SOME CONSIDERATIONS OF THE CHEMICAL LIMNOLOGY OF LAKE MARY, VILAS COUNTY, WISCONSIN

by

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CHAPTER I

INTRODUCTION

Although there have been numerous studies of meromictic lakes, stratified fjords, and unmixed oceanic trenches throughout the world, the majority of these studies have examined a minimum number of parameters in these incompletely-circulated bodies of water. Relatively few detailed studies of the chemical limnology of meromictic lakes or similar bodies of water are available. Previously there have been no studies of Lake Mary, one of the meromictic lakes in Wisconsin, that have examined the behavior of more than one or two chemical species within this lake.

Lake Mary, located in the northwest corner of Vilas County, Wisconsin, is the second lake in a chain of five interconnected lakes. The first lake in this chain, Lake Rose, is of similar size to Lake Mary and is a typically dimictic lake. These two lakes, of approximately equal size and located in the same biotope, offer an opportunity for a comparison of the chemical limnology of a meromictic lake with that of a dimictic lake, both lakes existing under essentially the same environmental conditions.

This study was undertaken with several objectives in mind. The first of these goals was to verify the source of the Lake Mary meromictic state and, if biological activity were the cause, to estimate the amount and location of this activity. This phase of the study involved mainly analysis of Lake Mary waters for the dissolved gas, CH_4. In addition, an attempt was made to define the possible mixing processes occurring within Lake Mary. Finally, the chemical limnology of Lake Mary was compared to that of Lake Rose and the similarities and differences discussed.

The following chapter presents a review of the fundamental aspects of meromixis in general and the basic principles of anaerobic fermentation processes. A brief review of the literature concerning anaerobic conditions in aquatic environments and a summary of the previous work concerning Lake Mary are also presented.

CHAPTER II

LITERATURE REVIEW

Understanding the chemical characteristics of a meromictic lake requires a knowledge of several different topics. These areas of background material include the general features of meromixis, the biochemical and microbiological aspects of anaerobic digestion, anaerobic digestion within sediments, and evidence of anaerobic digestion occurring in lakes and in anoxic basins of the oceans. Since this study deals with the interpretation of the chemical characteristics of meromictic Lake Mary in northern Wisconsin, some of the previous work dealing with this lake is also of importance. A brief discussion of each of these topics follows.

CHARACTERISTICS OF MEROMIXIS

The need for the category of lake-type classification of "meromictic" lake has arisen because such a lake has distinguishing chemical and biological characteristics that differentiate it from most other lakes. One of the most distinctive of these characteristics is the distribution of oxygen content with lake depth.

Findenegg (38, 39) first noticed the year-round absence of oxygen in the deep waters of some of the lakes of Carintha. Even at time of maximum water circulation these lakes showed complete absence of oxygen in the lower waters. In addition, these lakes were often characterized by temperature inversion. The temperature of the lakes decreased to a minimum midway down the water column and then increased with increasing depth to the bottom. Findenegg defines lakes of this type as being meromictic, with their principal feature being that some water remains either partially or completely unmixed with the main water mass at the times of maximum circulation. This lack of complete mixing, attributed to a significant density difference existing between the lake's layers, distinguishes meromictic lakes from holomictic lakes, ie., lakes which experience periods of complete circulation. The more dense layer of unmixed, deep water is termed the monimolimnion. This corresponds to the hypolimnion of a holomictic lake during stratification. Hutchinson (48) later called the upper layer of a meromictic lake (corresponding to the epilimnion of a holomictic lake) the mixolimnion. The layer between the monimolimnion and the mixolimnion is termed the chemocline, and is a layer of rapidly changing chemical characteristics.

Findenegg (39) further classified meromictic lakes according to the types of processes that formed them. He considered a meromictic lake as being of either static or dynamic origin. Those lakes with a static origin exhibit stratification due to some geologic feature. An example of such is a lake that, due to a phenomenon such as an earthquake or a tidal wave (tsunami), contains some very saline water. This more dense saline water forms the the monimolimnion and creates the permanent stratification. A dynamically-formed meromictic lake is stratified due to the processes of decomposition and solution that occur continuously in the lower waters. These processes cause the permanent enrichment of the bottom waters with ions such as bicarbonate and silicate that under normal lake conditions would be in equal concentrations throughout the lake at the time of circulation.

This early classification of meromixis origins has been expanded. Hutchinson (48) classified meromixis of all lakes as being one of three types, either ectogenic, crenogenic, or biogenic meromixis. A discussion of each of these categories follows.

Ectogenic meromixis. An external catastrophe that brings into a lake water of different density than the water already present produces ectogenic meromixis. Such an occurrence could bring either fresh water into a saline lake or salt water into a fresh-water lake. Some mixing would occur at the time of the water's entrance, but two distinct layers would quickly form.

Angino and Armitage (7) and Angino, Armitage, and Tash (6, 8) have described the stratification of two Antarctic lakes. The lakes considered to have ectogenic origins of their permanent stratification are Lake Bonney and Lake Fryxell. Each of these lakes contains a dense, saline-water layer that remains unmixed with the overlying water. Lake Bonney is a 33-m deep lake with a surface height approximately 38 m above present-day sea level. The saline-water layer begins at a depth of 15 m and has a maximum specific gravity of approximately 1.2. The concentrations and ratios of cations in this saline water and the present surface height above sea level suggest that this layer of water is actually sea water. Alternatively, the monimolimnetic water may have come from volcanic hot springs or from an ancient glacial lake located in the same area. The mixolimnetic water may have originated from fresh water flow from melting glaciers. A similar analysis was made to determine the history of Lake Fryxell. This lake is a shallow (total depth, 13 m) basin located in Taylor Valley. Because of this location, the lake's main source of water is glacial runoff, which forms the mixolimnion. The dominant ionic species present in the monimolimnion are Na^+ and Cl^- ions, but HCO_3^- and SiO_3^{-2} also occur. Angino _et al_. (6) concluded that these four main ions were allochthonous to the lake and proposed four possible sources. These included (1) ocean spray blowing 4.5 km to the valley, (2) small sources of Na^+ and Cl^- from NaCl and $NaSO_4$ common to glacial moraines, (3) relic sea water, or (4) thermal water from volcanic hot springs. Although the authors were unable to determine the exact source(s) of the more dense water, they suggested that because of its location the lake could have been an arm of the sea or could have been near some volcanic hot springs. Boswell, Brooks, and Wilson (10) studied trace element ratios in lakes Bonney and Fryxell and compared them with those of sea water. Their study indicated that the saline water in both of these lakes could be ancient sea water. The results of these studies verify the ectogenic origins for the meromixis of lakes Bonney and Fryxell.

Strom (104) reported the saline characteristics of the deep, unmixed water of Lake Tokke. This Norwegian lake is located near the sea and has the characteristic features of a fjord except that it is sealed from the sea. The waters from 132-147.5 m in this lake are completely unmixed with the upper waters. There is no indication of the existence of saline springs. A chemical comparison of the ionic ratios of the monimolimnetic waters with those for ocean waters shows these ratios to be nearly identical. The only composition differences appear in the SO_4^{-2}, HCO_3^-, and NH_4^+ contents. Virtually no SO_4^{-2} was present in the lower lake water (sea water of equivalent chlorinity contains 1283 mg/l SO_4^{-2}), whereas the HCO_3^- content was 3800 mg/l (comparable sea water contains 69 mg/l). Sea water contains no NH_4^+ ions; Lake Tokke water from the monimolimnion contained 145 mg/l. These differences can be explained by the fact that the bottom waters of the lake have been anaerobic for a long period of time. During this time the SO_4^{-2} ions have been reduced to sulfide ions. The large increases in HCO_3^- and NH_4^+ concentrations are due to the processes of anaerobic fermentation. Thus, the unmixed water in Lake Tokke is apparently ancient sea water. This water could likely have originated from either of two sources. Possibly this lake was once an arm of the sea which was blocked from the sea by a landslide. Over an extended period of time the saline upper water may have become diluted by rainfall and land runoff to produce the present-day composition while the water below 132 m remained unmixed and largely unchanged. Strom favors the possibility of sea-water intrusion as the source of this lake's meromixis. At some time when sea level was higher than it presently is some water may have entered into the basin of Lake Tokke and flowed to the bottom, forcing some of the fresher water from the basin. Presumably, permanent stratification ensued.

Man may presently be inducing ectogenic meromixis in some lakes. Schraufnagel (93) notes that in Wisconsin the spreading of deicing chemicals upon highways may have adverse effects upon water quality. The most commonly used chemical for deicing is rock salt. Winter road runoff water near Chippewa Falls, Wisconsin, had a measured Cl^- ion concentration of 10,250 mg/l as compared to a summer maximum Cl^- ion concentration of 16 mg/l for runoff waters. An influx of such highly saline water into a farm pond, gravel quarry, or lake may cause meromictic conditions to develop within that water body.

Crenogenic meromixis. Crenogenic meromixis is a second meromictic type whose origin is largely dependent upon hydrologic and geologic features. It arises due either to the presence of saline springs in a lake or to a similar benthic source of a large quantity of saline water. The entering saline water from the springs forces some of the fresher water out of the lake. There will probably be an equilibrium position reached in the lake before the saline water replaces all of the fresh water. At some depth near the surface, wind action and fresh water runoff from the land combine to produce a layer of water less saline than the spring water. The thickness of this fresh-water layer depends largely upon the rate of discharge from the saline spring. If the spring flows at a steady rate and if the rate of fresh-water supply is approximately constant, then the chemocline will remain at a nearly-constant depth.

Likens and Johnson (69) report that Pingo Lake in Alaska is a meromictic lake of crenogenic origin. This is a 2.5 hectare (ha) lake that is stratified from 3-8.8 m depths. This lake was formed by hydraulic pressure causing water to rise through cracks in the permafrost. As this water rose, it uplifted the ice mound above the permafrost and the layer of earth covering this mound. Once the ice was exposed to the atmosphere, it melted and formed a thaw lake. The existence of a subsurface spring is evidenced by the facts that there is no inflow to the lake, but there is an outflow, and that although there is no drainage basin for the lake, the lake level remains constant. In addition, the monimolimnetic water contains high concentrations of Li^+ and Sr^{+2} ions. The Li^+ concentration is 1 mg/l and the Sr^{+2} 1.5-2.0 mg/l. Since Li^+ is often a constituent of mineral springs, this high concentration supports the proposed existence of a subsurface spring.

Crenogenic and ectogenic meromixis are examples of static meromixis, dependent upon geological phenomena for their incipience. Often the maintenance of the meromictic state may be strictly a function of the hydrologic features of the lake environment. The third category of meromixis that Hutchinson (48) discusses is comparable to Findenegg's (39) classification of dynamic meromixis. The maintenance of this meromixis type is dependent upon processes that are continuously occurring within the lake system.

Biogenic meromixis. Biogenic meromixis is due to increased salt concentrations in the water caused by natural processes of anaerobic decay. These solution processes release the ions that are contained in decaying organic matter that settles to the lake bottom. Possibly one of the best examples of biogenic meromixis is that shown by deep, tropical lakes. In these lakes, due to the relatively high temperatures prevailing, the processes of solution are quite rapid and an anaerobic water layer can develop quite readily. In lakes in a temperate climate the process of biogenic meromixis formation is much slower. Hutchinson (49) theorizes that the ingredients for the formation of this type of meromixis are present after a severe winter when spring circulation of a holomictic lake is incomplete due to late ice-out and calm wind conditions. After this incomplete mixing, the lake enters summer stagnation without oxygenation of the entire water column. Inorganic ions accumulate in the hypolimnetic waters and during summer stagnation the concentrations of these ions increase. If the fall weather conditions are relatively calm, circulation may again be incomplete before ice cover occurs. Winter stagnation further increases the concentration of ions within the anaerobic layer. Each time that this incomplete circulation occurs the lake assumes further characteristics of a meromictic lake. Eventually, the lake may become permanently meromictic.

