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Effects of Thermal Discharges on the Chemical Parameters of Water Quality and Eutrophication

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ABSTRACT

The temperature dependencies of the major chemical reactions, which are directly involved in the quality of natural waters, are reviewed. The effects of temperature variations on both the position of equilibria and the rates at which equilibria are attained are considered for acid-base, precipitation, gas transfer, complexation, oxidation-reduction, sorption, and biochemical reactions. Because of the small enthalpies and activation energies of many of the chemical processes, temperature variations induced by meteorological conditions and properly designed thermal discharges have only slight effects on chemical equilibria and reaction rates and little or no effect on the chemical parameters of water quality. A review of the current knowledge of eutrophication indicates that, while temperature increases may increase the growth rates of algae, the nutrient flux rather than the temperature controls the biomass of algae during the summer recreational period and the rate of eutrophication of lakes.

RÉSUMÉ

On discute la relation de la température sur les principales réactions chimiques qui affectent directement la qualité des eaux naturelles. Etude des effets des variations de température tant sur la situation d'équilibre que sur les vitesses-de-réaction en ce qui concerne les réactions acide-base, de précipitation, de transfert gazeux, de complexation, d'oxydation-réduction, de sorption et les réactions biochimiques. A cause de peu d'enthalpies et d'énergies d'activation de nombre de ces processus chimiques, les variations de température provoquées par les conditions météorologiques et par des décharges thermiques bien conçues n'ont que de faibles effets sur les équilibres chimiques et les vitesses-de-réaction et peu ou pas d'effet sur les paramètres chimiques de la qualité de l'eau. Une revue des connaissances actuelles en matière d'eutrophication enseigne que, tandis que les hausses de température peuvent accélérer le rythme de croissance des algues, c'est le flux nutritif plutôt que la température qui contrôle la masse biologique des algues durant l'été période de régénération estivale et la vitesse d'eutrophication des lacs.

INTRODUCTION

Temperature is a significant intensive variable in the analysis of natural water systems because of the relatively large seasonal variations and the temperature dependencies of chemical and biological processes. The major sources of thermal energy in the environment are solar radiation, geothermal heating, and waste heat from power production. Since waste heat is released from point sources, man-induced thermal gradients have generated concern in regard to the effects of temperature variations on the chemistry of natural waters.

Thermal discharges differ from other forms of "pollution" in that it is energy rather than matter which is wasted to the environment. Because of the dynamic nature and magnitude of the heat budgets of aqueous environments, thermal energy can be readily dissipated, and residuals such as those imposed by chemical wastes do not persist. However, temperature increases in cooling waters and thermal plumes may affect water quality in the vicinity of the plume. Often those who advocate strict thermal discharge standards cite as justification the deleterious effects that such discharges may have on the various chemical parameters of water quality, such as reduced O_2 concentration and accelerated eutrophication of the receiving water. This paper reviews the effects of temperature variations on the chemistry of natural waters with emphasis on the chemical parameters of water quality and eutrophication. It does not attempt to review the effects of thermal discharges on aquatic organisms such as fish or zooplankton. These topics have received extensive review in the liter-

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ature. The reader is referred to the reviews edited by Krenkel and Parker (1969) and by Mount (1971).

MAGNITUDE OF TEMPERATURE VARIATIONS

In order to discuss properly the effects of thermal discharges to natural waters on the chemical parameters of water quality and eutrophication, consideration must be given to two distinctly different types of situations. One of these is where large amounts of heat are added to small bodies of water in such a way as to increase the temperature of a substantial part of the water 5 to 10° or more above ambient. The other situation is one where thermal discharges are made to a large body of water in a manner which causes highly localized, short duration heating in a thermal plume. The first type is similar to a large thermal discharge to a small lake, pond, or river. The second is analogous to a thermal discharge from electric generating stations on Lake Michigan or other large bodies of water. Each of these types of situations will be discussed in this paper.

The temperature rises induced by thermal discharges become superimposed upon normal seasonal variations of the receiving waters. Although natural water temperatures may vary from 0°C during ice-cover to more than 70°C in thermal springs (Brock, 1970), temperate lakes and streams seldom experience temperatures greater than 25 to 30°C. The utilization of properly designed thermal discharges allows the dissipation of immense quantities of waste heat even though the temperature of the plume remains less than 5°C above ambient water temperatures.

