogen. In full-strength seawater (35 ppt) with free amino-nitrogen content below about 0.1 mg/L, the conversion of hypochlorous acid (HOCl) to hypobromous acid (HOBr) is expected to be a dominant early reaction, occurring before chloramine formation (Helz et al. 1978). This reaction reaches completion in less than 10 sec, at a dose of 1 mg/L chlorine. Free or combined bromine oxidants remain thermodynamically stable in salinities as low as 1 ppt. As salinities increase, the relative amounts of bromine analogs also increase. A chlorine dose of 1.4×10^{-5} mM results in the following: at a salinity of 0.00 ppt--mainly chloroform ($CHCl_3$); at 1.06 ppt--half bromoform ($CHBr_3$) and half dibromochloroform ($CHBr_2Cl$); at 3.68-32.54 ppt--mainly bromoform ($CHBr_3$). However, the actual quantity produced is quite small (Helz 1981).

There may be a tendency for oxidants to decay faster with increasing salinity. Chlorine demand increases with salinity, reaching its maximum at a point where the concentration of Br^- exeeds the concentration of chlorine added (Sugam and Helz 1977). Goldman et al. (1979) similarly found decay more pronounced in waters containing bromide. Decreases in salinity favor the formation of the more stable monochloramine over the quickly decaying dichloramine.

pH

The pH of the receiving waters can be influenced to some extent by the form in which chlorine is added to the water. Chlorine gas decreases the pH

as it hydrolyzes to hypochlorous acid (HOCl) and then dissociates to H^+ and OCl^- (Sugam and Helz 1977). Calcium or sodium hypochlorite (NaOCl, bleach) on the other hand tends to increase pH. To a great extent, pH determines which chlorine species is present (Palin 1975). Chlorine is more active as an oxidizing agent under acidic conditions (Snead et al. 1980). In dilute solutions of aqueous chlorine with a pH range of 5-9, HOCl is the major reactive species for oxidizing reactions (Morris 1978). In the more acidic solutions below pH 5, Cl_2 predominates while in more basic solutions, essentially only OCl^- is present. Between these values, HOCl and OCl^- are about equal (Palin 1975).

Chloramines in the neutral pH range (around pH 7) are predominantly monochloramine (NH_2Cl) (White 1978). Decreases in pH (relatively high concentrations of H^+) favor the formation of dichloramines ($NHCl_2$) while increases in pH (higher OH^- concentrations) result in large amounts of monochloramine. In freshwater, pH ranges of 6-9 favor formation of OCL^- over HOCL and NH_2Cl over $NHCl_2$. Sugam and Helz (1977) found the formation of monochloramine fastest at a pH of 8.3. The formation of trichloramine (NCl_3), however, is not greatly pH dependent at pH values greater than 3.2 (Saguinsin and Morris 1975).

There are similar patterns for bromine analogs in seawater, but dissociation reactions occur at pH levels higher than those for the corresponding chlorine compounds. At seawater pH greater than 8, chloramines form (eq. 13). At pH less than 8, hypobromite (HOBr) predominates, leading to bromamine formation (eqs. 14 and 15; Inman and Johnson 1978). Both HOBr and OBr^- are unstable at a pH of 8. At pH 4, the dissociation of the bromine species in seawater containing bromide leads to an equilibrium distribution of about 3% HOBr and 17% Br_2; the remaining fraction is composed of several bromine-chloride complexes ($BrCl_2^-$, $BrCl_6^-$; Goldman et al. 1979). Dibromamine (NHBr) formation is favored at most pH levels.

$$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O \qquad \text{pH greater than 8} \qquad (13)$$

$$HOCl + Br^- \longrightarrow HOBr + Cl^- \qquad \text{pH less than 8} \qquad (14)$$

$$2HOBr + NH_3 \longrightarrow NHBr_2 + 2H_2O \qquad (15)$$

While pH plays an important role in the equilibria constants which govern the relative proportions of the various product chlorine species, little information exists on the effect of pH on chlorine toxicity (Brooks and Seegert 1978b). It is not known whether there is a synergistic toxic effect by pH levels and chlorine residuals on organisms or merely an indirect effect by pH levels influencing the types and amounts of chlorination products.

Nitrogen Concentration

The type and quantity of nitrogen compounds in the receiving water influences the chemical form of chlorine and, thus, its toxicity. For typical seawater ammonia-nitrogen concentrations, the formation of monobromamine (NH_2Br) will be minimal.

Ammonia-nitrogen is quickly consumed in receiving waters, so waters containing ammonia (NH_3) will have been subjected to recent pollution. High ammonia- or amino-nitrogen levels, such as the 10-40 mg/L found in wastewater effluents (White 1978a), favor chloramine formation. With equimolar or excess ammonia and a chlorine to amino-nitrogen weight ratio less than 5:1, monochloramine (NH_2Cl) is the dominant residual in fresh water or sea water (White 1978a).

Inman and Johnson (1978) have found that the critical factors in determining the predominance of bromamines or chloramines are bromine concentration or salinity, the ammonia nitrogen level and pH. At chlorine to ammonia-nitrogen weight ratios less than 5 and longer exposure times (chlorine dose less than 2.5 mg/L and ammonia concentrations greater than 0.5 mg/L), monochloramine (NH_2Cl) becomes the major component of the total oxidant concentration. For ammonia-nitrogen levels less than 0.4 mg/L and with sufficiently large chlorine doses, tribromamine (NBr_3) and hypobromous acid (HOBr) are the major products.

Similarly, Sugam and Helz (1977) found that both the chlorine to bromide ratio and the chlorine to ammonia ratio were critical factors in evaluating which chlorine species predominate. For the pH range of natural waters, only bromamines and free bromine contributed to total oxidant concentration in marine and estuarine waters at normal chlorine doses. Bromine-halide complexes dominated only at pH values less than 6, according to their model.

Nitrogen in the form of amino acids, peptides or proteins leads to the formation of organic chloramines which are generally thought to have little biocidal effect (White 1978a). Most are fairly unstable and so, even if toxic, may cause little harm. Helz et al. (1978) suggest that oxidative deamination of organic amino compounds dominates the nitrogen chemistry in cooling water chlorination.

Dissolved Organics

Sugam and Helz (1977) and Helz et al. (1978) are convinced that organic carbon plays a major role in the fast decay process. The removal of all organic material reduces the decay rate (Sugam and Helz 1977). There is a veritable cascade of chloro-organic products resulting from chlorination. Jolley and Pitt (1978) have discovered 74 compounds of relatively low volatility, many of which had been chlorinated, in effluents from domestic wastewater; they list all these compounds along with concentration and method of analysis. Glaze and Henderson (1975), similarly, detected over 100 identifiable compounds in a chlorinated secondary sewage. While they conceded that the superchlorination conditions used in their study (doses of 1500-2000 mg/L for one hour contact periods) were not representative of the usual wastewater treatment, they nonetheless felt that many of the same compounds would be formed in smaller quantities in conventional sewage plants. The content of organic material in cooling water depends on the time of year and the site (Høstgaard-Jensen et al. 1977).

Chlorine can react with organic material by:

1. Addition to a double bond in an organic compound.

2. Substitution forming an organic chlorocompound.

3. Oxidation where the organic material either is transformed to another with a higher oxidation level or is decomposed into carbon dioxide and water, reducing chlorine to chloride (Høstgaard-Jensen et al. 1977).

Fifty percent of the soluble organic matter in sewage effluents are humic substances, which are various complex organic substances obtained from humus and are insoluble in acids and organic solvents. These humic substances have been implicated as precursors to trihalomethane production during chlorination (Stevens et al. 1978; Kuo et al. 1977; Christman et al. 1981). Trihalomethanes--chloroform ($CHCL_3$) and bromoform ($CHBr_3$)--are potentially carcinogenic in drinking water. Sugam and Helz (1977) found bromine species to react faster and to a greater extent with humic acid than did chlorine species, making trihalomethane production a distinct possibility in chlorinated seawater. Christman et al. (1981) provide a comprehensive review of the reactions of aquatic humic materials with free chlorine (HOCl).

In addition, sewage effluents may contain free phenols and aromatic acids which are readily chlorinated to produce chlorinated analogs (Jolley et al. 1978, Tables I, II, III--lists of organic constituents in sewage effluent).

Jolley (1975) and Jolley et al. (1978) arrived at the following conclusions in studies of chlorinated sewage treatment plant effluents (chlorine residual: 1-2 mg/L)

1. Stable chloro-organic compounds are formed during the chlorination of sewage effluents at ppm chlorine concentration.

2. The chlorination yield of chloro-organic compounds (as Cl) is about 1% of the chlorine dosage when disinfection reaction conditions are used.

3. The types of organic products formed included chlorinated phenols, purines, pyrimidines and aromatic acids at the ppb concentration level.

They found similar conclusions in their study of cooling water from a steam power plant (chlorine dose: 2.1 mg/L; residual: 1 mg/L):

1. Over 50 stable chloro-organic compounds were formed.

2. The chlorination yield of the chloro-organic constituents is about 0.5% of the chlorine dosage under reaction conditions simulating those used for antifoulant treatment.

3. The HPLC chromatographic profile and peak elution positions were similar to those obtained for chlorinated sewage effluents.

Similarities in HPLC (^{36}Cl tracer-high pressure liquid chromatography) profiles of chlorinated sewage effluents and cooling waters suggest many of the same chloro-organic products are formed in each medium during chlorination. These profiles measure non-volatile compounds only--they could not measure chloroform or other volatile trihalomethanes. Three percent of the chlorine used in chlorination becomes volatile compounds--trihalomethanes (Kuo et al. 1977). The composition of cooling waters (containing animal excreta, plant and animal metabolites, microflora and microfauna) resembles that of dilute sewage effluents (Jolley et al. 1978). Since the presence of ammonia-nitrogen results in the formation of chloramines with lower oxidative powers, smaller quantities of chloro-organics would be anticipated in waters containing higher concentrations of ammonia. Hypochlorous acid (HOCl) may be the effective chlorinating agent for organic compounds in aqueous solutions.

Jolley et al. (1978) summed up their conclusions:

1. The chlorination reaction yields of chloro-organic products (as Cl) in chlorinated cooling waters and sewage effluents ranges from 0.5-3.1%.

2. Annually, the environmental impact of water chlorination on the aquatic ecosystems of the United States is estimated to include the introduction of several thousand tons of chloro-organic compounds.

3. Any or all of a large number of possible aqueous chlorination reactions may occur during water chlorination, depending on the presence of organic constituents, reactions kinetics and thermodynamics and other reaction parameters.

4. Complex mixtures of chloro-organic compounds are produced during chlorination, each at ppb concentration or less.

5. The nature of the chloro-organic products formed during the chlorination of sewage effluents and cooling water suggests a variety of possible effects relative to (a) genetics, (b) toxicity and (c) population, through altered chemical communications in aquatic ecosystems.

The oxidation of organics by chlorine is generally slow (Johnson 1978). Some of the possible organic products of chlorination include organic halamines, halogenated methanes, and other halogenated organic compounds.

Organic halamines

Formed from amino acids (Burleson et al. 1978), peptides and proteins, organic halamines are less stable than inorganic halamines (Murphy et al. 1975) and are generally thought to have little or poor biocidal effect (Johnson 1978; White 1978). They are difficult to distinguish analytically from inorganic chloramines or bromamines.

Halogenated Methanes

Halogenated methanes are formed when chlorine or bromine is incorporated into the carbon framework by a predominantly ionic pathway. Carpenter and Smith (1978) found evidence that bromoform production is but one of a host of competing reactions. Bromoform may result from the secondary reactions of Br^- with organic fragments generated by the oxidation of macromolecules. Helz et al. (1978) decided, however, that increased temperature and intense agitation in cooling water resulted not in haloform production but in relatively stable, halogenated macromolecules. Only 4% of the Cl_2 added produced bromoform ($CHBr_3$). They believe that a major portion of the large percentage of Cl_2 unaccounted for would be found as halo-organic compounds.

Bean et al. (1978) found bromoform to be the principal component of lab-chlorinated marine waters, with smaller quantities of dibromochloromethane and dichlorobromomethane. Interestingly, they found bromoform as well in all unchlorinated seawater samples they analyzed. Haloform concentrations in surface waters do not necessarily originate in chlorinated wastewater discharges (Hoehn et al. 1976, quoted by White 1978a). Dyrssen and Fogelquist (1981) found high bromoform levels (about 40-75 mg/L) in surface waters in unpopulated areas of the Arctic Ocean. They attributed this bromoform presence to production by algae belts. In populated areas, the levels were much higher (305-370 mg/L), probably as a result of chlorination of seawater.

The chronic or mutagenic effects of halogenated methanes are not well known. Stewart et al. (1979) studied the toxicity of three by-products of chlorinated or ozonated seawaters: bromate, bromoform and chloroform. There is some discrepancy as to whether or not bromate is a chlorination product. Peron and Courtot-Couper (1980), using bromine determination or electronic absorption, did not detect bromate formation in chlorinated seawater

Halogenated Organic Compounds

Formed by substitution reactions between chlorine and aromatic compounds (Larson and Rockwell 1979), these compounds are potentially highly toxic, or highly interfering with pheromone systems (Jolley et al. 1978). Many of the precursor compounds (phenols, cresol, citric acid, benzoic acid) enter the aquatic system through the breakdown of humic or fulvic acids, heme or chlorophyll.

Chlorine is readily incorporated into a carbon framework by a predominantly ionic pathway, but there is a decreasing reactivity of the aromatic nucleus with increasing chlorine substitution. Chow and Roberts (1981) found greater amounts of halogenated organics formed in nitrified wastewater effluent, presumably due to the greater reactivity of chlorine's free form over its combined form. In general, organic chloramines are less stable than are inorganic chloramine residuals (Murphy et al. 1975). Phenol is one of the more readily chlorinated aromatic compounds (Carlson and Caple 1978; Buikema et al. 1979) which also include amines, aldehydes, ketones and pyrrole (Murphy et al. 1975). Buikema et al. (1979) provide a review of the literature dealing with phenolics, including chlorophenols, in aquatic ecosystems.

When the bromide ion is present, the chlorination of waters containing phenol can result in brominated phenols (Sweetman and Simmons 1980). However, Murphy et al. (1975) found other organic compounds such as urea, furan, alcohols, methyl ketone and thiophene to remain unchlorinated, even under vigorous conditions. Stanbro and Smith (1979) studied the decomposition kinetics of N-chloroalanine, a rapidly formed chlorination product of the amino acid, alanine. They found that the N-chloroalanine formed during chlorination of natural water (pH of 5-9) would degrade in a few hours to products probably much less toxic. The decay rate was highly dependent on pH and temperature. More work needs to be done to predict both the toxicities and the lifetimes of chloro-organic materials under various environmental conditions (Brooks and Seegert 1978a; Stanbro and Smith 1979).

At low concentrations, chlorophenols are not metabolized. At high concentrations, chlorophenols adversely affect microbial populations, toxic effects being reflected in low BODs, which in tum reflect low microbial populations (Carlson and Caple 1978). Rosenblatt (1975) had previously mentioned such depressions in BOD by chlorination of unspecified organics. The toxicity of mixtures of chloro-organics is largely proportional to the concentration of the chlorophenol fraction. An increasing chlorine content of aromatics is correlated with a greater lipophilicity (Kopperman et al. 1978) which means that they have a greater bioaccumulation factor. While tri- and penta-chlorophenols are used as pesticides, only low levels of much less toxic mono-substituted phenols are formed under normal chlorination procedures. It is also possible that PCBs are formed: Rosenblatt (1975) cites an EPA study which found biphenyl converted to polychlorinated biphenyl under drastic chlorination conditions. Gaffney (1977) also reported the formation of PCBs in chlorinated wastewaters containing biphenyls. Since the chlorination of biphenyls ($C_{12}H_{10}$) proceeds very slowly, under the low chlorine concentration conditions of normal wastewater treatment only small amounts of chloro-biphenyls would be expected (Snider and Alley 1979). Polychlorinated aromatics are most likely not derived via a dilute aqueous chlorination process (Carlson and Caple 1978). Polynuclear aromatic hydrocarbons (PAH) were found to be degraded by chlorination practices, with an increased contact time, temperature and chlorine dosage resulting in a greater degradation rate (Harrison et al. 1976; Perry and Harrision 1977). Bean et al. (1978) found the production of halogenated components (presumably lipophilic), with the exception of haloforms, in the low-level chlorination of relatively pristine seawater to be very low.

Jolley et al. (1978) reviews the types of reactions and mechanisms involved in the formation of both N-chlorinated and C-chlorinated compounds.

Carlson and Caple (1978) believe that the basic principles of mechanistic organic chemistry can aid in elucidating the structure and/or evaluating the distribution of aqueous chlorination products. That is, if the parent aromatic organic content of a waste is known, then an estimate (a priori) of product type and distribution can be made. How much of this structural information can be transferred to the "real world" is unclear. This approach assumes that the individual wastewater constituents are known, which is not always the case in sewage treatment plants. If this assumption is false, then it is diffi-

cult to say anything about synergistic effects between chlorine and other (toxic) chemicals.

Temperature

The dissociation reaction of hypochlorous acid (HOCl) to hydrogen ions and hypochlorite ions depends on temperature, a high temperature encouraging this dissociation. Inorganic chloramine reactions also depend on temperature, the reactions increasing with an increase in temperature, while at lower temperatures disinfection is slower (Palin 1975; Johnson 1978; Snead et al. 1980). Low water temperatures require an increase in contact time or an increase in concentration to achieve the same efficiency in disinfection. Sugam and Helz (1977) found that increased temperatures reduced residual oxidants.

Brooks and Seegert (1978a) suggest, after reviewing the literature, that fish have some range within which temperature has litttle effect on chlorine toxicity; but outside this range, temperatures can increase the sensitivity of those fish to chlorine (Larson and Schlesigner 1978; Heath 1978; Goldman et al. 1978). The reactions are apparently species dependent. In another paper, however, Brooks and Seegert (1978b) determined that resistance of fish exposed to chlorine for short periods was inversely proportional to temperature.

Organisms may have physiological responses to an increase in temperature which add to the inherent toxicity of chlorine. Metabolism rates may speed up which, coupled with the lower dissolved oxygen levels at high temperatures, may increase mortality. Capuzzo (1979), in reviewing the literature, determined that temperature has a synergistic effect on the toxicity of both free chlorine and chloramine, perhaps due to an interaction of uptake rates and regulation of physiological rates. Larval stages may be present during the warmer seasons, and this life history stage may be more sensitive to chlorine compounds than the older or younger stages (Burton et al. 1979).

Dissolved Oxygen

The toxicity of oxidizing agents may be enhanced by low dissolved oxygen levels. Polluted waters downstream from sewage treatment plants may already have low dissolved oxygen concentrations. Zaloum and Murphy (1974) found that chlorination/dechlorination of filtered final effluents did not reduce biochemical oxygen demand nor create bioresistant organics, since there was no significant difference in the extent of carbon degradation between chlorinated/dechlorinated samples and unchlorinated samples.

Light

Ultraviolet radiation (sunlight) catalyzes the auto-oxidation of free chlorine oxidants. Rosenblatt (1975) considered the role played by the chlorine free radical to be more important than previously supposed and thought irradiation with sunlight could be an important factor in chlorine decay. Johnson

(1978) cited results obtained by Snoeyink and Markus (1973; 1974) in which free chlorine persisted ten times longer in dark (indoors) than in daylight (outdoors). Høstgaard-Jensen et al. (1977), in field measurements, found chlorine decay to be more rapid during the day than at night. They recommended, therefore, that chlorination of power plants should take place during the night to avoid persistent residuals in the effluents after release into receiving waters.

The decomposition reaction of hypobromite ions is also rapidly catalyzed by light. Many researchers have found light to increase chlorine decay rates and to induce bromate formation in chlorinated seawater (Haag 1981; Richardson et al. 1981). Macalady et al. (1977) found the intensity of sunlight caused up to 50% conversion of bromine to bromate (BrO_3), which is persistent and of an unknown toxicity. Carpenter and Smith (1978) and Carpenter et al. (1981) reported that the oxidative capacity in the added chlorine was substantially converted to bromate ion while bromoform ($CHBr_3$) production was reduced in sunlight. The toxicity and persistence of bromate in seawater needs to be determined (Carpenter et al. 1981). In contrast, Peron and Courtot-Couper (1980) did not detect bromate formation in chlorinated seawater using bromine determination or electronic absorption spectra.

Dichloramine ($NHCl_2$) and trichloramine ($NHCl_3$) are unstable even in the dark while monochloramine (NH_2Cl) may persist for days. Sugam and Helz (1977) and Helz et al. (1978) feel that decay induced by UV is too slow to contribute to the fast phase of decay during which most of the chlorine disappears, especially when this fast phase occurs inside a power plant (Sugam and Helz 1977).

Reducing Agents

Manganese (Mn_2), iron (Fe_2), nitrite (NO^-_2), sulfide (S_2^-) and sulfite (SO_2^-) in anoxic waters are reducing agents which react rapidly with chlorine (Sugam and Helz 1977). Exerting a chlorine demand, they can contribute to a lowering of the effluent toxicity. They also can react producing new oxidizing agents that, with current analytical methods, can be mistaken for free chlorine by analytical methods (Johnson 1978). However, Helz et al. (1978) rejected these inorganic reducing agents as major chlorine consumers because either the concentration of the agent in its reduced form was too small, relative to typical chlorine doses, or the redox reaction is too slow to explain the large chlorine decay.

Kuzminski et al. (1970) found calcium bicarbonate to interfere with the disinfection process of both chlorine and bromine. They hypothesized the formation of barriers restricting chlorine's passage into the target cell. Chlorination substantially reduces the copper complexing capacity of seawater (Carpenter et al. 1981).

Particulates

Carpenter and Smith (1978) found some evidence that particulate matter reacted with chlorine-produced oxidants, forming products other than bromoform. Helz et al. (1978) found chlorine decay in an estuarine water sample significantly slowed if the sample is first subjected to ultrafiltration. However, Sugam and Helz (1977) found no major effect of particulate matter on the decay pattern. White (1974) also discards the importance of suspended solids in the efficiency of the wastewater chlorination process. In lab experiments testing the efficiency of chlorination of drinking water, LeChevallier et al. (1981) found disinfection efficiency negatively correlated with turbidity. Total organic carbon was found to be associated with turbidity and was shown to interfere with maintenance of a free chlorine residual by creating a chlorine demand. Bacteria also were embedded in turbidity particles, shielding them from the effects of chlorine. Hejkal et al. (1981), in wastewater field experiments, found some protection of viruses from chlorination when viruses were associated with particles larger than 0.3 mm.

RECOMMENDATIONS FOR FURTHER RESEARCH

The basic reactions of chlorine in both freshwater and seawater appear to be fairly well understood, although with the analytical methods currently available (see next chapter) there is some difficulty in distinguishing the individual chlorine species produced. In need of further understanding are the reaction mechanisms and the kinetics involved in the creation of the "cascade" of chlorination products. Helz (1982) recommends that all the chlorine added to effluents be accounted for in a complete mass balance equation, a formidable task given the aggressively reactive nature of chlorine and the multitude of possible products. The use of modeling to predict the products of chlorination and their concentrations first assumes a knowledge of wastewater constituents, information that may not always be readily available. Helz (1981) raises the question of whether it is possible to generalize the various chlorination rections to the point where a model could have widespread application, but still accurately reflect real, localized conditions.

The stability (persistence) and decay rates of chlorination products, such as bromochloramine, bromamines, organic halamines and bromate in the aquatic environment need to be further assessed. Photochemical degradation, while documented in laboratory studies, needs to be assessed in field situations.

The use of fixed chlorine dosages to produce breakpoint chlorination in treatment plants needs to be reassessed. Fluctuations in the nitrogen content of wastewaters would produce a fluctuation in the chlorine dosage necessary for breakpoint reactions. A fixed chlorine dosage may be inappropriate.

Finally, the ultimate environmental fate of chlorination products and their possible toxicity in individual species of aquatic organisms need to be determined. Possible synergisitic effects on toxicity caused by environmental parameters, e.g., pH, need further study.

III

Analytical Techniques

While the various chlorine species differ in their disinfection capabilities, present analytical techniques do not separate and measure chlorine residuals on the basis of germicidal capabilities (White 1978a). The ability to selectively detect and measure only the effective disinfectant chemical species of chlorine could lead to more control over the chlorination process: such an ability would allow managers to regulate chlorine dosages for more precisely minimizing formation of toxic chlorination by-products (Johnson 1978).

In waters containing large amounts of ammonia, the preferred disinfectants are hypochlorous acid (HOCl) and monochloramine (NH_2Cl); yet none of the analytical methods currently available adequately measure the concentration of HOCl, the free residual chlorine. Most methods actually measure a variety of oxidants. HOCl is about 80 times more powerful than the hypochlorite ion (OCl^-) in the disinfection of bacteria (Palin 1974). OCl^- is not available to kill microorganisms; yet perhaps because of its ionic state, it is an oxidizing agent and is available to the analytical reagents for measuring free available chlorine (Johnson 1978). Manganese dioxide (Johnson 1978), bromine (Carpenter et al. 1977; Dimmock and Midgley 1979); nitrites, iron (Opresko 1980) and organic compounds (Wajon and Morris 1980) also can interfere in the analysis of free residual chlorine. In water containing nitrogenous organic compounds, N-chloro compounds form which may result in an overestimation of the disinfecting potential of the added chlorine when free chlorine is measured by Standard Methods (Wajon and Morris 1980). If the types of organic nitrogen compounds are known, then analytical methods can be altered to deal with them.

Opresko (1980) listed a number of factors to consider when selecting an analytical method: (1) types of residuals to be measured, free or combined; (2) level of sensitivity and degree of accuracy required; (3) presence of potential interference compounds; (4) amount of organic material in sample; (5) conditions under which the test is to take place (i.e., field or laboratory test; marine, estuarine or fresh water sample). Analytical measurements developed for freshwater represent abstractions of chemical processes which may not be directly comparable to those occurring in saline waters (Davis and Middaugh 1978; Carpenter et al. 1981). Carpenter et al. (1981) describe a technique applicable to seawater which avoids the underestimation by current analytical methods of the residual oxidants in chlorinated seawater. Since errors of underestimation depend on such factors as rate of titration and solution pH (Carpenter et al. 1977), strict documentation of the test and site conditions

(analytical parameters as well as environmental parameters such as turbidity, sunlight, oxygen, phenol content, proteinaceous nitrogen, iron, manganese) should be included in order to make the data more useful and to allow comparisons between experiments (Davis and Middaugh 1978, discussion).

Opresko (1980) provides a thorough discussion of current analytical methods based on the work of Lishka et al. (1969), Lishka and McFarren (1971), Marks (1972), White (1972), Palin (1975) and Johnson (1976). He describes the theory behind each method in the colorimetric, tritrametric, electrochemical and photometric techniques. A brief description of each method, taken mainly from Opresko (1980), follows. The American Public Health Service report "Standard Methods for the Examination of Water and Wastewater" contains procedural details for most of the methods. Helz (1981) also provides a discussion of analytical methods, describing the theory and limitations of each.

COLORIMETRIC

In colorimetric methods, organic reagents (indicators) added to sample solutions react with the residual oxidants to produce compounds with a characteristic color. The concentration of oxidant in the solution determines the amount of indicator oxidized, which is proportional to the color intensity produced. The color of the sample can then be compared with color standards or analyzed spectrophotometrically to determine oxidant concentrations.

1. Ortho-tolidine (ORTHO): ortho-tolidine reacts with residual chlorine to form a yellow-colored complex. The test is carried out at low pH (pH 1.3) where interference from combined residuals can cause overestimations of disinfection capabilities (White 1972). Chloramine decomposition is caused by acidification at these low pH values (Johnson 1975). Unstable color complexes form a modification of ORTHO, the ortho-tolidine-arsenite method (OTA) attempts to differentiate between free and combined residuals. However, monochloramine ($NHCl_2$) and manganese dioxide (MnO_2, Johnson 1976) interfere in the test for free residual chlorine. Both of these analytical methods have been dropped from standard methods because of their low levels of accuracy and precision (Opresko 1980). Another method, the stabilized neutral ortho-tolidine method (SNORT), attempts to eliminate the interference from combined chlorine and other compounds. Conducted at a higher pH where interference from (NH_2Cl) decreases, the technique relies on buffered stabilizers to prevent decomposition of the ortho-tolidine reagent. There is still interference from MnO_2, however. This method is still included as a standard method.

2. Leuco-crystal violet (LCV): chlorine oxidizes the indicator 4,4',4"-methyldynetris (N,N-dimethylaniline), producing a blue-colored complex. There is only a low interference of (NH_2Cl) in the test for free residual chlorine (Johnson 1976). However, it is susceptible to interference from MnO_2. A standard method, it is accurate with reproducible results although rather complicated, requiring a large number of buffers and reagents (which makes it unsuitable for routine field work).

3. Syringaldazine (SYRING or FACTS): syringaldazine reacts with free chlorine to form a violet-colored compound. The spectral absorbance of this product determines the initial chlorine concentration. This method is specific for free chlorine, although in seawater there is interference from bromine and bromamines. There is little or no interference from NH_2Cl or MO_2 (Johnson 1975). Interpretation is difficult at low concentrations, as the color fades slightly (Johnson 1976).

4. N,N-diethyl-para-phenylenediamine (DPD): standard method DPD reacts selectively with free chlorine to produce a red-colored complex. The solutions are compared against standard color solutions prepared from potassium permanganate. One of the problems with this method is the instability of its reagents. Another is that there is more interference from combined chlorine than in SNORT, LCV or FACTS, although there is less interference than that found in OTA.

TITRAMETRIC

In titrametric methods, the residual chlorine is titrated with a standardized reducing agent. The end point of the titration is measured by colorimetric, amperometric or potentiometric techniques. Since the end point of the reaction is sometimes difficult to discern, or easily passed, the back-titration method is sometimes used. An excess of the reducing agent is initially added to the test solution which is then titrated with a standard iodine or iodate solution (Palin 1974).