An example of a biogenic meromictic lake is Sodon Lake in Michigan. Newcombe and Slater (77,78) have described the physical features and temperature characteristics of Sodon Lake. The basin of this lake closely approximates a cone and is, therefore, ideally suited for the development of meromixis because of its relatively large depth/width ratio. Generally, lakes with cone-shaped basins are located in sheltered areas. This environment allows less mixing than a wind-swept area and assists the development of permanent meromixis. One prominent feature of Sodon Lake is its temperature profile. As is the case with many meromictic lakes, the temperature curve shows an inversion. Newcombe and Slater list three possible causes for the temperature inversion in this lake. These explanations are (1) the heat produced by the decomposition of organic material in the benthic water and bottom muds causes the warming of the water;

(2) there is heat of conduction from the benthic soil; and/or (3) there is addition of heat to the lake by inflowing warm, subterranean ground waters that are enriched with salts. Although they cannot rule out the latter two possibilities on the basis of their work, these workers consider Sodon Lake to be a meromictic lake of biogenic origin. The temperature inversion is, thus, assumed to be due to the processes of anaerobic decomposition.

Although there are these three categories for meromixis origin, meromictic types may overlap within a lake. Often the characteristics of biogenic meromixis appear in lakes of crenogenic or ectogenic origin. When this occurs, the processes of biogenesis contribute to the density differences already existing between the lake's layers. A lake which became meromictic through an ectogenic or crenogenic occurrence may develop a large anaerobic microbial population that is readily able to utilize the organic substrates provided to it. If this occurs, then the decomposition processes may continually increase the density differences between the monimolimnion and the mixolimnion. Thus, there may be different degrees of meromixis. Several authors have verified this possibility.

Strom (103) compared three Norwegian lakes of different degrees of meromixis. The types of meromixis represented ranged from "temporary" to "extremely stagnant". Vassjøtjern was a truly meromictic lake during the period of study. However, this investigation was conducted during two seasons of unusually cold winters and of ice breakup in mid-May. The salt concentrations throughout the monimolimnion were not uniform. Strom suggested that this lake would again mix after a less severe winter. Thus, Vassjøtjern exhibited "temporary" meromictic features. Maena was classified as a "typically" meromictic lake, with a temperature inversion curve and with a bottom-water temperature higher than that of maximum water density. The deep, anaerobic waters showed increased salt concentration over that in the mixolimnion. Strom theorized that this lake could mix under the proper meteorological conditions of a mild, windy winter. The third lake, Blankvatn, was a small, sheltered, 55-m deep lake. Strom classified it as being "extremely stagnant". Because this lake was perpetually stratified from 20 m to the bottom and maintained a constant temperature of from 5.04-5.09 °C in the monimolimnetic waters, Strom suggested that it had possibly remained uncirculated since glacial times. This is a striking example of true, permanent meromixis.

Stewart, Malueg, and Sager (102) considered the chemical characteristics of four meromictic lakes in Wisconsin. These authors stress that the absolute values of ionic concentrations in the mixolimnion and the monimolimnion are not the most important factors contributing to meromixis. The relative increases in ionic concentrations with lake depth are more indicative of the degree of meromixis. Those constituents of particular importance to establishing the degree of meromixis are total solids, total Fe, total P, total S, and Cl^-. Generally, an increase in meromictic stability is associated with increased concentration differences for these constituents between the mixed and the anaerobic waters. Hutchinson (48) used the term "meromictic stability" to indicate the amount of work that would be needed to completely mix (to a uniform ionic concentration) the waters of the monimolimnion with the waters of the mixolimnion through an isothermal water column.

Many researchers have chosen to look at meromictic stability in a qualitative, rather than a quantitative manner. Likens and Hasler (68) used a radiotracer to study the movement of water in a small, meromictic Wisconsin lake. These researchers injected ^{24}Na into the monimolimnion of Stewart's Dark Lake and observed its dispersion pattern. This small, bog lake is approximately two acres in surface area and has a maximum depth of 8.8 m. It is considered to be mainly a seepage lake. It is stagnant below a depth of 6 m. Likens and Hasler found a very rapid horizontal movement of the ^{24}Na of approximately 18 m/day in all directions from the point of release. They speculated that this horizontal movement could be due to either biological transport or some physical transport features such as a seiche, eddy diffusion, or currents. They felt that the results of this work indicated two distinct bodies of water that had no intermixing. Other workers using radiotracers have drawn essentially the same conclusions (75,35).

Edmondson (34) found that the monimolimnion of Hall Lake was not a completely isolated layer of water, however. He noted that this lake, a seepage, meromictic lake in Washington, produced a dense layer of algae in the mixolimnion. In view of the humic water of this lake and its low dissolved solids content, Hall Lake appeared to be unusually productive. This productivity was especially high in comparison with similar lakes in the area. Edmondson suggested that this productivity was due to an increased PO_4^{-3} content in the mixolimnion. He further indicated that this increased phosphorus content was due to fall mixing occurring between the stagnant monimolimnion and the mixed surface layers. This mixing enhanced the fertilization of the lake. Since this type of mixing is not common to meromictic lakes, he suggested that the amount of mixing might simply be a function of the degree of meromixis. This lake might be classified as being temporarily meromictic.

A meromictic state in a lake is characterized by the division of the lake into at least two separate and chemically-distinct layers. The predominant differences consist of the absence of oxygen in the lower water layer, the temperature of the bottom layer often higher than that in part of the upper layer, and a higher concentration of ionic species in the lower layer than in the upper layer. The extent of the differences in the chemical characteristics of the two layers dictates the degree of meromixis.

PRINCIPLES OF ANAEROBIC FERMENTATION

Of the features characteristic of meromixis the most important is the anaerobic condition that develops in the monimolimnion. Generally this condition helps to create a strong degree of meromixis. This, in turn, helps effectively separate the monimolimnion from the mixolimnion and hinders mixing so that anaerobic conditions are maintained. For best appreciation of the characteristics of meromictic conditions, one should consider the process of anaerobic fermentation.

Anaerobic fermentation is a complex process involving many factors that influence both the rate and the extent of the reaction, the products formed, the relative amounts of products, and the compounds that are fermentable. Much work encompassing the whole area of anaerobic digestion has been carried out. Papers covering both theoretical and applied engineering aspects of the anaerobic digestion process in detail were presented at the Manhattan Conference on Anaerobic Digestion (72). Detailed studies on the kinetics of methane fermentation have been performed by Andrews, Cole, and Pearson (4) and by Lawrence and McCarty (66). These presentations thoroughly discuss most aspects of the anaerobic fermentation process. To understand the phenomena that are observed in meromictic lakes a knowledge of all of these influencing factors is not essential. However, it is necessary to become acquainted with the biochemical processes occurring during anaerobic fermentation.

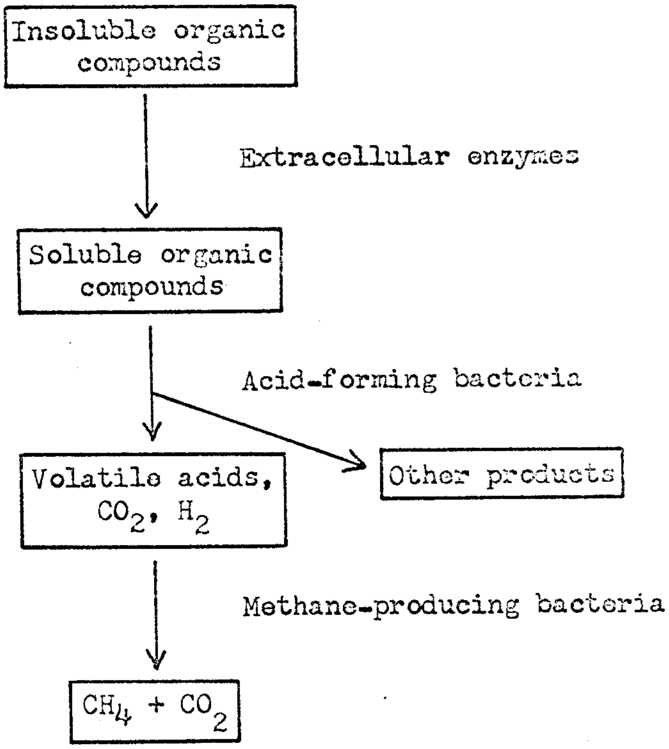
McCarty (73,74) describes the anaerobic fermentation process as consisting of two phases. The first phase, the breakdown of complex organic compounds such as proteins, carbohydrates, and fats into short-chain fatty acids by "acid-forming" bacteria consists of two steps. The bacteria excrete extracellular enzymes that hydrolyze the complex organic materials into amino acids, simple sugars, and fatty acids. Then direct bacterial action converts the intermediate products into short-chain fatty acids. The second phase of the fermentation process consists of the formation of CH_4 and CO_2 from the fatty acids by "methane-producing" bacteria. Figure 2.1 is a simple schematic diagram of this process. Synthesis of microbial cell material accompanies each step of the process.

McCarty (73) states that the bacteria responsible for the degradation of the complex organic materials into the short-chain fatty acids constitute a wide varitey of anaerobic and facultative anaerobic organisms. The bacteria that produce CH_4 and CO_2 are of a much smaller number and are well known.

The methane-producing bacteria have very strict growth requirements. The most stringent of these is that they are obligate anaerobes. Exposure to even a small amount of oxygen is lethal to these microorganisms. Also, they are very substrate specific. Generally, each bacterial species will act on only one or a few substrates. Barker (12,13) summarized the knowledge of the substrate specificity of methane-producing bacteria. Table 2.1 is a list of all the substrates that methane bacteria are known to decompose. In Table 2.2 the specific substrates that each isolated species of methane bacteria is known to decompose are enumerated. It should be noted that because of the great difficulty of isolating a pure culture of a methane-producing bacterium, it is unknown if these species include all of the methane-producers. Barker (11), Stadtman and Barker (98,99), Johns and Barker (53), and Pine and Vishniac (84) have extensively studied the mechanisms of decomposition of these substrates. The general equation

FIGURE 2.1

PATHWAY FOR PRODUCTION OF METHANE FROM COMPLEX ORGANIC COMPOUNDS*



*After Andrews (5).

TABLE 2.1

SUBSTRATES KNOWN TO BE UTILIZED BY METHANE-PRODUCING BACTERIA*

Fatty Acids	Alcohols	Gases
Formic	Methanol	Hydrogen
Acetic	Ethanol	Carbon monoxide
Propionic	Propanol, n-, iso-	Carbon dioxide
n-Butyric	Butanol, n-, iso-	
n-Valeric	1-Pentanol	
n-Caproic		

*After Barker (13).