In order to dissipate waste heat efficiently, large volumes of cooling waters are required, and sufficiently large areas are needed for the thermal plume. Temperature distributions and areas for thermal plumes originating from various magnitudes of thermal discharges have been discussed in the literature (see Parker and Krenkel, 1969). Pritchard (1970) has recently reviewed the size and temperature distribution of thermal plumes from large electric power generating stations located on large lakes such as the Great Lakes. He reported that the heat discharged from a 1000 MWE nuclear power plant with a 20°F temperature rise above ambient may be cooled to 1 to 2°F above ambient in approximately 100 acres of area using a high velocity off-shore discharge into a large lake. Although this paper deals primarily with chemical changes occurring in the mixing-zone of thermal discharges, it may equally apply to chemical changes during normal temperature variations due to upwelling in larger lakes (Mortimer, 1970).

In order to understand the role of heated discharges on chemical parameters of water quality, one must consider the path of a pollutant molecule, piece of particulate matter, etc., as it goes through the period of elevated temperature. As this molecule of particulate matter enters the intake works, it is subjected to a greatly increased velocity and shear forces, and passes through the condensers of the electric generating station where there is a rapid rise in temperature in the order of 10 to 20°F. Dependent on the design of the discharge, the elevated temperatures will persist for several minutes and, upon exposure to the lake water and the atmosphere, the chemical pollutant is rapidly cooled in the matter of a few minutes to a few hours to its original ambient condition. It should be noted that by far the majority of the chemicals and organisms present in a thermal plume, arising from a high velocity jet off-shore discharge from a thermal electric generating station, do not pass through the heat exchange condensers of the station. Rather, they are entrained in the discharge water from the lake. Under these conditions, Pritchard (1970) has computed that the maximum period that an organism or chemical molecule that moves with the water would be exposed to elevated temperatures greater than 2°F above ambient from a 1000 MWE nuclear power plant with a condenser discharge temperature of 20°F above ambient is approximately one hour.

With this information as background to the discussion, it is appropriate to consider the various types of chemical reactions that may occur in natural waters and the reactions which influence water quality as a result of increasing the temperature of the water.

TEMPERATURE EFFECTS ON CHEMICAL EQUILIBRIA

Dissociation Constants

Variations in temperature affect the lake system directly through temperature coefficients of various equilibrium constants of the chemical processes and the reaction rate constants which govern the speed of these reactions. The temperature dependence of equilibrium constants for acid-base, complexation, and precipitation reactions are derived from the energy changes due to the hydration of the ions. The dissociations or reactions with positive enthalpies (endothermic processes) vary directly with temperature. For example, the ion product of water varies reversibly from approximately $10^{-14.9}$ at 0°C to $10^{-13.3}$ at 50°C (Hutchinson, 1957). This indicates that the pH of pure water will decrease from approximately 7.4 to 6.6 during a 50°C increase in temperature. Similarly, the first and second dissociation constants for carbonic acid increase from $10^{-6.58}$ and $10^{-10.62}$, respectively, at 0°C to $10^{-6.35}$ and $10^{-10.33}$, respectively, at 25°C (Hawley, 1967). These data indicate that, if the temperature of a lake which has an alkalinity of 3.14 meq/l (as $CaCO_3$) and pH of 8.0 was increased from 0°C to 25°C, the pH may be expected to decrease to 7.78 if only the change in the dissociation constants is considered (Lee and Delfino, 1969). However, the above prediction of the effect of temperature on the pH of natural water is inaccurate because it neglects other more significant temperature dependent processes such as gas solubility.

Gas Solubility

The solubility of dissolved chemical species varies markedly with temperature. The solubility of dissolved gases in natural water varies inversely with temperature, while the overall exchange rate between the atmosphere and water increases with increasing temperature. Of particular interest to the above discussion on the temperature – pH relationship of the water is the temperature dependence of CO_2 solubility in the water. The solubility of CO_2 in pure water at a CO_2 partial pressure of 0.25 mm Hg decreases from 1.1 mg/l at 0°C to 0.48 mg/l at 25°C (Hutchinson, 1957). If an aqueous CO_2 system remains at equilibrium with a CO_2 partial pressure of 0.25 mm Hg as the temperature is raised, the net effect is a decrease in the dissolved CO_2 with a corresponding increase in the observed pH.

Consider a water with an alkalinity of 3.14 meq/l as ($CaCO_3$), pH of 8.0, and a temperature of 0°C at equilibrium with a CO_2 partial pressure of 0.25 mm Hg; if the temperature slowly increases to 25°C during the summer, the net change in the pH of the system is an increase from 8.00 to 8.76 (Lee and Delfino, 1969) rather than a decrease, which was predicted from dissociation constant effects alone.