1. Iodometric: a standard method, chlorine reduces to chloride in the presence of potassium iodide along with the oxidation of iodide to free iodine (Eq. 16) (Jenkins and Baird 1979). In the presence of starch, iodine forms a blue-colored complex which is titrated to a clear end point with a standardized reducing agent such as sodium thiosulfate or phenylarsine oxide. Back titration is used to avoid interference by other compounds. The difference between the reducing agent added and that remaining is equal to the total chlorine residual (White 1972).

$$Cl_2 + 2I^- \xrightarrow{pH=4.0} 2\,Cl^- + I_2 \qquad (16)$$

2. DPD titrametric method (DPD-FAS): the oxidized DPD is titrated with ferrous ammonium sulfate to a clear end point. Iodide catalyzes the reaction: a small amount causes monochloramine (NH_2Cl) to react with DPD, while an excessive amount causes dichloramine to react. Modifications to the method can determine other halogen residuals (Opresko 1980). This method does not appear suitable for measuring low concentrations of residual oxidants (0.1-0.01 ppm) since the visual end point is not sharp in these dilute solutions (Carpenter et al. 1977). In free chlorine tests, the pH is critical: at low pH values, more NH_2Cl reacts while at too high a pH value dissolved oxygen reacts. Temperature and manganic and copper ions can also interfere in the test.

3. Amperometric titration: the end point in titration is marked by a sudden drop in the current generated by the oxidizing agent in an electrolytic cell. In the back titration method, an excess of reducing agent is first added, with an oxidant used as the titration solution, and the end point is determined by the appearance of the induced currents. The pH of the solution determines what oxidant residuals are being measured. Interference from other oxidants, pH values, volatilization, contamination of the electrodes can all affect the results. Rapid stirring and quick addition of titrant can reduce volatility and reduction losses (Johnson 1975). The technique is considered to be less satisfactory than methyl orange, DPD-FAS and SNORT, but more satisfactory than iodometric, OTA and LCV.

ELECTROCHEMICAL

In electrochemical techniques, the current generated by an oxidizing agent in an electrolytic cell by the depolarization of the cathode is measured. The concentration of oxidants in the electrolytic cell will be directly proportional to the current. The electrodes in the technique can be immersed directly in the solution (direct amperometric method) and separated from the test solution by a membrane (amperometric electrode); or the potential in a redox cell can be measured (potentiometric method).

1. Direct amperometric method: the concentration of oxidants in the cell is directly proportional to the current produced. Both free and total chlorine are measured, but free chlorine measurements may have interference from monochloramine (NH_2Cl) and manganese. The electrode, directly immersed in the test solution, can become fouled with a filmy coating (Johnson 1975).

2. Amperometric membrane electrode: a platinum or gold electrode is separated from the test solution by a semi-permeable membrane which allows the selective transport of hypochlorous acid (HOCl) but not of ionic species like manganic and hypochlorite ions (Dimmock and Midgley 1979). By altering the potential, NH_2Cl can be measured. The electrodes respond to bromine and bromine analogs, making this technique less specific in seawater. The current is also affected by temperature, the surface area of the electrode, the thickness of the membrane and the permeability coefficient of the oxidant in the membrane (Dimmock and Midgley 1979).

3. Potentiometric: internal iodide reference element and a platinum-sensing element measures total residual oxidant concentrations by quantitating the ratio I_2: I^-, which is directly related to total residual chlorine (Jenkins and Baird 1979). Potentiometric techniques are easily adapted for continuous, infield monitoring (EPCO n.d.), although electrodes may be subject to chemical poisoning. This technique has a sensitivity of less than 0.01 mg/L.

PHOTOMETRIC

In photometric techniques, the light absorption of a solution is measured at a predetermined wavelength associated with a particular oxidant species. In the methyl orange method, free residual chlorine bleaches quantitatively a solution of methyl orange. At pH 2, the test is specific for free chlorine; pH is very important, since color development is incomplete at higher pH values. Suspended solids and other ions can interfere.

Ultraviolet spectrophotometric methods can determine monochloramine (NH_2Cl), dibromamine ($NHBr_2$)and tribromamine (NBr_3)—each has its own characteristic absorbance.

DIFFERENCE PULSE POLAROGRAPHY OF PHENYLARSINE OXIDE

A known amount of reducing agent is added in excess to an oxidant sample, resulting in a mixture of phenylarsenous acid and an oxidation product, phenylarsenic acid. Polarography is then used for the quantitative measurement of these acids (Carpenter et al. 1977). Smart et al. (1979) compared this method with amperometric titration for the determination of total residual chlorine in tap water, sewage treatment plant effluent and river water at a treatment plant outfall. While they found it compared favorably with standard volumetric analysis, they noted that the method had additional benefits: The addition of excess phenylarsine oxide immediately stopped reactions involving the oxidants, thus making possible the fixing of samples in the field. Measurements for total chlorine, free chlorine and ozone in the parts per billion range were determined from samples as small as 5 ml.

FRESHWATER STUDIES

Several studies comparing the precision and accuracy of the different methods of chlorine measurement have been conducted. Johnson (1975), in his review of analytical techniques, enthusiastically describes an amperometric membrane probe for measuring free residual chlorine species with a sensitivity that decreased correspondingly with their decreasing toxicities. There was no interference from manganese dioxide and the measurement was independent of pH. While Johnson claimed that the probe could measure down to 0.03 mg/L, he pointed out that there was a corresponding 100% error at this level and conceded that there is a choice to be made between selectivity and sensitivity.

Wajon and Morris (1980) compared seven Standard Methods (including DPD, ORTHO, OTA, LCV, SNORT and SYRING) and their effectiveness in the presence of nitrogenous organic compounds in freshwater. None of the methods gave a reliable measurement of free available chlorine (combined chlorine reacted as if it were free chlorine). DPD and SYRING methods, since they employ a neutral pH, were the most specific for free chlorine when only amino acids were present along with ammonia.

Brooks and Seegert (1979) describe an amperometric titration method for freshwater which has extremely low detection limits (0.0018 mg/L) and is 3-4 times more precise than previous amperometric methods. They suggest that any consistent underestimation of chlorine residuals may be due to the method by which the calculated chlorine values are arrived at and not necessarily the fault of the amperometric method.

Otson and Williams (1980) compared residual chlorine measurements in freshwater from the amperometric titration, chlorine electrode (potentiometric) and DPD ferrous titrametric methods at two different laboratories. They judged amperometric titration the best method due to its precision of measurements, ease and simplicity of operation, and capacity for measuring both total and free chlorine residuals. They also found that storage of samples before analysis affected determinations of chlorine residuals. The rapid decay rate of total residual chlorine in samples made correlation with other water parameters impossible.

Jenkins and Baird (1979) compared the freshwater performance of an Orion 97-70 residual chlorine electrode with the phenylarsine oxide back-titration method (iodometric). They found the electrode to be much more precise for chlorine samples less than 1 ppm than was the back-titration method, although both methods gave comparable results for samples with larger concentrations of chlorine. Sample turbidity, color and ionic strength did not appreciably interfere with the electrode, while temperature and high organic content were found to be critical.

SALINE WATER STUDIES

The chlorination of seawater results in the rapid formation of hypobromous acid (HOBr)(Carpenter et al. 1977). Measurement methods based on the reaction of the residual oxidant with iodide to produce iodine can give false measurements in seawater when the resulting HOBr reacts with iodine to produce a mixture of iodine and iodate (Carpenter et al. 1977). Subsequently, the iodate reacts with the excess iodide to produce additional iodine. The method badly underestimates the residual oxidants in chlorinated seawater by threefold or more. Carpenter et al. (1977) suggest that increasing the acidity and potassium iodide concentration eliminates the errors in estimation. Wong (1980) found no formation of iodate by the reaction between hypobromite and iodide, but did find a significant error in the amperometric titration method due to the rapid stirring and subsequent loss of molecular bromine via volatilization.

Wong (1980) looked at the determination of residual chlorine in seawater by the amperometric titration method. While Carpenter et al. (1977) found errors in the method due to the oxidation of iodide to iodate by bromine, Wong (1980) found no evidence of iodate formation. He suggested that the loss of measured oxidant was due to volatilization of molecular bromine, although he conceded that at chlorine concenterations less than 1 mg/L, iodate may interfere. Wong determined that in the amperometric titration method, the reagent potassium iodide must be added to the sample before the addition of the

acid buffer, and the addition of these two reagents should not be more than one minute apart. The stirring time between the addition of the reagent and the buffer contributed to the loss of the total residual chlorine. Goldman et al. (1979) found this method adequate for measuring total chlorine residuals in seawater.

Wong (1980) further cautioned on the use of concentration units, preferring the µM which contains equal numbers of active halogen atoms (the chlorine ion is considered chemically inert). The unit mg/L Cl must be used with care since it may contain different numbers of reactive halogen atoms. Wong feels that the unit ppm should be avoided entirely in seawater, since density varies with salinity, and the unit ppm assumes a density of 1 liter of water weighing 1 kg (or 1 g/cm^3). Seawater density can vary, introducing an error that may not be consistent over a wide range of salinities.

Using a potentiometric method, Pinsky and Weber (1977) were able to differentiate easily between bromine and chlorine in a dilute alkaline solution. In such a solution, hypochlorite did not react with thiosulfate, so the determination of hypobromite, which did react quantitatively, proceeded rapidly. Using conventional iodometric methods, the amount of total residual oxidant was determined. The difference between TRO and hypobromite was thus chlorine.

Dimmock and Midgley (1979) tested an amperometric membrane probe for its effectiveness in determining free residual chlorine in saline cooling waters. They found that the probe responded to hypochlorous acid, dichloramine, nitrogen trichloride, bromine and iodine, but not to ionic forms such as hypochlorite, hypobromite or manganese. The probe did not distinguish between free and combined residual chlorine. They found readings in estuarine waters difficult, requiring frequent calibration because of the variation with salinity. The probe was about five times more sensitive to bromine than it was to chlorine, and was more sensitive to molecular halamine than to hypohalamous acid. Changes in salinity which favor formation of Br_2Cl^-, which reduces the concentration of free bromine available to cross the probe's membrane, would tend to underestimate the halogen concentration.

The probe has two advantages: it can be automated, and it is free from ionic interferences, although it is susceptible to interferences from oxidizing agents such as iodate, bromine, cupric, manganese dioxide and dissolved oxygen as well as organic compounds (Jenkins and Baird 1979).

RECOMMENDATIONS FOR FURTHER RESEARCH

There are limitations inherent in all the analytical techniques currently available: interference from combined residuals in the free residual test (ORTHO, OTA, DPD colorimetric, iodometric); interference from manganese dioxide (ORTHO, OTA, SNORT, LCV, DPD-FAS, methyl orange, direct amperometric); interference from bromine and bromamines (SYRING, amperometric, membrane amperometric); instability of reagents or indicators (ORTHO, DPD colorimetric); complicated procedures or equipment (LCV, difference pulse polarography); poisoning of electrodes (direct amperometric, potentiometric).

Most procedures measure chlorine residuals in the 0.01-10.0 mg/L range (Opresko 1980). However, some organisms seem to be affected by chlorine residuals in the parts per billion (µg/L) range. Those techniques which do measure chlorine levels below 0.01 mg/L do so by sacrificing accuracy and reproducibility. The iodometric method can detect chlorine at levels as low as 0.04 mg/L, but its minimum accurate detection is 1 mg/L (Opresko 1980). The amperometric method similarly has a minimum detection level of about 0.002 mg/L, but is accurate only down to 0.1 mg/L. Johnson (1975), while enthusiastic about the selective response of amperometric membrane probes, admitted that there is a trade-off between sensitivity, selectivity and accuracy.

The methods most frequently recommended because of their practicality, sensitivity and reliability are DPD-FAS, amperometric titration and automatic direct amperometric methods. The ability of the membrane/electrode methods (membrane amperometric) to differentiate between the various chlorine species (particularly OCl^- and HOCl) make these methods look promising for future exploitation, especially if the detection limits can be lowered to small concentration levels.

Methods are needed to detect organic chloramines in the presence of excess concentrations of dechlorinating agents; this is especially important because of the increasing use of dechlorination throughout Maryland.

Helz (1981) stresses improved ease of operation as well as improved low-level detection as important goals in analytical technique research. Also in need of further improvement is the ability to measure chlorine in seawater, and the capability for detecting organic chloramines in the presence of excess concentrations of dechlorinating agents. The latter has become especially important because of the increasing use of dechlorinating agents: there is no way of quantitatively determining if dechlorination agents reduce chlorination (Helz and Kosak-Channing 1984).

IV

Chlorination Alternatives

The concern about the possible toxic effects from chlorination has been instrumental in the search to find adequate alternatives for water treatment. These alternatives include chlorine minimization, chlorination/dechlorination, halogenation, ozonation and irradiation. Some of these alternatives may be better suited for power plant biofouling control than for sewage treatment plant disinfection. For example, some methods of chlorine minimization, or the use of a minimal amount of chlorine to achieve adequately reduced levels of microbial populations, are not appropriate for sewage treatment plants, which require a continuous disinfection of effluents. Ozonation, on the other hand, is now receiving substantial consideration as a chlorination alternative in wastewater treatment. Used for more than 50 years in Europe as a drinking water disinfectant, ozone has only recently been considered a viable wastewater disinfectant.

This section describes the various available alternatives to chlorination. Much of the information presented here has been taken from Sawyer (1976), White (1978a) and Opresko (1980). Opresko (1980) reviews some methods suitable only for power plants, such as mechanical cleaning, special condenser coatings and thermal controls. For a more detailed description of these methods, the reader is referred to these sources.

CHLORINE MINIMIZATION

Chlorine minimization is the lowering of chlorine doses and the frequency and duration of the treatments to the minimum required for adequate control of microbial organisms. Some of these methods, involving little or no chlorination, include intermittent chlorination, zero discharge of effluents, magnetism, lagoons of submerged aquatic vegetation, and better design of chlorination systems leading to a more rapid mixing of chlorine with effluent.

Intermittent Chlorination

Although continuous chlorination is necessary for proper disinfection of municipal sewage effluents, intermittent chlorination may be sufficient for biofouling control in power plants. Using this strategy, a chlorine dose of perhaps 1-2 mg/L is applied to the cooling effluent for 5-60 min. at a time, up to 4 times a day (Opresko 1980). Intermittent chlorination does not necessarily reduce the toxicity of the chlorine residuals to the environment, however.

Brooks and Liptak (1979) found that Lake Michigan phytoplankton suffered irreversible damage after a 30 min. exposure to effluents with a total residual chlorine concentration greater than or equal to 1 mg/L. The difference in the total residual chlorine concentrations between nearly full recovery of algae after exposure to intermittent chlorination effluents and no recovery at all was quite small. Therefore, the control of the concentrations of chlorine residuals in the effluent must be very carefully controlled even in intermittent chlorination to preserve the integrity of the ecosystem.

The possible impacts of chlorinated effluents from a power plant unit on the receiving water can be further minimized by diluting the chlorinated stream of water with the discharge from the other, unchlorinated units. Generally, the units in a power plant are not all chlorinated at the same time.

Another way to lessen the impact from chlorinated effluents may be to restrict chlorination to the daylight hours when photodecomposition of chlorine residuals can hasten the decay rate, thus exposing the receiving waters to a briefer period of chlorine.

Zero Discharge

Also applicable only to power plants, zero-discharge plants release no water into the environment. The water is recycled many times and is retained within the plant; thus, it is possible to avoid the environmental guidelines regulating discharges. Lihach (1981) gives a review of this option and discusses the Energy Power Research Institute's interest in this process. There are more than 30 such plants now in operation in the U.S., most located in the West. Although the design and operation of zero-discharge systems has yet to be perfected, Lihach feels that these systems will become more attractive as environmental standards tighten and water supplies decrease.

Magnetism

Drapeau and Laurence (1981) describe a promising, experimental disinfection technique in which magnetite (Fe_3O_4) is added to the wastewater. Virus, algae, as well as suspended solids and dissolved phosphorus, adsorb to the magnetite in the presence of other coagulants. A magnetic field applied to the water then removes the magnetite and associated particles. This method resulted in the removal of bacteriophage T_7 and Poliovirus Type 1 with an efficiency of 98-99%, although it became less effective as the number of viruses in the water increased. Magnetism does not have a wide application yet, having only been researched during the last ten years.

Submerged Aquatic Vegetation

Although limited to small treatment plants (about 25,000 gallons per day) which have large areas, the removal of dissolved nutrients as well as bacteria and virus from wastewater by aquatic vegetation has recently been studied at

the Moulton Niguel Water District of Laguna, California (Pope 1981) and at Michigan State University. This type of water treatment system consists of a series of trenches or lagoons; the first in the series removes coarse suspended solids while the succeeding water bodies remove dissolved materials and microbes. In the Laguna study, domestic wastewater was successfully treated, meeting the secondary effluent quality standards with a minimal amount of mechanical equipment and manpower. This method is still in its infancy, but could become more attractive as energy costs rise.

IMPROVED CONTACT CHAMBER DESIGN

The design of the contact chambers in which the chlorine dose is added to the sewage stream is currently inadequate in many sewage treatment plants. Longley (1978) studied the efficiency of chlorination as a function of conventional contact chamber design at the Fort Meade Sewage Treatment Plant #2 in Maryland. He found virus inactivation to be very poor in the system, most inactivation occurring in the period immediately following the mixing of the effluent with the added chlorine. He recommended a highly turbulent, plug flow design to encourage the rapid mixing of the added chlorine dose with the sewage in the chamber. It is thought that rapid mixing exposes more virus to hypochlorous acid (HOCl), a more powerful form of chlorine species than hypochlorite or chloramines. Longley hypothesized that rapid mixing would achieve the required degree of disinfection by using less chlorine, resulting in fewer chlorine residuals discharged into the receiving stream.

Sepp (1981) compared an "optimized" pilot plant with six existing sewage treatment plants in California. The pilot plant, through rapid initial mixing of chlorine with effluent, direct residual control of chlorine dosage, and adequate contact time in a plug flow contact tank, saved up to 50% in chlorine use while discharging an effluent that was significantly less toxic to fish. Sepp, however, found that it was not possible to eliminate all chlorine-induced toxicity by optimum design alone. Dechlorination with sulfur dioxide resulted in less toxic effluents than unchlorinated or chlorinated effluents. Dechlorination will be addressed more fully in the following section.

CHLORINATION/DECHLORINATION

There are two main methods of dechlorination, or removal of the total combined chlorine residual remaining after chlorination: either a sulfur compound or activated carbon is added to the chlorinated effluent, the latter yielding two relatively innocuous acids (Tan et al. 1980). White (1978a), Ward and DeGraeve (1978) and Sepp (1981) cite a study in which dechlorinated effluents were less toxic to aquatic life than both chlorinated and unchlorinated waters. Adequate prior contact time is essential to chlorinated/dechlorinated strategies, since the removal of chlorine will halt disinfection. White (1978b) gives details of operations and the necessary equipment for dechlorination systems. A recent review by Helz and Kosak-Channing (1984) surveys dechlorination chemistry processes.

Sulfur Compounds

Dechlorination with sulfur compounds is desirable because, according to White (1978b), it is inexpensive, easy to control, quickly reactive and arithmetically convenient (1:1 removal ratio); moreover, chlorination equipment can be used with modification. Sulfur dioxide (SO_2) is highly soluble in water (Sawyer 1976) and reacts nearly instantaneously with both free and combined chlorine residuals (White 1978b), reducing all chlorine to the chloride ion (Sawyer 1976) at a 2:1 weight ratio (Seegert and Brooks 1978).

$$SO_2 + H_2O \longrightarrow H_2SO_3 + HOCl \longrightarrow H_2SO_4 + HCl \quad (17)$$

$$NH_2Cl + H_2SO_3 + H_2O \longrightarrow NH_4HSO_4 + HCl \quad (18)$$

Sulfure dioxide is applied as a liquified gas using chlorination equipment (Sawyer 1976). However, the switching back and forth from chlorination to dechlorination using the same equipment is not recommeneded (White 1974). Rapid and complete mixing is essential, but contact time is not important (White 1974; Sawyer 1976; WPCD 1978). Current practice is to add an excess of SO_2 so there will a surplus of sulfite ions. There is some concern that an excess of sodium sulfite (Na_2SO_3) used to generate SO_2 could remove dissolved oxygen in a dechlorinated effluent (White 1978b), since it is a reducing agent (Sawyer 1976). White (1978b), however, feels that this reaction would be too slow to create any detectable oxygen depletion. Re-aeration may be necessary to meet effluent standards (Sawyer 1976).

A feed forward system and device to provide for sulfonation shut-down and to avoid over-feeding (a fail-safe mechanism) is described by White (1974; 1978b) and Witkowski et al. (1980). Tan et al. (1980) give results for a wide range of reaction-rate parameters so that dechlorination units can be easily designed for once-through power plant cooling systems.

Activated Carbon

Activated carbon reacts with both free and combined chlorine residuals as follows (Bauer and Snoeyink 1973; White 1975):

$$C^* + HOCl \longrightarrow CO^* + H^+ + Cl^- \quad (19)$$

$$C + 2HOCl \longrightarrow Co_2 + 2H^+ 2Cl^- \quad (20)$$

$$C + 2NH_2Cl + 2H_2O \longrightarrow CO_2 + 2NH_4^+ + 2Cl^- \quad (21)$$

$$C + 4NHCl_2 + 2H_2O \longrightarrow CO_2 + 2N_2 + 8H^+ + 8Cl^- \quad (22)$$

The pH of the effluent has a significant effect on the adsorption of both chlorophenol and the humic substances (Murin and Snoeyink 1979) in potable water. While granular activated carbon was found to reduce the concentrations of chlorinated products of humic substances (McCreary and Snoeyink 1981), Seegert and Brooks (1978) found that except for a short initial period, activated carbon was not 100% effective in chlorine removal at the µg/L

level from municipal water for fish culture purposes. Activated carbon does have the advantage of removing ammonia and chemical oxygen demand from municipal wastewaters (Sawyer 1976).

Although White (1978b) reported that the high cost of activated carbon used as a continuous dechlorinated agent makes it uncompetitive with sulfur compounds, Seegert and Brooks (1978) describe an effective and relatively inexpensive system incorporating both carbon and sulfite dechlorination which has operated trouble free for one year.

HALOGENATION

Halogens other than chlorine and halogen compounds have been used as alternates for disinfection; these include chlorine dioxide, bromine chloride and iodine.

Chlorine Dioxide

Chlorine dioxide (ClO_2) was first introduced for the treatment of water supplies in 1944 (White 1978b); for more than 30 years it also has been used in industry for bleaching and oxidizing purposes (Rauh 1979). Termed the chlorine-chlorite process (Roberts and Vajdic 1974; Sawyer 1976; Rauh 1979; Longley et al. 1980), it is applied as a gas generated on site from sodium chloride ($NaClO_2$) solution and Cl_2 solution (Rauh 1979). White (1978b) gives a detailed description of the machinery and operations involved in chlorine dioxide disinfection.

Also used for biocontrol and control of industrial odors, chlorine dioxide is a selective biocide (Rauh 1979). It is also a true dissolved gas in solution in that it doesn't react with water (White 1978b). A selective oxidant, it tends to favor oxidation over chlorine substitution (Rauh 1979) but doesn't readily oxidize ammonia/ammonium, unsubstituted aromatics, primary amines and many other organic compounds (Rauh 1979); thus, the toxicity due to chloramines (Roberts and Vajdic 1974; Sawyer 1976; White 1978b) and trihalomethanes (Aieta et al. 1980; Roberts et al. 1981) are avoided. Since it doesn't react with ammonia (White 1978b), it retains a high degree of germicidal effectiveness over the pH values normally found in effluents. Although not pH dependent in the range of 7-10 (White 1978b), ClO_2 reduces to chlorite ClO_2^- (which may be toxic to humans--WPCD 1978) at pH values greater than 4, and it reduces to chlorous acid at pH values less than 4; the acid in turn produces ClO_2, chlorate (ClO_3) and chloride ion (Cl^-).

ClO_2 decays by photodecomposition (Anon. 1981), volatilization and demand reactions (Opresko 1980; White 1978b). The residual decay rate may be faster than that of chlorine residuals (White 1978b), reducing the length of time that receiving waters are exposed to toxic residuals. In addition, ClO_2 forms lower quantities of halogenated by-products (Sawyer 1976; Aieta et al. 1980). Less than 10% of the total organic halogens formed by HOCl are formed by ClO_2 (Roberts et al. 1981).

While ClO_2 at low dosages is similar to chlorine in disinfection capabilities in acidic, organic-free environments (Rauh 1979), it exceeds chlorine's performance in alkaline environments (Roberts and Vajdic 1974; Rauh 1979). For a given contact time, the concentration of residuals required to give a known fractional kill of coliforms was 2-70 times smaller for ClO_2 than for Cl_2 (Roberts et al. 1981). For a West Coast municipality using sewage effluent for utility power plant cooling water, chlorine-treated water (chlorine dose of 1.0 mg/L Cl_2) gave plate counts of more than 2400 organisms/100 ml; chlorine dioxide-treated water gave plate counts of 100 organisms/100 ml (Rauh 1979).

ClO_2 is a more rapid disinfecting agent than Cl_2 (Aieta et al. 1980), although in studies comparing the two, little inactivation occurred after the first three minutes following the addition of ClO_2 to the effluent stream (Longley et al. 1980). It is a more effective virucide (Poliovirus I, coliphage inactivation) (White 1978a; Aieta et al. 1980; Longley et al. 1980; Roberts et al. 1981). A chlorine dose of 2 mg/L is as effective as a chlorine dose of 10 mg/L in inactivating coliphage (Aieta et al. 1980).

The disadvantages of ClO_2 dioxide are a lack of field experience (White 1978b), its high oxidant demand (White 1978b; Aieta et al. 1980; Longley 1980), and its expense (Sawyer 1976; Aieta et al. 1980; Roberts et al. 1981). Organic wastewater exerts a high ClO_2 demand and high dosages may be necessary to accomplish disinfection (Sawyer 1976). This initial oxidant demand is greater for ClO_2 than Cl_2 (White 1978b; Aieta et al. 1980; Longley 1980). While Sawyer (1976) and WPCD (1978) state that there is no adequate method of determining low residuals, Aieta et al. (1980) and White (1978b) state that it provides a measurable residual, using DPD-FAS and amperometric methods which measure ClO_2, ClO_2^-, HOCl and NH_2Cl.

ClO_2 is a more expensive chemical to use in disinfection, costing 2-5 times as much as chlorine (Roberts et al. 1981). It works more rapidly than does chlorine as a disinfectant; thus, a smaller contact chamber with a shorter contact time may result in some financial savings. Nevertheless, the actual chemical costs are higher for the ClO_2 technique than they are for conventional chlorination (Aieta 1980).

There is some question about the toxicity of chlorite to humans (Roberts and Vajdic 1974; WPCD 1979; Bull 1980; Opresko 1980; Anon. 1981), although it has been reported that treatment with activated carbon seems to decompose chlorites (Anon. 1981). There is also evidence that suspended solids can shield bacteria and perhaps increase ClO_2 demand (Aieta et al. 1980; Roberts et al. 1981).

Bromine Chloride

Bromine chloride (BrCl) is applied similarly to chlorine, and chlorination plants can be easily retrofitted for BrCl feeding (Greene 1981). Its cost in wastewater disinfection is equivalent to ozone (Sawyer 1976), and a field test at a secondary waste-treatment plant in Sykesville, Maryland (Greene 1981) was found to be competitive with chlorination/dechlorination.

BrCl is a highly reactive oxidizing agent (Sawyer 1976; WPCD 1978) and appears to hydrolyze immediately and exclusively to hypobromous (HOBr) in water (Sawyer 1976; Greene 1981).

$$BrCl + H_2O \longrightarrow HOBr + HCl \quad (23)$$

BrCl solubility increases in the presence of the chloride ion (Sawyer 1976). Approximately 69% reactive, bromine is available from BrCl, which is 40% higher than the bromine contributed from Br_2 for substitution reactions (Sawyer 1976).

It has disinfecting characteristics similar to bromine (Sawyer 1976), but its lower residual toxicity of chlorobrominated effluent may be due to a more rapid dissipation of oxidant (Opresko 1980; Greene 1981). Bromamines are much less stable than are chloramines and decay in one hour (Greene 1981). Thus, even though residual bromamine chloride, when present in sufficient concentrations, was potentially as toxic as chlorine, the relatively reduced stability of bromine chloride in comparison with chlorine reduced this potential toxicity (Ward and DeGraeve 1978). The chlorination of seawater generates free bromine residuals as well as chloramines and bromamines; bromochlorination results in only bromamines (Opresko 1980). In estuarine waters with low ammonia, different results may be expected; in high salinities without ammonia, chlorination and bromochlorination yield identical results. (Opresko 1980).

For equivalent concentrations, BrCl is as effective a biofouling control agent as chlorine (Burton and Margrey 1979; Opresko 1980). Biocide effects are either similar to or less than those of chlorine, depending on the organisms (Liden et al. 1980). In continuous-flow bioassay tests, zooplankton appeared to be less affected by bromine chloride than by chlorine, while toxic effects of bromine chloride on entrained phytoplankton were identical to those of chlorine. In contrast to chlorine, salinity may not affect the types of BrCl residuals present and thus their toxicity. The species of chlorine present, with their characteristic toxicities, are closely tied to the salinity concentration, while bromine chloride seems to be independent of salinity (Burton and Margrey 1978). Coliform tests at a secondary wastewater treatment plant in Sykesville, Maryland, showed fecal coliforms well below the permit limitation of 200 MPN/100 ml (Greene 1981).

With regard to residual toxicity, size and age within species, as well as species themselves, play an important role in total residual BrCl toxicity (Burton and Margrey 1978). Mature blue crabs, for example, exhibited a slower response to residual bromine chloride toxicity than did grass shrimp. However, juvenile blue crabs were affected by a lower concentration of BrCl residuals than were mature crabs.