TABLE 2.2

SUBSTRATES KNOWN TO BE UTILIZED BY SPECIFIC METHANE-PRODUCING BACTERIA*

Microorganism	Compound(s) Fermented
Methanobacterium formicicum	hydrogen, carbon dioxide, formate
Methanobacillus omelianskii	hydrogen, ethanol, primary and secondary alcohols
Methanobacterium suboxydans	butyrate, valerate, caproate
Methanosarcina barkerii	hydrogen, carbon monoxide, methanol, acetate
Methanobacterium propionicum	propionate
Methanobacterium sohngenii	acetate, butyrate
Methanococcus mazei	acetate, butyrate
Methanococcus vannielii	formate, hydrogen
Methanosarcina methanica	acetate, butyrate

*After Barker (12,13).

for the energy-obtaining reactions of the methane-producing bacteria is

$$4\ H_2A + CO_2 \longrightarrow 4\ A + CH_4 + 2\ H_2O \qquad (2.1)$$

(Barker, 11),

where H_2A represents an oxidizable compound and A is its oxidation product. Those substrates whose fermentations do not follow the pattern presented by this general equation include CH_3COOH, CH_3OH, and CO. The individual reactions for the fermentation of these species appear below.

$$C^*H_3C^+OOH \longrightarrow C^*H_4 + C^+O_2. \qquad (2.2)$$

$$4\ C^*H_3OH \longrightarrow 3\ C^*H_4 + C^*O_2 + 2\ H_2O \qquad (2.3)$$

(Pine and Vishniac, 84).

$$CO + 3\ H_2 \longrightarrow CH_4 + H_2O \qquad (2.4)$$

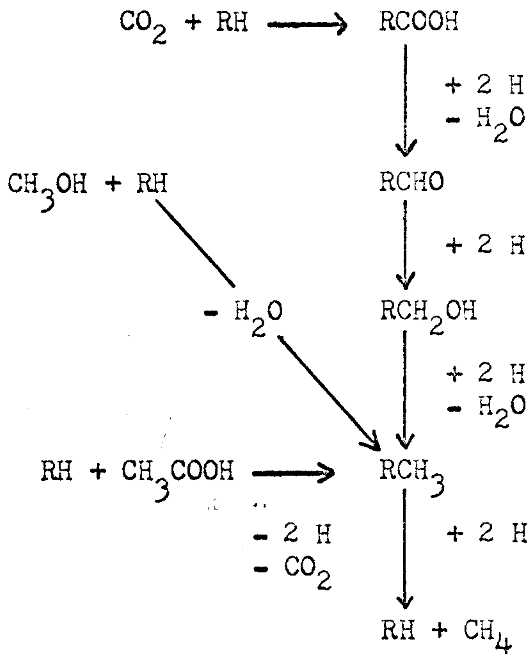
(Stephenson and Stickland, 101).

Barker (13) has proposed mechanisms for the formation of CH_4 from all sources. Figure 2.2 presents this reaction series. In this sequence R represents an as yet unidentified organic compound. This series of reactions presents CO_2, CH_3OH, and CH_3COOH as the important substrates in the reactions producing CH_4. For the other substrates listed in Table 2.1, acetic acid, carbon dioxide, or methanol are intermediates before they are finally converted into CH_4.

Because of the high degree of specificity exhibited by the methane-producing bacteria, it is apparent that several species of these bacteria together with acid-forming bacteria may be necessary for the complete destruction of just one complex organic substrate.* Thus, a well-balanced population of bacteria is necessary for the complete fermentation of a mixture of complex organic compounds. Such a bacterial population occurs naturally in anaerobic sludge digestion chambers of sewage treatment plants. This mixed population of methane-producers plus acid-forming bacteria is able to degrade most organic carbon sources.

FIGURE 2.2

PROPOSED MECHANISMS FOR PRODUCTION OF METHANE



R represents an as yet unidentified organic compound.
*After Barker (13).

Several batch process anaerobic fermentation studies have determined the "digestability" of various organic substrates. Buswell and Mueller (24) state that hydrocarbons, ethers, and lignins are not anaerobically degradable at measurable rates while most other naturally-occurring, carbon-containing compounds are anaerobically fermented at measurable rates. Buswell and Neave (23) performed laboratory tests in batch digester studies to determine the degradability of certain carbohydrate substrates common to sludge digesters. Their findings showed that most of the carbohydrates studied were readily degradable; ie., the total gas production in three months was greater than 400 ml of gas/gm of substrate. These readily-fermentable substrates included cellulose, starch, dextrin, raffinose, salicin, adonitol, dulcitol, mannitol, sucrose, maltose, lactose, fructose, dextrose, and glycerol. They also found that several proteins, peptides, and fatty acids were rapidly fermented by the digester microbial populations.

Jeris and McCarty (52), using similar batch process studies, also determined the degradability of representative fats, carbohydrates, and proteins. These workers were interested in the relative amounts of CO_2 and CH_4 produced by the fermentation of various substrates. In general, the fermentation of long-chain fatty acids will produce a gas consisting of from 67-100 percent CH_4, with the remaining gas fraction being CO_2. For carbohydrate fermentation the sample substrates were glucose, starch, and cellulose. The fermentation pathway for these compounds followed the sequence of

$$\text{substrate} \longrightarrow 1\ \text{glucose} \longrightarrow 2\ \text{acetate} + CO_2 + CH_4 \longrightarrow 3\ CO_2 + 3\ CH_4. \tag{2.5}$$

The fermentation of carbohydrates produces a gas consisting of approximately 67 percent CH_4. For proteinaceous material Jeris and McCarty stated that CH_4 constituted about 72 percent of the gas produced during the fermentation. From these results they concluded that approximately 70 percent of the gas produced from properly digesting sludges should be CH_4.

Although CO_2 and CH_4 are the major products of anaerobic fermentation, there are also several minor products formed. Davis and Squires (27) report ethane, acetylene, and ethylene formation during the anaerobic fermentation of sewage sludge. Pine and Barker (83) state that there is a widespread ability for anaerobic bacteria to fix N_2. Some methane-producing bacteria (notably Methanobacillus omelianskii) may produce NH_3 by N_2 fixation. The reverse of nitrogen fixation is also possible, with the production of N_2 by the denitrification of NO_2^- ions. Zobell (109) discussed the formation of H_2 gas in an anaerobic environment.

The anaerobic fermentation of organic materials is a widely-occurring natural process. A large and varied microbial population is necessary to perform the complete digestion of organic material, producing CO_2 and CH_4 as the principal end products. Although the greatest amounts of work with anaerobic fermentation have been with sewage sludge, anaerobic digestion of organic material is a widespread occurrence in the aquatic environment and the associated sediments.

ANAEROBIC FERMENTATION IN SEDIMENTS

The sediments of a lake (if not influenced by industrial waste discharges) are a complex combination of inorganic and organic remnants of terrestrial erosion, undecomposed organic material produced within the lake and settled to the bottom, and inorganic compounds formed as precipitates within the lake. Much of the organic material in this complex matrix will be fatty-acid, carbonaceous, and proteinaceous materials. These materials in the lake's sediments can undergo anaerobic fermentation in a manner similar to the material in sewage sludges. The study of the fermentation of lake sediments has been approached in a manner analogous to the study of sludge digestion.

Koyama (65) studied the mechanism of the production of CH_4 and CO_2 from acetic acid that had been added to sediment samples. He found the mechanisms of CH_4 production to be identical to those previously described for microbial populations in a sludge digester. In a previous study, Koyama (63) incubated muds and observed the varying concentrations of the gaseous products with time. He found that CO_2 production began immediately in the mud. As soon as the sediments became anaerobic, H_2 formation began, and then CH_4 formation started. Accompanying the increasing CH_4 concentration was a decreasing CO_2 concentration due to the reduction of CO_2 to CH_4. These studies indicate that the same types of microbial populations are responsible for anaerobic fermentation in lake sediments as are active in an anaerobic sewage sludge digester.

In some sediments the formation of H_2 may be an important process. Zobell (109) reports that the formation of H_2 in anaerobic marine sediments is a common occurrence. H_2 gas is liberated from carbohydrates and polyhydroxy alcohols. However, large concentrations of H_2 gas are generally not found in sediments because H_2 is readily utilized by certain aerobic and anaerobic bacteria. Among others, sulfate-reducing bacteria and some methane-producing bacteria compete for the available H_2. Large concentrations of H_2 might indicate that the microbial population present was not "balanced". That is, the ecological niche was not filled by organisms that could most efficiently utilize the available substrates. In the environment little H_2 is found.

As some workers report finding hydrocarbons other than CH_4 in anaerobic, sewage sludge digesters, so Emery and Hogan (37) report small concentrations of several volatile organic compounds in Pacific sediment cores. Found as gases were methane, ethane, propane, n-butane, isobutane, and ethene. They also report traces of such compounds as hexane, isopentane, cyclobutane, cyclopentane, benzene, toluene, and xylene as being present. These authors were searching for the presence of oil and concluded that, because of the types of organic materials characterized, there was quite possibly oil in nearby sediments.

In situ studies by Koyama (62,64) have shown that the concentrations of anaerobically-produced gases in the sediments may vary considerably from lake to lake. The greatest CH_4 concentrations occurred at a depth of 15-35 cm from the sediment surface. Possibly the upper 10-15 cm of the lake's sediment were sufficiently well mixed as to allow relatively rapid gas release to the overlying water. The overall quantities of CH_4, N_2, and H_2 in the sediments increased with increasing lake depth. The CO_2 content decreased with increasing depth of the lake. The total pressure of the gases in the sediments was always slightly greater than hydrostatic pressure, but gas bubble formation in the sediments was rare. Finally, the work indicated that the dominant reactions of the nitrogen cycle were different in different sediments. In some instances nitrification occurred predominantly, in other cases denitrification was the major process, and for still other lake sediments the two processes apparently balanced themselves.

Allgeier, Peterson, Juday, and Birge (1) performed gross analyses of the digestion of Lake Mendota sediments (samples were taken from an 18-m depth). These workers found that the maximum destruction of organic material (11.9 percent of the total organic carbon was destroyed in 200-210 days) occurred at the greatest incubation temperature, 55°C. Analyses of the gases produced showed that CH_4 was the main fermentation product, constituting 65-85 percent of the evolved gas. CO_2 comprised 3-30 percent of the gas; H_2, 1-3 percent; and N_2, 3-22 percent. The considerable amount of N_2 produced was suggested as coming from decomposition of nitrogenous compounds. However, other workers (21,26) have been unable to duplicate the production of N_2 gas from Lake Mendota sediments under conditions similar to those used by Allgeier et al. They proposed that inadequate analytical procedures produced the large apparent N_2 concentrations.

Anaerobic digestion occurs in the sediments of many lakes. Apparently the bacterial population performing the decomposition is similar to that found in sewage treatment plants because the gaseous products found in the sediments are present in approximately the same ratios as occur in a sludge digester. These main gaseous products are CO_2 and CH_4, with N_2, NH_3, and H_2 being produced in much lower concentrations. Often studies in lakes or in the ocean do not measure gaseous concentrations in the sediments but look instead at concentrations in the waters above the muds. Brezonik (21) analyzed the hypolimnetic waters of Lake Mendota for CH_4. He found maximum concentrations of approximately 6-7 mg/l in the deepest water. This type of study may be an attempt to view the overall effect of anaerobic conditions in the lake or oceanic basin.

ANAEROBIOSIS IN LAKES AND OCEANIC TRENCHES

Thus far the discussion of anaerobic fermentation reactions has been limited to the production of mainly gaseous end products that may appear from fermentation of organic compounds containing only carbon and oxygen atoms. Little thought has been given the fate of nitrogen, phosphorus, and many trace metals when released from decomposing organic material. These do, however, effect the chemistry of the environment. Various researchers have used model equations to explain the effect of anaerobic fermentation on the chemical characteristics observed in the environment.