Solubility

The effects of temperature on the solubility products of salts are similar to the effects of temperature on dissociation constants of acids and bases. In general, the solubility of a salt with a positive heat of hydration increases with increasing temperature. However, the hydration of some processes goes through a transition from exothermic to endothermic in the temperature range of interest (the same is true for some of the dissociation constants of weak acids) (Butler, 1964). The solubility of such salts decreases with increasing temperature to the transition temperature and then increases with higher temperature. An example of the importance of this type of reaction in natural waters is the calcium carbonate system.

The solubility for calcium carbonate at an ionic strength of 6.4 mmols/l decreases from 9.48×10^{-9} at 0°C to 4.55×10^{-9} at 25°C. To demonstrate the significance of the effects of temperature on the calcium carbonate system in natural waters, consider the lake system described above in which calcium is added to the system to produce a calcium concentration of 0.76 mmols/l.

If the water remains at equilibrium with the atmospheric CO_2, the solubility constant at 0°C is 9.48×10^{-9}, while the measured ion activity product (IAP) is 3.60×10^{-9}. Therefore, the system is undersaturated with respect to calcium carbonate. As the water temperature rises, the pH increases owing to the lowering of the CO_2 concentration causing an increase in the carbonate/bicarbonate ratio as defined by the second dissociation constant for carbonic acid. Thus, while the Ksp decreases to 8.19×10^{-9} at 5°C, the IAP increases to 19.2×10^{-9}, and the system is supersaturated with respect to calcium carbonate. At 25°C, the IAP/Ksp ratio approaches 10, and the water is grossly supersaturated by the increased temperature.

The precipitation of calcium carbonate from the supersaturated water is largely controlled by the kinetics of nucleation and particle growth. The rates of nucleation are influenced by the degree of supersaturation and presence of some ions such as magnesium. In Lake Mendota, Wisconsin, the epilimnion waters remain supersaturated during the summer months and do not equilibrate with respect to calcium carbonate (Hawley, 1967). If no precipitation occurs, the cooling of the water to near 0°C in the winter returns the system unaltered to the initial conditions. However, the marl sediments of the lake suggest that calcium carbonate precipitation has occurred, either chemically or through photosynthetic activity of phytoplankton.

When the water is cooled following a period of calcium carbonate precipitation, the system may be expected to have an ion activity product less than that of the previous year. The constancy of the calcium concentrations and alkalinity in Lake Mendota in recent years indicates, however, that the undersaturated waters equilibrate with calcium carbonate in the sediments and the runoff waters brought in during the period of high spring flows and ground water that enters the lake. Thus, although the temperature fluctuations in natural waters may have a significant effect on the dissociation and solubility constants of dissolved species, the effects are largely reversible,and little change in the overall water quality can be attributed to them. Many of these same processes would be expected to occur in the thermal discharge plume; however, where the natural variations in temperature do cause changes in water quality as a result of their effect on the chemical parameters, the slight increase in temperature in the relatively small area of the discharge plume would not have a significant effect above that expected for the natural temperature variations.

Sorption

Other important types of reactions that occur in natural waters and are influenced by temperature are sorption type reactions. These reactions are discussed separately from the other types of reactions since the magnitude of the temperature effect is often different from that found in most acid-base, complexation, precipitation, and redox reactions. Sorption phenomena may be divided into chemisorption processes with the enthalpy of the reaction being 10 to 20 Kcal/mole and physical sorption with the enthalpy of the reaction being approximately 2 to 6 Kcal/mole (Hayward and Trapnell, 1964). Since the entropy decreases in sorption reactions, the processes are exothermic, and a temperature increase normally results in a decrease in the extent of adsorption. For many physical adsorption processes, the enthalpies of the desorption reactions are similar to those of crystallization and condensation, and small temperature changes do not significantly affect the extent of sorption. It should be pointed out that the experimentally observed enthalpy is the "apparent enthalpies", since it is a composite energy change of hydration and solubility in addition to sorption. For example, the adsorptions of dieldrin and lindane on sands have enthalpies of -2.75 and -4.88 Kcal/mole, respectively, which are typical for physical adsorption processes (Boucher, 1967). Similarly, the sorptions of sulfonated alkyl benzene compounds on carbon have enthalpies of approximately -1.4 Kcal/mole (Weber, 1967) and show only small temperature dependence. Therefore, normal sorption processes, which are likely to occur in natural waters such as the uptake of phosphate by clay minerals, show little temperature dependence, and the amount of sorption in the temperature range of natural waters is largely independent of temperature. Any chemical species whose concentration is likely to be influenced by the sorption process would be unaffected by small variations in temperature.