Iodine

Discovered in 1811 by Curtois (White 1972), iodine was first used in water treatment by Vergnoux in World War I. It is the least reactive of the halogens

(Sawyer 1976; Opresko 1980). Stable residuals of molecular iodine (I_2) and hypoiodous acid (HOI) are the primary forms in solution (Sawyer 1976).

$$I_2 + H_2O \longrightarrow HIO + H^+ + I^- \quad (24)$$

$$HIO \longrightarrow H^+ + IO^- \quad (25)$$

At a neutral pH, approximately 50% of the iodine in solution will be HOI (Sawyer 1976; Opresko 1980). Normally, iodine does not react with ammonia (Sawyer 1976; Opresko 1980).

It exists in solution as I_2, HIO, IO^- (hypoiodate), I_3^- (iodate) (Chang 1958--cited from Opresko 1980).

HOI is effective as a bactericide (Opresko 1980) while I_2 is an effective cysticide (Opresko 1980); I_2 is also an effective virucide: Apostolov (1980) found iodine to effectively inactivate Newcastle disease virus after a 15 sec incubation at 37°C. The dosages required for a given disinfection may be higher than those required for chlorine (Sawyer 1976). It retains good disinfecting power at higher, more alkaline pH values.

Its advantages include no apparent health effects to humans (Sawyer 1976) and no lasting toxic residual: no iodamines (Sawyer 1976; Opresko 1980). Its main disadvantage is its expense (Sawyer 1976).

OZONATION

First recorded in 1785 by Van Marum, ozone was named by Schonbein in 1840 from the Greek work "ozein," meaning to smell. It was first used as a water treatment bactericide in 1893 in the Netherlands. It has been used continuously for drinking water treatment at Nice, France, since 1906. The first sewage treatment plant to use ozone for disinfection was Indiantown, Florida, in 1975 (Rauh 1979). Rosen (1979) reviews the state of the art of ozonation; he observes that international use is increasing rapidly, while, in the United States, the number of wastewater ozonation systems has increased from one in Indiantown, Florida, in 1975 to 33 that were expected to be in operation by 1981.

Ozone is generated by passing air or oxygen between electrodes (WPCD 1978; Stover 1981). Oxygen (O_2) is converted to ozone (O_3) by the addition of energy to a stream of dehydrated air or pure oxygen (Sawyer 1976). The gas is then applied through porous diffusers at the bottom of the contact tank (Stover 1981) or mixed with a liquid before addition to effluent (Sawyer 1976). The composition of the oxygen-contained feed gas is important--air produces concentrations of 1-2% by weight, while oxygen produces 3-4% (Rosen 1977; WPCD 1978); the process is inefficient in that 90% of the input energy is lost as heat (Rosen 1973; Stover 1981). The capital costs for generation are relatively high (Rice et al. 1979); electric power is the major source of operating expense (Stover 1981). WPCD (1978) cites a cost comparison study that found ozonation to be approximately twice as expensive as chlorination.

O_3 is more than 13 times as soluble as oxygen in water (Sawyer 1976). It decomposes to atomic oxygen in solution, which is highly reactive, and is capable of oxidizing a variety of organic and inorganic compounds (Equation 26) (Rosen 1980).

$$O_3 \longrightarrow O_2 + O \tag{26}$$

In seawater, ozone oxidizes bromide ions to generate free bromine (Williams et al. 1978; Crecelius 1979) and it reacts with ammonia to form bromamines (Opresko 1980). Further oxidation of either bromine or chloride ion to hypochlorite was not observed (Williams et al. 1978).

The compounds most susceptible to treatment with ozone include unsaturated hydrocarbons, unsaturated fatty acids and esters. Compounds largely unchanged by ozonation conditions at the upper Thompson Sanitation District Treatment Plant in East Park, Colorado, include aromatic hydrocarbons, chlorinated hydrocarbons, alkanes and fatty acids (Chappell et al. 1981). Ozone treatment makes humic material more biodegradable. Combined ozonation and adsorption treatment (used in German utilities) results in nearly complete removal of bacteria and viruses, while improving removal of dissolved organic compounds by adsorption (Kühn et al. 1978). Ozonation of seawater oxidizes bromide to free residual oxidants and then to bromate. If seawater is ozonized for more than 60 min., essentially all bromide is converted to bromate. Bromate, while toxic at high concentrations, was not acutely toxic at levels of concentration produced by ozonation of power plant cooling waters (Crecelius 1979). McNulty et al. (1977) and Richardson et al. (1981) found results of ozonation experiments consistent with a free radical mechanism of ozonation (the hydroxyl radical {$^{\bullet}OH$} is the predominantly active species). Ozonation is independent of pH (Opresko 1980).

The required absorbed ozone concentration to achieve specific levels of disinfection depended on water quality and stage of treatment at an ozone pilot facility in Massachusetts (White 1972; Stover et al. 1981). The inactivation of microorganisms doesn't occur until a threshold level of ozone is reached (Sawyer 1976). This initial slow rate of deactivation when adding ozone to a batch system is due to the rate of mass transfer of ozone into the solution, followed by a first order reaction between virus units and dissolved ozone (McNulty et al. 1977; Hacker and Lockowitz 1977). Large doses may be necessary to overcome organic interferences (ozone demand--Sawyer 1976). Demand can be reduced by effective coagulation and sedimentation in the early stages of treatment (Kuo et al. 1977). Demand may be higher for industrial effluents which contain non-biodegradable materials (Nebel et al. 1973). As the viscosity of a synthetic sewage increases, treatment time to achieve 99% destruction of virus increases (Hacker and Lockowitz 1977). Hacker and Lockowitz theorized that the lowered diffusion rate and an increase in competing demand reactions were responsible for the longer time required for inactivation.

Ozone is a powerful but non-selective oxidant (Rosen 1973; Rice et al. 1979). It doesn't, however, oxidize highly halogenated organics (Rice et al. 1979) and doesn't produce halogenated organics (Kuo et al. 1977; Rice et al.

1977). It does oxidize phenols rapidly (Rosen 1980) and converts many non-biologically degradable organics to oxidation products which are biodegradable (Rice et al. 1979). It is a powerful disinfectant and virucide over wide temperature and pH ranges, but leaves no residual as it decays much faster than does chlorine (Nebel et al. 1973; Rice et al. 1979; Opresko 1980 Richardson et al. 1981). Ozone operates much more rapidly than chlorine: A chlorine dose of 0.1 mg/L required 250 min. to reduce the total plate count of a sample by 99.9%, while 0.1 mg/L ozone needed only 0.8 min. (Sliter 1974). Nebel et al. (1973) found that ozonation of secondary effluent destroyed viruses quickly and completely, reducing bacteria and carbonaceous material also. Viral inactivation occurred faster than bacterial kill. McNulty et al. (1977), studying the effects of ozonation of hospital wastes noted a reaction rate maximum at temperatures between 40-50°C and at alkaline pH. Thus, there is a strong influence by both pH and temperature on reaction rates. Ozone does react with ammonia below pH 9 (Rice et al. 1979).

The biocidal activity of ozone is equal to or greater than that of free chlorine (Opresko 1980). It is a fast-acting virucide and bactericide (Opresko 1980). While it does add dissolved oxygen to water (Rice et al. 1979), there is some concern that ozonation can result in toxic products (Kuo et al. 1977), such as acetic and oxalic acids which are toxic at high concentrations. Ozonated effluents (freshwater and marine) can produce toxic effects greater than or equal to that of chlorinated effluents if the residual oxidants are maintained at their initial level (Ward, cited from Opresko 1980). However, under normal conditions in receiving waters, ozone dissipates quickly from the water due to the dilution effect of the receiving waters. In a study comparing the toxicity of chlorine, bromine chloride and ozone, ozone was found to have the least potential for toxicity under normal operating conditions. Hall et al. (1981) found striped bass eggs to be significantly more sensitive to ozone-produced oxidants in freshwater than in estuarine water. The toxicity of chlorine and ozone was similar for striped bass eggs and larvae in estuarine water. Ozone in freshwater tends to remain longer in the more reactive molecular phase (Hall et al. 1981).

Ozonation in conjunction with UV radiation had a synergistic effect, increasing the rate of oxidation reaction with hospital wastes (Kuo et al. 1977; McNulty et al. 1977).

The main advantages of ozonation are its disinfection capabilities: the reduction of BOD and COD; the increased dissolved oxygen; the oxidation of secondary sludge organics; and the break-up of colloid structures (Rosen 1973). Nevertheless, there are operational and cost problems. Rakness and Hegg (1980) discuss some of the operational problems associated with full-scale ozonation of a wastewater treatment plant at Upper Thompson Sanitation District, Colorado. Because sewage treatment plants are designed conservatively, for larger flows than they actually handle, lower ozone production levels result in inefficient power utilization (Rakness and Hegg 1980; Stover 1981). Because of the expense, the use of ozone for cooling waters doesn't seem justified yet (Williams et al. 1978).

RADIATION TREATMENTS

Several techniques utilizing different wavelengths of light have been used for disinfection purposes, including ultraviolet, gamma and longer wavelengths.

Ultraviolet Irradiation

Ultraviolet light must strike organisms for inactivation to occur. Therefore, the effluent must enter the irradiation area in the form of a thin hydraulic film free from hindering suspended matter (WPCD 1978). Among the advantages of UV irradiation of water is that the small radiation dose requires only a brief contact period (Sawyer 1976; WPCD 1978): the most effective germicidal radiation is in the range of 250-260 nanometers (Sawyer 1976). Moreover, no chemicals need be added and there are no residuals (WPCD 1978). UV irradiation of filtered seawater can be an effective disinfectant if used at proper dose and concomitantly with other sanitary procedures (Brown and Russo 1979). There are synergistic effects from oxygen, ozone, chlorine and iodine; raising temperatures above 57°C can increase the disinfection efficiency of irradiation (Woodbridge and Cooper 1979). UV irradiation can be used to reduce chloramines, chloro-organics and free chlorine in dechlorination processes of municipal water (Seegert and Brooks 1978). One hundred percent chlorine removal is possible, but is considerably more expensive than a combined carbon-sulfite system. Seegert and Brooks (1978) estimated that the annual operating costs for the ultraviolet system would be $2,850 compared with $171 estimated for the carbon-sulfite system.

Gamma Irradiation

Gamma rays create ionization and excitation along their paths, which result in three very reactive species, e^-_{aq}, H^o and OH^o (Equations 27, 28, 29) (Woodbridge and Cooper 1979):

$$H_2O + \gamma \longrightarrow H_2O + e^-_s \qquad (27)$$

$$H_2O + \gamma \longrightarrow \underset{\text{excited water}}{H_2O^*} \quad H^o + OH^o \qquad (28)$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^o \qquad (29)$$

$$e^-_s \longrightarrow e^-_{aq} \quad \text{hydrolized electrons} \qquad (30)$$

Gamma radiation is applied in the same way as UV radiation and has many of the same characteristics (WPCD 1978). The irradiation sources include cobalt-60 and cesium-137 as the ionizing radiation (Sawyer 1976). There may be a possible radiation hazard (WPCD 1978), although Woodbridge and Cooper (1979) think the energies of the rays are too low to cause residual radioactivity.

The creation of UV radiation within wastewater and immediately adjacent to microorganisms results in an increase of disinfection capabilities (Woodbridge and Cooper 1979). Radiation having no residual effect may not be adequate for biofouling control in power plants where the disinfectant must remain effective throughout pipe systems (Opresko 1980).

Photodynamic Oxidation

The penetration power of UV light is severely limited. Gerba et al. (1977) experimented with light in the wavelength 670 nm and the generally innocuous dye methylene blue to achieve disinfection of wastewater. Temperature, pH, dye concentration, sensitization time and light intensity all have an effect on the numbers of microorganisms that could be inactivated. Coliforms were far more senstivie to dye and photo-inactivation than poliovirus. Wavelengths in 670 nm range are not absorbed by organics and can penetrate to much greater depths. Solar energy was found to be a practical alternative to artificial light sources.

RECOMMENDATIONS FOR FURTHER RESEARCH

Practical alternatives to chlorination do not appear to be attractive on a large scale. While economic issues are important, there may be less interest to alternatives because of expense and an insubstantial gain in benefits. Better design and increased operating efficiency of existing chlorination systems in sewage treatment plants appear to be the most practical and attainable chlorine minimization alternative. Intermittent chlorination appears to be the most appropriate minimization method for power plant biofouling control, although the subtle, sublethal effects need to be further understood. The other methods, zero discharge, magnetic fields and submerged aquatic vegetation, require a great deal of further research and may be feasible in only a few, specific geographic locations.

The chlorination/dechlorination method has been shown to be effective, having a lower toxicity to some organisms than either chlorinated or untreated waters. The combined carbon-sulfite system investigated by Seegert and Brooks (1978) appears to add the inexpensiveness of the sulfur system to the effectiveness of the activated carbon system. Helz and Kosak-Channing (1984) point to the need for better SO_2 application and control systems; moreover, the role of water composition on SO_2 overdose and contact time must be assessed.

The alternative halogens available for disinfection all have the disadvantage of being more expensive than chlorine. Chlorine dioxide and bromine chloride both appear to decay faster in the receiving waters than does chlorine; therefore, these halogens may exert less of a lasting toxic effect once they are released into the environment. More studies on their levels of toxicity are needed before they can replace chlorine as the major disinfectant.

Ozonation may be the most practical alternative to chlorination currently available. Decades of use in Europe have resulted in an extensive literature dealing with the various aspects of ozonation--this review has sampled just a fraction of what is available. The major disadvantages with ozonation are its high operating costs and the uncertainty of the toxicity of some of its by-products, such as acetic and oxalic acids. In addition, the conversion of conventional treatment plants to ozonation may produce problems.

The radiation methods (ultraviolet, gamma and longer wavelengths) are currently either too expensive or too unreliable to replace chlorination at the present time. These methods require more developmental research and feasibility studies.

V

Effects of Chlorine on Microorganisms

INTRODUCTION

Large numbers of microorganisms occur naturally in estuarine environments such as the Chesapeake Bay. As components of complex and interdependent ecological networks, they play significant roles in recycling nutrients, as primary producers, as consumers and as decomposers (Buffaloe and Ferguson 1981).

However, the bacteriology and virology of the Bay are also affected by man's use of the Bay's riverine system--in wastewater from municipal sewage treatment plants, in fertilizer runoff, and in industrial and power plant effluents along the shorelines. While not all microbial agents are pathogenic (capable of causing disease), we are concerned primarily with those that are.

The microbiology of wastewater, especially of effluents from waste treatment plants, concerns indigenous enteric potential pathogens such as Shigella shiga, enteropathogenic Escherichia coli, Proteus mirabalis, Salmonella typhimurium, Streptococcus faecalis and other human and animal associated bacteria such as Vibrio and Mycobacterium. These bacteria may cause a variety of ailments including: gastroenteritis with diarrhea and stomach cramps, diarrhea of newborns, chills, fever, and swollen lymph nodes at the site of infection (Silvey et al. 1974; Geldreich 1972). Of recent public health concern is the report of the appearance of the bacteria Listeria monocytogenes, one agent of meningitis, in higher numbers in sewage than some Salmonella species. This would tend to suggest substantial association of the agent with human and animal population (Watkins and Sleath 1981) as well as the potential for waterborne disease transmission. High numbers of acid-fast Mycobacteria, in addition to Mycobacteria tuberculosis, which are capable of causing human infections (Goslee 1976), have been reported in untreated wastewater (Engelbrecht et al. 1974; Engelbrecht et al. 1977; Carson et al. 1978). High concentrations of bacteria have been reported contaminating the air vents of cooling towers using back up river water that has been polluted with wastewater effluent. The Serratia, Bordetella and Pseudomonas found in these waters are of public health concern because they can potentially cause upper respiratory tract infections (Adams et al. 1980).

The potential threat to public health has led to widespread use of waste water disinfection as the first line of defense against the spread of pathogens in the aquatic environment. And chlorine has largely been the disinfectant of choice.

Recently, however, its efficiency in eliminating bacteria and viruses has been questioned. In turn, organic compounds that may be mutagenic were recovered after treatment by chlorine (Maruoka and Yamanaka 1980). The concern over current techniques for assessing disinfection efficiency has resulted in numerous studies leading to (1) a reevaluation of the various assays for enumeration of enteric bacteria and viruses in water; (2) an introduction of new assay techniques for indexing water quality with respect to the absence of bacteria and viruses; (3) attempts to define new indicator microorganisms for evaluation of disinfection efficiency; and (4) proposals for alternative disinfectants for chlorine.

This chapter surveys these studies and reviews the research dealing with chlorine as a bactericidal and virucidal agent.

BACTERIA

Effectiveness of Chlorination in Eliminating Bacteria in Water

Historically, little consideration was given to the physiological effects of chlorination on indigenous and pathogenic microorganisms in the Chesapeake Bay. More recently, critical assessments of the usefulness and efficiency of chlorine were undertaken. Haas et al. (1980) and Gould and Haas (1981) reviewed current data on the microbiological aspects of disinfection of water. While they focused on survival of viruses and lethality following various treatment processes, they emphasized mechanisms of action of chlorine on viruses and bacteria.

Mode of Action

Camper and McFeters (1979) studied chlorine injury to E. coli, an inhabitant of the gut in human beings and animals, and showed that the disinfectant inhibited respiration and active nutrient transport. The following additional effects have been reported:

1. Chlorine affects the bacterial dehydrogenase, aldolase (Green and Stumpf 1946; Knox et al. 1948).
2. Unbalanced metabolism results from destruction of key enzymes (Wyss 1961).
3. Protein synthesis is disrupted (Benarde et al. 1967).
4. Oxidative decarboxylation of amino acids yields to nitriles and aldehydes (Pereira et al. 1973).
5. Chlorine reacts with purines and pyrimidines of nucleic acids (Hoyano et al. 1973).
6. Chromosomal aberrations result (Ingols 1958).
7. Lesions occur in the DNA as demonstrated by loss of DNA transforming ability (Shih and Lederberg 1976).

8. Inhibition of oxygen uptake and oxidative phosphorylation results in loss of macromolecules due to leakage (Venenkobachar et al. 1975).

Haas and Engelbrecht (1980), in studies on the mechanism of chlorine injury, compared the effects of chlorine on E. coli with its effects on acid-fast bacteria and yeasts. They concluded that in E. coli lethal effects occur at or near the cell membrane and involve the DNA as well; on the other hand, yeasts and acid-fast organisms are more resistant because of their thicker cell walls. An understanding of the physiology of chlorine-injured bacteria is necessary to ensure the index bacteria is at peak function in enumeration assays comparing unchlorinated and chlorinated receiving waters. These assays are used to assess the effectiveness of chlorine as a disinfectant.

Effect of Various Chlorine Species

Snead et al. (1980), studying the ability of chlorine residuals to offer continued bactericidal protection, reported a 0.2 mg/L free chlorine residual afforded 99.9% bacterial protection, whereas an equal concentration of combined chlorine afforded only 90% bactericidal inactivation for 0.1% sewage level contamination of a water distribution system. Hypochlorous acid (HOCl), because of its low molecular weight and electrical neutrality, easily penetrates cell walls and is thus the most effective chlorine species against bacteria. Pure monochloramines, on the other hand, are poor bactericidal agents (Selleck et al. 1978).

Species Resistant to Inactivation by Chlorination

In municipal water systems where free chlorine levels range between 0.2-0.4 mg/L, strains of Mycobacteria were found to be 20-100 times more resistant to free chlorine residuals in concentrations up to 1.0 mg/L (Carson et al. 1978).

Ridgway and Olson (1980) used a membrane filter method to quantitate the resistance of natural microorganisms in distribution waters. Their experimental data revealed that bacteria in the chlorinated system were 80-fold more resistant than in the unchlorinated system. Haas and Morrison (1980) suggested that low chlorine levels select for resistant bacterial strains.

Development of Most-Probable-Number Techniques for Indexing the Efficiency of Chlorine Disinfection

Standard Most-Probable-Number (S-MPN) for Enumeration of Fecal Coliforms

The Standard Most-Probable-Number (S-MPN) assay recommended by the APHA (1970) represents an indirect approach to assessing waters for certain pathogens of human or animal origin. Coliforms (most commonly E. coli) are the indicator organisms that the assay is designed to detect. As outlined in Figure 5, the procedure consists of (1) a presumptive test to detect gas within

24-48 h from fermentation of the sugar lactose; (2) a 24 h confirmation test to check for the presence of lactose positive colonies on solid media inoculated from the positive presumptive cultures; and (3) a completion of the confirmation as indicated by the presence of gas with 24 h lactose fermentation and identification of the typical rod-shaped gram-positive bacteria of non-spore forming type (Buffaloe and Ferguson 1981; APHA 1970). The assay is not without problems, however. Hussong et al. (1981) recently showed that in estuarine waters interactions among bacteria other than coliforms can sometimes yield false positives in the presumptive test, necessitating routine use of the confirmation assay. Hussong et al. (1980) also recommended strict adherence to the assay including the completed test for estuarine waters, especially when temperatures fall below 15°C, to check for false positive results in the confirmed test. This suggests another major drawback of the S-MPN assay which is in the requirement for the 72 h incubation time before results can be demonstrated.

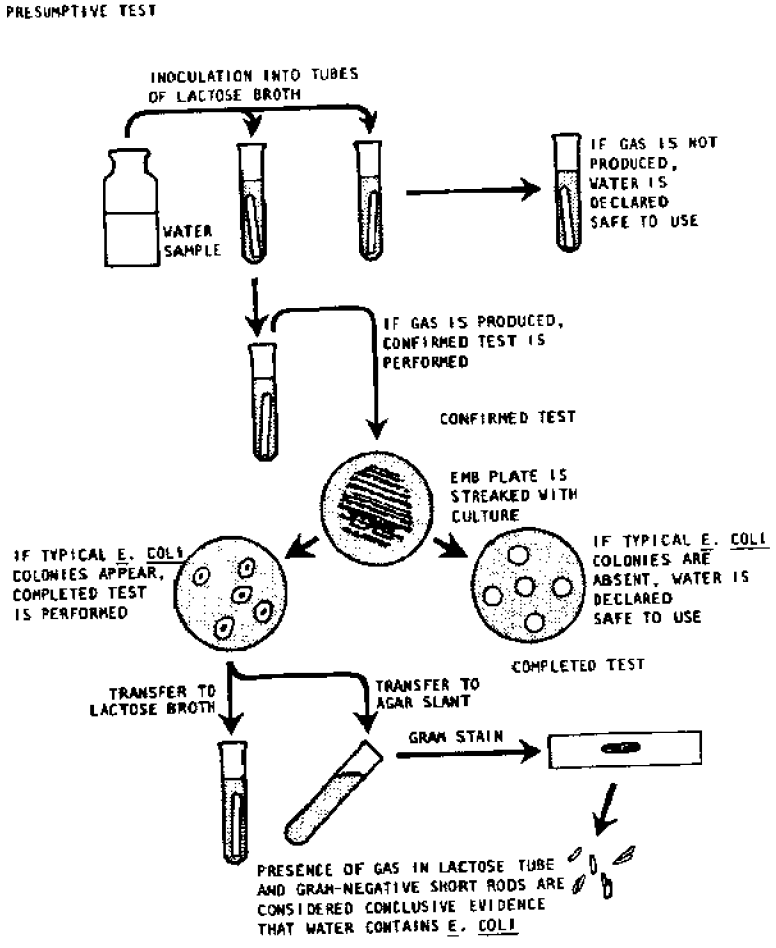

Figure 5. Schematic of S-MPN assay.

Braswell and Hoadley (1974) reported that the S-MPN technique was not applicable for fecal coliform enumeration in chlorinated waters, because of the failure of chlorine-injured microbes to recover. Thus, Munoz and Silverman (1979) developed a single-step MPN method to detect fecal coliforms in chlorinated effluents from sewage treatment plants. This method had the advantage of being completed in 18 h or less depending on whether growth was detected visually or by comparison of the electrical impedence ratios of the sample vs. the control. Comparative testing of this single-step MPN method with the S-MPN method using chlorinated and unchlorinated samples indicated agreement of fecal coliform counts within the 95% confidence limits. The single-step MPN method, however, was not applied to waters contaminated with a variety of wastes, nor to potable or recreational waters (Munoz and Silverman 1979). It is not clear from research results whether the assay is acceptable for use in these cases; consequently, the S-MPN assay is still used.

Studies by Evans et al. (1981) indicated that interference with qualitative coliform detection by the S-MPN assay can lead to the false assumption that water is free of bacteria. Coliform masking due to overgrowth by non-coliforms occurs in the presumptive, confirmed and completed phases of the S-MPN assay. This overgrowth occurs because environmental injury, especially due to chlorination, can slow coliform growth. Means and Olson (1981) presented data indicating that certain bacteria, in chlorinated as well as unchlorinated waters, produce bacteriocin-like substances (BLS) which could contribute to this interference in the detection of coliforms via the S-MPN procedure. Likewise, pseudocin-like substances (PLS) produced by Pseudomonas have recently been shown to inhibit coliform growth on lab media for MPN and Membrane Filter enumeration of coliforms.

Erkenbrecher (1981), while studying a shellfishing subestuary of the lower Chesapeake Bay, reported lowered density of indicator coliform bacteria in sites where salinity was highest. He speculated that an unidentified bactericidal property of seawater contributed to these results. Furthermore, it is known that diluent composition, exposure time in diluent and temperature of the diluent can affect the recovery of chlorine injured bacteria in the S-MPN test. Although enrichment or refrigeration of the diluent increases the recovery rate of injured coliforms (McFeters et al. 1982), these refinements do not make the S-MPN assay an optimum system.

Evans et al. (1981c), recognizing this interference, developed a modified MPN procedure (M-MPN) that is superior to the S-MPN and even to the standard membrane filter (S-MF, see below) procedure for coliform detection in potable as well as untreated surface waters. This procedure used the same basic media as the S-MPN procedure with the exception that in each step of the assay, provisions were made to recover coliforms from test tubes and plates that were initially read as negative for coliforms.

Dexter (1981) tested 572 seawater samples for fecal coliforms and found that a 24 h incubation, rather than the standard 48 h inoculation recommended by the APHA (1970), was adequate to yield positive results in the presumptive test. He recommended this modification to the S-MPN procedure for seawater.

Standridge (1981) compared the 24 h MPN assay (with 3-h preincubation at 35°C) with the two-step MPN technique in APHA (1976) for detecting fecal coliforms in chlorinated secondary sewage treatment plant effluents. While results obtained in the comparative study were statistically equivalent, the modified procedure requires further testing on wastewater samples from many locations (Standridge 1981).

Development of Membrane Filter Techniques For Determining the Efficiency of Chlorine Disinfection

The Standard Membrane Filter Assay (S-MF), a commonly used technique for enumerating bacteria when they occur in small numbers in a sample, has largely replaced the S-MPN assay. The assay was accepted by APHA (1971) as an alternative method for fecal coliform enumeration in water. In this procedure, a known sample volume is filtered and the bacteria trapping filter pad is allowed to incubate on the surface of a solid medium. The assay has the advantages of: (1) being completed in 24 h rather than the 72 h required for the S-MPN assay; (2) being useful when attempting to detect small numbers of coliforms; and (3) yielding a quantitative estimate of the number of coliforms present in polluted waters. Its disadvantage, however, is the possibility for interference in bacterial growth on the medium if the water contains much particulate matter (APHA 1971; Buffaloe and Ferguson 1981).

A modified membrane filter technique (M-MF) was developed by Green et al. (1977) for recovering fecal coliforms from chlorinated effluents (the standard MF technique showed average recovery with these effluents that was only 14% of the S-MPN procedure). This technique called for a 5 h incubation at 35°C to allow cells injured by chlorine to acclimate. Studies using the technique on laboratory and plant chlorinated effluents revealed a greater recovery rate (Green et al. 1977).

Stuart et al. (1977) incorporated the enriched and selective medium of Rose et al. (1975) in an injury-mitigating membrane filter (IM-MF) assay and held the plates for 1.5 h at room temperature before exposing them to higher incubation temperatures. The medium included glycerol and acetate as metabolic intermediates with reducing agents to eliminate chlorine residuals. The assay was designed for recovery of environmentally stressed coliforms (Stuart et al. 1977).

As with the S-MPN technique, coliform masking is apparent in the MF technique and increases with increased turbidity of chlorinated waters. Because particulates inhibit the effectiveness of chlorination of water, regulations have established certain maximum turbidity levels, especially applicable to drinking waters (LeChevallier et al. 1981).

DuFour et al. (1981) devised a membrane filter (MF) technique to quantitatively recover, with 90% accuracy, *E. coli* from marine and estuarine waters. The technique allowed for a 2 h resuscitation of these environmentally damaged cells. The M-Tec procedure provided greater specificity for marine and estuarine waters than freshwater or sewage effluents (DuFour et al. 1981).

Six investigators compared three other membrane filter methods. M-Tec was preferred because of (1) a high recovery accuracy, especially for chlorine stressed fecal coliforms; (2) the low false-positive results; and (3) a high degree of selectivity (Pagel et al. 1981).

Various media were used for coliform recovery by the MF technique. Grabow et al. (1981) evaluated the effectiveness of Standard and Modified Fecal Coliform (M-FC), MacConkey and Teepol media. He found the highest recovery numbers with M-FC agar without rosolic acid; the acid tended to inhibit growth of injured bacteria. Furthermore, this assay procedure eliminated the need for pre-incubation or other resuscitation steps for stressed bacteria. It must be noted, however, that Grabow et al. (1981) concluded that the fecal coliform tests were not reliable indicators of active E. coli titers.

Assuming that sanitary drinking water is defined in part by the absence of any coliforms, coliform detection and verification must be made as sensitive as possible. Towards this end, Evans et al. (1981) proposed a rapid, single-step technique for verifying, in m-lactose broth via gas production, the MF total coliform counts from untreated and potable waters.