Richards, Cline, Broenkow, and Atkinson (87) studied the accumulation of dissolved gases and ionic species in an anaerobic fjord, Lake Nitinat, on Vancouver Island, British Columbia. Through the use of a plankton model consisting of chosen ratios of C, N, O, and P atoms, these workers attempted to explain the ratios of the inorganic ions that they found in the lake's monimolimnetic waters. They present, as a typical reaction for the aerobic decomposition of plankton, the equation

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 106\ O_2 \longrightarrow 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 106\ H_2O. \qquad (2.6)$$

This model for decomposition applies only when free O_2 is available. For anaerobic decomposition of this plankton model, the equation

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \longrightarrow 53\ CH_4 + 53\ CO_2 + 16\ NH_3 + H_3PO_4. \qquad (2.7)$$

was suggested. By using these two equations, or modifications of them to include such processes as sulfate reduction, the authors were able to explain most of the observed chemical characteristics of the waters including the ratios of most of the chemical constituents. They were unable, however, to explain the ratios of CH_4 to some of the ions by the use of this latter equation.

Later work by Atkinson and Richards (10) explained their previous inability to correlate all of their data for Lake Nitinat. They found that the primary source of CH_4 in Lake Nitinat is not from the destruction of organic material as Equation 2.7 suggests. Instead, the $\Delta CO_2:\Delta CH_4:\Delta S:\Delta NH_3:\Delta H_3PO_4$ ratios indicate that the primary CH_4 source is from the decomposition of carbohydrates and fatty acids produced by other processes, such as sulfate reduction. These findings are consistent with those of McCarty (73). The studies of Lake Nitinat indicate that successful environmental models can be proposed if adequate data is available.

Deevey and co-workers (28,29,30) have chosen to look at an aspect of anaerobic fermentation other than simple gas production. They have quantitated the fractionation of isotopes by microorganisms within a lake. It is well known that metabolizing microorganisms selectively utilize the different isotopes of an element. Therefore, the chemical species produced during metabolism will be richer in one or two isotopes of an element than would be expected based on strict natural abundance percentages of the element's isotopes. Fractionation of isotopes is particularly evident in the comparison of the isotopic ratios in epilimnetic waters with those in anaerobic, hypolimnetic waters. The metabolic reactions that occur in each of these water layers follow different pathways, and one layer may be enriched in one isotope of an element while the other layer is enriched with another isotope of the element (probably appearing as a different chemical species of the element).

Because of the permenent stratification of meromictic lakes, isotopic fractionation differences are often quite pronounced between the mixolimnetic and the monimolimnetic waters. It was a meromictic lake that Deevey _et al_. studied, Fayetteville Green Lake in New York. Eggleton (36) has presented a thorough limnological description of this lake. Green Lake lies in a sheltered valley that rarely receives strong wind action upon the water's surface. This 59-m deep lake is permanently stratified below a depth of 25 m. Isotopic fractionation is characteristic of light and chemically-active elements. Two such elements are carbon and sulfur. The fractionation of the isotopes of both of these elements has been enhanced by the permanent meromictic state of Green Lake. This is because oxidized compounds of both carbon and sulfur tend to be richer in the heavy isotopes of the elements than do the reduced compounds. This lake has layers of permanently-oxidizing and permanently-reducing environments.

Deevey et al. have found that the fractionation of carbon and sulfur isotopes in Green Lake is much the same as would be predicted. The CO_2 produced by ordinary oxidative metabolism is ^{13}C rich, whereas that produced by the methane fermentation process is poor in ^{13}C. The overall sulfur species in the monimolimnion show an ^{34}S enrichment. For an unknown reason, the outlet of this lake preferentially removes ^{32}S from the mixolimnetic waters. This causes less total sulfur to be in the mixolimnion than is in the monimolimnion. (Limnological features suggest saline springs as a source of some water to the monimolimnion; these may carry in more sulfur-containing compounds.) If a perfect balance could be made of the import and export of sulfur and carbon to and from the lake, it might be possible to determine the age of the meromixis by the amount of isotopic fractionation observed. Thus far, such a determination has been impossible.

PREVIOUS LAKE MARY STUDIES

Lake Mary is a 1.2 ha, dystrophic, meromictic lake located in the northwest section of Vilas County, Wisconsin. Nearly all previous studies concerning this lake have been of a general survey nature. The workers were investigating one particular aspect of the lake's chemical or biological characteristics. No comprehensive studies have been performed.

One of the most striking and most obvious limnological features of Lake Mary is the high color of the lake waters. This color is associated with relatively large concentrations of organic materials in the water. Juday and Birge (56) report that the color of Lake Mary water increases from 118 chloroplatinate-Pt color units in the surface waters to 218 color units in water from a 20-m depth. Over an irregular, five-year sampling period the color of the surface waters ranged from 100-122 color units. Birge and Juday (15,17) also compared the distribution of the lake's organic material between the dissolved portion and the planktonic fraction. A series of 114 samplings from all depths of the lake produced a mean value of 2.35 mg/l of planktonic material. During the summer of 1926 a maximum plankton concentration of 4.06 mg/l was observed at a depth of three m. The concentration of plankton decreased with depth, as would be expected. The total dissolved organic matter remained nearly constant throughout the top 15 m of the lake at approximately 40 mg/l. A sample from 20 m showed approximately 52 mg/l, however. In general, the organic content appeared to be constant throughout the lake.

Some studies have been performed on Lake Mary water to determine its nutrient content. Juday, Birge, and Meloche (57) compared the concentrations of nitrogen species in the mixed, surface waters with those in the monimolimnion. They found no detectable NO_2-N in any of the water samples. The NO_3-N concentrations were approximately the same throughout the water column, ranging from 0.04-0.06 mg/l. The NH_3-N concentrations in the mixolimnetic waters ranged from a trace to 0.01 mg/l, whereas the concentrations in the deep, unmixed water were as great as 4.00 mg/l. Juday, Birge, Kemmer, and Robinson (55) and Birge and Juday (16) analyzed the lake water for various forms of phosphorus. Their studies showed that both soluble and organic phosphorus concentrations increased with increasing lake depth. Total phosphorus concentrations in the surface waters were from 0.000-0.050 mg/l soluble-P during the study period. Organic-P contributed approximately 0.04 mg/l to the total. In the monimolimnetic waters, soluble-P concentrations of up to 0.700 mg/l were found with accompanying organic-P concentrations of up to 0.100 mg/l. Because of the high color of the waters of this lake and the low nitrogen and phosphorus content of the surface waters, Lake Mary is classed as a dystrophic lake.

Allgeier, Hafford, and Juday (2) investigated the oxidation-reduction potential of the waters and sediments of Lake Mary. On the occasion of their study, oxygen was present in only the upper four meters of water. The Eh of the upper two m of water was approximately constant at + 0.470 volts. From this point the Eh decreased rapidly with increasing depth to a value of + 0.150 volts at eight m depth. The redox potential then decreased slowly to a minimum value of 0.070 volts in the lake sediments. It was shown by this data that a rapid drop in potential accompanies the rapid increase in number of chemical species present as the chemocline is crossed.

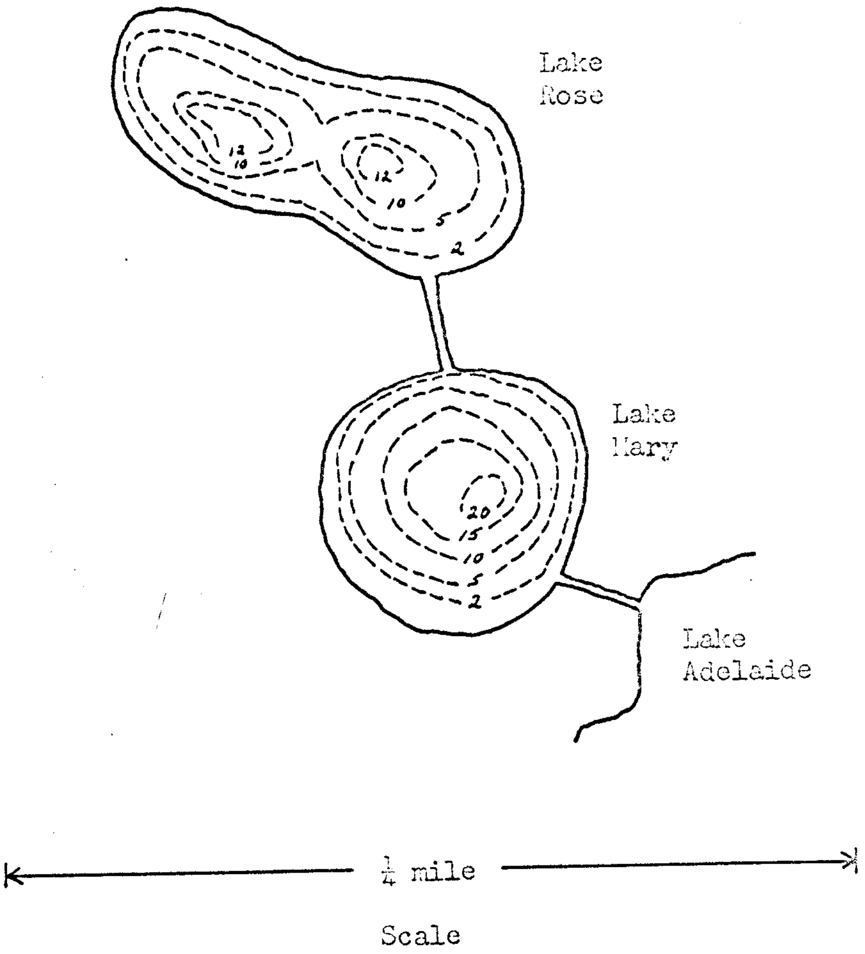
CHAPTER III

EXPERIMENTAL METHODS

Analyses of various chemical parameters in Lake Mary and Lake Rose were performed over a 21-month period. The analyses for some of these constituents were conducted only one or two times to provide a knowledge of their concentration levels. Because this study was to a large extent concerned with the nature and the amounts of dissolved gases in the waters, a major emphasis was adapting an analytical method for dissolved gases for use under the conditions presented in this investigation. In addition to the presentation of analytical procedures, descriptions of field sampling techniques and general hydrographic characteristics of lakes Mary and Rose are included.

ENVIRONMENTS OF LAKES MARY AND ROSE

Lake Mary and Lake Rose, small drainage lakes, are located in the northwest corner of Vilas County, Wisconsin. Lake Rose is a typical dimictic lake, whereas Lake Mary is a permanently meromictic lake. Both lakes are located in small basins, sheltered from wind action by well-forested hills. Lake Rose is fed apparently by drainage from the surrounding area, both as land runoff and groundwater inflow. The only visible sources of water for Lake Mary are land runoff and a small stream connecting lakes Mary and Rose. An outlet from Lake Mary transports water to Lake Adelaide, the third lake in a chain of five interconnected lakes. Figure 3.1 presents hydrographic maps of Lake Rose and Lake Mary and depicts their interlinking with each other and with Lake Adelaide. Summaries of the pertinent morphometric and hydrographic data for lakes Mary and Rose are presented in Tables 3.1, 3.2, and 3.3.



HYDROGRAPHIC CHARTS OF LAKES MARY AND ROSE
After Juday and Birge (58).

FIGURE 3.1

TABLE 3.1

HYDROGRAPHIC DATA FOR LAKES MARY AND ROSE*

Parameter	Lake Mary	Lake Rose
Length-m	125	210
Width-m	120	92
Area-ha	1.2	1.43
Maximum depth-m	21.5	13.0
Mean depth-m	7.76	5.17

*After Juday and Birge (58).

TABLE 3.2

MORPHOMETRIC DATA FOR LAKE MARY*

Depth	Area		Stratum	Area Between Contours-ha	Volume	
m	ha	% total	m		m^3	% total
0	1.2	100.0	0-2	0.25	21,430	23.2
2	0.95	79.1	2-5	0.23	25,000	27.0
5	0.72	60.0	5-10	0.33	27,270	29.4
10	0.39	32.5	10-15	0.20	14,340	15.5
15	0.19	15.8	15-20	0.17	4,450	4.8
20	0.02	1.6	20-21.5	0.02	110	0.1

*After Juday and Birge (58).