Chemical Kinetics

The velocity of a chemical reaction is directly related to the temperature through the Arrhenius equation:

$$\frac{d \ln k}{dt} = \frac{E_{a_2}}{RT}$$

where k is the rate constant, E_a is the energy of activation, T is the absolute temperature, and R is the gas constant. If the reaction process is viewed as the formation of an activated complex which dissociates into products of reaction, the enthalpy of activation is approximately equal to E_a, since changes in the pressure and volume may be neglected in aqueous systems. Because the enthalpies of activation for a wide variety of chemical reactions are of the same order of magnitude, it is generally estimated that the rate of a chemical reaction increases by a factor of two with each 10°C rise in temperature. Similar approximations have been made for the rates of biochemical reactions, although the temperature range for which the approximation holds is much more limited. Studies by Stumm and Lee (1961) have shown that some chemical processes, such as the reactions between ferrous iron and dissolved oxygen, do not have activation energies sufficiently large for the reaction rate to double for a 10°C increase in temperature. This reaction, in particular, has a much smaller activation energy and, therefore, has a much smaller temperature dependence than most chemical reactions.

As a pollutant molecule passes through the electric generating station, there is an opportunity, prior to the time that it cools to ambient conditions in the lake, for an increase in the rate of chemical reactions. The fact that most chemical reactions are more rapid at increased temperatures will not, however, result in a significant effect on the chemical parameters of water quality, except in those situations where large amounts of chemical pollution of the waters have recently occurred or where two water masses of distinctly different chemical characteristics are mixed just prior to entering the intake works of the electric generating station. In other words, for most natural waters the rate of change in the chemical parameters of water quality is sufficiently slow, compared with the excess temperature-time relationship normally associated with the thermal plume, so that significant changes in the chemical parameters of the water are unlikely. Also, many of the chemical-biochemical transformations that occur in natural waters result in a diminution of pollutants and enhance more desirable water quality characteristics. Therefore, any hastening of the normal rates of self-purification may result in improved water quality rather than its deterioration.

Toxicity of Pesticides

One of the alleged effects of heated discharges, which is supposed to result in deteriorated water quality, is the effect of such discharges on the toxicity of pesticides to aquatic organisms. There is no general relationship between the temperature of natural waters and the chronic toxicity of pesticides to aquatic organisms, because pesticides comprise extremely variable classes of chemical compounds and aquatic organisms have extremely variable responses to them. While it is true that the acute toxicity of many chlorinated hydrocarbons to fish increases with increasing temperatures, there are exceptions such as DDT, where the toxicant is more toxic at lower temperatures (Schoettger, 1970). There are considerable differences between laboratory conditions, where the pesticide is added to a water and the fish or other organism is allowed to accumulate chronic levels, and the much more complex natural water systems, where many factors are acting on the pesticide to influence its concentration and toxicity. The rates of chemical and biological reactions such as hydrolysis and oxidation increase with increasing temperature. Thus, although the toxicity of some pesticides may increase with an increase in temperature, the rate of degradation of the chemical in a heated natural water may also increase. For example, the organophosphorus pesticides degrade initially through hydrolysis of an ester bond. An increase in temperature would result in a much greater rate of increased degradation of these compounds. Chlorinated hydrocarbons such as DDT are dechlorinated to DDE and other metabolites at increased rates with increased temperatures. Also, increased temperatures increase the vapour pressure of the pesticide and favour the loss to the atmosphere where photooxidation can occur.

While it cannot be stated with any degree of certainty whether the toxicity would increase, decrease, or remain unchanged as a result of heating the water, it is appropriate to state that, based on our current degree of understanding of the effect of temperature on these various chemical and biochemical processes that influence the concentration and toxicity of pesticides in natural waters, the normal thermal discharge from an electric generating station would not cause a significant increase in the toxicity of any pesticides present in the discharge plume waters to the aquatic organisms that might be associated with these waters.

TEMPERATURE DEPENDENCE OF OXYGEN UTILIZATION

An examination of the role of temperature on the concentration of dissolved oxygen (DO) illustrates the interactions between physicochemical and biological processes in the chemistry of natural waters. Based on the fact that an increase in temperature increases the rate of oxidation of organic matter and decreases the solubility of oxygen, it may be presumed that waste heat discharges would significantly lower the concentration of DO in the receiving water. However, the observed levels of DO are the result of the interplay between thermodynamic factors such as gas solubility and kinetic processes such as the rate of oxidation of organic matter (BOD), rate of oxygen uptake by the sediments, photosynthetic activity, and rate of reaeration, each of which shows slight temperature dependencies. Since the reaeration rate also increases with increasing temperature, predictions that thermal discharges would significantly lower the DO concentrations in low-BOD waters are generally not substantiated by data from existing plumes (Moore,1958; Slack and Clarke,1965; Davidson and Bradshaw,1967).