Toward New Indicators of Disinfection Efficiency

According to Dutka (1973), indicators of disinfection efficiency must be:

- Present in greater number than the pathogens
- Low in proliferation rate compared to the pathogens
- More resistant to the disinfectant than the pathogens
- Easily identifiable.

For a number of years, studies on the efficiency of disinfection as a measure of water quality have utilized MPN or MF techniques to enumerate the reduction of total coliforms or fecal coliforms (Berg et al. 1978), and in some cases fecal Streptococcus (Kjellander 1960). However, while fecal coliforms are the accepted indicator microbes (Berg et al. 1978), there has been some question about their suitability for indicating the removal of viruses following disinfection (Durham and Wolfe 1973; Berg et al. 1978; White 1978a). Moreover, the recent finding that Vibrio cholerae survives better in estuarine waters than E. coli has raised concern about fecal coliforms as adequate indicators of water quality, especially for monitoring the occurence of V. cholerae (Hood and Ness 1982). A number of researchers argue that they are inadequate (Dutka 1973; Carney et al. 1975; Matson et al. 1979) because they fail to meet all of the necessary criteria. Although a new indicator has yet to be established, others have been suggested.

Bisson and Cabelli (1980) compared the densities of E. coli and Clostridium perfringens, an agent shown to be associated with human fecal waste in chlorinated and unchlorinated wastewater. They suggested Clostridium in conjunction with other indicator microbes as a "conservative tracer" of post-chlorinated waters. The specific choice of indicator species depended on the use of the treated water, i.e., drinking, swimming.

Resnick and Levin (1981a) suggested using the ratio of the bifidobacteria to E. coli as an indicator of the effectiveness of treatment of sewage effluent. Bifidobacteria are found in human feces in numbers sufficient to be useful as an indicator organism of fecal contamination in fresh and marine waters. They can be effectively eliminated by chlorination and are found to satisfy all criteria for an indicator microbe (Resnick and Levin 1981a). A quantitative, selective and differential membrane filter technique using medium YN-6 has been developed for easy enumeration of these anaerobes in natural waters (Resnick and Levin 1981b). However, this isolation procedure has not yet been tested using post-chlorinated or contaminated estuarine waters.

Smedberg and Cannon (1976) recognized the need for a practical and inexpensive model system for viral detection in wastewater and suggested analysis for the presence of the non-pathogenic blue-green bacterial virus LPP-1. This cyanophage has been isolated whenever coliform bacteria are present and is absent when coliform bacteria are absent. It is more resistant to chlorination than fecal coliform and could serve as a conservative indicator for the presence of animal viruses in post-chlorinated waters (Smedberg and Cannon 1976). Bausum et al. (1982) presented data which indicated that resistance of F-2 phage to chlorination gives it value as an experimental indicator organism, especially for aerosol contamination from chlorinated effluents. However, although this and the other organisms may hold promise, none has yet come close to replacing E. coli test systems as the indicators of fecal pollution.

VIRUS

More than 100 types of human and non-human viral isolates have been recovered from untreated wastewater. Viruses have been isolated from surface waters (Sattar and Westwood 1978; Metcalf et al. 1974; Pittler et al. 1967) as well as polluted lake water (Bitton et al. 1981) and drinking water (Hoehn et al. 1977; Nestor 1980).

A recent review of viral occurrence in estuarine and fresh waters indicated that viruses survive equally well in both environments, that they are quite stable in seawater and that association with sediment offers protection for them in the marine environment (Roy et al. 1981).

Several factors account for the occurence of pathogenic viruses in Chesapeake Bay waters. They may be shed in feces and urine of human beings or animals with viral infections and may not be removed during primary or secondary wastewater treatment (Mahdy 1979). In fact primary treatment, while it removes 50% of bacteria in wastewater, adsorbs only a small percentage of the virus population. Secondary treatment with "trickling filters" is relatively ineffective in inactivating or removing viruses from the waste stream because filtration is intended only to clear wastewaters of particulates prior to some form of disinfection or tertiary treatment (Culp et al. 1980). Of greater significance is the observation that viruses are ineffectively removed by chlorine disinfection (Mahdy 1979).

Viruses in wastewater discharges suggest a possible health hazard and may directly cause diseases ranging from mild skin rash to fatal outbreaks of meningitis (Grabow 1968; Mahdy 1979). To cite but a few potential waterborne diseases, enteroviruses may cause paralysis, aseptic meningitis, myocarditis and pericarditis. Viral hepatitis can lead to liver damage. Reoviruses can act as agents of infantile gastroenteritis infection. Cytomegalic inclusion disease in newborns may lead to mental retardation and even death. Among the adenoviruses are some 35 types capable of causing minor to acute respiratory problems, gastroenteritis and eye infections (Mahdy 1979). Table 2 summarizes major human waterborne diseases of viral etiology.

Table 2

Common Human Viruses Discharged* in the Water Environment and Associated Diseases

Virus	Number of Types	Excreted Feces	Excreted Urine	Disease
Enteroviruses Poliovirus	3	+	+	Paralytic poliomyelitis, aseptic meningitis.
Coxsackie A	23	+	?	Herpangina, aseptic meningitis, paralysis.
Coxsackie B	6	+	+	Pleurodynia (Bornholm disease), aseptic meningitis, acute infantile myocarditis.
Enterovirus	31	+	+	Aseptic meningitis, rash and fever, diarrheal disease, respiratory illnesses
Hepatitis	72	+	+	Infectious hepatitis.
Reovirus	3	+	+	Fever, respiratory infections and diarrhea.
Cytomegaloviruses	1	+	+	?
Reo-like viruses	?	+	?	Infantile gastroenteritis
Adenovirus	35	+	+	Respiratory and eye infections, gastroenteritis.

* These are usually of fecal-oral transmission.

Techniques to Quantitate Viruses in Water

While pathogenic viruses do occur in waters, their number may be well below the optimum concentration necessary to be detected by available isolation techniques. Still, because small numbers of viruses may be capable of causing infection in a susceptible host, efficient techniques for virus detection and isolation from water are required for assessing water quality and for assessing the effectiveness of wastewater treatment systems. Such techniques usually involve concentration procedures to isolate small numbers of viruses from large volumes of water. This section summarizes the development of these techniques to quantitatively measure viruses in water.

Tube and plaque assays have been used for virus recovery. The tube assay examines the cytopathic effect on appropriate tissue culture cells of viruses in samples serially diluted in tubes. The plaque assay is similar to the bacterial plate count. Appropriate cells are grown in sheets on the surface of a petri dish and a dilution of the virus suspension to be assayed is applied. Viruses lyse the cells, leaving clear areas (plaques) which represent one viral infective unit. However, because both assays require small fluid volumes and optimum viral concentrations, they are inadequate. Ultra-centrifugation steps can be used to concentrate viruses and enhance recovery, but this is quite laborious and requires expensive apparatus. Even with this modification, only a 10-20 fold concentration of virus is reported (Pittler et al. 1967).

Hill et al. (1971) reviewed the procedures and efficiency of several promising methods for quantitative measurement of viruses in water under field conditions. These techniques were either an adsorption type—adsorption of the virus to membranes, precipitable salts, iron oxide or polyelectrolytes--or a separation type making use of aqueous polymer or soluble alginate filters. Roy et al. (1981), reviewing current methods for viral isolation and detection, indicated that most involve adsorption and elution techniques using filter media. Problems hampered efficient viral recovery from water via the tentative standard method (TSM) recommended in APHA (1976) (cited by Sobsey et al. 1980a). However, addition of polyvalent cations such as $MgCl_2$ or $AlCl_3$ eliminated the problem of interference of materials in virus recovery, and elution with less alkaline solutions solved the problem of virus inactivation at this step (Sobsey et al. 1980b).

Recommended fiberglass filters, which were found to give comparable and reproducible results, were easy to handle and cost effective (Morris and Waite 1980a). BGM cell lines were found to be best suited for virus screening assays (Morris and Waite 1980b). Other cell lines such as Madin-Darby bovine kidney (MDBK), rhesus monkey kidney (LLC-MK_2) and human embryonic intestinal (intestinal 407) have also been shown to be sensitive. Reoviruses in excess of 100/L of raw sewage have been detected in the MDBK immunofluorescent cell count assay (Ridinger et al. 1982).

Improved methods for virus concentration were developed for field sampling of waters (Wallis et al. 1972) to include sea water (Gerba et al. 1978). However, coliphage tends to be more sensitive to the extreme pH levels of previous assay techniques (Gerba et al. 1978). Subsequently, Bitton et al.

(1981) succeeded in developing a simple and inexpensive method for field recovery of these enteroviruses from wastewater effluents via flocculation or aggregation. Although the mechanism for recovery is unclear, the magnetite-organic flocculation procedure is expected to become the one-step method for phage and enterovirus recovery from sewage effluents and contaminated waters. The viral aggregation is complete in 30 min. and 100% of the coliphage can be recovered (Bitton et al. 1981). This technique can then be applied to assay estuarine waters, such as the Chesapeake Bay, for presence of enteropathogenic viruses. Further studies are needed to determine if the presence or absence of coliphage would represent an appropriate index of viral contamination.

Most recently Brashear and Ward (1982) compared five general methods for recovering indigenous viruses from raw wastewater sludge. Each method included elution, concentration and disinfection steps. An elution method was found to yield the greatest virus recovery. The technique may eventually be adapted to estuarine waters.

Virus Removal Via Primary, Secondary and Tertiary Wastewater Treatment Techniques

Although wastewater treatment procedures are primarily aimed at removing bacteria, some viral removal can be accomplished. This section outlines basic wastewater treatment procedures currently in practice at sewage treatment plants and notes the potential for viral elimination at each step.

Long-term storage is a simple although impractical way of reducing viruses in wastewater (Berg 1966). With primary treatment, removal depends on adsorption of the virus onto particles that eventually settle out of the wastewater (Culp et al. 1980). However, "primary settling," a common method for treating sewage before disposal, yields a low efficiency of effluent viral removal when compared to untreated effluents (Berg 1966).

Secondary treatment in the trickling filter system, where the wastewater effluent is sprayed over a bed of crushed stone and sand and allowed to trickle through for removal of organic matter via bacterial degradation and absorption (Culp et al. 1980; Buffaloe and Ferguson 1981), can remove 90-95% of the viruses, but does not inactivate them (Culp et al. 1980). A 99% virus reduction is obtained if, instead of stone, a coal and sand filter bed is used. (Roy et al. 1981). A similar secondary treatment system using activated carbon adsorption is shown to be unreliable for viral removal since very coarse particles may tend to clog the pores of the granular activated carbon filter units that adsorb organic particles within their surface pores. The system is useful, however, for removing soluble organic materials (Culp et al. 1980).

The microbial activity occuring in secondary treatment procedures can aid in virus removal from wastewaters. Coxsackie A-9 (an enterovirus) is susceptible to the degradative action of proteolytic enzymes of bacteria (Cliver and Herrmann 1972; Hermmann and Cliver 1973) which inactivate the virus by degrading the viral protein coat (capsid) with subsequent release of the RNA virus genome material. Poliovirus types 1-3 and Coxsackie B1 and B3, however, are resistant to this proteolytic action (Herrmann and Cliver 1973).

Use of such chemicals as alum or lime and anionic polymers in coagulation-flocculation is highly effective for removal of viruses as well as bacteria from wastewater, the chemical "flocs" (large aggregates) carrying microorganisms out of the wastewater stream (Culp et al. 1980).

While filtration of secondary effluents (tertiary treatment) is important primarily for turbidity reduction, virus removal depends on the type of filtration media (polymers or anthracite with silica and sand additions). Use of more than one filtration media (mixed media) is not uncommon (Culp et al. 1980). In a study of five advanced wastewater treatment plants in Los Angeles County, viruses were isolated from approximately 50% of the secondary effluents but only 16% of the unchlorinated effluents following tertiary treatment (Dryden et al.1979). Thus, tertiary treatment can contribute considerably to reduction of viral numbers prior to disinfection procedures.

Virus Removal Via Chlorination

Mode of Action

While much research has dealt with chlorine action on indicator bacteria, very little experimental data exist on the effects of chlorine on viruses. It is only within the last ten years that modes of viral inactivation via chlorination have been investigated (Kruse et al. 1971; Kim and Min 1979; Dennis et al. 1979).

Chlorine acts primarily on the capsid. In particular, the aromatic amino acids tryptophan, tyrosine and histidine may be oxidized and ring substitutions made. Also, the viral nucleic acid may be altered to the extent that the virus can no longer reproduce in host cells (Kruse et al. 1971). In recent years, researchers have used F-2 bacteriophage, which is physically and chemically similar to human enteroviruses, to lend experimental support to the proposal that it is the viral RNA that is the main target of chlorine action (Kim and Min 1979; Dennis et al. 1979).

Comparative Effectiveness of Different Chlorine Species

Differing virucidal capacities have been ascribed to the different chlorine species present in water. In a comparative study of viral inactivation by chlorine, Scarpino et al. (1972) found hypochlorite (OCl^-) to be seven times more effective against poliovirus I than hypochlorous acid (HOCl). These data contradicted a previous report by Weidenkopf (1958) that inactivation of Type I Poliomyelitis virus was greater when the HOCl species predominated. Lab studies on the inactivation of enteric viruses by free available chlorine (HOCl) revealed a wide range of susceptibilities to inactivation, even among related viruses. Thus, a single virus cannot be expected to serve as a standard to determine the effectiveness of disinfection via chlorination of waters (Engelbrecht et al. 1980).

Free chlorine residuals (HOCl and OCl^-) are difficult to maintain; hence the general practice is to maintain combined residuals--monochloramines, dichloramines and nitrogen trichloride (Kruse et al. 1971). At normal disinfect-

ing levels in wastewater (i.e., standard temperature and pH), chlorine is present as equal parts mono- and dichloramines. These species result from the reaction of chlorine with nitrogenous substances in polluted waters (White 1972; Young and Cameron 1977) and are predominant in chlorinated wastewaters (Aieta 1980). (See Chapter 2, "Chlorine Chemistry.") It has been suggested, however, that organic chloramines have poor virucidal capacity (Kruse 1971). In support of this suggestion, Snead et al. (1980) presented data indicating that in waters contaminated with virus due to 0.1% sewage level contamination, exposure (2 h, pH 8.0) to 0.2 mg/L combined chlorine residuals afforded no viral inactivation whereas equal levels of free chlorine residuals yielded 90% viral inactivation.

Environmental Factors Affecting the Inactivating Capacity of Chlorine

Variations in salinity, pH and ionic capacity affect the capability of chlorine to inactivate viruses in Chesapeake Bay waters. A study of 20 human enteric viruses has shown that those occurring under natural environmental conditions are more resistant to free chlorine residuals than those subjected to the laboratory environment (Liu et al. 1971). A poliovirus type 1 isolate from a modern water treatment plant maintaining chlorine residuals of 1 mg/L was shown to have much higher titers after chlorination when compared to the same virus strain that was maintained in the laboratory environment (Shaffer et al. 1980). These data suggest some acquired resistance through long-term exposure of the virus to the low levels of chlorine that exist in distribution systems. Thus, data collected in the laboratory on virus inactivation by chlorine may not be applicable to field conditions.

Dennis et al. (1979), using the F-2 bacteriophage and radioactively labelled aqueous chlorine (^{36} Cl), found the rate of inactivation varied with changes in pH. More labelled chlorine is found associated with RNA at pH 5.6 than at pH 7.6 and above. Likewise, inactivation rates for poliovirus 1 are greater at pH 6 than pH 10 (Engelbrecht 1980). On the other hand, analysis of chlorine reaction kinetics of Echovirus 1 at pH 6 indicated that some virions became temporarily resistant to chlorine due to capsid conformational changes which slowed HOCl penetration into the virion. Whether this conformational change occurred as a result of exposure to the chlorine species was not revealed in the experiments (Young et al. 1977).

Sensitivity of viruses to inactivation via chlorine is affected by the ionic nature of the environment as well as pH. At pH 6, OCl^- species destroyed poliovirus type 1 (Mahoney) more rapidly in presence of 0.1 M NaCl than HOCl species with or without salt (Sharp et al. 1980). Sharp and Leong (1980), examining inactivation rates of poliovirus 1 (Brunhilde) in the presence of the same salt concentration, found a 3-fold increase in the effectiveness of the OCl^- species at pH 10 when compared to HOCl at pH 6. They speculate that the increase in ionic strength at higher pH weakens the protective coat, thus making the virus more susceptible to inactivation even by the weak disinfecting form OCl^-. This effect can have important implications for experiments on viral chlorination which must take into count the variation of ionic strength in sea water (Sharp and Leong 1980).

Particulates or organic materials in water can also affect the disinfecting action of chlorine. Studies have shown that bacteriophage MS-2 associated with suspended solids or attached to clay particles is still able to infect as it is somehow protected from inactivation by HOCl (Stagg et al. 1977). Earlier, Moore et al. (1975) had shown in lab models using Poliovirus Type 1 (Mahoney) that adsorption of the virus to clay particles was enhanced in the presence of 0.01 M $CaCl_2$. While these data allow speculation on the possible results of chlorination for virus removal from estuarine waters, no supportive field data are currently available.

Failure of MPN to Effectively Detect Virus Inactiviation via Chlorination

Fecal coliforms represent the standard bacterial indicators in wastewater (Berg et al. 1978) with fecal streptococci serving as the indicator in some situations (Kjellander 1960). Total coliforms is the indicator system used to detect pollution in drinking water. However, it has been reported that indicator bacteria do not reflect the concentration of enteric viruses in marine waters (LaBelle et al. 1980).

Viruses are known to be more resistant to inactivation by chlorination than bacteria (White 1972). Berg et al. (1978) were able to isolate viruses from water deemed safe for recreational use (200-400 MPN/100 ml fecal coliform counts) based on MPN tests. Thus, absence of fecal coliforms does not necessarily assure absence of viruses (Berg et al. 1978). A comparison of the quality of tap water under field conditions indicated that a chlorine concentration which successfully inactivated coliform bacteria did not inactivate enteroviruses (Nestor 1980). Indeed, many investigators suggest that the MPN testing procedure is an inadequate system for virus detection (Berg et al. 1978; Nestor 1980), or for determining if water is free of viruses and, therefore, sanitary (Burns and Sproul 1967).

VIRUCIDAL AND BACTERICIDAL CAPACITY OF OTHER DISINFECTANTS

In a recent review, the National Academy of Science (1979) concluded that chlorine, ozone and chlorine dioxide come closest to being ideal water disinfectants. These alternatives were given considerable attention at a 1981 conference on chlorine use in estuaries (Chlorine--Bane or Benefit 1982). Among the alternative disinfectants, chlorine dioxide, bromine chloride, ozone and irradiation are discussed here, particularly their modes of action and their effectiveness when compared with chlorine.

Chlorine Dioxide

The first reported use of chlorine dioxide as a disinfectant was in 1944 at the Niagra Falls water treatment plant. By 1963, only 8 of 11,590 plants reported using it as a disinfectant (Calabrese et al. 1978).

There is evidence that chlorine dioxide works to inactivate dehydrogenase enzymes located in the bacteria cytoplasmic membranes. While protein synthesis may be slightly inhibited, cell death does not occur. DNA is unaffected by levels of chlorine dioxide used in treatment plants as indicated by a lack of inhibition of transforming activity in Hemophilus influenza, under laboratory conditions (Roller et al. 1980).

In a field study that attempted to compare the bactericidal effects of chlorine and chlorine dioxide, Aieta et al. (1980) used secondary effluent from activated sludge processed sewage. Chlorine dioxide was found to have a statistical advantage over chlorine as a bacterial disinfectant. Suspended solids, however, offered some physical protection for the bacteria.

The same researchers, comparing virucidal effectiveness, found that coliphage yielded only "conservative performance data" on the disinfection efficiency of chlorine dioxide (Aieta et al. 1980). Other studies, however, have indicated that chlorine dioxide was superior to chlorine for inactivating viruses in wastewater (Longley et al. 1980; Alvarez and O'Brien 1982). Wastewater, on the other hand, exerted a greater demand on the chlorine dioxide than on chlorine (Longley et al. 1980), while chlorine dioxide was found to disinfect more rapidly with greater inactivation than chlorine over a short contact time (Aieta et al. 1980).

Inactivation rates differ for different viruses. Virus F-2 was found to be more sensitive to chlorine dioxide than poliovirus type 1 at pH 5.72 or 9.0, although both viruses became more sensitive with increasing pH (Hauchman et al. 1982). RNA infectivity of F-2 virus appears not to be destroyed by chlorine dioxide treatment (Olivieri et al. 1982).

Studies on the mode of action of chlorine dioxide on poliovirus type 1 (Mahoney) verify that 0.5 mg/L chlorine dioxide, pH 10, does not affect RNA but does degrade the capsid into smaller (80s) particles. The virus is not, however, degraded at pH 6, where inactivation occurs at a much slower rate (Alvarez and O'Brien 1982).

To date, many of the studies evaluating chlorine dioxide as an alternative disinfectant to chlorination have focused on mammalian toxicity and health effects. Unfortunately, there is a paucity of data on the specific effects of chlorine dioxide on viruses and bacteria.

Bromine Chloride

LeBlanc (1982) presented data supporting bromine chloride (BrCl) replacement of chlorine as a disinfectant for wastewater. Bromamines are stronger oxidants than chloramines and their bactericidal and virucidal properties are comparable with chlorine. Because residuals are less stable, the need for chlorination-dechlorination procedures is eliminated, especially in "hot spots" (breeding grounds) of the Chesapeake Bay. However, depending on effluent quality a greater BrCl demand may be exerted and this could influence the effectiveness of the residual. A back-up chlorine system may be required to ensure proper residuals are available (LeBlanc 1982).

Keswick et al. (1981) evaluated the comparative effectiveness, under laboratory conditions, of BrCl and chlorine. Bromamines did not cause detectable changes in the structure of Poliovirus type 1 used in their study. HOBr was found to be the most effective disinfectant. HOBr and bromamines react with the protein coat, but cause no detectable change in the structure or infectivity of the RNA. Further studies are needed to elucidate specific modes of attack for viral inactivation.

Although Poliovirus type 1 was more resistant to chlorine than bacteria under field conditions, BrCl was found to inactivate virus and bacteria with equal effectiveness. Furthermore, BrCl residues were more effective in reducing major enteric viruses such as echo-, coxsackie- and reo-viruses than even higher residuals of chlorine. Disinfection of natural populations of bacteria and viruses in wastewater effluents, under field trials, proved BrCl more effectively removed viral populations, whether aggregated or attached to particles, than did chlorine at the same mg/L concentration. BrCl requires shorter contact time than chlorine (Keswick et al. 1980).

Ozone

Ozone was first used in the 19th century in Ireland and in Paris for odor control and disinfection in sewage treatment plants (Burns 1982). A 1978 study examining use of chlorine and ozone for wastewater treatment found lower concentrations of ozone to be a more effective biocide than chlorine (Keenan and Hegemann 1978). Quantitative studies of disinfecting capacity are difficult because of the instability of ozone in solution. There is no effect of pH on inactivation capacity but there must be microbial contact with ozone residuals (Keenan and Hegemann 1978). Colberg (1979) suggests that the oxidation capacity of ozone for bacterial spores is greatest at high pH. But the concentration must be greater than 1.0 mg/ml ozone for 10 min. as some spores were found to be resistant to this concentration.

Laboratory studies revealed rapid inactivation of F-2 phage during the first 5 sec of exposure to ozone concentrations as low as 0.09 mg/L. Further inactivation occured at a slower rate. Plaque forming units (PFU) and specific adsorption to host bacterial cells was reduced. Freed RNA showed a reduced infectivity for spheroplasts, suggesting that infectivity may be retained following ozonation. The F-2 protein capsid is broken into smaller subunits via attack on the amino acid components, namely cysteine, tryptophan and methionine, which are most sensitive to ozone (Kim et al. 1980). Katzenelson et al. (1979) presented a dose response relationship for the concentration of ozone required to inactivate Poliovirus type 1, and it follows, in part, first order inactivation kinetics in that most of the virus present were inactivated in the first step, which lasted from 0.2-1.0 sec. The remainder of the type 1 virus were inactivated over a longer time interval (Katzenelson et al. 1979). Cell-associated poliovirus are even more difficult to inactivate. Likewise, complete inactivation of coxsackie A-9 virus associated with cells was not attained under the experimental conditions simulating current treatment plant use. Consequently, filtration for removal of particles is a necessary step preceding ozonation (Emerson et al. 1982). The amount of ozone required for dis-

infection is dependent on the level of contamination of the effluent, and it can be an expensive procedure when compared to chlorination. It has been suggested that ozone is useful for oxidizing organic compounds from wastewater prior to chlorination (Keenan and Hegemann 1978).

Exposure of bacteria to ozone results in non-specific cell lysis. However, ozone treated water (0.4 ozone mg/L) tended to become less bactericidal in a shorter time than chlorine treated waters. Suspended organics can protect bacteria from ozone induced lysis (Rusanova et al. 1979).

Radiation

Ultraviolet doses between 25,000-35,000 μW-S/cm^2 are used for disinfection of waters. But at these doses cysts of the protozoan Giardia lamblia, agent of giardiasis, can survive. Coliforms, on the other hand, can be reduced by 99.9% with doses of 3,000 μW-S/cm^2 (Rice and Hoff 1981). Sewage treatment plant effluents irradiated with UV retained fewer coliforms resistant to streptomycin but more coliforms resistant to tetracycline and chloramphenicol (Meckes 1982). There are no field studies on the specific efficiency of ultraviolet radiation as a bactericide or virucide. Hoehn (1976), however, suggests that technological developments would make ultraviolet radiation a cost-effective technique.

Gamma radiation also has potential to reduce the incidence of waterborne diseases. Some vesicular disease virus, vesicular stomatitis virus and blue tongue virus, were irradiated under conditions most protective for the viruses with the result that no infectious agents survived 4.0 M rads of gamma irradiation (Thomas et al. 1982).

RECOMMENDATIONS FOR FURTHER RESEARCH

1. For estuarine environments field data are needed that are predictive of the effects of salt concentration on adsorption of viruses to particles, resulting in viral protection against chlorine inactivation.

2. MPN procedures need further study to assess their adequacy for determining whether waters are free of human viruses.

3. More data on the mode of action of chlorine dioxide on both pathogenic and non-pathogenic microorganisms must be obtained.

4. Laboratory data are necessary on the mode of action of bromine chloride in virus inactivation.

5. UV irradiation as an alternative to chlorination may be cost effective. However, the danger of generating microbial mutant varieties (perhaps more virulent and antibiotic resistant) as a result of UV exposure remains to be assessed.

6. Evaluative and comparative studies are needed on enumeration assays in order to discover a better indicator microbe and to develop a better procedure for indexing the quality of chlorinated and unchlorinated waters.

7. To assess whether viruses and bacteria can acquire resistance to low level exposures of chlorine, correlations between field and laboratory measurements are required.

8. False negative and positive MPN tests occur under certain conditions; a more direct measure of the presence of pathogens is still sought.

VI

Effects of Chlorine on Aquatic Macroorganisms

In recent years, a number of literature reviews regarding chlorine toxicity on aquatic life have been published (Brungs 1973; Tsai 1975; Whitehouse 1975; Brungs 1976; Morgan and Carpenter 1978; Morgan 1979; Graybeal 1980). The most recent power plant chlorination literature reviews by Hall et al. (1981b) and Hall et al. (1982a) covered a range of information. In addition to discussing power plant chlorination issues, chlorine chemistry and methodologies for chlorine toxicity studies, they compiled data on relationships between chlorine toxicity and both freshwater organisms and estuarine-marine organisms. Although their tables and references are sometimes inconvenient to use--they are not presented in alphabetic order--nevertheless, they are comprehensive; moreover, the subject index is useful and the recommendations for further research are well-defined.

Hall et al. (1981b), in an interpretive literature review on the effects of power plant chlorination on estuarine and marine organisms, documented their data systematically. Many useful general conclusions were delineated--though the reader will have to refer to the original literature to find the supporting data--and detailed recommendations for research are well justified. Graybeal (1980) published a short literature review along with tables showing some lethal and sublethal levels of chlorine to estuarine organisms. Crumley et al. (1980) evaluated factors affecting the toxicity of chlorine to aquatic organisms. In the spring of 1981, a conference was held in Fredericksburg, Virginia, on the uses of chlorine in estuaries. The proceedings (Chlorine--Bane or Benefit? 1982) offers the most up-to-date information on research regarding chlorination of power plant and sewage treatment plant effluents in the United States and why chlorination is not a common practice in the United Kingdom. This chapter examines research on the effects of chlorine primarily on Chesapeake Bay macroorganisms and provides detailed summaries of toxicity testing on invertebrates and fish.

TOXICITY TESTS

Chlorine toxicity tests are conducted with either (1) a static water system, in which the solution is replaced at regular intervals to maintain a relatively stable chlorine concentration, or (2) a flow-through system, in which the concentration of chlorine is kept constant. While chlorinated sewage water sometimes has been used, such attempts to simulate actual environmental situations lead to variable levels of ammonia and organic matter, etc., that then must be considered in interpreting the results.

Toxicity may be lethal or sublethal. Lethal toxicity in this chapter is expressed as LC50, TL50 or TLm where:

LC50 is the lethal concentration for 50% of test organisms.
TL50 is the tolerance limit for 50% of test organisms to survive.
TLm is the median tolerance limit for survival of test organisms.

Where sublethal toxicity is being considered, EC50 is the concentration at which 50% of specific responses are effected. Sublethal toxicity effects are expressed in a number of ways; for example, mortality, growth rate, reproduction (sperm or egg viability, egg number or stage of ovary, maturation), embryonic development, serum constituents, osmoregulatory mechanisms, respiration (oxygen consumption, gill movement),. shell movement, water pumping rate, changes in enzyme activity and histological or morphological abnormalities.

There is some difficulty in comparing the results of different studies among researchers: analytical methods vary and reported chlorine concentrations are based on several methods of estimation. Some investigators use actual figures obtained from water analysis, while others calculate the concentrations based on the amount of chlorine applied. Moreover, applied concentrations and the resulting concentrations vary greatly.