TABLE 3.3

MORPHOMETRIC DATA FOR LAKE ROSE*

Depth	Area		Stratum	Area Between Contours-ha	Volume	
m	ha	% total	m		m^3	% total
0	1.43	100.0	0-2	0.38	24,700	33.4
2	1.05	73.4	2-5	0.39	25,440	34.4
5	0.66	46.1	5-10	0.45	20,690	28.0
10	0.21	14.6	10-12	0.13	2,850	3.9
12	0.08	5.5	12-13	0.08	216	0.3

*After Juday and Birge (58).

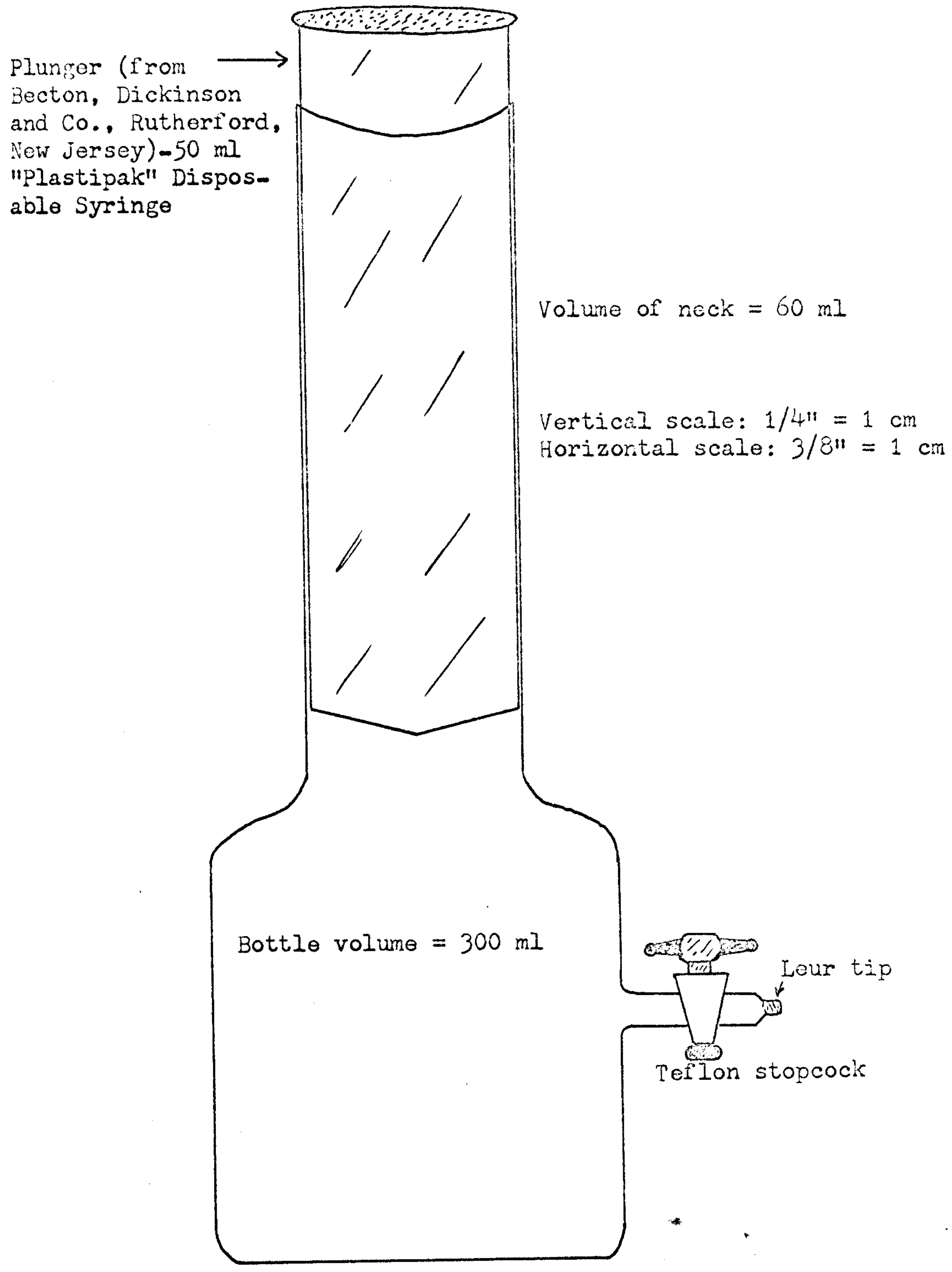
FIELD SAMPLING PROCEDURES

The collection of water samples from lakes Mary and Rose was performed from the fall of 1966 through the spring of 1968. During times of open water, sampling was done from a canoe. When ice cover prevailed on the lakes, equipment was transported manually or by the use of a snowmobile. *In situ* measurements made from the canoe or from the ice included measurements of water transparency by the use of a Secchi disc and the determination of temperature vs. depth profiles of the water columns with a thermistor-type underwater thermometer. During the latter half of the study *in situ* dissolved oxygen (DO) measurements were also performed, using a Yellow Springs Instrument Company model 54RC oxygen meter (see Kluesener, 61). When this meter was used to measure DO, it was also used to determine the temperature profiles for the lakes. Water samples were collected with a plastic water sampler similar to the Van Dorn sampler often used in oceanographic surveys (Anon., 9). This sampler was lowered to the desired depth in the lake and then closed with an appropriate tripping mechanism. Water samples collected in this manner were then brought to the surface and transferred, through rubber tubes attached to the sampler, to bottles for temporary storage before analysis. This method of transfer from the sampler minimized dissolved gas transfer to or from the water samples.

Generally four sample bottles were filled for analysis. In the early part of the study before the acquisition of the YSI DO meter, a fifth sample was also taken for a Winkler DO determination. From anaerobic waters additional samples for sulfide analysis were also collected. The four samples routinely gathered included separate samples for nitrogen species analysis, phosphorus species analysis, dissolved gas analysis, and general analysis (refers to sample taken for analysis of those chemical parameters not requiring preservation). The samples for nitrogen species analysis were placed into one-l polyethylene bottles. To each of these samples was added approximately two ml of a saturated water solution of Hg_2Cl_2. The samples taken for analysis of phosphorus species were placed into glass bottles of approximately 300 ml volume; these bottles had been previously washed with a solution of 1:1 HCl and then rinsed several times with distilled water. Phosphorus samples were preserved by the addition of about two ml of $CHCl_3$ to each bottle. The samples for general analysis were placed into one-l polyethylene bottles; no prevervative was added. The sulfide samples were collected in glass BOD bottles of 300-ml volume which had been flushed with approximately three volumes of sample water to minimize contamination of the sample with oxygen. These samples were preserved by the addition of one ml of 1 M NaOH and one ml of 1 M $Zn(C_2H_3O_2)_2$. All preservative agents were added in the field. Nitrogen, phosphorus, and general samples returned to Madison were stored in the dark at a temperature of 4^oC. The nitrogen and phosphorus samples were seldom stored for more than two weeks before analysis.

The samples taken for dissolved gas analysis were placed into bottles of the type shown in Figure 3.2. The procedure for filling these sample bottles was similar to that used for filling the bottles for the sulfide samples. Water was added through the neck of the bottle and allowed to flush through both the neck and the stopcock, using about two volumes of water for this flushing operation. After the stopcock was closed and water overflowed the neck of the bottle, the plunger was inserted (about ½"-1" into the neck) with the stopcock now open. The stopcock was then closed and the sample was ready for transportation to the analysis site.

The dissolved gas samples were transported in a large, wooden container. Since these water samples, when collected, were brought from the



GAS SAMPLING BOTTLE

FIGURE 3.2

lake into an atmosphere of lower total pressure (ie., hydrostatic pressure had been relieved) and often of warmer temperature than the lake water, there was a tendency for the gases dissolved in the water to form bubbles and to collect at the top of the sample bottle. To avoid bubble formation, snow (when available) was packed around the samples in their storage box to maintain them at an approximately constant, low temperature. The above procedure was used for the analysis of dissolved gas samples from September, 1967, to March, 1968. Previously, sample collection bottles were 300-ml BOD bottles that were filled according to the procedure used for filling bottles for sulfide samples. Use of this type of sample bottle was discontinued because of difficulties in sample transfer during a later step in the dissolved gas analysis procedure.

FIELD ANALYSIS PROCEDURES

Standard Chemical and Physical Methods

Because of the unique nature of some aspects of this study, it was mandatory that certain analyses be performed on-site, or as close to on-site as circumstances permitted. Originally, the on-site analyses were performed in the Water Chemistry field truck equipped with the necessary equipment and stationed at Lake Mary. When dissolved gas sample bottles of the type shown in Figure 3.2 were introduced into the study, the site of analysis became the Kemp Biological Station (University of Wisconsin Agricultural Experimental Station) located near Woodruff, Wisconsin. Several types of analyses were performed* at these "on-site" stations. Except for the dissolved gas analysis, all of these analyses were performed on the non-preserved sample collected for general analysis. A brief discussion of each of these analytical methods follows.

The turbidity of an unfiltered sample was evaluated with a Hellige Turbidimeter (see Hellige instruction manual, 43). For color analysis, the samples were first filtered through Whatman No. 1 filter paper. A Hellige model 611 Aquatester was used to compare the color of the water to standard, non-fading, colored-glass discs.

The pH of the samples was measured using a Beckman model N or model G pH meter. A combination glass electrode was used for all of the measurements. This system was calibrated with a 6.86 pH buffer and the calibration was then checked against a 4.04 pH buffer.

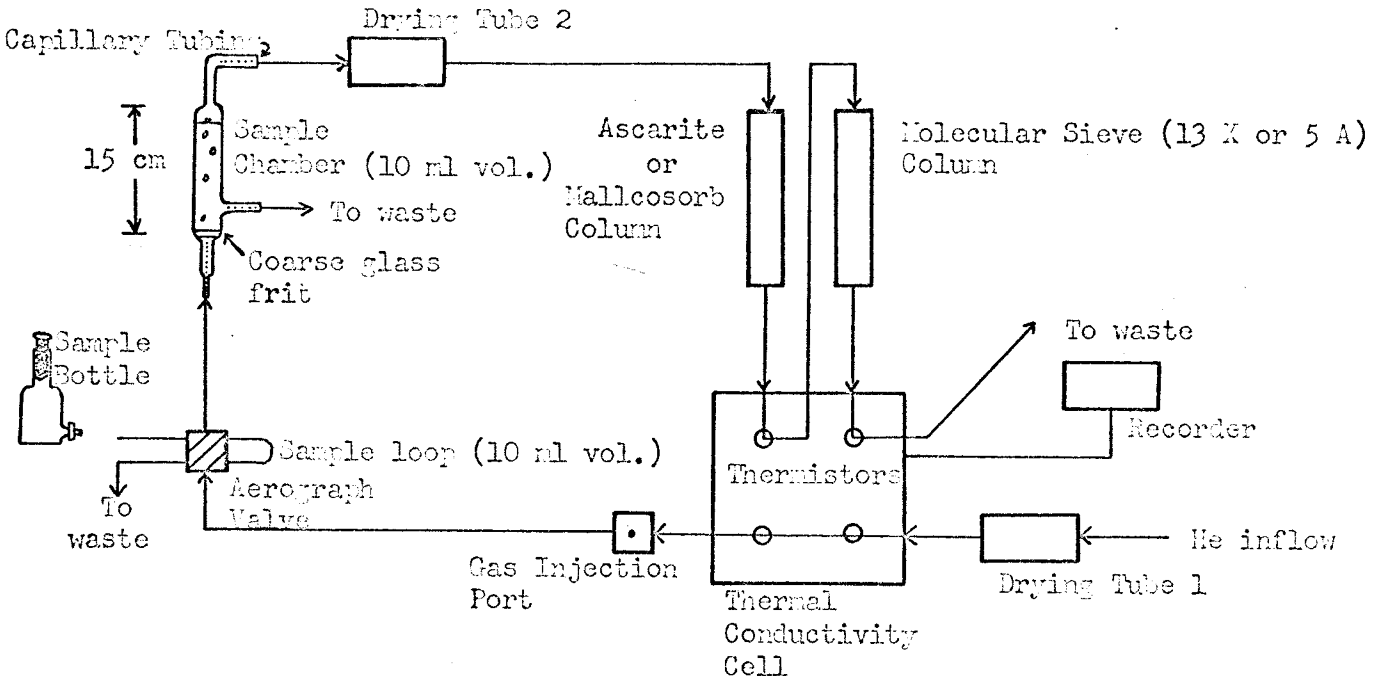
An Industrial Instruments model RC 1682 conductivity bridge equipped with a fill-type conductance cell (cell constant = 1.00) was used to measure the samples' specific conductance values. Since the samples were not all at the same temperature at the time of the conductivity measurements, the temperatures of the samples were measured in addition to the specific conductance values. The conductivity values for the samples were later corrected to a standard temperature through the use of the calibration data for specific conductance vs. temperature presented in Chapter IV.