To demonstrate the effect of temperature on the DO in low-BOD waters, consider a 20°C to 25°C increase in the temperature of water from the near-shore regions of Lake Michigan. Based on the Fox values for the oxygen solubilities, the 5°C temperature rise would decrease the DO (at saturation) from 9.17 mg/l to 8.38 mg/l at 1 atmosphere, the temperature coefficient averaging approximately 2.5 per cent of the 15°C equilibrium value per °C (R. A. Taft Sanitary Engineering Center, 1958).

Superimposed upon the equilibrium DO concentrations are the removal of DO by deoxygenation processes and the input of oxygen through reaeration and photosynthesis. A first order approximation at modelling these kinetic processes is described by the Streeter-Phelps equation (Fair and Geyer,1961) which neglects the benthic DO demand and photosynthesis. This equation of the form:

$$D = \frac{k_1 L}{k_2 - k_1}\left[e^{-k_1 t} - e^{k_2 t} + D_o e^{-k_2 t}\right]$$

where D is the DO deficit at time t, D_o is the initial DO deficit, L is the ultimate BOD of the water, k_1 is the deoxygenation rate, and k_2 is the reaeration rate, is a convenient method of estimating the DO deficit.

The average 5-day BOD of the near-shore water of Lake Michigan is approximately 1.4 mg/l (U.S. Dept. of Int., 1970). If it is assumed that the water contains an ultimate BOD of 5.0 mg/l, k_1 of 0.23 day^{-1} at 20°C, a k_2 of 0.40 day^{-1}, and no initial DO deficit, the Streeter-Phelps equation would predict that the DO deficit after 1 day and 5 days at 20°C would be 0.90 mg/l and 1.23 mg/l, respectively.

If the temperature of the water is raised to 25°C, each of the operationally defined parameters above increases slightly through the activation energies of the respective processes. The dependence can be estimated with the van't Hoff-Arrhenius equation of the form:

$$X_2 = X_1 e^{C_x(T_2 - T_1)}$$

where X is the parameter of interest, T is the temperature, and C_x is a constant for the respective process. The predicted oxygen deficit at 25°C after 1 day and 5 days would be approximately 1.05 mg/l and 1.31 mg/l, respectively.

It is obvious that the deficit varies directly with the BOD loading, and a polluted stream may exhibit a much larger deficit per °C temperature increase. However, in low-BOD waters such as many of the large lakes, a deficit may not be observed because of increased reaeration through wave action and/or photosynthetic activity.

The previous calculations suggest that a body of water containing organic wastes would have adequate amounts of oxygen to maintain desirable fish life at one temperature, while at an elevated temperature the rate of exertion of the BOD would be increased sufficiently to cause a critical depletion in the dissolved oxygen concentration. Such a situation would occur, however, only if two other conditions are also present: the intake waters of the electric generating station must be grossly polluted, i.e., where large amounts of untreated municipal and/or industrial wastes are discharged immediately adjacent to the intake works, and the elevated temperatures must persist for periods of many hours to days. This type of situation would not be encountered in the majority of the electric generating stations located on large lakes such as Lake Michigan. Commonly, the BOD of the lake waters is in the order of only 1 to 3 mg/l. Increasing the temperature of the water a few degrees will not cause a significant depletion in the dissolved oxygen of the water as a result of increased BOD exertion. This situation is a good example of why it is necessary to consider each individual electric generating station with regard to its potential water quality problems.

A special situation arises in a thermal discharge plume which would tend to counter the full development of the predicted DO deficit. The turbulence levels in many discharge plumes may be such that the supersaturation of the water, with respect to the gases arising from heating the water in the condensers, is not lost to the atmosphere before the water is cooled to ambient conditions. The relatively slow rates of gas transfer that occur in many natural waters would tend to minimize the effects of heating the water in electric generating stations on dissolved gas concentrations. Therefore, for normal situations, where the intake waters do not contain large amounts of organic wastes or are already at critically low oxygen levels, the effect of using the water for cooling purposes probably would have little or no effect on the amount of dissolved oxygen in the water.

MISCELLANEOUS AND CHEMICAL PARAMETERS

Tastes and Odours

The taste and odour characteristics of natural waters are often intensified at elevated temperatures. Therefore, the increase in the temperature of the water could cause a deterioration of water quality. It is unlikely that water supply intakes would be located immediately adjacent to the discharge works of large electric generating stations, and, unless the water has been raised more than 2° when it reaches the water supply intake, there would be no significant deterioration in water quality resulting from tastes and odours in the water. Increasing the temperature of water as it passes through an electric generating station and in the plume of the station's discharge in the order of a few degrees would not be normally expected to change the colour, turbidity, alkalinity, ammonia, various toxic metals and non-metals, aquatic plant nutrients such as nitrogen and phosphorus, and organic compounds to such a degree that there would be a measurable deterioration in water quality.