Capuzzo et al. (1977) compared the concentrations of applied free chlorine and chloramine with the corresponding residual levels in seawater. Recovery of residual toxicant concentrations was dependent on the form of chlorine applied and the turnover time in the assay units. In an assay system with a turnover time of 1.5 h, the recovery of applied chloramine (87%; $r = 0.99$) was greater than the recovery of applied free chlorine (approximately 45%; $r = 0.97$). In another system with a turnover time of 3 h, recovery of the two chlorine forms was equivalent (18%; $r = 0.88$).

MACROINVERTEBRATES

Lethal Toxicity

In both lethal and sublethal tests, bivalves have demonstrated a higher sensitivity to chlorine than have fish or crustacea.

Table 3 shows that for most representative species, LC50s are between 0.1 and 0.5 mg/L TRC (total residual chlorine). LC50 for such organisms as the hard clam Mercenaria mercenaria was as low as 0.001 mg/L TRC (Roberts et al. 1975), while for others such as the mud crab Panopeus herbstii LC50 was as high as 10 mg/L ClO (chlorine-induced oxidants) (Vreenegoor et al. 1977).

Latent mortality should be taken into account when considering lethal effects of chlorine toxicity. The grass shrimp Palaemonetes pugio, for example, could tolerate 2.5 mg/L TRC for 3 h with only 2% immediate mortality; but by 96 h, following the 3 h exposure, 98% of the shrimp had died (McLean 1973). McLean found similar effects for the amphipod Gammarus tigrinus.

Table 3
Lethal Levels of Chlorines to
Macroinvertebrates

ORGANISMS			CRITERION	CHLORINE		SALINITY[1]	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Acartia tonsa	Copepod	adult	TL50, 24h	<0.05	TRC	18-20		Roberts et al. 1975
		adult	TL50, 48h	0.05	TRC	18-20		Roberts et al. 1975
		immature and adult	LC50, 48h	0.028-0.175	CPO	10-12	15	Heinle and Beaven 1977
Anonyx sp.	Amphipod	adult	LC50	0.15	TRO	28	14.8	Thatcher 1978
Balanus improvisus	Barnacle	larvae	LC80, 3h after 0.08h exposure	2.5	TRC		12-17	McLean 1973
Callinectes sapidus	Blue crab	adult	LC50, 48h	0.75	CPO	10	25	Vreenegoor et al. 1977
		adult	LC50, 144h	0.63	CPO	10	25	Vreenegoor et al. 1977
		adult	LC50, 96h	0.86	CPO	10	25	Vreenegoor et al. 1977
		female	LC50, 96h	0.86	CPO		14-21	Laird and Roberts 1980
		male	LC50, 96h	0.84	CPO		14-21	Laird and Roberts 1980
		adult	LC50, 48h	0.97	CPO		14-21	Laird and Roberts 1980
		adult	LC50, 48h	1.40	CPO		14-21	Laird and Roberts 1980
		juvenile	LC50, 48h	0.42	CPO			Roberts 1978
		juvenile	LC50, 96h	0.32	CPO			Roberts 1978
Crangon nicricauda	Shrimp	adult	LC50, 96h	0.13	TRO	28	14.8	Thatcher 1978
Crassostrea virginica	American oyster	adult	LC50, 96h	0.026	TRC	20	19-28	Roberts and Gleason 1978
		adult	TLm, 48h	0.005	TRC	E	14.2-16	Bellanca and Bailey 1977

Table 3, Cont.

ORGANISMS			CRITERION	CHLORINE		SALINITY[1]	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Crassostrea virginica	American oyster	larvae, 7 days	LC50, 48h	0.12	FC		25	Goldman et al. 1978
		larvae, 7 days	LC50, 48h	0.01	chloramine		25	Goldman et al. 1978
		larvae	LC50	0.15	chloramine	30-31	20	Capuzzo and Lawrence 1976
		larvae	TL50, 48h	0.005	TRC	18-20	17-28	Roberts et al. 1975
		larvae	TL50, 2h	0.75	TRC	18-20	17-28	Roberts et al. 1975
		larvae	TL50, 24h	0.27	TRC	18-20	17-28	Roberts et al. 1975
		larvae	TL50, 48h	0.11	TRC	18-20	17-28	Roberts et al. 1975
		embryos	LC50, 48h	0.027-0.046	CPO	E		Roberts 1980
		embryos	LC50, 48h	0.220	CPO(Br)	E		Roberts 1980
		larvae	EC50, 48h	0.21	CPO(Br)	20	19-28	Roberts and Gleeson 1978
		larvae	EC50, 48h	0.02	FC	20	19-20	Roberts and Gleeson 1978
		larvae	LC50	0.86	FC	30-31	20	Capuzzo and Lawrence 1976
		larvae, 7 days	LC50	0.12	FC	30-31	20	Capuzzo 1977
		larvae	TL50, 24h	0.001-0.006	TRC	18-29	19-28	Meldrim et al. 1974
		larvae	TL50, 48h	0.11	TRC	18-29	19-28	Meldrim et al. 1974
		juvenile	EC50, 96h	0.006	TRC	18-29	19-28	Meldrim et al. 1974
		straight hinge larvae	LC69-91, 72-96h	0.1	CPO	12-14		Roosenburg et al. 1980
		straight hinge larvae	LC61-100, 48-96h	0.3	CPO	12-14		Roosenburg et al. 1980
Elminius modestus	Barnacle	adult	LC>80 10 min.	0.5	TRC			Waugh 1964
		adult	LC100, 10 min.	2.0	TRC			Waugh 1964

Haliotis cracherodii	Abalone	adult	LC100, 25 days	28.2	TRC		9.7-13	Behrens and Larsson 1976
Hemigrapsus nudus	Shore crab	juvenile and adult	LC50, 96h	1.42	TRO	28	14.8	Thatcher 1978
Heptacarpus pictus	Transparent shrimp	adult	LC100, 2h	1.6	TRC	33.5	9.7-13	Behrens and Larsson 1976
		adult	LC100, 20h	3.7	TRC	33.5	9.7-13	Behrens and Larsson 1976
Homarus americanus	American lobster	stage IV	LC50, 48h	2.90±0.10	FC		25	Goldman et al. 1978
		stage IV	LC50, 48h	0.30±0.05	chloramine		25	Goldman et al. 1978
Melita nitita	Amphipod	adult	48h after 3h exposure	2.5	TRC		12-17	McLean 1973
	Amphipod	adult	96h after 3h exposure	2.5	TRC		12-17	McLean 1973
Mercenaria mercenaria	Hard clam	larvae	TL50, 48h	0.001	TRC	18-20	19-28	Roberts et al. 1975
	Hard clam	larvae	TL50, 96h	0.001-0.006	TRC	18-28	19-28	Meldrim et al. 1974
Mulinia lateralis	Coat clam	larvae, 48h	LC50	0.038	CPO	15-23	18.3-28	Roberts 1980
		embryo, 48h	LC50	0.01-0.10	CIO	15-23	18.3-28	Roberts et al. 1979
		embryo, 2h	LC50	0.072	CIO	15-23	18.3-28	Roberts et al. 1979
Mya arenaria	Soft shell clam	larvae, straight hinge	LC50, 12h	0.35	CPO		17-20	Roosenburg et al. 1977
		larvae, straight hinge	LC50, 16h	0.27	CPO		17-20	Roosenburg et al. 1977
		larvae, pediveligers	LC50, 24h	0.5	CPO		17-20	Roosenburg et al. 1977

Table 3, Cont.

ORGANISMS			CRITERION	CHLORINE		SALINITY[1]	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Mya arenaria	Soft shell clam	larvae, pediveligers	LC50, 48h	0.25	CPO		17-20	Roosenburg et al. 1977
		larvae, pediveligers	LC50, 72h	0.165	CPO		17-20	Roosenburg et al. 1977
		larvae, pediveligers	LC50, 96h	0.125	CPO		17-20	Roosenburg et al. 1977
Neomysis sp.	Mysid shrimp	adult	LC50, 96h	0.162	TRO	28	14.8	Thatcher 1978
Pagurus longicarpus	Hermit crab	larvae	LC50, 24h	0.405	CIO	17-20	15-16	Roberts 1978
		larvae	LC50, 48h	0.310	CIO	17-20	15-16	Roberts 1978
		larvae	LC50, 96h	0.098	CIO	17-20	15-16	Roberts 1978
		adult	LC50, 96h	0.210	CIO	18.9	26.9	Roberts et al. 1979
Palaemonetes pugio	Grass shrimp	adult	LC50, 24h	0.86	CPO	24.3	26.6	Roberts 1980
		adult	LC50, 48h	0.47	CPO	24.3	26.6	Roberts 1980
		adult	LC50, 96h	0.30	CPO	24.3	26.6	Roberts 1980
		adult	LC50, 24h	1.13	TRC(BR)	20	19-28	Roberts and Gleeson 1978
		adult	LC50, 48h	0.82	TRC(BR)	20	19-28	Roberts and Gleeson 1978
		adult	LC50, 96h	0.70	TRC(BR)	20	19-28	Roberts and Gleeson 1978
		adult	TLm, 24h	0.38	TRC(BR)			Roberts et al. 1979
		adult	TLm, 96h	0.22	TRC(BR)			Roberts et al. 1979
		adult	TLm, 96h	0.22	TRC		14-16	Bellanca and Bailey 1977
Penaeus kerathurus	Shrimp	adult	LC50, 168h	0.37	TRC	30	20	Saroglia and Scarano 1979

Pandalus danae	Coon striped shrimp	adult	LC50, 96h	0.133-0.293	TRC	28.5-31	Δ2-12	Capuzzo et al. 1976, 1977
		adult	LC50, 96h	0.5	TRO	30	12.5	Thatcher 1977
		juvenile and adult	LC50	0.178	TRO	28	14.8	Thatcher 1978
		adult	LC50, 96h	0.295	TRC	28.5-31	8±2	Gibson et al. 1976
		adult	LC50, 96h	0.178	TRC	28.5-31	8±7	Gibson et al. 1976
		adult	LC50, 96h	0.133	TRC	28.5-31	8±12	Gibson et al. 1976
		adult	LC50, 96h	0.210	TRC	28.5-31	15±10	Gibson et al. 1976
Pandalus goniurus	Shrimp	adult	LC50, 96h	0.09	TRO	28	14.8	Thatcher 1978
		adult	LC50, 96h	0.295	TRO	28.5-31	8±2	Gibson et al. 1976
		adult	LC50, 96h	0.178	TRO	"	8±7	Gibson et al. 1976
		adult	LC50, 96h	0.210	TRO	"	15±10	Gibson et al. 1976
		adult	LC100, 1 month	0.18	TRO	28.5-31	16	Gibson et al. 1976
Panopeus herbstii	Mud crab	eggs	LC100	0.21	CIO			Roberts 1980
		eggs	LC75	0.05	CIO			Roberts 1980
		larvae from eggs exposed	LC74	0.05	CIO			Roberts 1980
		larvae from eggs exposed	LC92	0.08	CIO			Roberts 1980
		larvae	LC50, 24h	0.70	CIO	17-20	15-16	Roberts 1978
		larvae	LC50, 48h	0.41	CIO	17-20	15-16	Roberts 1978

Table 3, Cont.

ORGANISMS			CRITERION	CHLORINE		SALINITY[1]	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Panopeus herbstii	Mud crab	larvae	LC50, 24h	1.0	CIO	17-20	July	Roberts 1978
		larvae	LC50, 48h	0.13	CIO	17-20	July	Roberts 1978
		larvae	LC50, 96h	0.038	CIO	17-20	July	Roberts 1978
		larvae	LC50, 96h	0.024	CIO		23.7-26.6	Roberts et al. 1979
		juvenile	LC50, 96h	0.50	CIO		23.7-26.6	Roberts et al. 1979
		adult	LC50, 96h	0.50	CIO		23.7-26.6	Roberts et al. 1979
Pontogeneia sp.	Amphipod	juvenile	LC50, 96h	0.687	TRO	28	14.8	Thatcher 1978

[1]E = estuarine water

Sublethal Effects

Sublethal effects make themselves evident in a variety of ways, depending on the species and the nature of the experiment (Table 4). Laird and Roberts (1980) reported that for the blue crab Callinectes sapidus, a 96 h exposure to 1.04 mg/L CPO (chlorine-produced oxidant), higher concentration than the 96 h LC50 in their experiment, did not cause significant changes in respiration rate; neither were osmotic imbalances observed as judged by levels of serum constituents such as protein, total ninhydrin-positive substances (TNPS), chloride, potassium, sodium and calcium. Vreenegoor et al. (1977) did observe, however, osmoregulatory changes at 0.81 mg/L CPO for the same species. Laird and Roberts found a significant increase in serum magnesium at 1.04 mg/L CPO.

The American oyster Crassostrea virginica, in contrast to the blue crab, was sensitive to very low concentrations of chlorine. Rhoderick et al. (1977) found that shell deposition was inhibited at 0.07 mg/L CPO at 15°C and by 0.01 mg/L CPO at 25°C. Roberts et al. (1975) reported that for juvenile oysters, the 96 h EC50 for shell deposition was 0.023 mg/L TRC; they later reported that growth was inhibited more than 50% at 0.018 mg/L TRC at 20°C and ceased at 0.128 mg/L TRC (Roberts 1980). Standard respiration rate of oyster larvae was inhibited by 0.1 mg/L applied free chlorine or chloramine (Capuzzo and Lawrence 1976).

While eggs of the sea urchin Strongylocentrotus purpuratus were not affected by 0.77 mg/L hydrochloride for 5 min. exposure (Muchmore and Epel 1973), sperm of the sea urchin in sewage with 0.05 mg/L available chlorine, lost motility and died after detachment of flagella.

Setting of the mussel Mytilus sp. was inhibited in sewage at applied chlorine concentration of about 0.5 mg/L (James 1966). Holmes (1969, 1970) later found that chlorine interfered with the attachment of the mussel Mytilus edulis by inhibiting byssus thread production at this concentration; growth was also inhibited. Holmes also found that after nine weeks in a chlorine residual of 1.0 mg/L bysuss formation was only 25% compared with animals kept in unchlorinated seawater. Beauchamp (1969) found a weight loss following the detachment caused by 0.5 mg/L applied chlorine.

For the soft shell clam Mya arenaria, an increasing percentage of pediveligers detached as CPO was increased to between 0.2 and 0.5 mg/L. The mortality of the detached clams was much higher than those remaining attached.

In laboratory experiments, sublethal effects on hatchability have been demonstrated. For example, although the fertilized eggs of coon striped shrimp Pandalus damae exposed to $\geq$0.16 mg/L TRO did hatch, the process was delayed for several days (Thatcher 1977). For the larvae of mud crab Panopeus herbstii, only 25.9% of eggs exposed to 0.05 mg/L ClO survived whereas 40.9% of the control group survived; moreover, development was slower for the exposed eggs. At 0.21 mg/L ClO, no hatching occurred. At concentrations as low as 0.09 mg/L ClO, larvae developed only to the zoea II stage.

Table 4
The Sublethal Effects of Chlorines to Macroinvertebrates

ORGANISMS			CRITERION	CHLORINE		SALINITY[1]	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Bimeria franciscana	Hydroid	adult	growth rate decline, 96h	>1.0	TRC	10-11	19-23	McLean 1973
Callinectes sapidus	Blue Crab	adult	respiration rate increased	1.04	CPO	10	25	Laird and Roberts 1980
		adult	LCO, 96h	0.65	CIO	10	20.5-27	Laird and Roberts 1980
		juvenile	LCO, 0.08-4h	0.30	TRC	5-5.5	+Δ2	Hall et al. 1979
		juvenile	LCO, 0.08-4h	0.30	TRC	5-5.5	+Δ6	Hall et al. 1979
		juvenile	LCO, 0.08-4h	0.30	TRC	5-5.5	+Δ10	Hall et al. 1979
Cancer productus	Crab	adult	ammonia excretion increased 4-fold, 96h	0.68	TRC	30	11	Roesijadi et al. 1979
Crassostrea virginica	American oyster	adult	pumping reduced	0.01-0.05	FC		18-24	Galtsoff 1946
		juvenile	EC50 for shell deposition, 96h	0.023	TRC	18-20	17-28	Roberts et al. 1975
		juvenile	shell deposition reduced 15 days	0.5	appl. chlorine	2	31±1	Liden et al. 1980
		juvenile	shell deposition 69% less than control	0.018	RC	24	20	Roberts 1980
		juvenile	shell deposition 0%	0.128	RC	24	20	Roberts 1980
		juvenile	shell deposition 1%	0.246	RC	24	20	Roberts 1980
		juvenile	shell growth, 75% of control, 15 day exposure	<EC50	TRC(Br)	24	20	Roberts and Gleason 1978

Crassostrea virginia	American oyster	adult	LC0, 15 days	0.081	TRC(BR)	32±0.6	30-31	Liden et al. 1980
		adult	LC10, 15 days	0.045	TRC(BR)	32±0.6	30-31	Liden et al. 1980
		adult	LC5, 15 days	0.020	TRC(BR)	32±0.6	30-31	Liden et al. 1980
		adult	LC0, 15 days	0.062	TRC	32±0.6	30-31	Liden et al. 1980
		adult	LC8, 15 days	0.032	TRC	32±0.6	30-31	Liden et al. 1980
		larvae, straight hinge	LC<14, 6-36h	0.01	CPO	12-14		Roosenburg et al. 1980
		straight hinge	LC10, 6-12h	0.05	CPO	12-14		Roosenburg et al. 1980
		straight hinge	LC27, 12-72h	0.05	CPO	12-14		Roosenburg et al. 1980
		straight hinge	LC54, 96h	0.05	CPO	12-14		Roosenburg et al. 1980
		straight hinge	LC40, 6-48h	0.1	CPO	12-14		Roosenburg et al. 1980
		straight hinge	LC8, 8h	0.3	CPO	12-14		Roosenburg et al. 1980
		straight hinge	LC30, 24h	0.3	CPO	12-14		Roosenburg et al. 1980
		straight hinge	LC51-100, 48-96h	0.3	CPO	12-14		Roosenburg et al. 1980
		setting pediveliger	LC1-4, 6-24h	0.05	CPO	12-14		Roosenburg et al. 1980
		setting pediveliger	LC10-14, 24-72h	0.05	CPO	12-14		Roosenburg et al. 1980
		setting pediveliger	LC<30, 72-96h	0.05	CPO	12-14		Roosenburg et al. 1980
		adult	LC0, 15 days	0.062	TRC	2	31±1	Liden et al. 1980
		adult	LC8, 15 days	0.032	TRC	2	31±1	Liden et al. 1980
		adult	LC0, 15 days	0.014	TRC	2	31±1	Liden et al. 1980

Table 4. Cont.

ORGANISMS			CRITERION	CHLORINE		SALINITY[1]	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Crassostrea virginica	American oyster	juvenile	growth <50% of control	0.018	TRC	24	20	Roberts 1980
		juvenile	growth 0%	0.128–0.246	TRC	24	20	Roberts 1980
Dendraster excentricus	Sand dollar	adult	sperm viability EC50, 0.08h	0.002–0.013	TRO		28–31	Stober et al. 1978
Gammarus daiberi	Amphipod	adult	LC13, 0.6h	0.05	TRC		1.2–3; 15.3–26.7	Ginn and O'Connor 1978
Gammarus tigrinus	Amphipod	adult	mortality 4.8% after 3h exposure	2.5	TRC	E	6.1–7.8	McLean 1973
		adult	mortality 15.8%, 48h after 3h exposure	2.5	TRC	E	6.1–7.8	McLean 1973
		adult	mortality 24.8%, 96h after 3h exposure	2.5	TRC	E	6.1–7.8	McLean 1973
Haliotis cracherodii	Abalone	adult	LC0, 15 days	9.6, 14.2	TRC	33.5	9.7–13.1	Behrens and Larsson 1976
		adult	LC0, 10 days	18.1	TRC	33.5	9.7–13.1	Behrens and Larsson 1976
Heptacarpus pictus	Transparent shrimp	adult	LC0, 24h	0.2	TRC	33.5	9.7–13.1	Behrens and Larsson 1976
Melita nitida	Amphipod	adult	mortality 27%, 3h exposure	2.5	TRC	E	12.2–16.7	McLean 1973
		adult	mortality 3.2%, 3h after 0.08h exposure	2.5	TRC	E	12.2–16.7	McLean 1973
Mytilus edulis	Mussel	adult	byssus thread production reduced 50–70%, 1 wk	0.5	applied chlorine			Holmes 1969
		adult	survival 95%, 1 wk	0.2	TRC			White 1966, 1969
		adult	growth reduced, 1 wk	0.2–0.4	TRC			White 1966, 1969

Oreonectes propinqus	Crayfish	adult	LC0, 96h	0.071	TRC(Br)*		25	Ward et al. 1976
Pagurus longicarpus	Hermit crab		development reached:					
			pro-zoea II	0.18	CIO	18.9	26.9	Roberts et al. 1979
			zoea II,	0.36	CIO	18.9	26.9	Roberts et al. 1979
			megalopa	0.09	CIO	18.9	26.9	Roberts et al. 1979
			megalopa, but days later than control	0.05	CIO	18.9	26.9	Roberts et al. 1979
			megalopa, 1 day later than control	0.01	CIO	18.9	26.9	Roberts et al. 1979
Palaemonetes pugio	Grass shrimp	adult	LC28, 0.08h	0.30	TRC	5-5.5	+Δ10	Hall et al. 1979
		adult	LC40, 1h	0.30	TRC	5-5.5	+Δ10	Hall et al. 1979
		adult	LC7, 0.08h	0.15	TRC	5-5.5	+Δ6	Hall et al. 1979
		adult	LC13, 1.0h	0.15	TRC	5-5.5	+Δ6	Hall et al. 1979
		adult	LC19, 2h	0.15	TRC	5-5.5	+Δ6	Hall et al. 1979
		adult	LC30, 3h	0.15	TRC	5-5.5	+Δ6	Hall et al. 1979
		adult	LC43, 4h	0.15	TRC	5-5.5	+Δ6	Hall et al. 1979
		adult	gill damage	<1.0	CPO	24.3	26.6	Roberts 1980

*100% effluent

Table 4, Cont.

ORGANISMS			CRITERION		CHLORINE	SALINITY[1]	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Pandalus danae	Coon striped shrimp	egg	hatching delayed 2-7 days	0.16	TRO	30	12.5	Thatcher 1977
Pandalus goniurus	Shrimp	adult	growth rate decreased 75% vs. control, 1 month	0.08	TRO	28.5-31	16	Gibson et al. 1976
		adult	growth rate decreased 67% vs. control, 1 month	0.01	TRO	28.5-31	6	Gibson et al. 1976
Phragmatopoma californica	Annelid	adult	sperm motility decreased 78% vs. control	0.2	available chlorine**			Muchmore and Epel 1973
		adult	sperm motility decreased 25% vs. control	0.4	available chlorine**			Muchmore and Epel 1973
		adult	sperm motility decreased 14% vs. control	1.0	available chlorine**			Muchmore and Epel 1973
Rangia cuneata	Clam	adult	LC0, 15 days	0.062	TRC*	2	31±1	Liden et al. 1980
		adult	LC20, 15 days	0.032	TRC	2	31±1	Liden et al. 1980
		adult	LC0, 15 days	0.014	TRC	2	31±1	Liden et al. 1980
		adult	LC0, 19 days	0.081	TRC(BR)	2±0.63	30-31	Liden et al. 1980
		adult	LC10, 19 days	0.045	TRC(BR)	2	30-31	Liden et al. 1980
		adult	LC5, 19 days	0.020	TRC(BR)	2	30-31	Liden et al. 1980
		adult	LC0, 19 days	0.062	TRC(BR)	2	30-31	Liden et al. 1980

* 100% effluent

** Sewage

Rangia cuneata	Clam	adult	LC20, 19 days	0.032	TRC(BR)	2±0.63	30-31	Lawrence and Burton 1980
		adult	LC0, 19 days	0.14	TRC(BR)	2±0.63	30-31	Lawrence and Burton 1980
Strongylocentrotus purpuratus	Sea urchin	sperm	lost motility	0.05	available chlorine**			Muchmore and Epel 1973
		egg	no effect, 0.08h	0.77	hypochloride			Muchmore and Epel 1973
Urechis caupo	Fat innkeeper worm	adult	fertilization success 78%	0.2	available chlorine**			McLean 1973
		adult	fertilization success 0%	0.4	available chlorine**			McLean 1973

[1] E = estuarine water

** Sewage

FISH

While laboratory research on the effects of chlorine on fish has been quite extensive, it is often difficult to compare results because of variations in such experimental conditions as water temperature and salinity, duration of exposure, stage of development of the fish, and the type of chlorine tested. Nevertheless many data are available and this section reviews that data relevant to the Chesapeake Bay.

Lethal Toxicity

Tables 5 and 6 summarize the lethal and sublethal toxicity of chlorine for various marine-estuarine and freshwater fishes. Most of the LC50 or TLm values are between 0.05 and 0.3 mg/L. Most fish exposed to TRC for more than 48 h and up to several days can tolerate 0.02 mg/L TRC with no apparent toxic effects. For the Atlantic silverside Menidia menidia, however, LC50 was as low as 0.01-0.05 mg/L TRC and for juvenile striped bass Morone saxatilis, 0.04 mg/L TRC; for one 2 h exposure, the LC50 for naked goby Gobiosoma bosci LC50 was as high as 0.6 mg/L TRC (Roberts et al. 1975).

Sublethal Toxicity

Laboratory experiments have demonstrated a variety of sublethal effects on different species. Capuzzo et al. (1977) found that for juvenile killifish Fundulus heteroclitus, on chlorine concentrations near the lethal level, an exposure of 0.5 h resulted in a significant decrease in respiration rate. At a lower concentration, distended gills and erratic swimming behavior, indications of environmental stress, were observed. Middaugh et al. (1980) reported that for juvenile spot Leiostomus xanthurus, at a relatively high temperature of $30\pm1^{\circ}C$, oxygen uptake rate decreased to 50% of that of the control at CPO concentrations near the LC50 level. At higher concentrations, gill damage occurred as indicated by the epithelial tissue sloughing away from the underlying pillar cells. Middaugh et al. (1977) also observed similar results in the larvae and juveniles of striped bass M. saxatilis. However, Fobes (1971), working with isolated gill tissue of the white sucker Catastomus commersoni, was unable to detect any effects of chloramine at 1.0 mg/L TRC. Striped bass M. saxatilis larvae and white perch Morone americana larvae hatched from eggs that were exposed to chlorine around the LC50 level had body lengths shorter than those of the control (Morgan and Prince 1977, 1978).

Abnormalities, such as scoliosis and other mass deformation, were observed in 15% of the larvae of blueback herring Alosa aestivalis that were hatched from eggs treated with TRC near LC50 levels (Morgan and Prince 1978).

NON-BIOLOGICAL FACTORS AFFECTING CHLORINE TOXICITY

Temperature

Generally, chlorine or CPO becomes more toxic as chlorine concentration, temperature and/or duration of exposure increases. In experiments with juvenile killifish F. heteroclitus, Capuzzo et al. (1976) found that at 25°C, LC100 was 0.65 mg/L TRC; at 30°C, LC100 decreased to 0.25 mg/L TRC. For spot Leiostomus xanthurus that were exposed to chlorine for 8 days at 10°C, LC50 was 0.12 mg/L; at 15°C, LC50 decreased by half to 0.06 mg/L (Middaugh et al. 1977). When striped bass M. saxatilis prolarvae were exposed to 0.15 mg/L TRC for 2 h at 20+ Δ10°C, the mortality was 80%; but at 20+ Δ2°C, mortality decreased to 62% (Burton et al 1979). Similar results have been found in macroinvertebrates (Hall et al. 1981c).

High temperature can be more harmful than chlorine. For example, Lauer et al. (1974) demonstrated with mysid shrimp Gammarus sp. that with water temperature above 31°C, the mortality of shrimp exposed to chlorinated water was attributable primarily to the temperature.

Acclimation temperature is a factor that should be taken into account when evaluating the impact of power plant discharges (Hall et al. 1981b). Hall and his colleagues (personal communication) found that for juvenile striped bass acclimated to 15°C, the avoidance response at 0.15 mg/L TRC decreased from 60% to 15% as ΔT increased. But when acclimation temperature was 20, 25 and 30°C, preference for ΔT of 6°C did not override a chlorine avoidance response. At 25°C, however, with TRC of 0.15 mg/L and ΔT of 0°C, the fish did not exhibit a strong (≈60%) avoidance response, although the 96 h LC50 value for juvenile striped bass is around 0.19 mg/L TRC. Hall et al. (1982b) also found that in juvenile Atlantic menhaden Brevoortia tyrannus there was a significant difference in the response surface at 25 and 30°C in their chlorine-ΔT-avoidance responses. Greater avoidance of all TRC conditions up to 0.15 mg/L occurred at 30°C. The significance of the work by Hall et al. (1981c) is their demonstration that striped bass and Atlantic menhaden can avoid adverse conditions of a combination of ΔT and chlorine which would likely occur near power plant discharges. Although there are few papers (Sprague and Drury 1969; Giattina et al. 1981; Osborne et al. 1981) reporting the actual avoidance to chlorine under field conditions, laboratory results of avoidance of chlorine and temperature are thought to be in good agreement with field observations (Sprague and Drury 1969; Stauffer et al. 1976); thus, laboratory results may be applied with caution in the prediction of what might actually happen in the field.