A modification of the <u>Standard Methods</u>, twelfth edition, (1965) method was used for the determination of total sulfide in the samples. The sample was initially preserved by adding one ml of 1 M NaOH and one ml of 1 M $Zn(C_2H_3O_2)_2$. The NaOH raised the pH of the sample so that all of the sulfide was present as the S^{-2} species. This species then precipitated as ZnS upon the addition of the $Zn(C_2H_3O_2)_2$. Before the analysis was performed, the ZnS precipitate was dissolved by the addition of a small amount of mineral acid to the sample. Sulfide was quantitated colorimetrically by a procedure involving the formation of methylene blue from a solution containing p-aminodimethylanaline, ferric chloride, and the sulfide ion under appropriate reaction conditions. The absorbance of the methylene blue color was measured at a wavelength of 662 nanometers (nm) with a Spectronic 20 spectrophotometer.

The total alkalinity of the water samples was determined by titration with 0.02 N H_2SO_4 (Standard Methods, 1965). The endpoint was detected in one of two ways. Originally, the endpoint of the titration was taken as the methyl purple colorimetric endpoint. However, due to the high color of the Lake Mary waters this endpoint was difficult to detect. Endpoint detection was later achieved by performing a conductometric titration of the alkalinity (Park and Oliphant, 82). This latter method permitted the determination of a more readily discernible endpoint.

Dissolved Gas Analytical Procedure

Much of this project's analytical emphasis involved the analysis of the lake waters for dissolved gases, particularly the N_2 and CH_4 species. The basic procedure for the analysis of these gases involved (1) introducing the water sample into a specially-designed sample chamber, (2) stripping the dissolved gases from the water sample by using He carrier gas, (3) separating the gases from one another by using gas-solid chromatography, and (4) analyzing the components of the gas mixture by using thermal conductivity measurements. This technique was first developed by Swinnerton, Linnenbom, and Cheek (106). The main parts of the experimental apparatus involved in this analysis include the gas-stripping chamber, a Fisher model 25 gas partitioner (modified), a temperature stabilizer for this gas partitioner, and a Honeywell one millivolt recorder. A schematic diagram of the flow system is shown in Figure 3.3. The He carrier gas is dried before entering the reference side of the thermal conductivity cell which provides the reference thermal conductance of the gas stream. This carrier gas then strips the dissolved gases from the water sample contained in the sample chamber. Before re-entry into the thermal conductivity cell, the sample stream passes through a



Drying tubes (Tygon tubing) 1 & 2 contained 10/20 mesh Drierite; drying tube 1, 6" x 1"; drying tube 2, 18" x $\frac{1}{4}$".
Ascarite or Mallcosorb CO_2-removing columns contained 10/20 mesh ascarite or 30/60 mesh Mallcosorb; column size, 10" x $\frac{1}{4}$" Tygon tubing.
Molecular sieve column contained 30/60 mesh molecular sieve 13 X or 5 A; column size, 12' x 1/8" or 18' x 1/8" aluminum tubing.

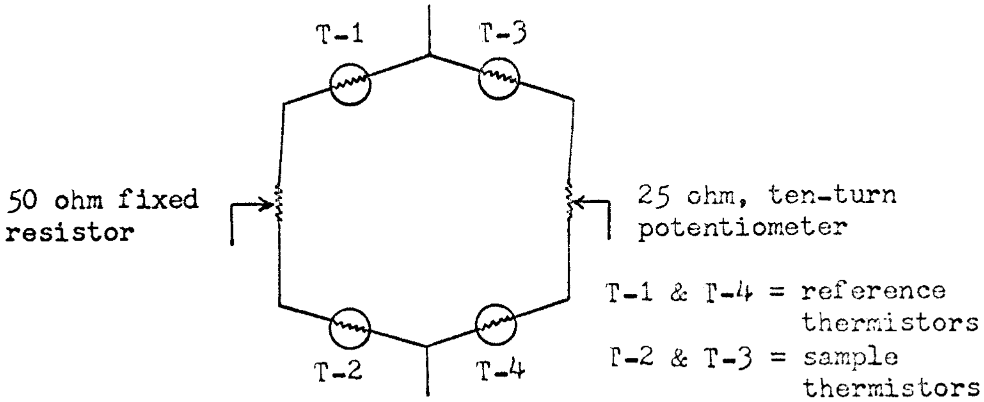
DISSOCIATED GAS ANALYTICAL SYSTEM

FIGURE 3.3

column to remove all traces of water and through a column to absorb CO_2 and other acidic gases. Passage of the sample past the third thermistor quantitates the total amount of gas in the sample. The molecular sieve column separates the sample mixture into its individual gaseous components before each of these gases is measured by the final thermistor.

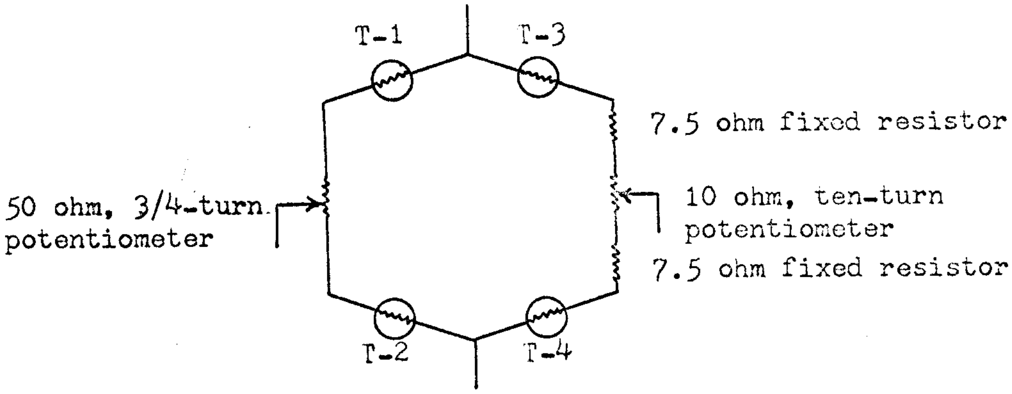
The column materials for the drying tubes and the molecular sieve columns were preconditioned before placement into the system. The Drierite material was maintained at a temperature of approximately 110°C for two to three days to remove any traces of volatile materials. After removal from the oven it was placed in a tightly-closed container to help avoid recontamination. The molecular sieve was preconditioned by placement in another gas chromatograph (held at a temperature of 160°C) for 24 hours while flushing with He carrier gas at a rate equivalent to that used for the dissolved gas analysis set-up. This conditioning was performed to remove any volatile materials that might later come off the chromatographic matrix. The ascarite or Mallcosorb columns for CO_2 removal were not preconditioned.

The thermal conductivity cell was slightly modified from the normal instrumental state. Figure 3.4-a shows a schematic of the original wiring of the thermal conductivity bridge. The 50-ohm resistor was fixed. Instrumental balance was obtained by using the 25-ohm, ten-turn potentiometer. With these instrumental controls, it was found to be quite difficult to obtain a steady baseline; ie., to perfectly balance the instrument. The modification involved replacing the 50-ohm resistor with a 50-ohm, three-quarters-turn potentiometer and replacing the 25-ohm potentiometer with two 7.5-ohm resistors and a 10-ohm, ten-turn potentiometer. A schematic of this modification is shown in Figure 3.4-b. With this



Wiring of original thermal conductivity cell

(a)



Wiring of modified thermal conductivity cell

(b)

WIRING OF THERMAL CONDUCTIVITY BRIDGE

FIGURE 3.4

arrangement the 50-ohm potentiometer was used as a coarse adjustment and the 10-ohm potentiometer was used as a fine balance control. This modification enabled a more sensitive balance adjustment of the current flowing through both sides of the bridge and aided baseline stabilization.

Experimental operating conditions were maintained approximately constant for each set of analyses. The thermal stabilizer was maintained at approximately 30°C. This held the gas partitioner at nearly constant temperature if 10-12 hours were allowed for initial temperature equilibration between the gas partitioner and the temperature controller. A delivery pressure of approximately 22 psi on the He tank allowed adjustment of the carrier gas flow to about 40 ml/min. It should be noted that, although equivalent operating conditions for each experiment were desirable, they were not required because the instrument was recalibrated each day.

Several calibration techniques were tested. The most successful of these involved the injection of a measured sample of air or CH_4 into the instrument's flow system. This gas sample was transported by the carrier gas through the glass frit in the gas-stripping chamber and was bubbled through a ten-ml volume of gas-free water. Thus, this calibration gas traversed approximately the same course that a sample of gas stripped from the water would follow, and produced a similar diffusion pattern as readout. The ml of gas injected were converted to an equivalent number of mg/l of gas stripped from the ten-ml water sample. A sample calculation of this conversion follows.

For CH_4

Assume: Barometric pressure = 750 mm Hg = 0.986 atmospheres
Air temperature = $24^{\circ}C = 297^{\circ}K$

Using the ideal gas law, PV = nRT, where

$P = 0.986$ atmospheres
$R = 0.082$ l atm/mole-degree (K)
$T = 297^{\circ}K$,

if we want to determine the volume of CH_4 that would be equivalent to 40 mg/l, then

$$n = \frac{40 \text{ mg}}{1} \times \frac{1 \text{ gm}}{1000 \text{ mg}} \times \frac{1 \text{ mole}}{16 \text{ gm}}$$
$$= 2.5 \times 10^{-3} \text{ moles/l.}$$

The volume of gas equivalent to this number of moles of CH_4 is

$$V = \frac{nRT}{P}$$
$$= \frac{(2.5 \times 10^{-3}) \times (297) \times (0.082)}{(0.986)}$$
$$= 0.0617 \text{ l} = 61.7 \text{ ml.}$$

Since the water volume taken for determination is only ten ml, then the volume of gas equivalent to a total 40 mg/l concentration is 61.7 ml/100 = 0.617 ml.