EFFECT OF TEMPERATURE ON EUTROPHICATION

The eutrophication of natural waters is one of the most significant water quality problems facing North America today. Large amounts of funds will have to be expended in controlling the excessive fertilization of natural waters. One of the frequently cited deleterious effects of thermal discharges in natural waters is an accelerated rate of eutrophication (U.S. Dept. of Int., 1970). The basis for the claim that thermal discharges will cause an increased eutrophication of Lake Michigan and other bodies of water is a result of confusion regarding the relationships involved in algal growth rates at increased temperature, seasonal secession of algae, effect of temperature on nutrient recycling, and the amounts of heating that will take place from a thermal discharge. Three major factors governing the growth of algae in lakes are the temperature of the water, amount of light penetration in the water, and the amounts of aquatic plant nutrients present in the water. Major changes in any one of these will alter the degree of eutrophication of a body of water. For example, in a lake with a certain amount of light and concentration of aquatic plant nutrients at a temperature of 0°C, heating the water to 20 to 25°C will likely produce more algae and also a change in the predominant species. However, the anticipated thermal discharges to large lakes such as Lake Michigan will not cause a measurable change in the overall or even near-shore lake temperature. Based on Pritchard's (1970) calculations, a 1000 MWE nuclear generating station discharge will heat the water a few degrees above ambient for a few hours. Under these conditions, no change in the numbers and types of planktonic algae would be expected in the discharge plume water. This results from the fact that the time-temperature relationship of the water in the plume compared with the growth rates of planktonic algae in natural waters is too small to produce any significant increase in the total number of algae in the water. Algae in natural waters normally require several days to double in numbers. Even if several 1000 MWE electric generating plants were located on the southern Lake Michigan shore, there still would not be an expected effect on the total numbers of algae nor a shift in type, since all reliable estimates of the potential increased temperature show that it would be less than one degree above ambient during the critical recreational period of the summer.

Temperature changes of a much larger magnitude are frequently found in the surface waters of lakes. In Lake Mendota, Madison, Wisconsin, a warm period during the summer will increase the surface temperature of the lake 3 to 5°C above the normal average temperature for that time of the year. These elevated temperatures may persist for several weeks, during which time there is no increase in the numbers of bluegreen algae over those normally found for the cooler water temperatures of the season.

The short-term variation in temperatures that is normally found in a lake during the summer cannot be correlated with changes in the numbers and types of algae present in the lake. It is important to emphasize that the anticipated thermal discharges to large bodies of water such as Lake Michigan will result in small temperature changes in a limited area of the lake. This type of change should not be equated to the seasonal changes in lake temperature that occur from winter to summer. The latter type of temperature change will influence algal numbers and types. However, the former will not cause an accelerated eutrophication in large bodies of water.

Algae and other aquatic plants generally grow at a more rapid rate as the temperature of the water is increased. However, this does not mean that the total biomass, i.e., amount of algae present in the water, will be increased as a result of the increased temperature. The total amount of algae and other aquatic plants present in a given body of water is primarily dependent on the availability of aquatic plant nutrients rather than on temperature. Some of the most productive areas of the world's oceans are the cold waters in the Antarctic and the upwelling areas of cold water from deep within the ocean, while many of the tropical waters are sparsely populated with aquatic organisms. The differences are primarily due to the rate of nutrient supply and have little or no relationship to the temperature of the water. Therefore, unless it can be shown that heating water for a short time, a few degrees above ambient, would increase the nutrient availability within the water, there is no reason to believe that thermal discharges will have any effect on the degree of eutrophication of a given body of water.

While it is true that the rates of mineralization of nitrogen and phosphorus compounds from dead algae and other aquatic organisms increase with increasing temperature, it will be generally found that the time-temperature relationship that will exist in the normal thermal discharge plume of large electric generating stations located on large lakes will not alter to any measurable degree the rate of remineralization of nitrogen and phosphorus compounds in the lake water. The relatively short period of time over which this increase in temperature takes place is too short to be of any significance compared with the normal rates of mineralization of nitrogen and phosphorus compounds. However, thermal discharges to small bodies of water, which increase the temperature of the water 5 to 10°C above ambient, will increase the growth rate of algae and the recycling rate of aquatic plant nutrients from dead algae and sediments. The net result would be an expected increase in biomass of algae in spring and fall for temperate bodies of water.