Duration of Exposure

For most species, the toxic effects of chlorine increase as exposure time is increased. For example, mortality of American oyster C. virginica straight hinge larvae was 10% at 0.05 mg/L CPO with a 6-12 h exposure. As exposure time was increased to 96 h, mortality reached 54% (Roosenburg et al. 1980). For striped bass M. saxatilis prolarvae, 0.15 mg/L at 20+Δ 6°C caused a

Table 5
Lethal Levels of Chlorines
to Fish

ORGANISMS			CRITERION	CHLORINE		SALINITY	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Alosa aestivalis	Blueback herring	eggs	LC50	0.33	TRC	1±0.2	21	Morgan and Prince 1978
		larvae	LC50, 24h	0.28	TRC	1±0.2	21	Morgan and Prince 1978
		larvae	LC50, 48h	0.24	TRC	1±0.2	21	Morgan and Prince 1978
		larvae	LC50, 48h	0.32	TRC	1±0.2	21	Morgan and Prince 1978
		larvae	LC50, 72h	0.38	TRC	1±0.2	21	Morgan and Prince 1978
		eggs stage e	LC50±4	0.38	TRC	1±0.2	21	Morgan and Prince 1978
		eggs	LC95, 80h	0.70	TRC	1±0.2	21	Morgan and Prince 1978
		eggs	LC100, 80h	0.57	TRC	1±0.2	21	Morgan and Prince 1978
		larvae, 1 day	LC95, 24h	0.42	TRC	1±0.2	21	Morgan and Prince 1978
		larvae, 1 day	LC95, 48h	0.35	TRC	1±0.2	21	Morgan and Prince 1978
		larvae, 1 day	LC100, 24h	0.36	TRC	1±0.2	21	Morgan and Prince 1978
		larvae, 2 days	LC95, 24h	0.67	TRC	1±0.2	21	Morgan and Prince 1978
		larvae, 2 days	LC95, 48h	0.81	TRC	1±0.2	21	Morgan and Prince 1978
		larvae, 2 days	LC100, 24h	0.40	TRC	1±0.2	21	Morgan and Prince 1978
		larvae, 3 days	LC100, 24h	0.15	TRC	1±0.2	21	Morgan and Prince 1978
Ammodytes hexapterus	Pacific sand lance	adult	LC50, 96h	0.82	TRC	28	14.8	Thatcher 1978
		adult	LC50, 96h	0.15	TRC		25	Gullans et al. 1977
Apeltes quadracus	Fourspine stickleback	adult	LD 50, 24h	0.75	TRC			Anderson 1975

Brevoortia tyrannus	Atlantic menhaden	adult	LC50, 48h	0.22	TRC(Br)			Roberts and Gleason 1978
		adult	LC50, 96h	0.15	CPO	25		Hoss et al. 1977
		adult	LC50, >8 min	0.03	FRC	10,30	15	Hoss et al. 1975
		adult	LC50, >5 min	0.03	FRC	10,30	15+Δ10	Hoss et al. 1975
		adult	LC50	0.18	CPO		15	Hoss et al. 1977
		adult	LC50	0.15	TRC		25	Gullans et al. 1977
Carassius auratus	Goldfish	adult	TL50, 96h	0.195–0.278	TRC		25	Ward et al. 1976
Catostomus commersonii	White sucker	adult	LC50	0.132	TRC			Arthur et al. 1975
Clupea harengus	Pacific herring	adult	LC50, 96h	0.065	TRO	28	14.8	Thatcher 1978
Cymatogaster aggregata	Shiner perch	adult	LC50, 1h	0.30	TRO	28.8–30.8	13	Stober et al. 1978
		adult	LC50, 1h	0.32	TRO	28.8–30.8	13±Δ3	Stober et al. 1978
		adult	LC50, 1h	0.23	TRO	28.8–30.8	13±Δ20	Stober et al. 1978
		adult	LC50, 8–13h	0.11–0.19	TRO	28.8–30.8	13±Δ20	Stober et al. 1978
		adult	LC50, 96h	0.071	TRO		14.8	Thatcher 1978
Cynoscion nebulosus	Spotted seatrout	eggs, 2,10h	TLm, 48h	0.21	NaOCl	30	25	Johnson et al. 1977
		eggs, 2h	TLm, 48h	14.14	chloramine	30	25	Johnson et al. 1977
		eggs, 10h	TLm, 48h	0.57	chloramine	30	25	Johnson et al. 1977
		larvae, 1h	TLm, 48h	5.75	chloramine	30	25	Johnson et al. 1977
		larvae, 1h	TLm, 48h	0.17	chloramine	30	25	Johnson et al. 1977

Table 5, Cont.

ORGANISMS			CRITERION	CHLORINE		SALINITY	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Fundulus heteroclitus	Mummichog	juvenile	LC100, 0.5h	0.65	TRC	30-31	25	Capuzzo et al. 1977
		juvenile	LC100, 0.5h	1.20	chloramine	30-31	25	Capuzzo et al. 1977
		juvenile	LC100, 0.5h	0.25	TRC	30-31	30	Capuzzo et al. 1977
		juvenile	LC100, 0.5h	0.85	chloramine	30-31	30	Capuzzo et al. 1977
Gasterosteus aculeatus	Threespine stickback	adult	LC50, 96h	0.17	TRO	28	14.8	Thatcher 1978
Gobiosoma bosci	Naked goby	adult	TL50, 2h	0.64	TRC	18.2-20.4		Roberts et al. 1975
		adult	TL50, 24h	0.08	TRC	18.2-20.4		Roberts et al. 1975
		adult	TL50, 48h	0.08	TRC	18.2-20.4		Roberts et al. 1975
		adult	TL50, 96h	0.08	TRC	18.2-20.4		Roberts et al. 1975
		eggs, 2h	TLm	14.14	chloramine	18.2-20.4		Roberts et al. 1975
		eggs, 10h	TLm	0.57	chloramine	18.2-20.4		Roberts et al. 1975
		larvae, 1h	TLm	5.57	chloramine	18.2-20.4		Roberts et al. 1975
Ictalurus melas	Bullhead	adult	LC50, 96h	0.28	TRC(Br)		25	Ward et al. 1976
Ictalurus natalis	Yellow bullhead	adult	LC100, 96h	0.29	TRC(Br)		25	Ward et al. 1976
		adult	LC50, 96h	0.177**	TRC(Br)		25	Ward et al. 1976

** 100% effluent

Leiostomus xanthurus	Spot	juvenile	TL50, 48	0.09	CPO	26-31	30±1	Middaugh et al. 1980
		juvenile	TL50, 1.6h	0.36	CPO	26-32	30±1	Middaugh et al. 1980
		juvenile	TL50, 1.5h	0.37	CPO	26-31	30±1	Middaugh et al. 1980
		juvenile	TL50, 6.7h	0.13	CPO	26-31	30±1	Middaugh et al. 1980
		juvenile	LC50, 196h	0.12	TRC		10	Middaugh et al. 1977a
		juvenile	LC50, 196h	0.06	TRC		15	Middaugh et al. 1977a
		juvenile	LC50, 24h	0.48	TRC	E	variable	LeBlanc et al. 1978
		juvenile	LC50, 48h	0.31	TRC	E	variable	LeBlanc et al. 1978
		juvenile	LC50, 96h	0.23	TRC	E	variable	LeBlanc et al. 1978
		juvenile	LC50, 144h	0.23	TRC	E	variable	LeBlanc et al. 1978
		juvenile	TLm, 24h	0.14	TRC	E	14.2-16	Bellanca and Bailey 1977
		juvenile	TLm, 96h	0.09	TRC	E	14.2-16	Bellanca and Bailey 1977
		juvenile	TLm, 48h	0.22	TRC(Br)	E	variable	Roberts and Gleeson 1978
		juvenile	LC50, 24h	0.41-0.48	TRC(Br)	12-20	variable	Roberts 1980
		juvenile	LC50, 48h	0.31-0.38	TRC(Br)	12-20	variable	Roberts 1980
		juvenile	LC50, 96h	0.23	TRC(Br)	12-20	variable	Roberts 1980
		juvenile	LC50, 144h	0.23-0.25	TRC(Br)	12-20	variable	Roberts 1980
		juvenile	LC50, 24h	0.41	TRC(Br)	E	variable	LeBlanc et al. 1978

Table 5, Cont.

ORGANISMS			CRITERION	CHLORINE		SALINITY	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Leiostomus xanthurus	Spot	juvenile	LC50, 48h	0.38	TRC(Br)	E	variable	LeBlanc et al. 1978
		juvenile	LC50, 96	0.25	TRC(Br)	E	variable	LeBlanc et al. 1978
		juvenile	LC50, 144h	0.25	TRC(Br)	E	variable	LeBlanc et al. 1978
		adult	LC50, 24h	0.48	TRC(Br)		16.8-27.6	Roberts 1980
		adult	LC50, 48h	0.31-0.38	TRC(Br)		16.8-27.6	Roberts 1980
		adult	LC50, 96h	0.23	TRC(Br)		16.8-27.6	Roberts 1980
		adult	LC50, 144h	0.25	TRC(Br)		16.8-27.6	Roberts 1980
		adult	LC50, 48h	0.22	TRC(Br)			Roberts and Gleeson 1978
		adult	LC50, 96h	0.21	TRC(Br)		16.8-27.6	Roberts and Gleeson 1978
		juvenile	LC100, 96h	0.16	TRC(Br)		14.2-16	Bellanca and Bailey 1977
Lepomis sp.	Sunfish	adult	TL50, 96h	0.195-0.28	TRC			Ward and DeGraeve 1978b
Menidia beryllina	Tidewater silverside	eggs	LC50, 24h	0.26	TRC			Morgan and Prince 1977
		eggs	LC50, 48h	0.21-0.25	TRC			Morgan and Prince 1977
		eggs, 4-cell	LC50, 24h	0.23	TRC			Morgan and Prince 1977
		eggs, 24h	LC50, 48h	0.32	TRC			Morgan and Prince 1977

Menidia beryllina	Tidewater silverside	eggs, 2h	LC95, 24h	0.41	TRC			Morgan and Prince 1977
		eggs, 2h	LC95, 48h	0.44	TRC			Morgan and Prince 1977
		eggs, 3h	LC95, 24h	0.37	TRC			Morgan and Prince 1977
		eggs, 3h	LC95, 48h	0.28	TRC			Morgan and Prince 1977
		eggs, 24h	LC95, 48h	0.43	TRC			Morgan and Prince 1977
Menidia menidia	Atlantic silverside	eggs	LC50, 2h	0.38	TRC			Morgan and Prince 1977
		eggs	LC50, 48h	0.30	TRC			Morgan and Prince 1977
		eggs	LD50, 24h	0.20	TRC			Anderson et al. 1975
		adult	TL50, 24h	0.095	TRC	18-20	17-28	Roberts et al. 1975
		adult	TL50, 48h	0.038	TRC	18-20	17-28	Roberts et al. 1975
		adult	TL50, 96h	0.037	TRC	18-20	17-28	Roberts et al. 1975
		adult	TLm, 96h	0.037	TRC	E	14.2-16.0	Bellanca and Bailey 1977
		adult	LC50, 24h	0.23	TRC (Br)	20	>19	Roberts and Gleason 1978
		adult	LC50, 48h	0.23	TRC(Br)	20	>19	Roberts and Gleason 1978
		adult	LC50, 96h	0.23	TRC(Br)	20	>19	Roberts and Gleason 1978
		eggs, 2h	LC95, 24h	1.23	TRC			Morgan and Prince 1977

Table 5, Cont.

ORGANISMS			CRITERION	CHLORIDE		SALINITY	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Menidia menidia	Atlantic silverside	eggs, 2h	LC95, 48h	0.56	TRC			Morgan and Prince 1977
		adult	LC100	>0.2	CFO	19-25	25.6-29.3	Roberts 1980
Micropterus dolomieu	Smallmouth bass	adult	TL50, 168h	0.261	TRC			Arthur 1971
Micropterus salmoides	Largemouth bass	adult	TL50, 96h	0.24	TRC			Arthur et al. 1975
		adult	TL50, 168h	0.26	TRC			Arthur et al. 1975
Morone americanus	White perch	eggs	LC50, 24h	0.27	TRC			Morgan and Prince 1977
		prolarvae	LC50, 24h	0.31	TRC			Morgan and Prince 1977
		larvae	LC50, 24h	0.31	TRC			Morgan and Prince 1977
		eggs	LC100, 70-90h	>0.55	TRC		18	Morgan and Prince 1977
		eggs	LC100, 70-90h	0.55	TRC	2.5±0.2	15	Morgan and Prince 1977, 78
		eggs	LC95, 24h	0.46	TRC	2.5±0.2	15	Morgan and Prince 1977, 78
		adult	LC50, 96h	0.15	CFO		25	Gullans et al. 1977
		adult	LC50, 96h	0.21	CFO		15	Gullans et al. 1977
Morone saxatilis	striped bass	eggs, 13h	LC50, 48h	0.20	TRC			Morgan and Prince 1977
		eggs, 24-40h	LC50, 48h	0.22	TRC			Morgan and Prince 1977
		eggs, 40h	LC50, 24h	0.36	TRC			Morgan and Prince 1977
		larvae, 12 day	LC50, 48h	0.07	TRC			Morgan and Prince 1977
		larvae, 24h	LC50, 24h	0.02	TRC			Morgan and Prince 1977
		larvae, 70h	LC50, 24h	0.19	TRC			Morgan and Prince 1977

Morone saxatilis	Striped bass	prolarvae, 2 days	LC50, 48h	0.04	TRC	13-30	18±1	Middaugh et al. 1977b
		prolarvae, 12 days	LC50, 48h	0.07	TRC	13-30	18±1	Middaugh et al. 1977b
		juvenile, 30 days	LC50, 48h	0.04	TRC	13-30	18±1	Middaugh et al. 1977b
		eggs	LC100, 40h	0.21	TRC	13-30	18±1	Middaugh et al. 1977b
		eggs	LC96, 40h	0.07	TRC	13-30	18±1	Middaugh et al. 1977b
		eggs	LC77, 40h	0.01	TRC	13-30	18±1	Middaugh et al. 1977b
		eggs	LC84, 4h	0.30	TRC	2	22	Burton et al. 1979
		eggs	LC100, 36h	0.06	TRC			Hall et al. 1981b
		eggs, <13h	LC95, 48h	0.39	TRC		22	Morgan and Prince 1977
		eggs, 24-40h	LC95, 48h	0.50-0.99	TRC		22	Morgan and Prince 1977
		eggs >40h	LC95, 24h	2.15	TRC		22	Morgan and Prince 1977
		eggs, 13h	LC100, 48h	0.43	TRC		22	Morgan and Prince 1977
		eggs, 24-40h	LC100, 48h	0.50	TRC		22	Morgan and Prince 1977
		eggs, 70h	LC100, 24h	0.40	TRC		22	Morgan and Prince 1977
		eggs, 12h	LC62, 2h	0.15	TRC	2	22+Δ10	Burton et al. 1979
		eggs, 12h	LC82, 2h	0.30	TRC	2	22+Δ6	Burton et al. 1979
		eggs, 12h	LC86, 2h	0.30	TRC	2	22+Δ10	Burton et al. 1979
		eggs, 12h	LC56, 4h	0.15	TRC	2	22+Δ2	Burton et al. 1979
		eggs, 12h	LC54, 4h	0.15	TRC	2	22+Δ6	Burton et al. 1979
		eggs, 12h	LC90, 4	0.30	TRC	2	22+Δ6	Burton et al. 1979
		larvae	LC75, 96h	0.06	TRC		18±1	Hall et al. 1981b

Table 5, Cont.

ORGANISMS			CRITERION	CHLORINE		SALINITY	TEMP.	REFERENCE
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Morone saxatilis	Striped bass	larvae	LC100, 4h	0.25	TRC		18±1	Hall et al. 1981b
		prolarvae, 72h	LC78, 0.08h	0.15	TRC		20+Δ6	Burton et al. 1979
		prolarvae, 72h	LC96, 0.08h	0.15	TRC		20+Δ10	Burton et al. 1979
		prolarvae, 72h	LC60, 0.08h	0.30	TRC		20+Δ2	Burton et al. 1979
		prolarvae, 72h	LC62, 2h	0.15	TRC		20+Δ2	Burton et al. 1979
		prolarvae, 72h	LC76, 2h	0.15	TRC		20+Δ6	Burton et al. 1979
		prolarvae, 72h	LC86, 2h	0.15	TRC		20+Δ10	Burton et al. 1979
		prolarvae, 72h	LC100, 2h	0.30	TRC		20+Δ6	Burton et al. 1979
		prolarvae, 72h		0.30	TRC		20+Δ10	Burton et al. 1979
		prolarvae, 72h	LC100, 4h	0.15	TRC		20+Δ2	Burton et al. 1979
		prolarvae, 72h		0.15	TRC		20+Δ6	Burton et al. 1979
		prolarvae, 72h		0.30	TRC		20+Δ6	Burton et al. 1979
Mugil cephalus	Striped mullet	adult	LC>50, 8 min.	0.03	FRC	10,30	15	Hoss et al. 1975
		adult	LC>50, 6 min.	0.03	FRC	10,30	15+Δ10	Hoss et al. 1975
		adult	LC>50, 2 min.	0.05	FRC	10,30	15+Δ10	Hoss et al. 1975
Notemigonus crysoleucas	Western golden shiner	adult	LC55	0.095	TRC(BR)		25	Ward et al. 1976
		adult	TL50, 96h	0.19	TRC		25	Envelt et al. 1971
		adult	TL50, 96h	0.040	TRC		25	Ward and DeGraeve 1978b
		adult	TL50, 96h	0.090	TRC(Br)		25	Ward et al. 1976
		adult	TL50, 96h	0.120*	TRC(Br)		25	Ward et al. 1976

Notemigonus crysoleucas	Western golden shiner	adult	TL50, 96h	0.140	TRC(Br)		25	Ward et al. 1976
		adult	LC100, 2 days	0.178	TRC	17.5-18	0.4-12	Holland et al. 1960
Notropis anogenus	Pugnose shiner	adult	LC100, 24h	0.161*	TRC(Br)		25	Ward et al. 1976
		adult	LC100, 96h	0.211**	TRC(Br)		25	Ward et al. 1976
		adult	TL50, 96h	0.045	TRC		25	Ward and DeGraeve 1978b
		adult	TL50, 96h	0.109*	TRC(Br)		25	Ward and DeGraeve 1978b
		adult	TL50, 96h	0.136**	TRC(Br)		25	Ward and DeGraeve 1978b
Notropis cornutus	Northern common shiner	adult	LC100, 24h	0.161*	TRC(Br)		25	Ward and DeGraeve 1978b
		adult	LC100, 96h	0.211**	TRC(Br)		25	Ward and DeGraeve 1978b
Oncorhynchus gorbuscha	Pink salmon	juvenile	LC50	0.23	TRO	28	14.8	Thatcher 1978
		juvenile	LC50	0.052	TRO	28	14.8	Thatcher 1978
		juvenile	LC100, 2 days	0.178	TRC	17.5-18	0.4-12	Holland et al. 1960

* 60% effluent

** 100% effluent

Table 5, Cont.

ORGANISMS			CRITERION	CHLORINE		SALINITY	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Oncorhynchus kisutch	Coho salmon	adult	TL50, 24h	0.10	TRC	28	11.2-16	Buckley and Matsuda 1972
		adult	TL50, 96h	0.10	TRC	28	11.2-16	Buckley and Matsuda 1972
		adult	TL50, 24h	0.20-0.23	TRC	28	8.0-24.3	Buckley and Matsuda 1972
		adult	TL50, 96h	0.20-0.23	TRC	28	8.0-24.3	Buckley and Matsuda 1972
		adult	LT50, 19-33h	0.11-0.19	TRO	28	14.8	Thatcher 1978
		adult	LC50	0.11-0.19	TRO	28	14.8	Thatcher 1978
		adult	LC50, 96h	0.07	TRC	28	10-14	Buckley 1976
Oncorhynchus tshawytscha	Chinook salmon	juvenile	LC50, 96h	0.038	TRO	28	14.8	Thatcher 1978
		juvenile	LC50, 96h	0.065	TRO	28	14.8	Thatcher 1978
		adult	LC60, 96h	0.066	TRC(Br)*		16	Ward et al. 1976
		adult	TL50, 96h	0.059	TRC(Br)**		16	Ward et al. 1976
Paralichthys sp.	Flounder	adult	LC>50, >7 min	0.03	FRC	10,30	15	Hoss et al. 1975
		adult	LC>50, >3 min	0.03	FRC	10,30	15+Δ10	Hoss et al. 1975
		adult	LC>50, >3 min	0.05	FRC	10,30	15	Hoss et al. 1975

* 60% effluents

** 100% effluents

Paralichtys sp.	Flounder	adult	LC>50, >2 min	0.05	TRC	10,30	15+Δ10	Moss et al. 1975
		adult	TL50, 96h	0.095	TRC		25	Ward et al. 1976
Parophrys vetulus	English sole	adult	LC50, 96h	0.073	TRC	28	14.8	Thatcher 1978
Perca flavescens	yellow perch	adult	TL50, 168h	0.205	TRC			Arthur et al. 1975
Pimephales promelas	fathead minnow	adult	TL50, 96h	0.05–0.16	TRC			Zillich 1969
		adult	TL50, 168h	0.082–0.115	TRC			Arthur 1971
		adult	TL50, 96h	0.082–0.095	TRC		25	Ward et al. 1976
		adult	LC>50, <2h	1.5	chloramine			Grothe and Eaton 1975
		adult	LC100, 96h	0.29	TRC(Br)*			Ward et al. 1976
		adult	LC100, 96h	0.25	TRC(Br)**			Ward et al. 1976
		adult	LC100, 96h	0.33	TRC(Br)**			Ward et al. 1976
		adult	LC100, 96h	0.32	TRC(Br)**			Ward et al. 1976
		adult	LC85, 96h	0.18	TRC(Br)**			Ward et al. 1976
		adult	TL50, 96h	0.185–0.193	TRC(Br)*		25	Ward et al. 1976
		adult	TL50, 96h	0.133–0.193	TRC(Br)**		25	Ward et al. 1976

* 60% effluent
** 100% effluent
*** 36% effluent

Table 5, Cont.

ORGANISMS			CRITERION	CHLORINE		SALINITY	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Pleuronectes platessa	Plaice	eggs, 4 day	LD50, 72h	0.70	TCL	5.4-9.3		Alderson 1972
		eggs, 5 day	LD50, 192h	0.12	TCL	5.4-9.3		Alderson 1972
		larvae, stage 1c	LD50, 96h	0.024	TCL	5.4-9.3		Alderson 1972
		larvae, stage 3c	LD50, 96h	0.034	TCL	5.4-9.3		Alderson 1972
		metamorphosed fish	LD50, 96h	0.084-0.095	TCL	5.7-17		Alderson 1974
Pseudopleuronectes americanus	Winter flounder	adult	LD50, 24h	0.5	TRC			Anderson et al. 1975
		larvae	LT50, 15 min	2.5	TRC	30		Gentile et al. 1976
		juvenile	LC100, 0.5h	0.55	TRC	30-31	25	Capuzzo et al. 1977
		juvenile	LC50, 0.5h	2.55	chloramine		25	Alderson 1972
Salmo namaycush	Lake trout	adult	LC100, 96h	0.154	TRC(Br)**	14		Ward et al. 1976
Salvelinus namaycush	Lake trout	adult	TL50, 96h	0.102	TRC(Br)***	14		Ward et al. 1976
Sebastes mystinus	Blue rockfish	adult	LC50, 20 min	1.10	TRC		11.0-14.6	Wilson 1977
Solea solea	Sole	larvae	LC50, 48h	0.028-0.059	TCL		12-17	Alderson 1974
		larvae	LC80	0.12-0.15	TCL		12.5-13.0	Alderson 1969
Stenotomus versicolor	Scup	juvenile	LC100, 05h	0.65	TRC	30-31	25	Capuzzo et al. 1977
		juvenile	LC100, 05h	3.10	chloramine	30-31	25	Capuzzo et al. 1977
Stizostedion vitreum	Walleye	larvae	TL50, 168h	0.15	TRC			Arthur et al. 1973

Syngnathus fuscus	Northern pipefish	adult	TL50, 24h	0.28	TRC	18.2-20.4	17-28	Roberts et al. 1975
		adult	TL50, 48h	0.27	TRC	18.2-20.4	17-28	Roberts et al. 1975
		adult	TL50, 96h	0.27	TRC	18.2-20.4	17-28	Roberts et al. 1975

* 36% effluent
** 100% effluent
*** 36% effluent

Table 6
Sublethal Effects of Chlorines to Fish

ORGANISMS			CRITERION	CHLORINE		SALINITY	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Alosa aestivalis	Blueback herring	eggs, stage e	survival 85 ± 4%	0.14	TRC	1±0.2	21	Morgan and Prince 1978
		eggs, stage e	survival 76 ± 3%	0.31	TRC	1±0.2	21	Morgan and Prince 1978
		eggs, stage e	survival 47 ± 4%	0.38	TRC	1±0.2	21	Morgan and Prince 1978
		eggs, stage e	LC5, 80h	0.15	TRC	1±0.2	21	Morgan and Prince 1978
		larvae, 1 day	LC5, 24h	0.18	TRC	1±0.2	21	Morgan and Prince 1978
		larvae, 1 day	LC5, 48h	0.16	TRC	1±0.2	21	Morgan and Prince 1978
		larvae, 2 day	LC5, 24h	0.15	TRC	1±0.2	21	Morgan and Prince 1978
		larvae, 2 day	LC5, 48h	0.075	TRC	1±0.2	21	Morgan and Prince 1978
		larvae	development not effected	0.14–0.31	TRC	1±0.2	21	Morgan and Prince 1978
		larvae, 60h	comatose, 24h	0.16–0.25	TRC	1±0.2	21	Morgan and Prince 1978
Brevoortia tyrannus	Atlantic menhaden	juvenile	survival 97%, 19 days	0.014–0.062	TRC*	2.0	31.2	Liden et al. 1980
		juvenile	survival 100%, 19 days	0.032	TRC*	2.0	31.2	Liden et al. 1980
Carassius auratus	Goldfish	adult	survival 65%, 96h	0.127	TRC(BR)*		25	Ward et al. 1976
Catostomus commersonii	White sucker	gill, tissue culture	respiration rate, no effect	1.0	chloramine			Fobes 1971
Fundulus heteroclitus	Mummichog	juvenile	respiration rate decreased slightly	2.0	applied chloramine		25	Morgan and Prince 1977
		juvenile	respiration rate decreased slightly	2.0	applied chloramine		25	Morgan and Prince 1977
		juvenile	respiration rate decreased slightly	4.0	applied chloramine		25	Morgan and Prince 1977

*Effluent

Fundulus heteroclitus	Mummichog	juvenile	respiration rate increased	0.5h	TRC	30-31	25	Capuzzo et al. 1976
		juvenile	behavioral aberration	0.32	TRC	30-31	25	Capuzzo et al. 1976
		juvenile	behavioral aberration	0.65	chloramine	30-31	25	Capuzzo et al. 1976
Leiostomus xanthurus	Spot	juvenile	O_2 uptake, decrease 43%, >48h	0.09	CPO	26-31	30±1	Middaugh et al. 1980
		juvenile	O_2 uptake, decrease 27%, >48h	0.13	CPO	26-31	30±1	Middaugh et al. 1980
		juvenile	O_2 uptake, decrease 34%, 0.5h	0.37	CPO	26-31	30±1	Middaugh et al. 1980
		juvenile	O_2 uptake, decrease 70%, 1.0h	0.37	CPO	26-31	30±1	Middaugh et al. 1980
		juvenile	opercular ventilation rate, elevated	0.09-0.12	CPO	26-31	30±1	Middaugh et al. 1980
		juvenile	blood pH, lowered	0.09-0.12	CPO	26-31	30±1	Middaugh et al. 1980
		juvenile	survival, 81%	0.081	TRC(Br)	2±0.6	30-31	Liden et al. 1980
			survival, 75%	0.045	TRC(Br)	2±0.6	30-31	Liden et al. 1980
		juvenile	survival, 73%	0.020	TRC(Br)	2±0.6	30-31	Liden et al. 1980
		juvenile	survival, 78%	0.062	TRC	2±0.6	30-31	Liden et al. 1980
		juvenile	survival, 76%	0.032	TRC	2±0.6	30-31	Liden et al. 1980
		juvenile	survival, 73%	0.014	TRC	2±0.6	30-31	Liden et al. 1980

Table 6, Cont.