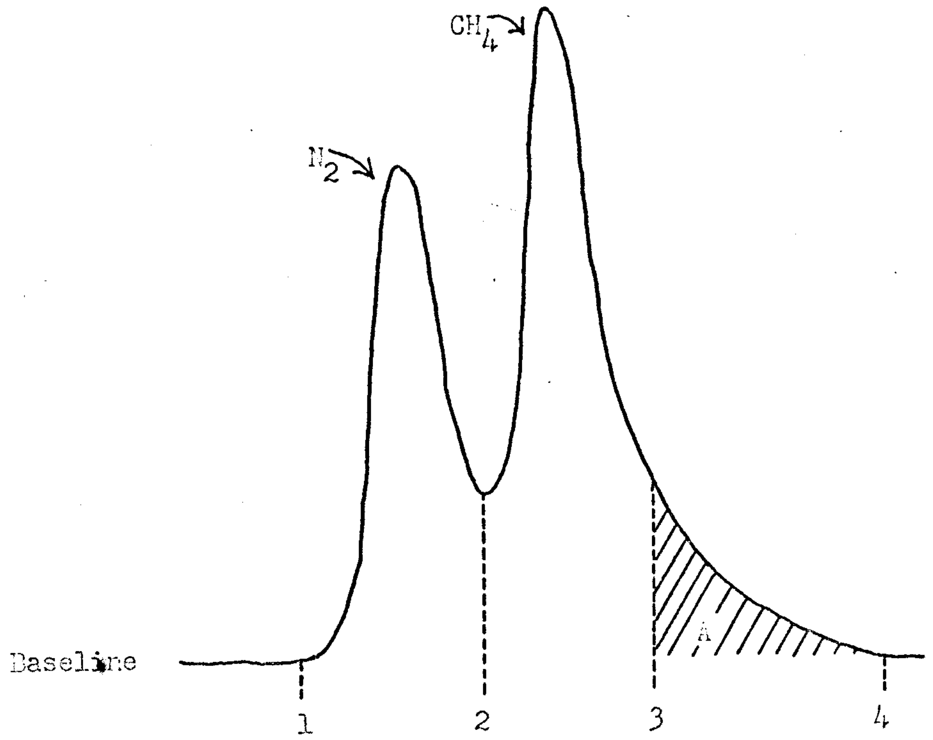
There was no barometer available for atmospheric pressure readings at Lake Mary or at the Kemp Biological Station laboratory; therefore, daily barometer readings were obtained from the weather bureau for a station at Green Bay, Wisconsin. This pressure reading was necessary because the calibration procedure involved the injection of measured volumes of gases. The barometric pressure readings were corrected for the elevation of Lake Mary.

The sampling valve used in this system was a two-position, six-way, linear valve (Aerograph). There are six entrance or exit portals protruding from this valve. Two of these are connected to the sample loop (a 1/8" O.D. polypropylene tube holding a ten-ml volume), two serve as an inlet or outlet valve to the sample loop, and the remaining two portals are connected directly to the gas flow system.

The water samples were put into the sample loop through the inlet portal. Two different methods for placing the water samples into the sample loop were used. When BOD bottles were used for the collection of samples, a flexible, plastic tube attached to the inlet portal was placed into the BOD bottle and a syringe was attached to the plastic tube fastened to the outlet portal. The syringe then drew the water sample into the sample loop. This sampling procedure was faulty because it allowed an unknown quantity of dissolved gases to escape from the sample to the atmosphere while the top of the BOD bottle was removed. In addition, the suction action of the syringe may have extracted some amount of gas from the water samples.

The second method of sample introduction utilized the sample bottle previously shown in Figure 3.2. The outlet of this bottle was fitted with a glass, Leur tip. This fit directly into a Leur coupling that was attached to the inlet tube on the valve. The sample was injected into the sample loop by pressing the plunger of the sample bottle. A sample injection system of this type introduced the water sample into the gas partitioner without allowing any exposure to the atmosphere.

Different techniques were used to quantitate the data output on the chart paper. The most reliable methods were integration of peak areas with a planimeter by hand or an integration of the areas by the use of a Disc Integrator attached to the Honeywell recorder. Each of these methods provided a factor of X square units equivalent to one mg/l of CH_4 or N_2. This factor was used for the quantitation of the unknown peaks, as shown in Figure 3.5. Because of the general tailing characteristics of the N_2 peak, the total N_2 area was assumed to be equal to the area under the N_2 peak from point 1 to point 2 plus area A, the peak area from point 3 to point 4. The total CH_4 area was then assumed to be equal to the total enclosed



METHOD OF QUANTITATION OF OVERLAPPING N_2 AND CH_4 GAS CHROMATOGRAPHIC PEAKS

FIGURE 3.5

area from points 2 to 4 minus area A.

STANDARD LABORATORY ANALYSES

Analyses of suspended and dissolved solids, chemical oxygen demand (COD), and analysis for the chloride ion were performed as outlined in Standard Methods, twelfth edition, (1965). Total solids determinations were performed on non-filtered samples. Samples to be analyzed for dissolved solids were first filtered through 0.45 μ membrane filters. Chloride ion was determined by titration of the sample with $Hg(NO_3)_2$, using diphenylcarbazone as an indicator in the presence of xylene cyanol FF. COD analyses were performed using a dichromate-sulfuric acid oxidation employing back titration to the ferroin endpoint with a standard $Fe(NH_4)_2(SO_4)_2$ solution.

A Perkin-Elmer model 303 Atomic Absorption spectrophotometer, equipped with the appropriate lamps, was employed for the analyses for calcium, magnesium, sodium, and potassium ions. The pH of the samples for calcium analysis was lowered to 2.5-3.5 before aspiration, as recommended by Bentley and Lee (14).

Sulfate analyses utilized a method presented by Rainwater and Thatcher (86). This method involves the reaction of the Ba^{+2} ions from a $BaCl_2$ solution with the SO_4^{-2} ions of the water sample to form a $BaSO_4$ precipitate. Excess Ba^{+2} ions react with the Thorin indicator in an 80 percent ethanol solution to produce a color change detectable with a Spectronic 20 spectrophotometer.

Total iron analyses were performed according to the procedure described by Plumb (85). The samples were heated (after the addition of concentrated HCl) to solubilize the iron. A $NH_2OH \cdot HCl$ reducing agent converted all iron to the Fe^{+2} form. This solution was buffered to a pH of 4.5-5.0 and a 2,4,6-tripyridal-s-triazine (TPTZ) reagent was added.

This TPTZ forms a colored complex with ferrous iron that is quantitated in a Beckman DU spectrophotometer at a wavelength of 593 nm.

Dolfino (31) described the persulfate procedure used for the analysis of total Mn. $(NH_4)_2S_2O_8$ is added to preconcentrated water samples and the solutions are boiled for a short time. This oxidation step converts all Mn species present to the MnO_4^{-2} species whose absorbance is measured at 525 nm with a Spectronic 20 spectrophotometer.

Technicon AutoAnalyzer systems were used for the colorimetric analyses of all the nitrogen and phosphorus species. The modules used included the peristaltic pump, the heating bath, a continuous digestor (used for the organic-N analysis only), a continuous-flow, single-beam colorimeter, and a recorder for readout.

Analyses for both total phosphorus and soluble, orthophosphate were performed. The analytical methods were identical to those used by Shannon (94). Samples for soluble orthophosphate analysis were filtered through HCl-washed 0.45 μ membrane filters. Total phosphorus samples were digested with an HNO_3-H_2SO_4 mixture. After filtering or digestion, the samples were analyzed by the stannous chloride-acid molybdate procedure. This technique involves the reaction of orthophosphate with the molybdate ion to form a molybdophosphoric acid. Stannous chloride reduces this acid to a blue-colored complex whose absorbance is measured at a wavelength of 651 nm.

The water samples were analyzed for three nitrogen species, NO_3-N, NH_3-N, and organic-N. The nitrate analytical procedure was a modification of that used at the Federal Water Pollution Control Administration Cincinnati Water Laboratory, Cincinnati, Ohio (41). This procedure involves the reduction of NO_3^- to NO_2^- by using a basic copper sulfate-hydrazine sulfate solution. The nitrite ions then react with a diazotizing-coupling reagent in the presence of acetone to produce a pink color, quantitated at a wavelength of 535 nm.

The ammonia analytical procedure consisted of the reaction of ammonia with an alkaline phenol solution and a hypochlorite solution to yield a blue-colored compound. This compound is thought to be related to indophenol. The blue color is measured at a wavelength of 610 nm. This procedure is described by Technicon Controls, Inc. (32).

Organic-N analyses were performed employing the system described by Kammerer, Rodel, Hughes, and Lee (59). The sample was digested with a Se-H_2SO_4 digestion reagent to convert much of the organic-N to NH_3-N. After neutralization, the sample was analyzed by the standard ammonia procedure described above.

CHAPTER IV

RESULTS AND DISCUSSION

Because of some unique problems encountered in the analysis of the Lake Mary water samples (ie., low mineral content of the water, high water color, long distance from Madison laboratory facilities), extensive checking of the precision of some of the analytical methods was requisite. The first section of this chapter is an evaluation of some of these experimental procedures. The precision of the analytical techniques dictates the types of data interpretation possible.

EVALUATION OF EXPERIMENTAL TECHNIQUES

Field Techniques

Many of the so-called "standard" field analyses were performed to provide a complete picture of the chemical limnology of lakes Mary and Rose. As such, the methods employed were procedures generally accepted as being applicable to nearly all limnological conditions. These analyses included measurement of temperature profiles of the lakes, determination of dissolved oxygen content, color, turbidity, pH, and specific conductance of the water samples. The preceding chapter contains discussions of the determinations of color, turbidity, pH and temperatures.

Dissolved Oxygen

The Yellow Springs Instrument Company model 54 RC dissolved oxygen meter was used for DO determinations during the final six months of the study. Before use of this instrument, the linearity of its response was checked throughout the anticipated DO range by comparison with Winkler determinations; the readout of the meter was found to be linear. This instrument was calibrated prior to each use, employing two complementary methods. The first involved laboratory calibration by immersing the probe into a water solution saturated with air and noting the temperature of the water. The instrument was then adjusted to indicate the appropriate DO concentration. The calibration was checked in situ by submersing the probe to a level of Lake Mary known to be free of oxygen and then adjusting the calibration to zero DO. This double check was found to provide adequate meter calibration.

Specific Conductance

Specific conductance measurements in the field or at the Kemp Biological Station laboratory were performed on waters of various temperatures. Consequently, it was necessary to determine the temperature of each water sample at the time of the specific conductance measurement and to correct these conductivity values for the effects of the temperature differences. To determine the specific conductance change/temperature change, four water samples were allowed to warm from 5-30°C. During this period of warming, conductivity measurements were taken at 3-4 C° intervals. The conductance change upon warming was expressed as percent conductivity change/C° and was constant within the temperature range investigated. The four water samples tested represented both anoxic and oxic waters from lakes Mary and Rose. Table 4.1 presents the results of this study. These were the values used for the adjustment of all specific conductance measurements to specific conductance at 25°C.