It is unlikely that the total biomass present at any time would increase in the summer months, since the planktonic algal growth at this time is primarily limited by the nutrient content of the water. However, the frequency of algal blooms would likely increase, resulting in an overall deterioration in water quality. The magnitude of the effect of an increase in temperature on the biomass of planktonic algae is difficult to predict because of the fact that the temperature coefficients of each of the processes involved are not known.

A temperature increase in a body of water may limit algal production for several reasons. The aqueous environmental chemistry of aquatic plant nutrients such as N_2 and P is such that some part of the nutrients present in a phytoplankton population becomes refractory (chemical forms which are not recycled). Therefore, an increase in frequency of planktonic algal blooms may increase the rate at which refractory compounds are formed and deposited in the sediments. Another way in which an increase in overall temperature for a body of water could limit phytoplankton growth in hard water lakes would be in coprecipitation (sorption, solid solution formation, and occlusion) of aquatic plant nutrients such as phosphorus and other trace elements with calcium carbonate precipitation. As previously discussed, the solubility of calcium carbonate decreases with increasing temperature. Therefore, an overall temperature increase in a body of water, especially during the summer period of highest temperatures and pH, would tend to limit algal production in hard water lakes by possibly removing nutrients essential for algal growth.

Special consideration must be given to the growth of attached algae in the region of the discharge plume, since some forms of these algae, especially *Cladophora* do cause a significant deterioration of water quality. At the present time, the factors that influence the growth of *Cladophora* are poorly understood. However, it is clear that there are many factors other than temperature which tend to control its growth. Based on the limited knowledge available, it is reasonable to predict that if a suitable substrate for the attachment of *Cladophora* occurred in the region of the discharge plume, *Cladophora* would be present at an earlier date each spring as a result of heating the water in the order of a few degrees above ambient. This would occur only in the region of the discharge plume. This does not mean that there would be increased amounts of *Cladophora* occurring with the lake or within the discharge plume; it means only that they would occur earlier in the spring. This may not represent a significant effect on water quality, since the amount of increased growth that would occur at a few degrees above ambient may not be perceptible, and the area over which such growth would occur would likely be insignificant in most bodies of water. Observations by the authors on the amount of *Cladophora* present along the shore of Lake Mendota show that the total biomass of this organism is not controlled by temperature in the 15 to 25°C temperature range. Periods of several weeks with temperatures 5° above normal, average summer temperatures do not lead to increased biomass of this organism. To the contrary, often there is an inverse relationship between the total biomass present and maximum summer temperatures. This suggests that some of the growth of *Cladophora* or other attached algae in the discharge areas from electric generating stations may be due to the increased velocity of the water in the area, since increased velocities transport larger amounts of aquatic plant nutrients to the *Cladophora* than would the normal lake circulation.

An often cited effect that could be caused by thermal discharge is a change in the type of algae present in a given lake. Normally, the secession of algae proceeds from diatoms to green to blue-green algae as the water is warmed in the spring and summer. It is generally believed that the blue-green algae has a preference for warmer waters. Since blue-green algae often cause a greater deterioration in water quality than diatoms or green algae, any factors that would promote the presence of blue-green algae would represent a potentially significant deterioration of water quality. However, the factors influencing the secession of the various types of algae are not well understood. While it is generally found that blue-green algae are dominant during the warmer summer months, they are not restricted to this period, and, in fact, some of the highest concentrations ever encountered by the authors have been found under the ice in winter.

If it is accepted that blue-green algae would be more dominant under warmer conditions, then one must ask if the conditions that are likely to be encountered in the thermal discharge would promote the growth of blue-green algae. It is likely that the few degrees rise in temperature that will persist over a period of a few hours will not have a significant effect on the rate of growth or the numbers of blue-green algae in a natural water. The primary reason for this statement is that planktonic algae normally grow at a very slow rate compared with the time that they will be present in the discharge plume.

Reversibility of Thermal Effects

While all available evidence points to the fact that the discharge of heated effluent from electric generating stations located on Lake Michigan and other large bodies of water, as currently contemplated, will not have a significant deleterious effect on water quality, it is not possible to be absolutely certain that no effects will be encountered. It is important to consider whether the discharge of a heated effluent to Lake Michigan could cause irreversible damage to the lake if subtle effects of the heated discharge are found at some future date. It can be unequivocally stated that thermal discharges, unlike other discharges, do not leave a residue in the water which must be flushed from the lake upon termination of the input. The thermal discharges continuously equilibrate with the atmosphere, and there are no long-term effects on water quality after the discharge is stopped.