ORGANISMS			CRITERION	CHLORINE		SALINITY	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		ug/L	Species	°/oo	°C	
Leiostomus xanthurus	Spot	juvenile	survival 100%, 96h	0.04	TRC		14-16	Bellance and Bailey 1977
		juvenile	survival 78.3%, 19 days	0.062	TRC			Liden et al. 1980
		juvenile	survival 76%, 19 days	0.032	TRC			Liden et al. 1980
		juvenile	survival 74%, 19 days	0.014	TRC	2±0.6	14-16	Liden et al. 1980
		juvenile	survival 100%, 19 days	0.02-0.04	TRC			Middaugh et al. 1977a
Menidia beryllina	Tidewater silverside	eggs, 2h	LC5, 24h	0.17	TRC	19-24	10-15	Morgan and Prince 1977
		eggs, 2h	LC5, 48h	0.14	TRC	19-24	10-15	Morgan and Prince 1977
		eggs, 4 cells	LC5, 24h	0.15	TRC	19-24	10-15	Morgan and Prince 1977
		eggs, 4 cells	LC5, 48h	0.16	TRC	19-24	10-15	Morgan and Prince 1977
		eggs, 24h	LC5, 48h	0.24	TRC	19-24	10-15	Morgan and Prince 1977
		eggs, 80h	survival, 100%	0.24-0.52	TRC	19-24	10-15	Morgan and Prince 1977
		eggs, f48h	survival 100%	0.22-0.27	TRC	19-24	10-15	Morgan and Prince 1977
Menidia menidia	Atlantic silverside	eggs, 2h	LC5, 24h	0.12	TRC	19-24	10-15	Morgan and Prince 1977
		eggs, 2h	LC5, 48h	0.16	TRC	19-24	10-15	Morgan and Prince 1977
		adult	LC100	f0.2	CPO	19-25	26-29	Roberts 1980
Micropterus salmoides	Largemouth bass	adult	survival, 100%, 96h	0.095*	TRC(BR)		25	Ward et al. 1976

*Effluent

Morone americana	White perch	eggs	LC5, 76h	0.15	TRC		15.1	Morgan and Prince 1977
		eggs, stage e	survival 69±3%	0.046	TRC	2.5±0.2	15.1	Morgan and Prince 1978
		eggs, stage e	survival 54±5%	0.16	TRC	2.5±0.2	15.1	Morgan and Prince 1978
		eggs, stage e	survival 39±5%	0.35	TRC	2.5±0.2	15.1	Morgan and Prince 1978
		eggs	edema, blistering	>0.40	TRC			Morgan and Prince 1977
		eggs	osmoregulatory and respiration breakdown 1-8h	0.8	TRC	14	15	Block et al. 1978
		eggs	loss of body equilibrium, >2h	1.3	CPO	14	15	Block et al. 1977
		eggs	blood pH decrease, 0.5h	1.3	CPO	14	15	Block et al. 1977
		prolarvae	LC5, 24h	0.20	TRC			Morgan and Prince 1977
		prolarvae	survivals had shorter body length than average	0.31	TRC			Morgan and Prince 1977
		larvae, 25 day	survival 74%, 3h	0.19	TRC	1.5	18	Hall et al. 1979
		larvae, 25 day	survival 69%, 3h	0.24	TRC	1.5	18	Hall et al. 1979
		larvae, 25 day	survival 64%, 3h	0.30	TRC	1.5	18	Hall et al. 1979
		larvae, 25 day	survival 64%, 4h	0.12	TRC	1.5	18	Hall et al. 1979
		larvae, 25 day	survival 59%, 4h	0.20	TRC	1.5	18	Hall et al. 1979
		larvae, 25 day	survival 54%, 4h	0.25	TRC	1.5	18	Hall et al. 1979
		larvae, 25 day	survival 88%, 0.1h	0.14	TRC	1.5	18	Hall et al. 1979
		larvae, 25 day	survival 83%, 0.1h	0.23	TRC	1.5	18	Hall et al. 1979
		larvae, 25 day	survival 88%, 1h	0.10	TRC	1.5	18	Hall et al. 1979
		larvae, 25 day	survival 83%, 1h	0.22	TRC	1.5	18	Hall et al. 1979
		larvae, 25 day	survival 79%, 1h	0.28	TRC	1.5	18	Hall et al. 1979
		larvae, 25 day	survival 83%, 2h	0.13	TRC	1.5	18	Hall et al. 1979

Table 6, Cont.

ORGANISMS			CRITERION	CHLORINE		SALINITY	TEMP.	REFERENCES
Scientific Name	Common Name	Stage		mg/L	Species	°/oo	°C	
Morone americana	White perch	larvae	survival 79%, 2h	0.23	TRC	1.5	18	Hall et al. 1979
		larvae	survival 74%, 2h	0.29	TRC	1.5	18	Hall et al. 1979
		larvae	LC5, 24h	0.20	TRC	1-2.8	15-21	Morgan and Prince 1978
		larvae	decline of development	0.16-0.35	TRC	1-2.8	15-21	Morgan and Prince 1978
Morone saxatilis	Striped bass	eggs	hatchability 23%, 40h	0.01	TRC	1-3	22	Middaugh et al. 1977b
		eggs, <13h	LC5, 48h	0.10	TRC	1-3	22	Middaugh et al. 1977b
		eggs, 24-40h	LC5, 48h	0.048	TRC	1-3	22	Middaugh et al. 1977b
		eggs, >40h	LC5, 24h	0.060	TRC	1-3	22	Middaugh et al. 1977b
		eggs, 12h	mortality 26%, 36h after 0.08h exposure	0.15		2	22+ΔT6	Burton et al. 1979
		eggs, 12h	mortality 30%, 36h after 0.08h exposure	0.15		2	22+ΔT10	Burton et al. 1979
		eggs, 12h	LC42, 42%, 2h	0.15	TRC	2	22+ΔT2	Burton et al. 1979
		eggs, 12h	LC 46%, 2h	0.15	TRC	2	22+ΔT2	Burton et al. 1979
		larvae >24h	LC5, 24h	0.068	TRC	13-30	18±1	Morgan and Prince 1977
		larvae 70h	LC5, 24h	0.14	TRC	13-30	18±1	Morgan and Prince 1977
		larvae >24h	LC5, 24h	0.59	TRC	13-30	18±1	Morgan and Prince 1977
		larvae 70h	LC5, 24h	0.25	TRC	13-30	18±1	Morgan and Prince 1977
		eggs, stage e	survival 96.3%	0.051	TRC	2.8	18±1	Morgan and Prince 1978
		eggs, stage e	survival 51±2	0.19	TRC	2.8	18±1	Morgan and Prince 1978
		larvae	development declined	0.15-0.19	TRC	2.8	18±1	Morgan and Prince 1978
		juvenile	gill damage	0.21-2.36	TRC	13-30	18±1	Middaugh et al. 1977

Morone saxatilis	Striped Bass	larvae	body length shorter than control after eggs exposure	0.15–0.35	TRC	17.5–18	64–11.9	Morgan and Prince 1977, 1978
Oncorhynchus kisutch	Coho salmon	adult	survival 100%, 9 days	0.173	TRC	17.5–18	64–11.9	Holland et al. 1960
		adult	survival 79%, 96h	0.153	TRC(BR)*		16	Ward et al. 1976
Pimephales promelas	Fathead minnow	adult	LC5, 14 days	0.082	TRC(Br)*			Ward et al. 1976
Pseudopleuronectes americanus	Winter flounder	juvenile	behavioral aberration	0.20	TRC	30–31		Capuzzo et al. 1977
		juvenile		1.50	chloramine	30–31		Capuzzo et al. 1977
Salmo gairdneri	Rainbow trout	adult	LC43, 96h	0.153	TRC(Br)		16	Ward et al. 1976
Salmo trutta	Brown trout	adult	LC20, 96h	0.066	TRC(Br)*		16	Ward et al. 1976
Stenotomus versicolor	Scup	juvenile	behavioral aberration	0.5	TRC	30–31	25	Capuzzo et al. 1977
		juvenile		2.20	chloramine	30–31	25	Capuzzo et al. 1977

* Effluent

mortality of 78% for 0.08 h exposure; with a 2 h exposure; mortality was 76%; and for a 4 h exposure, mortality was 100% (Burton et al. 1979). On the other hand, for northern pipefish Syngnathus fuscus, the TL50 for 24, 48 and 96 h was essentially the same (Roberts et al. 1975).

Dissolved Oxygen

In an avoidance study using the Atlantic silverside Menidia menidia, Meldrim and Fava (1977) found that as dissolved oxygen decreased below saturation, avoidance occurred at a higher concentration. With DO saturated and temperature between 13-27°C, avoidance occurred at 0.10 mg/L TRC; when DO dropped below saturation, avoidance occurred at 0.15 mg/L TRC. At lower temperatures between 0-12°C, the effect of DO was less obvious: avoidance appeared at practically the same TRC level with saturated and unsaturated DO.

Light Intensity

Research on the effects of light intensity on chlorine toxicity is limited; nevertheless, there are possible impacts that the discharge time of wastewater treatment plants may have on the macrofauna and the issue is an important one. Meldrim and Fava (1977), in their avoidance threshold study, found that at temperatures between 13-27°C with high light intensity (1070 lux), Atlantic Silverside reacted to 0.20 mg/L TRO, whereas at lower light intensity (430 lux) the threshold dropped to 0.10 mg/L.

Salinity

Although the effects of water chemistry are discussed in Chapter 2, it should be pointed out here that salinity does affect chlorine toxicity and avoidance behavior of fish: higher salinity under otherwise equal conditions results in higher thresholds of avoidance (Meldrim and Fava 1977). Under similar temperature, light intensity and DO conditions, Atlantic silverside Menidia menidia was sensitive to 0.11 mg/L TRO when salinity was 5.0-7.0 ppt. But the threshold for avoidance increased to 0.64 mg/L TRC with salinity 2.5-4.0 ppt. Larvae of white perch M. americana reacted similarly.

Interaction Of Chlorine, Elevated Temperature and Duration of Exposure

Burton et al. (1980) experimented with grass shrimp P. pugis and mysid shrimp Gammarus sp. under conditions similar to those at a once-through power plant. With TRC between 0.15 and 0.30 mg/L, and a range of temperatures, 15°C plus Δ2,6 and 10°C, and exposure times of 0.08, 2.0 and 4.0 h, the dominant cause of mortality was TRC. Although elevation of temperature alone was of little importance, a two-way interaction between TRC and ΔT was observed for the mysid shrimp. A second-order linear inter-

action appeared between TRC and exposure time for grass shrimp. Blue crabs Callinectes sapidus were not significantly affected under conditions similar to those mentioned above.

Burton et al. (1979) used models and also conducted experiments to study survival of striped bass eggs and larvae when subjected to varying combined conditions of chlorine concentrations, elevated temperature and exposure times. At each exposure period, as TRC concentration and ΔT increased, mortality of eggs and prolarvae increased. As exposure time increased, mortality also increased. With exposure time kept equal, eggs were more tolerant than prolarvae to the combined effect of TRC and ΔT. (Models are discussed more fully in Chapter 7, "Chlorine Models and Their Application to the Field.")

Chemistry of the Water Body

The chemistry of the water body receiving chlorinated water greatly affects the toxicity of the residual chlorine. Reducing agents such as sulfides, iron and manganese in water elevate the chlorine demand. (On chlorine demand, see Chapter 2.) Organic matter, ammonia and other nitrogenous compounds and bromine also have affect chlorine demand. The toxicity of the resulting chlorine compounds has not been well studied, except for some chloramines and bromides.

BIOLOGICAL FACTORS AFFECTING CHLORINE TOXICITY

Life Stage

Organisms have different capacities for surviving chlorine concentrations at different stages of development. Both for fish and macroinvertebrates, early life stages are generally more sensitive to chlorine toxicity. For example, hatchability of eggs of the mud crab Panopeus herbstii was not affected at 0.08 mg/L ClO; for larvae, the 96 h LC50 was 0.12 mg/L CLO; for juveniles and adults, the LC50 increased to 0.50 mg/L (Roberts 1978). Larvae and adults of the American oyster C. virginica were much more susceptible to low concentrations: LC50 for larvae was 0.005 mg/L TRC (Roberts 1975) and for the adult 0.026 mg/L TRC (Roberts and Gleeson 1978).

The LC50 for striped bass varied at different developmental stages, although even here experimental conditions differed for each researcher, thus making it difficult to draw comparisons. For striped bass eggs, LC50 ranged from 0.20 to 0.36 mg/L TRC by Morgan and Prince (1977) and 48 h LC50 of 0.01 mg/L by Mattice and Zittel (1976); for prolarvae, from 0.04 to 0.07 mg/L by Middaugh et al. (1977). Morgan and Prince (1977) noted that older eggs are more tolerant than younger ones, a conclusion based on experiments in which the 48 h LC50 for 13 h old eggs was 0.33 mg/L TRC, whereas for 40 h old eggs, it was 0.99 mg/L TRC.

Physical State of Organism

A factor requiring more attention is how the mechanical damage caused by entrainment may affect an organism's tolerance to chlorine. Marcy et al. (1978) stated that physical damage is the major cause of mortality during the normal operational cycle of a power plant, and that thermal and chemical stresses may be more variable. It appears that few studies have actually investigated how physical damage, which would weaken the organism, may affect their responses to chlorine toxicity. Differences in behavior such as avoidance would be expected between healthy and injured fish.

BIOLOGICAL SIGNIFICANCE OF AVOIDANCE RESPONSES TO CHLORINE BY ORGANISMS

Avoidance response as a mechanism for mobile organisms to escape from unfavorable environments is of great biological significance. On the other hand, if the discharge of chlorine is near the feeding or spawning grounds of aquatic organisms, the avoidance responses which would keep the organisms away may lead to an imbalanced distribution of population.

Tsai (1973) reported that no fish were found below sewage outfalls in freshwater of 0.37 mg/L TRC, and the species diversity of fish was zero at 0.25 mg/L TRC. Table 7 gives the avoidance threshold for various species. Unfortunately, data of LC50 for the same species under similar conditions are often unavailable.

Meldrim and Fava (1977) have reported that avoidance response of Atlantic silverside Menidia menidia is affected by light intensity and dissolved oxygen (DO). At 13-27°C, high light intensity of 1070 lux and saturated DO, the mean avoidance concentration was 0.20 mg/L TRO. But under similar conditions with light intensity dropping to 430 lux, fish avoid 0.10 mg/L TRO. When DO was unsaturated, and light intensity high, fish became very sensitive and responded to chlorine concentrations as low as 0.03 mg/L TRO. White perch larvae placed under similar conditions, however, did not display such great differences in avoidance thresholds. Stober et al. (1978) found that coho salmon Oncorhynchus kisutsch avoided TRC above 0.02 mg/L, whereas Meldrim et al. (1974) reported that white perch M. americanus, Atlantic silverside M. menidia, mummichog F. heteroclitus and hogchoker Trinectes maculatus did not display avoidance behavior until the TRC concentration reached 0.02-0.15 mg/L.

Hall et al. (1983a) studied the avoidance response of juvenile Atlantic menhaden B. tyrranus to simultaneous ΔT (0, 2, 4 and 6°C) and TRC (0.00, 0.05, 0.10 and 0.15 mg/L) and established a predictive avoidance model accordingly. The response surface developed at 25°C showed that avoidance increased with increasing TRC concentrations at each ΔT condition. Avoidance also increased with increasing ΔT conditions at each TRC concentration. A combination of the highest ΔT (6°C) and highest TRC (0.15 mg/L, which is the 96 h LC50 value at 25°C) resulted in the greatest avoidance response. TRC was found to be the most important factor to

trigger avoidance. The response surface developed at 30°C indicated higher avoidance responses; ΔT and TRC were both important factors influencing avoidance responses.

Hall et al. (1983b) has found that juvenile striped bass can avoid a series of combinations of simultaneous TRC concentrations up to 0.15 mg/L and ΔT up to 6°C. Their percent avoidance model showed that when acclimated to 15-30°C, the most important influencing factor at 15 and 20°C was TRC; at 25 and 30°C, ΔT became the major factor. Tests conducted at 15°C suggested that preference for a higher temperature overrides a chlorine avoidance response to 0.15 mg/L TRC (96 h LC50 at 25°C was 0.19 mg/L). But at acclimated temperatures of 20, 25 and 30°C, the preference for a higher temperature (ΔT 6°C) did not override chlorine avoidance responses. At a rather high temperature of 30°C, fish were most sensitive to all combinations of TRC and ΔT.

THE IMPACT OF DISCHARGE OF CHLORINATED WATER

James River, a Case Study

In 1973 and 1974, millions of fish in the estuarine portion of James River were killed. Although there has been dispute regarding the major cause of the fish kills and no doubt the pesticide kepone played an important role, circumstantial evidence indicates the cause to be the discharge of chlorinated effluent from waste water treatment plants. The total chlorine level at some outfall areas was as high as 2.2 mg/L. Field investigations, laboratory experiments and on-site tests showed that such concentrations in water would kill fish; moreover, when that water was dechlorinated, it no longer caused fish mortality. When the total chlorine level of the discharge was reduced to 1.0 mg/L (OT method), fish kills stopped completely and almost immediately (Bellanca and Baily 1977). It has also been proved that satisfactory disinfection can be achieved at 1.0 mg/L OT, the equivalent of 2.0 mg/L amperometric (Bellanca and Bailey 1977). Thus, combining the control of chlorine application in treatment plants and power plants with the prediction of dilution of the discharge should provide satisfactory protection to the macrofauna.

Biological Effect Of Dechlorination Of Chlorinated Water

Dechlorination of chlorinated water is one of the alternatives for eliminating or reducing chlorine-induced toxicity on aquatic organisms (Esvelt et al. 1973; Ward et al. 1977). Roberts (1980) simulated chlorination conditions of secondary treatment plant effluents with a residual level of chlorine of 2 mg/L. When sodium thiosulfate was used as the reducing agent, the chlorinated water, which would have been fatal to the Atlantic Silverside M. Menidia and the grass shrimp P. pugis without dechlorination, did not cause mortality. However, for the American oyster C. virginica, shell deposition was inhibited.

Table 7
Avoidance of Organisms to Chlorine

Organism Scientific Name	Common Name	Criterion	Toxic Level MG/L	Chlorine Species	Temp. °C	Reference
Alosa pseudoharengus	Ale Wife	Avoidance	<0.1	Mono-Chloramine		Bogardus et al. 1978
Callinectes sapidus	Blue Crab	Avoidance	>1.90	FRC		Meldrim et al. 1974
Crangon septimspinosa	Sand Shrimp	Avoidance	0.05	FRC		Meldrim et al. 1974
Gammarus daiberi	Mysid Shrimp	Avoidance	0.020	TRC	29.8	Ginn and O'Connor 1978
Gammarus daiberi		Avoidance	0.16	TRC	22.1	Ginn and O'Connor 1978
Palaemonetes pugio	Grass Shrimp	Avoidance	0.07	FRC		Meldrim et al. 1974
Lagodon rhomboides	Pinfish	Avoidance	0.02-0.04	CPO		Cripe 1979
Leiostomus xanthurus, juvenile	Spot	Avoidance	1.57	TRC		Middaugh et al. 1977a
Leiostomus xanthurus, adult		Avoidance	0.18	TRC	10	Middaugh et al. 1977a
Leiostomus xanthurus, adult		Avoidance	0.05	TRC	15-20	Middaugh et al. 1977a
Menidia menidia	Atlantic silverside	Avoidance	0.02-0.15	FRC		Meldrim et al. 1974
Morone americanus	White perch	Avoidance	0.02-0.15	FRC		
Morone saxatilis , larvae	Striped Bass	Avoidance	0.29-0.32	TRC	18±1	Middaugh et al. 1977b
Notropis nudsonius	Spottail Shiner	Avoidance	<0.1	TRC Mono-Chloramine		Bogardus et al. 1978
Oncorhynchus kisutsch	Coho salmon	Avoidance	>0.002	TRC		Stober et al. 1978
Trinectes maculatus	Hogchoker	Avoidance	0.02-0.15	FRC		Meldrim et al. 1974

Further studies regarding the relative toxicity of various reducing agents and resulting residuals used in dechlorination to aquatic organisms are essential.

Level Of Discharges Of Chlorinated Water In The Bay Area

The residual level allowed for chlorine in municipal waste-water treatment plants discharge is 0.05-0.2 mg/L. For power plant cooling systems, it is 0.05-0.1 mg/L but is as low as 0.01-0.02 mg/L TRC in many plants (Fox and Moyer 1975). Most power plants practice chlorination for control of fouling only when the ambient temperature reaches or exceeds 12.8°C (Guiland 1981*), whereas sewage treatment plants operate on a year-round basis.

In 1979, among 143 sewage treatment plants in the Chesapeake Bay region, namely, on the Chester River, Patuxent River, Nanticoke River Basin, Potomac River Basin, Choptank River Basin and in the upper Bay, 141 plants used chlorination techniques. The average total residual chlorine at the end of the pipe ranged from 0 to 19.0 mg/L. Only twenty-one of these plants kept the TRC concentration below or around 0.1 mg/L or had zero discharge; thirty-eight plants were between 0.2 and 2.0 mg/L while nine plants were above 10 mg/L.

The Baltimore area may serve as another example. In 1979, the approximate feed-rate of the sewage treatment plants was 2 mg/L gaseous chlorine. The actual concentrations of chlorine of the discharges were: Westpoint plant 0.09-0.4, average 0.17; Could Street 0.05-0.4, average 0.10; Wagner 0.019-0.23, average 0.03 (Bauereis, 1981**). However, many of the other plants did not obtain as good a record of discharge.

Lack of data on chlorine levels in various sites in the Bay and for water flow and dilution factors has made it difficult to judge the actual levels of residual chlorine in the receiving water bodies, or how the chlorine interacts with other chemicals or diluents in these environments. Models are critical for answering such questions so that informed decisions can be made on the protection of areas of ecological significance, such as oyster beds and spawning grounds of fish. This issue is discussed in the next chapter.

COMPARISON OF THE TOXICITY OF CHLORINE, BROMOCHLORINE AND CHLORAMINES

Few papers have dealt with the toxicities of chlorine and bromochlorine or chloramines under similar experimental conditions, thus making comparisons difficult.

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* Guiland, L.S. Letter to R.A. Roig, Department of Natural Resources, Maryland.

** Bauereis, E.I. 1981, Baltimore Gas and Electric, letter to H. Speir, Tidewater Administration, Maryland.

The scup Stenotomus versicolor showed behavioral aberration at 0.5 mg/L TRC with free chlorine and at 2.2 mg/L with chloramine. One hundred percent mortality occurred at 0.65 mg/L TRC with free chlorine and 3.1 mg/L with chloramine. Juvenile winter flounder Pseudopleuronectes americanus also showed a much lower toxic response to chloramine than to chlorine: one hundred percent mortality occurred at 0.55 mg/L TRC with free chlorine and 2.55 mg/L for chloramine. Behavioral aberration occurred at 0.20 mg/L and 1.5 mg/L, respectively (Capuzzo et al. 1977). It seems, however, that sensitivity of the American oyster C. virginica to the two chemicals is quite different from that of fish: for larvae of the oyster, 48 h LC50 was 0.12 ±0.01 mg/L TRC with free chlorine, and less than 0.01 mg/L for chloramine (Goldman et al. 1978).

While bromines are stronger oxidants than chlorides, there is apparently no great difference between chlorine and bromochlorine toxicity. But bromochlorine residuals decay more rapidly than chlorine residuals, and in some cases bromochlorine is less toxic than chlorine to aquatic organisms. Under the same experimental conditions, 100% survival of the American oyster was 0.081 mg/L TRC with chlorine and 0.062 mg/L for bromochlorine. For juvenile spot L. xanthurus, approximately 75% survived at 0.032 mg/L TRC with chlorine and 0.045 mg/L TRC with bromochlorine. Adult spot had an LC50 of 0.48 mg/L TRC for chlorine and 0.41 mg/L TRC with bromochlorine. The clam Rangia cuneata had 100% survival at 0.062 mg/L with chlorine and 0.81 mg/L TRC with bromochlorine (Liden et al. 1980).

ACCLIMATION OF ORGANISMS TO CHLORINE

During a seven-week experiment on the acclimation of fathead minnow Pimephalas promelas to chlorine or bromochlorine, Ward et al. (1976) reported that fish exposed to gradually increasing chlorine or bromochlorine concentrations were able to tolerate higher levels of the halogen to which they had been exposed than fish that had not been acclimated. For unacclimated fish, TL50 was 0.082-0.095 mg/L TRC. The acclimated fish could survive exposure of one week up to 0.138 mg/L TRC, whereas the unacclimated ones all died within 68 h. At a concentration of 0.504 mg/L TRC, 100% mortality for unacclimated fish occurred within 1.5 h whereas the acclimated fish lived for 20 h.

Roberts and Gleeson (1978) found that when American oysters were exposed to 0.026 mg/L TRC, at first their shell movement and pumping decreased, but they were later able to tolerate prolonged or repeated exposure. Galtsoff (1946) also reported the development of tolerance of American oysters to repeated treatment of chlorine. Both of these results indicate the importance of distinguishing between the physiological effect of acclimation on tolerance to chlorine and the effects of age and other biological factors on tolerance.

RECOMMENDATIONS FOR FURTHER RESEARCH

There is abundant literature concerning chlorine effects on aquatic life. Although previous literature review papers have discussed specific needs in research, there are several important issues which need more attention than has formerly been given.

1. The physiology and biochemistry of chlorine effects on aquatic organisms.

   Although a variety of physiological and biochemical parameters have been used in chlorine toxicity studies, the cause-effect relationships in most cases have not been well defined; neither are the biological significance of changes in these parameters, particularly the serum biochemical parameters, well established. Specifically:

   How does chlorine affect the biochemistry of the organism? For example, it has been reported repeatedly that oxygen uptake is impaired by chlorine toxicity. Although gill damage and heavy secretion of mucus of the gills have been related to chlorine toxicity, more research is necessary to define the specific mode and effect, for example, the effects on respiratory enzyme activities, cell membrane structure, and transportation of oxygen across the membrane.

   What is the mechanism of avoidance responses to chlorine? Avoidance responses allow motile organisms to avoid toxicants. But by comparing LC50 values and chlorine concentrations for avoidance, it is obvious that the thresholds for avoidance wanted a strong response and may differ greatly, depending not only on the species, but also on the experimental conditions. The dependence of these differences in threshold on physiological and environmental factors requires further study.

2. The interaction of chlorine and environmental factors such as ΔT, light intensity, dissolved oxygen (DO) and salinity.

   The study of the interaction of chlorine and temperature changes is well under way. How DO affects chlorine toxicity is beginning to draw attention. Meldrim and Fava (1977) showed that chlorine-avoidance response of Atlantic silverside M. menidia was most sensitive (0.03 mg/L TRO) with a combination of high light intensity and low DO and least sensitive (0.20 mg/L TRO) with high light intensity combined with high DO.

   If these results may be generalized, then the optimal time of day for discharge of chlorinated water should be determined by, among other parameters, the eutrophic level of the receiving waters. In receiving waters abundant in phytoplankton and/or macrophytes, it would be expected that DO would be low in the early morning when light intensity is low and become much higher on sunny days. The relatively low sensitivity of fish to chlorine at high DO could cause more harm than at other times of the day, because fish would not respond by avoidance behavior to

low, though potentially harmful, concentrations of chlorine.

Better understanding of these complicated situations requires development of predictive models to explain the nature and consequences of multi-factor interactions. Such an understanding is critical for the development of policies to regulate the discharge of chlorinated water.

3. The toxicity of chemicals used as chlorine alternatives and their derivatives to aquatic organisms.

Some work has been done on acute toxicities. Much more work must be done on sublethal effects.

4. The fate of chlorine in the Bay, and the toxicity of its various by-products formed under different water qualities.

Chlorine decays rapidly. In most cases, it is difficult to detect chlorine 1-2 km away from the discharge point. On the other hand, the detection limit of chlorine by methods used in most field studies is about 0.01-0.02 mg/L. In other words, when chlorine exists in the environment at concentrations sublethal to aquatic organisms or in chemical forms of which we are not well aware, they may not be detected. It is imperative that we know more precisely where all the chlorine goes in the estuary. Since both sewage and water in the estuary are rich in organic matter, it is especially important to examine organohalogens, which are known to be toxic. The possibility of a build up of these compounds in water and in aquatic life should also be investigated, although at present we may be limited by analytical technology.

5. Comprehensive field studies of chlorine effects.

Very few field studies have been conducted. Even the best field study, the James River fish kills in 1973 and 1974, is not conclusive. The gap between field investigations and laboratory experiments much be bridged before much of the valuable information obtained from laboratories can be applied to solving practical problems and to improving management of chlorination in power plant and sewage treatment plant chlorination practice.

In the process of writing this review paper, we became increasingly aware of the fact that, although it is well known that a large quantity of chlorine enters the Bay area daily and that it can do damage, there is in fact very little information documented regarding the actual concentrations of chlorine at these discharge points and at a certain distance away from discharge points. Even less is known about the actual effect of these discharges on aquatic life in the areas concerned. Since chlorine toxicity is dependent on its concentration, the evaluation of its actual impact in the Bay must be based on the knowledge of concentration of chlorine in the Bay. More in situ studies are essential.

It is apparent that only recently do we have the essential parameters of models which are capable of describing accurately the behavior of chlorine once it reaches the aquatic environment. Gowda's (1980) model would perhaps require some means of calibration other than the chloride ion in the estuarine environment; nevertheless, it may offer the best means currently available for providing predictive capability in the Chesapeake system.

The development of a detailed Bay-wide model through plant by plant examination is unrealistic, although useful information capable of limited extrapolation may be obtained from a preliminary study using key treatment plants. These may be selected on the basis of hydrographical characteristics, and the models obtained would require verification by field analyses. In addition to chlorine discharge levels that are currently available from the plants concerned, accurate records of both effluent flow and river flow would be required, together with water quality parameters likely to affect chlorine decay rates such as temperature, salinity and total organic nitrogen. Significant amounts of this information already exist through the U.S. Geological Survey Water Resources Data for Maryland and Delaware although to our knowledge there is a lack of sufficiently detailed data to initiate a modeling program at present.

By selection of "key" plants on the basis of chlorine discharge, water chemistry and hydrography of the receiving water, it may be possible to categorize discharge sites with reference to the "limited use zone" concept. It is clear that this represents a more realistic appraisal of the behavior of chlorine in the environment than other models currently available.

It is essential that more data are obtained on the effect of chlorine on biota in the environment. In order to determine if there is an unequivocal link to chlorine, the cooperation of power plant and sewage treatment managers must be sought. If, for example, advance notice can be given of periods of low or high chlorination (for whatever reason), then it may be possible to conduct meaningful "caged animal" experiments in selected areas. Data from such field experiments together with improved field analysis programs can only benefit the long-term protection of the Chesapeake Bay and its riverine system.

VII

Chlorine Models and Their Application to the Field

When assessing the impact of chlorine on the environment, the investigator is immediately confronted by the lack of available field data for chlorine produced oxidants and other chlorinated compounds.

Despite a comprehensive body of laboratory information regarding the toxicology of these compounds to a wide variety of organisms, we are still largely unable to evaluate their true impact in the field. When a chlorinated effluent is discharged into an estuarine environment we need to know the characteristics of its dispersal before we can assess possible damage to the ecosystem: Several important qeustions need to be addressed.

Within the context of the estuarine environment, does the river immediately impacted by the effluent represent an area of high sensitivity? For example, is this an area of particularly high productivity? Does it represent a potentially important nursery area for key species? We know, for example, that between them the Chesapeake and Delaware Canal and the Potomac River are responsible for more than half of the striped bass in the Chesapeake Bay system and that the Choptank and Nanticoke rivers supply another 10-15% of the Chesapeake Bay stocks of this species.