If it is found at some time in the future that a certain parameter of water quality is significantly adversely affected by thermal discharges and it is decided that this effect is of such proportions as to warrant the termination of further thermal discharges to the lake, it is reasonable to expect that, upon termination of these discharges, the affected parameter will return to normal.

Of particular concern to some water quality regulatory agencies is the reversibility of the eutrophication process in the Great Lakes and other large bodies of water. The reversibility of the eutrophication process has been documented in two instances. The first of these was the lower Madison, Wisconsin lakes. Lakes Waubesa and Kegonsa received the treated effluent from the city of Madison until 1959. During the time of discharge of this effluent to the lake, the concentrations of aquatic plant nutrients were excessively high, and these lakes had frequent blooms of planktonic blue-green algae which were sufficiently thick to enable the ducks, turtles, etc., to walk on the surface of the blooms. In December, 1959, a diversion of the waste waters from these lakes was completed. Shortly thereafter, a marked improvement of water quality was noted. The frequency and severity of blue-green algal blooms was much less after the diversion of the treated sewage effluent. This resulted in a marked improvement in the water quality in the lake (Lawton, 1961). Of primary interest is the fact that the diversion of Madison's waste waters in the lower Madison lakes did not change the temperature of the lakes; yet, the frequency and severity of the blue-green algal blooms decreased significantly during the summer period. Other types of algae, such as green algae, were much more prevalent after the diversion of waste waters from the lakes. This evidence suggests that it is the aquatic plant nutrients, rather than the temperature, that are controlling factors in blue-green algae growth and eutrophication of a body of water.

A second example of the reversibility of the eutrophication process is provided by the studies of Edmondson (1970) on Lake Washington in Seattle, Washington. Edmondson has found that, within a short period after diverting the city of Seattle sewage effluent from this lake, it began to show marked improvements in water quality with respect to the frequency and severity of obnoxious algal blooms in the lake.

Regulatory agencies are concerned about the number of thermal electric generating stations projected for bodies of water such as the Great Lakes and are placed in the dilemma of having to make decisions on the amount of heat that may be discharged to a body of water without having adequate field experience as the technical base for the decisions. The introduction of non-reactive pollutants to large bodies of water with long flushing periods requires that the conservative approach be used by regulatory agencies in developing regulations for the control of these chemicals. However, this same approach is not justified with regard to thermal inputs because of the rapid reversibility of any detrimental effects. There is a need for large scale field studies designed to determine the heat assimilative capacity of various types of natural waters. Regulations requiring the installation of cooling devices on existing, or soon to be completed, electric generating stations represent a needless waste of public funds and may result in significant water quality deterioration due to the potential detrimental effects on environmental quality of the cooling devices such as evaporative cooling towers.

SUMMARY AND CONCLUSIONS

Every body of water has a certain heat assimilative capacity. Any meaningful discussion of the effect of a thermal discharge on the chemical parameters of water quality and eutrophication must consider the relative magnitude of the thermal discharge versus the heat assimilative capacity of the receiving water. Thermal discharges may be conveniently divided into two types dependent on this ratio. The primary distinguishing feature between the two types is whether or not a significant part of the receiving water has a continuously elevated temperature of 5 to 10°C above normal temperatures for the type of water under investigation in that area. In general, the temperature dependence of a chemical parameter of water quality is such that increasing the temperature a few degrees above ambient for a few minutes to a few hours will not have a deleterious effect on the chemical parameters of water quality and eutrophication of receiving waters. On the other hand, increasing the temperature of a substantial part of the receiving waters 5 to 10° above normal ambient for extended periods of time (days or longer) may, in certain instances, create situations where there would tend to be greater water quality deterioration and increased frequency of algal blooms in the receiving water. Of particular concern is the reduced DO concentrations in heavily polluted receiving waters. It can also be expected that, if the increase in temperature results in a temperature from below 10 to 15°C to above 15 to 20°C, increased numbers of blue-green algae would be present in the water. However, the degree of eutrophication of a water is primarily dependent on the amounts of aquatic plant nutrients present in the water, nitrogen and phosphorus compounds being the more important. Temperature plays a minor role in determining the total biomass of algae present in a sample water during the summer, which is the period of time when eutrophication is of the greatest consequence to the public.

The complete and rapid reversibility of any detrimental effects of thermal discharges on the chemical parameters of water quality and eutrophication permits the opportunity for studying the potential detrimental effects of the large thermal nuclear power stations that are currently under construction on the Great Lakes and other large bodies of water without fear of causing irreversible detrimental effects on water quality.

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