With anadromous species, this raises the question of the completeness of the barrier to these organisms represented by an effluent plume from a sewage treatment plant or a power plant. In the latter case where volumes of water taken from the river system may be very large, the problem of entrainment of pelagic organisms in highly chlorinated water, at least for short periods, must also be addressed. For example, the Chalk Point Power Plant on the Patuxent River draws 1-2 million L of water through its condensers every minute, a flow rate approaching the summer freshwater flow rate in the entire river. The entrainment in such large volumes extends the problem beyond a simple consideration of the extent and effect of the effluent plume alone. In power plant effluents, the effects of temperature increases can never be entirely separated from those of chlorine.

Because of the paucity of field data on chlorine produced oxidants and chlorinated organics, it has been necessary to invoke models of varying complexities in order to assess the likely impact of chlorine on the environment. The conceptual model of Mattice and Zittel (1976) was developed, within the limits of known toxicological data, in response to a need to evaluate and limit chlorine discharge. The model is relatively simple with respect to chlorine

chemistry insofar as toxicity estimates are based on total residual chlorine only. The authors direct their remarks to power plant chlorination, although they acknowledge that very low levels of the type of organochlorine complexes likely to be associated with organically enriched effluents, for example from wastewater treatment plants, may significantly alter the toxicity profile of that effluent. From the inspection of a large body of experimental data concerning total residual chlorine toxicity to a large number of species, Mattice and Zittel (1976) constructed graphs relating exposure time to TRC concentrations for freshwater and marine organisms. Using the following conversion factor:

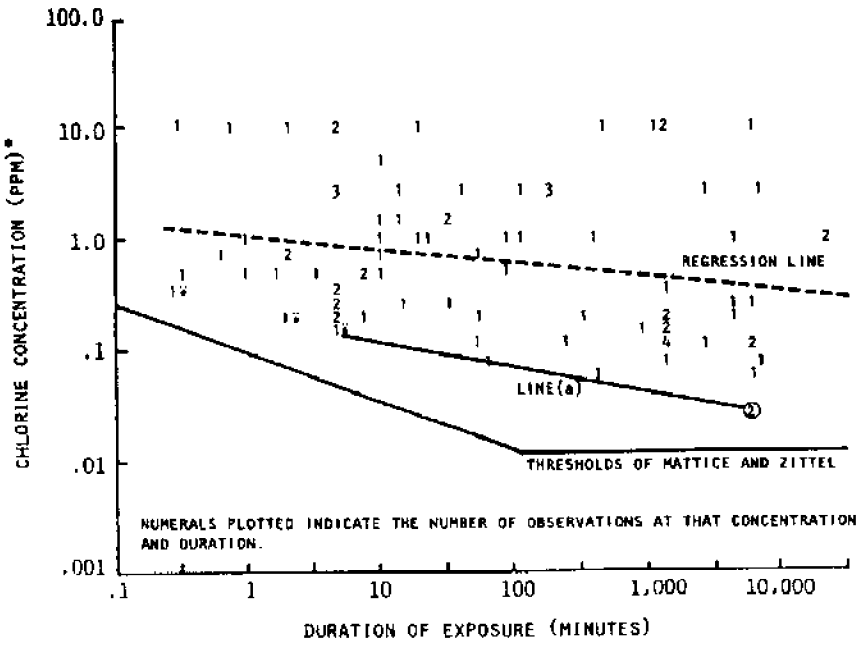
$$y = 0.37x,$$

where x = time (min.) to yield 50% mortality and,
y = maximum time (min.) to yield zero mortality,

Mattice and Zittel constructed acute and chronic toxicity thresholds encompassing all data points as they would exist after conversion from 50% to 0% mortality. These threshold lines are shown in Figure 6 and represent boundaries separating toxic from nontoxic effects. The Mattice and Zittel model represents a useful attempt to deal with the problem of chlorine toxicity in a practical way and has been accepted by the Environmental Protection Agency (EPA) as the basis of their permitted TRC concentrations. These criteria are 2 µg/L for salmonid fish and 10 µg/L for other freshwater and marine organisms.

However, the Mattice and Zittel model has been criticized for a number of reasons. The positioning of the acute and chronic toxicity threshold lines was seen by Thayer et al. (1978) to be somewhat arbitrary and determined by only a few data points. They further question the rationale for drawing both a chronic and an acute toxicity threshold line, and maintain that the data could equally well have been enclosed by a single line (line (a) in Figure 8) touching the lowest data points and almost parallel to the overall regression line. The inclusion of freshwater species in the determination of a median-to-zero (mortality) conversion factor which is applied to marine animals is considered by Thayer et al. (1978) to be unacceptable on the grounds that the difference in chlorine chemistry in saline and freshwater creates entirely different toxicity characteristics, thereby altering the slope of a dose-dependent toxicity curve and, therefore, the relationship between a "50%" and a threshold toxicity level. Using purely marine species, Thayer et al. (1978) arrived at a "marine conversion factor for median-to-zero mortality of 0.53.

A major criticism of the model of Mattice and Zittel was its lack of compatability among some data sets, insofar as the model included a mixture of results from studies of free residual chlorine, combined residual chlorine and total residual chlorine. Thayer et al. (1978) point out that TRO cannot be derived from data reporting concentrations of free or combined residual chlorine. Apart from differences in what is being measured the analytical techniques forming the basis of the Mattice and Zittel (1976) data base have also been seriously questioned on the grounds that the data were inadequately reported, imprecise (orthotolidine) or applied beyond their range of sensitivity.



STATISTICS CALCULATED FROM THE DATA

REGRESSION LINE

EQUATION: LOG CONCENTRATION = .03 + (-.15) LOG DURATION

ANALYSIS OF VARIANCE:

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F-VALUE	P
Attributable to Regression	1	3.5812	3.5812	8.0248	>.005 <.01
Deviation from Regression	90	40.1637	.4463		
Total	91	43.7440			

MULTIPLE CORRELATION: .29

STANDARD ERROR OF ESTIMATE: .67

*INCLUDES FREE RESIDUAL, COMBINED RESIDUAL AND/OR TOTAL RESIDUAL CHLORINE-INDUCED OXIDANT CONCENTRATIONS.

"POINTS CRITICAL IN DETERMINING SLOPE OF MATTICE AND ZITTEL'S ACUTE THRESHOLD.

POINTS CRITICAL IN DETERMINING POSITION OF MATTICE AND ZITTEL'S CHRONIC THRESHOLD.

Figure 6. Mattice and Zittel (1976) model (after Thayer et al. 1978). Data points refer to LC50 values. Numbers refer to number of observations per data point.

(iodometrically determined TRO less than 1 mg/L). A re-evaluation of the data base was made by Thayer et al. (1978) who included in a revised and updated model only information derived from investigations using ferrous DPD or amperometric techniques. The revised toxicity data plotted as log TRO concentration versus log exposure duration showed a highly significant correlation which led those authors to become skeptical of the existence of separate acute and chronic toxicity thresholds as defined by Mattice and Zittel. Thayer et al. (1978) derived an acute toxicity threshold line by lateral (and parallel) displacement of the overall regression line using a factor which protected the most sensitive species (i.e., that species whose set of data points have the greatest mean distance below the regression line). The existence of a chronic toxicity threshold was viewed with some skepticism by Thayer et al. (1978) although this threshold was included in their model (Figure 7) to ensure compatability with the Mattice and Zittel model. In an investigation of a wide range of species including Acartia, Crassostrea and Fundulus, Goldman et al. (1978) concluded that threshold levels of sublethal responses to total residual oxidants, could not be obtained for invertebrates although threshold levels for lethal responses were discernable for both vertebrates and invertebrates. In a study of the blood chemistry of coho salmon exposed to total residual oxidants, Buckley et al. (1976) found that some low halogen concentrations resulted in no noticeable effects even after long exposure times. It was this lack of certainty regarding boundary conditions for sublethal effects which prompted Thayer et al. (1978) to omit sublethal data from their model. The resulting "Envirosphere" model (Thayer et al. 1978) is less conservative than the Mattice and Zittel model. For example, at their widest point of divergence (>100 min. exposure time) the threshold levels differ by a factor of nearly 10.

It must be remembered that the thresholds and exposure times obtained from these models are derived from laboratory experiments and have questionable relationships to a field situation. It is only realistic to refer to exposure times where the boundaries of the contaminated water body and the biota densities within that water body can be clearly defined. In the field this has proved exceptionally difficult except perhaps within a power plant entrainment situation where measurement may be made of such parameters as the volume of water flow and residence time, number of organisms and levels of chlorination.

The entrainment situation provides a natural "laboratory" to study aspects of chlorine chemistry which have an important bearing on how the chemical may be expected to behave in the natural environment. Most of the work done in this regard concerns "within-plant" assessments of chlorine behavior and has been carried out to facilitate management practices which will ensure compliance with effluent limitations under the National Pollutant Discharge Elimination System. Current effluent limitations for power plants are based on measurement of free residual chlorine and stipulate a 30-day average concentration of 0.2 mg/L free residual chlorine to be applied at a single unit for a maximum period of 2 h within any 24 h period. The Federal Register (1976) gives an instantaneous maximum concentration of 0.5 mg/L free residual chlorine. For sewage treatment plants, 0.5 mg/L total residual chlorine is the recommended concentration required to provide a reduction in the coliform

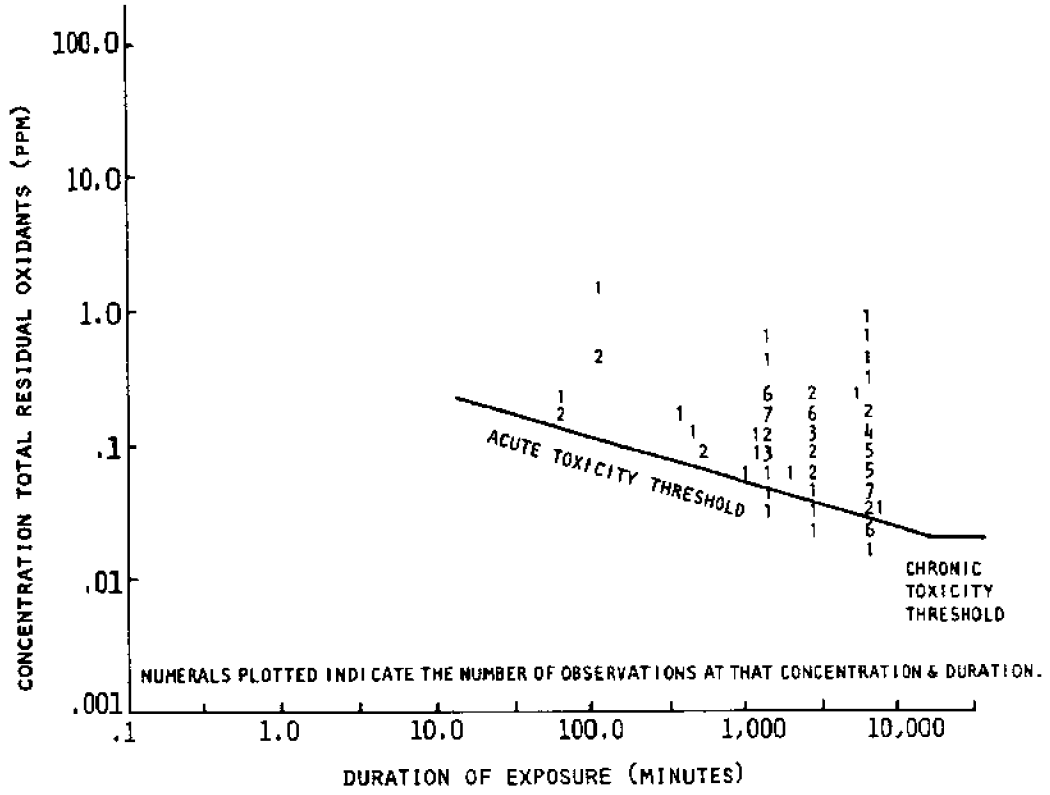


Figure 7. Alternative toxicity model (after Thayer et al. 1978). Data points refer to LC50 values. Numbers refer to number of observations per data point.

count, and a number of authorities (e.g., state of Ontario, Canada) regard this as a required level for contact chamber discharge. Most models relating chlorine feed to discharge levels have been developed for the electricity generating industry and begin with a mathematical model which may be modified empirically depending on site-specific field data. Work done by the Argonne National Laboratory (Draley 1973) showed that at a maximum concentration of 0.53 mg/L, about half of the combined chlorine species, were lost across a natural draft cooling tower. Their equations were formulated using a mass balance approach and involved no chemical reaction kinetics. Constants were used to match field data. A similar approach was used by the Environmental Protection Agency (Nelson 1973) to predict total residual chlorine levels for cooling tower blowdown. However, although eight operational alternatives were incorporated into the model, no field data were presented to validate the model.

The importance of field verification in developing such models is illustrated by the work of Sugam and Helz (1977), who measured oxidant levels in chlorinated water before and after passage through the condensers of the Chalk Point steam electric generating plant. These studies show that more than 90% of the oxidant added to the cooling waters disappears before the water emerges from the plant. After eliminating most of the obvious parameters affecting this decay, these authors conclude that reactions with organic carbon or organic nitrogen, either in the dissolved or suspended state, are largely responsible. Sugam and Helz (1977) also speculate on the possible influence of the component metals of the condenser tubing in catalyzing self-decomposition oxyanions. The high decay rate observed by Sugam and Helz (1977) means that, although the power plant normally uses a Cl_2 dose in the range 1-2 mg/L, the period of time that an entrained organism would be exposed to concentrations greater than 0.05 mg/L as Cl_2 is less than 30 min. The period of time that such an organism would be exposed to concentrations greater than 0.1 mg/L is probably less than 10 min. Bongers et al. (1977) also report similar decay characteristics from the Morgantown Power Plant on the Potomac River.

Mathematical models simulating chlorine decay on power plants have become more sophisticated in recent years and place increasing emphasis on the role of organic constituents of the water body in the decay process. The model of Zielke and Moss (1980), developed for closed cycle cooling systems, has been backed up by field work which indicates that the relationship between chlorine demand and time could be represented by the equation:

$$D = kt^n,$$

where D = chlorine demand
k = chlorine demand at a unit time
t = contact time
n = slope for plot of log chlorine demand versus log of time.

The value of the exponent n gives the speed of the reaction and is related to the types of compounds in the water reacting with chlorine. Low values of n indicate the presence of compounds causing rapid initial chlorine demand. Examples of such compounds are the inorganic ions S^{--}, Fe^{++} and NO^{-}_{2} which

reduce the chlorine to chloride. Higher values of n are indicative of slower reactions with more complex organic material. Field data reported by Zielke and Moss (1980) almost always resulted in a high value for n, (> 0.2) signifying the presence of larger and more complex nitrogen compounds that could represent a major portion of the chlorine demand. Bearing in mind the overriding importance of bromine in saline environments in creating bromine analogs to chlorine, it is clear that the organic nitrogen content of the water plays a very important part in the decay of the oxidant. The enormous number of chloro- or bromo- organics likely to be produced in a sewage treatment plant together with the estuarine environment presents engineers, modelers and biologists with two central problems.

1. The creation of a general model which accurately describes the level of oxidant at the outfall of a power plant or sewage treatment plant is a virtually impossible task, and most existing models contain a variety of tuning variables which correct empirically for characteristics intrinsic to the individual plant and environmental variables such as temperature, light, salinity and the organic content of the water.

2. Even where decay models reach an acceptable degree of accuracy in predicting, for example, total residual chlorine, an array of halogenated organic compounds is produced, particularly within a sewage treatment plant, many of which are close to or below detectable limits and which often have unknown toxicological characteristics.

Until recently the problem of modeling oxidant levels beyond the confines of the plant itself has not been addressed in any detail. In a Danish study attempting to model chlorine input from a throughflow power plant to a seawater environment, Høstgaard-Jensen et al. (1977) concluded: "During the investigations it became clear that through kinetic studies it was impossible to reach a quantitative description of general validity on the decay of chlorine because the chlorine/sea water system is so complex. It has been necessary to limit the studies to only one reactant of the chemical reactions, namely residual chlorine. What can be said of the other reactants and products is very limited and mostly based on speculations." In many ways their approach is similar to, though much less comprehensive than, Sugam and Helz (1977). Field data from the Danish study indicated that chlorine decay enabled a residual chlorine concentration of 0.05 mg/L to be reached by mixing with a volume of receiving water only 0.115-0.15 times that which would be required assuming dilution alone. Høstgaard-Jensen et al. (1977) found improved decay rates in the presence of light and advocated daytime chlorination where possible. In the field, a suite of residual chlorine measurements were used to draw isoconcentration lines. These indicated nighttime residual chlorine levels less than 0.05 mg/L within 300 m of the outfall. During the day this distance was reduced to 200 m.

Most of the models mentioned above were developed to assist power plant management and to facilitate compliance with effluent limits for residual chlorine. These in turn have been developed in response to toxicological data

(e.g., Mattice and Zittel 1976), but until recently attempts to model chlorine in the environment beyond to "end of pipe" situation have been virtually nonexistent. Although decay rates and associated parameters have been incorporated into these "compliance models," once the chlorine has been released into the environment it has essentially been treated as a conservative pollutant (i.e., effluent controls have been dictated by likely dilution effects only). In management terms, this makes sense as it leads to conservative estimates of permissable residual chlorine levels although it does little to indicate the "real world" situation.

In the absence of adequate field data, estimates of residual chlorine in an estuarine environment can only be made through the use of detailed models which go substantially beyond the end-of-pipe situation and which address the total impact of chlorine and chlorine produced oxidants on the estuarine system. Such models must equate effluent chlorine levels and effluent discharge rates with river water chemistry and hydrographical characteristics.

These considerations present extraordinarily complex problems to hydrographical engineers. An effluent discharged from a shoreline location or from a pipeline stretching some way from the shoreline will disperse in such a way as to produce concentration gradients in transverse (across the river), longitudinal (downstream) and vertical directions. The distance between the outfall and the point at which the effluent plume reaches both banks of the river/estuary is known as the "crossing distance." Even at this point, transverse concentration gradients may exist for the particular pollutant in question, and it is not until the pollutant concentration has become "homogenized" with respect to the cross-sectional area of the receiving stream that the end of the "mixing zone" is reached. In order to accommodate the conflicting needs of effluent discharge and the protection of biota, regulations adopted by water management agencies generally allow for localized areas within the mixing zone where the pollutant concentration exceeds a specified instream criterion. This is called the "limited use zone." The remaining portion of the receiving water, which represents a safe habitat for aquatic life is termed the "zone of passage." A schematic view of the mixing zone of a stream is shown in Figure 8.

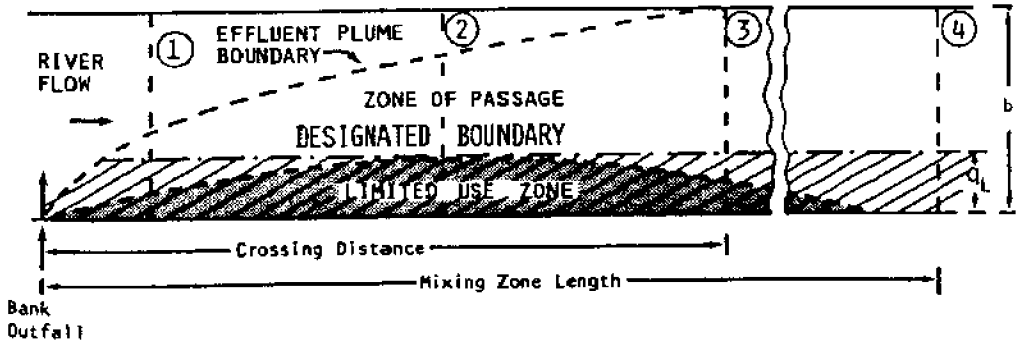


Figure 8. Schematic view of mixing zone (after Gowda, 1980a).

The boundary of the limited use zone in a relatively shallow river is generally identified by the transverse and longitudinal coordinates with respect to the outfall. Usually the lateral boundary of a limited use zone is limited to the range 0.2-0.4 times the river discharge. For a bank outfall, the maximum longitudinal boundary of the limited use, zone occurs along the discharge shoreline. Within the designated lateral boundary of the limited use zone a specified pollutant concentration criterion must be met. A longitudinal profile along the lateral boundary of the limited use zone indicates a maximum concentration of pollutant at a point (termed the "critical point") some distance (termed the "critical distance") downstream from the outfall. The variables affecting these parameters include river and effluent flow rates and the concentration of the pollutant in the effluent. This system has been investigated with respect to both ammonia and residual chlorine by Gowda (1978 a, b, c; 1980 a, b) in a series of papers which represent the most complete modeling study to date of chlorine in the aquatic environment. Gowda's model is a modification of the stream tube model, developed by Yotsukura and Cobb (1972) and aims (1) to account for longitudinal variabilities in decay rate coefficients for a non-conservative pollutant such as chlorine and for changes in hydraulic parameters of the channel and (2) to develop analytical expressions and procedures for computing critical point coordinates, allowable effluent concentration and maximal longitudinal spread of the limited use zone.

The model was calibrated with the chloride ion which was found to be a suitable marker for the plume from a number of sewage treatment plants and was tested with respect to chlorine on the Alliston sewage treatment plant on the Boyne River in Ontario using field data that have been gathered by Wisz et al. (1978). The model validation was tested at three transects A, B and C, respectively, 21, 61 and 183 m, below the Alliston outfall. None of the lower transects yielded TRC values. The relationships among observed TRC concentrations and those predicted using Gowda's model are shown in Figure 9. The values Q_e, Q_r, C_e refer to effluent flow rate, river flow rate and effluent TRC concentration, respectively. Based on these figures, the distribution of TRC along the lateral boundary of the limited use zone in the Boyne River has been plotted (Figure 10) for two different boundary conditions (P_L). These values of P_L are dimensionless insofar as they are expressed as a function of the river flow (Q). Where P_L = 0.25, the boundary of the limited use zone comes closer to the outfall bank and, therefore, has higher TRC concentrations.

Several important observations emerge from this work:

1. The close proximity of observed and predicted data indicates that the model accurately describes an environmental situation involving a chlorinated sewage effluent.

2. The critical point is clearly seen from the model and the verifying field data.

3. The Ontario Ministry of the Environment Water Quality Objective for TRC, like that of the U.S. Environmental Protection Agency, is 2>µg/L, a value clearly exceeded in this instance.

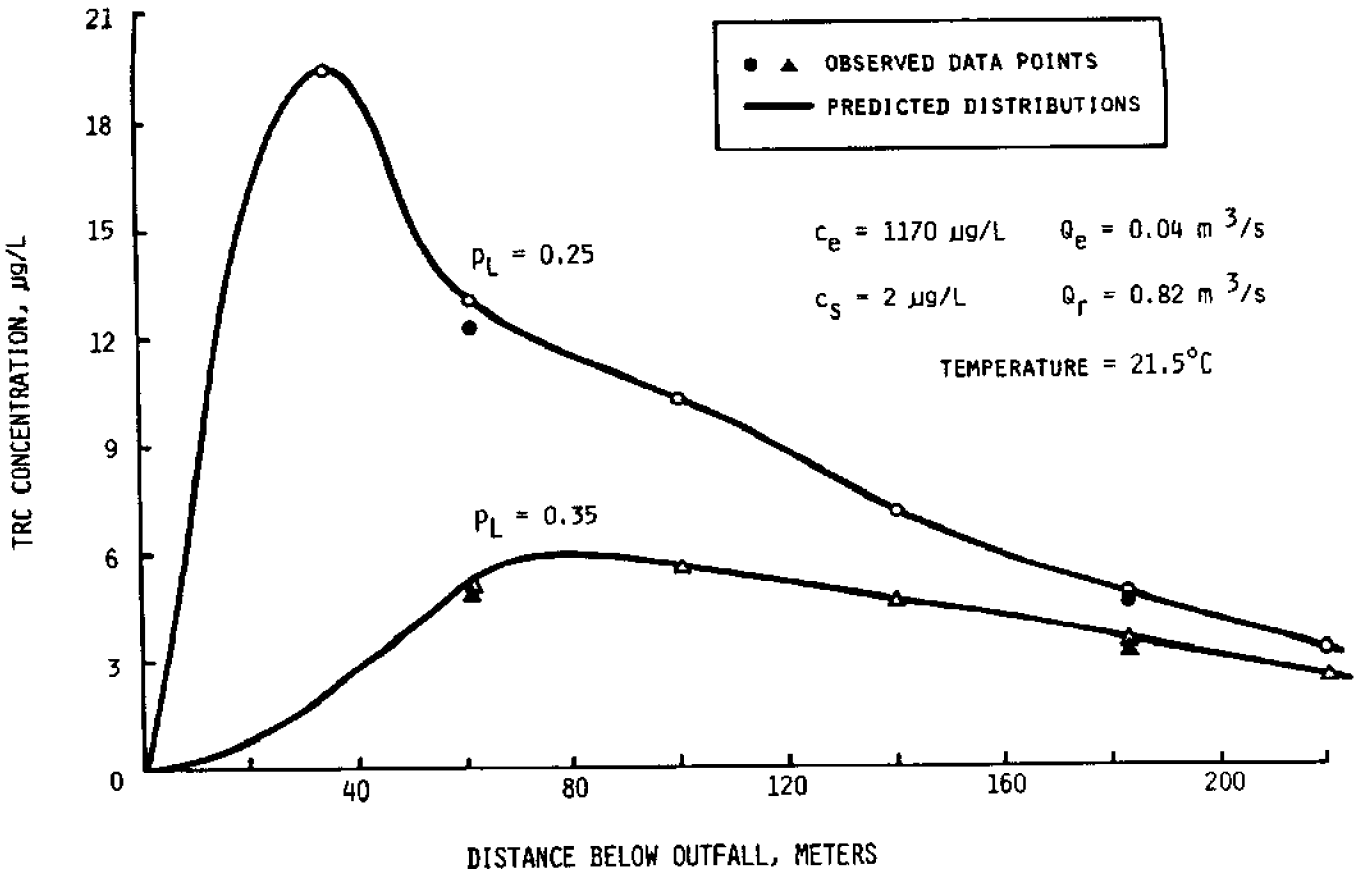


Figure 9. Distribution of TRC along the lateral boundary of Luz in the Boyne River (from Gowda, 1980a).

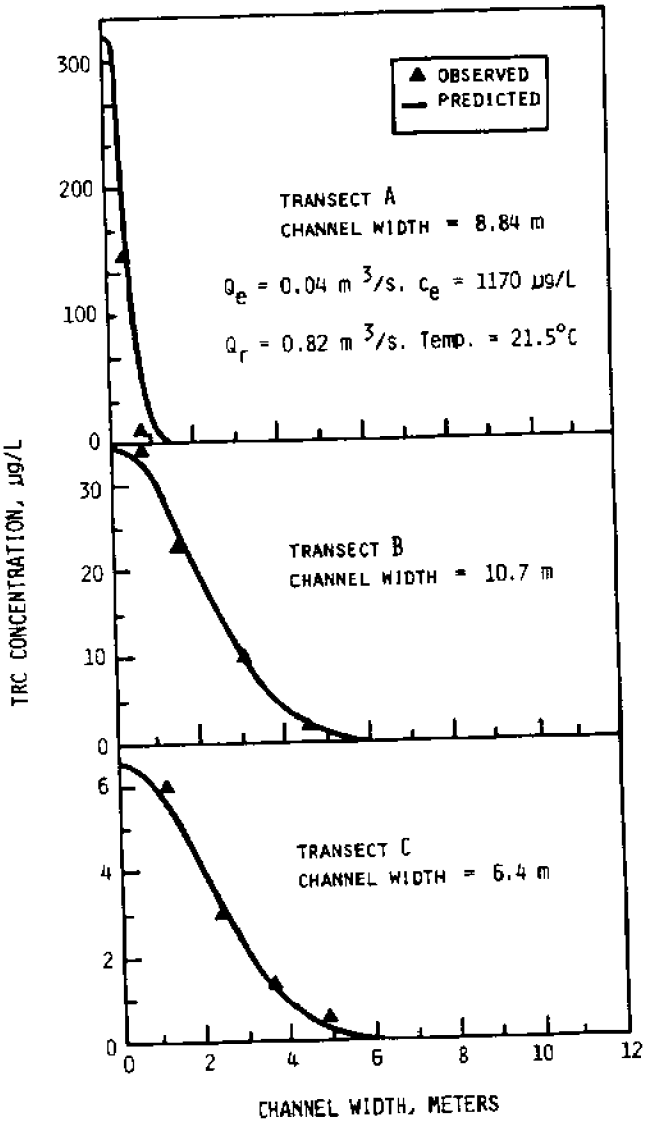


Figure 10. Distribution of TRC along the lateral boundary of the limited use zone in the Boyne River (from Gowda, 1980a).

In the case of discharge from a bank outfall, it is inappropriate to determine the allowable effluent chlorine concentration based on the assumption of instantaneous complete mixing (as well as the dilution ratio, streamflow rate, effluent flow rate) because (1) in some cases it may lead to a limited use zone with too large a lateral boundary (and, consequently, too small a zone of passage) due to an underestimation of treatment required; and (2) in other cases, it may result in too small a limited use zone due to the prediction of treatment requirements that are too stringent in comparison with those based on the limited use zone concept (Gowda 1980).

With improved knowledge of avoidance responses by fish to chlorine (see previous chapter) it may eventually be necessary to 'factor in' such responses to a model which describes the chlorine threat to an aquatic acosystem. Given the complexities of chlorine chemistry and the differential loading of the system by nutrients and organic contaminants it is likely that such a model will be at least river-specific and will have periodically updated components concerning pollutant-loading (e.g., nutrients, chlorine, organics), temperature, river flow, tidal/salinity regime (if appropriate) and fishery potential (e.g., species composition, numbers, spawning).

VIII

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