Alkalinity

Due to the high color of the water samples from Lake Mary, the detection of a colorimetric endpoint for alkalinity determinations was often difficult. Therefore, a conductometric endpoint was used for the alkalinity determinations. The standard deviation of this method was determined for ten replicate analyses of samples from two different depths of Lake Mary. Table 4.2 presents the results of these replicate titrations. A comparison

TABLE 4.1

SPECIFIC CONDUCTANCE-TEMPERATURE RELATIONSHIPS

Lake	Depth-m	Percent Conductivity Change/°C
Mary	1 (oxic water)	2.5
Mary	18 (anoxic water)	2.4
Rose	4 (oxic water)	2.5
Rose	10 (anoxic water)	2.2

TABLE 4.2

PRECISION OF CONDUCTOMETRIC ALKALINITY DETERMINATIONS

		Alkalinity-mg/l as $CaCO_3$		
Sample	Number of Replicate Analyses	Mean	Range	Standard Deviation
Lake Mary surface water	10	7.9	1.7	± 0.4
Lake Mary 17-m water	10	22.4	2.8	± 2.4

of the methyl purple endpoint with the conductometric endpoint for this same series of determinations indicated that the two endpoints agreed within ± 0.1 ml of the standard acid, with the methyl purple alkalinity generally requiring less acid for the titration. This 0.1 ml increment was equivalent to approximately 1.9 mg/l of alkalinity (as CaCO$_3$).

A spot check was also made to determine whether or not filtering of the samples would affect the apparent alkalinity. Analyses of four samples from selected depths in Lake Mary showed values for alkalinity that were within the standard deviation of the procedure; therefore, for these waters, filtering apparently does not measureably affect the titratable alkalinity.

Most of the alkalinity determinations were performed as soon as possible, usually within 8-10 hours after sample collection. It was felt that this immediate analysis was necessary because a loss of apparent alkalinity was observed during sample storage. Table 4.3 presents data showing this measurable alkalinity decrease. For samples from the 1-, 5-, and 9-m depths there was no measurable alkalinity change. For the sample from the 16-m depth (anaerobic waters), there was a finite, determinable decrease in the apparent alkalinity during the 44-day storage period. The greatest change in this observed alkalinity occurred during the first day of storage. (There is also the possibility that some alkalinity change occurred prior to the initial alkalinity determinations.) Part of the decrease in the apparent alkalinity of these anaerobic samples may have been due to a loss of sulfide species (through diffusion and/or oxidation) that were titrated as alkalinity. This would be an alkalinity decrease of less than 1 mg/l. The remainder of the loss is unexplained. The loss of sulfide may partially explain why no decrease in alkalinity was observed for the anaerobic waters from the 9-m depth, for only a trace of sulfide was present at this depth. The loss of this small amount of sulfide would

TABLE 4.3

APPARENT ALKALINITY DECREASE DURING STORAGE OF LAKE MARY WATER SAMPLES

Depth of Sampling-m	Date of Analysis	Initial pH	Conductometric Alkalinity mg/1 as $CaCO_3$
1	12-18-67	5.95	7.4
1	1-31-68	-	6.5
5	12-17-67	5.8	6.9
5	12-18-67	-	7.1
5	12-20-67	-	7.1
5	1-31-68	-	6.4
9	12-17-67	5.8	8.1
9	12-18-67	-	5.6
9	1-31-68	-	6.5
16	12-17-67	5.45	27.2
16	12-18-67	-	24.9
16	12-20-67	-	25.6
16	1-31-68	-	22.6

Samples were collected 12-17-67 and were unfiltered and unpreserved.

not have noticeably affected the titratable alkalinity. Although the data presented in Table 4.3 is for unfiltered, unpreserved samples, filtered and preserved (2 ml/l of $CHCl_3$) samples displayed the same apparent alkalinity decrease with time.

Sample Preservation

Since only a few analytical determinations were possible in the immediate vicinity of the sampling sites, most analyses were performed in the Madison laboratory. Thus, sample transport necessitated that either the chemical parameter of interest did not change with time or that the sample be preserved. The only chemical constituents thought to vary in their content or distribution of species with time were the nitrogen and phosphorus species. Hg_2Cl_2 was used as the nitrogen-species preservative. Jenkins (50) reported that samples preserved with Hg_2Cl_2 and stored at 4°C showed little change in nitrogen species composition for the first three weeks of storage. The insoluble, organic nitrogen fraction was an exception to this in that the concentration of this species was rather erratic over all time periods (he noted that this fluctuation may have been due to an inability to effectively sample this fraction). Since mineral nitrogen analyses for lakes Mary and Rose were limited to $NO_2^- + NO_3^-$-N, NH_3-N, and total organic-N, and since most of the analyses were performed within two weeks of the sampling date, it was felt that the nitrogen preservation methods used were adequate. In another report Jenkins (51) commented on the value of the preservation of phosphorus samples by the addition of $CHCl_3$ and storage at 4°C, the method used in this study. For storage up to one week, the soluble, orthophosphate and insoluble phosphorus fractions were well differentiated. Beyond this time, minor fluctuations occurred. For this study, analyses for soluble, orthophosphate and total phosphorus were performed within two weeks after sampling. By this time, there may have been some changes in the distribution of the phosphorus species; these were probably minor.

Laboratory Determinations

Miscellaneous Analyses

The laboratory procedures for supporting data generally were not checked to determine their standard deviation for Lake Mary water. These procedures included COD determination, Cl^- analyses, dissolved and suspended solids analyses, and the atomic absorption determinations of Ca^{+2}, Mg^{+2}, Na^+, and K^+. These analyses are performed routinely in water analyses and it was felt that no major interferences were present in Lake Mary waters that would adversely affect the determinations.

Manganese analyses were performed by J.J. Delfino. Delfino (31) discussed the precision of the persulfate oxidation method of manganese analysis. He also presented a statistical study of the modified methylene blue total sulfide analytical procedure. For a series of eight replicate analyses, Delfino obtained a total sulfide concentration of 3.50 ± 0.19 mg/l. It may be expected that the analyses of total sulfide in lakes Mary and Rose were not this precise since samples generally received rigorous handling during transport. Total iron analyses were performed by R.H. Plumb. Plumb (85) discussed the precision of the TPTZ method for iron quantitation in Lake Mary waters.

There were some procedures that did require modification before they were suitable for the analysis of Lake Mary waters*. A discussion of each of these procedures is presented below.

Sulfate Analyses

Of the procedures used for analysis of samples in this study, the procedure for the analysis of the sulfate ion was the most difficult to adapt for use with Lake Mary water. Numerous approaches to the analytical problem all failed to give completely satisfactory results. The difficulties in the development of an accurate and precise analytical procedure centered about two properties of the Lake Mary samples, namely, the low SO_4^{-2} concentration (less than 10 mg/l), and the high organic matter content (greater than 30 mg/l of organic carbon). This organic matter interferred with both spectroscopic and polarographic procedures.

Three analytical procedures and variations of them were tested. Initially, a modified Standard Methods (1965) turbidimetric procedure, based upon the formation of a $BaSO_4$ precipitate, was used. Sulfaver (Hach Chemical Company) replaced the standard $BaCl_2$ reagent. The high color of the water samples produced a blank reading that was higher than the lower limit of sulfate detectability, 10 mg/l of SO_4^{-2}. The use of untreated Lake Mary water as a blank was impossible because the addition of the Sulfaver and subsequent precipitation of $BaSO_4$ removed some of the water's color. Hence, often negative absorbance readings were noted after correction for the blank.

Mayer, Hluchaň, and Abel (110) discussed a micropolarographic method for the determination of sulfate. The chemistry of this procedure involved an exchange between a $BaCr_2O_7$ precipitate and SO_4^{-2} to produce a $BaSO_4$ precipitate. The released $Cr_2O_7^{-2}$ was reduced to CrO_4^{-2} and the Cr was then measured polarographically, the amount of Cr determined being equivalent to the amount of SO_4^{-2} in the water sample. This method gave a linear standard curve in the 1-10 mg/l SO_4^{-2} region, the concentration areas of major interest for the Lake Mary waters. The only difficulty encountered in the preparation of a standard curve was the consistently high blank value of approximately 1 mg/l SO_4^{-2}. There were some problems in adapting this method to the analysis of Lake Mary samples. To determine whether or not a water's natural organic compounds would interfer with this method, the sulfate ions were precipitated from some concentrated Lake Mary surface water, the organic carbon content of this Lake Mary concentrate determined, and enough of the concentrate added to each sulfate standard to be equivalent to the concentration of the organic carbon in Lake Mary. The results of this experiment indicated that the organic materials at the level found naturally interferred in a non-reproducible manner in this polarographic determination, with either a mercury pool or a saturated calomel electrode as a reference electrode.

Since these natural organic compounds interferred in a non-predictable manner, attempts to remove them were tried. Passing Lake Mary water through a column ($\frac{1}{2}$" x 8$\frac{1}{2}$"; flow rate, 1.5-2.0 ml/min) of activated coconut shell carbon (50-200 mesh) removed nearly all spectrophotometrically-measurable color (remaining color of 2-3 chloroplatinate-Pt color units). To aliquots of this Lake Mary "organic-free" water were added standard additions of known amounts of sulfate. The resulting sulfate determinations produced a broadly-scattered band of data points which had an apparent slope of less than that of a typical standard curve. Although the water was nearly free of colored organic materials, some organic compounds capable of fouling the polarographic electrodes were still present. Oxidation of the organic materials with acid, followed by neutralization with strong base was ineffective because of apparent trace metal contaminants in the reagents; these contaminants gave broad polarographic half-waves appearing at potentials interferring with the reduction of CrO_4^{-2}. Evidently, for a polarographic sulfate determination all organic materials must be absent from the sample to prevent random fouling of the mercury electrode. Most methods that would completely remove all of the organic materials without also introducing other contaminants are too time consuming to be of practical value.

The method finally adpoted for sulfate analysis was that presented by Rainwater and Thatcher (86). Briefly, this involved the precipitation of SO_4^{-2} by titration with Ba^{+2} in an 80 percent ethanol solution and in the presence of Thorin as an indicator. The titration with $BaCl_2$ was performed in a Spectronic 20 (wavelength, 520 nm) in a 1" cell with constant stirring. To correct for possible color interferences, the sample's absorbance was set at an initial value of 0.1. The $BaCl_2$ was added slowly to an absorbance of 0.3; the burette reading at this absorbance was taken as the endpoint of the titration. Generally, the change of absorbance was quite rapid and increased almost immediately from 0.1 to 0.3-0.4. Some difficulties did exist with this procedure. There was a large blank equivalent to approximately 1.2-2.0 mg/1 SO_4^{-2}; this procedure cannot differentiate between 0.0 and 2.0 mg/1 of SO_4^{-2}. Since the sulfate content of Lake Mary is between 0.0 and 6.0 mg/1 SO_4^{-2}, this high blank caused difficulty at these low sulfate levels. Also, just as the Sulfaver removed some of the color from the water as it precipitated $BaSO_4$, so may the $BaCl_2$ have removed some of the water's color; although this may have been of minor importance at a wavelength of 520 nm, only small absorbance changes were involved at best. This procedure was not totally satisfactory because of its inability to detect small concentrations of sulfate in colored water samples.

Nitrogen and Phosphorus Analyses

A Technicon AutoAnalyzer system was employed for the determination of all nitrogen and phosphorus species throughout the study. The most advantageous feature of this system is that it provides both samples and standards with identical treatment and eliminates inadvertent human errors. The accuracy and precision of analytical determinations using an AutoAnalyzer are comparable with those confirmed using manual techniques.

Of the nitrogen and phosphorus analytical methods employed, there was concern only for the technique for the NH_3 analyses. This method involved the absorbance measurement of the final solution at a wavelength of 610 nm. There was speculation that some of the high NH_3 concentrations found in the monimolimnetic waters (average concentration, 4.4 mg/l N) was due to light absorbance by some naturally-colored compounds. Because of the flow system in the AutoAnalyzer system this type of interference would be possible. To determine whether or not the naturally-colored compounds were interfering in this manner, a sample of surface water and a sample of monimolimnetic water were passed through a column of anion exchange resin to remove most of the color. The NH_3-N concentrations in these two treated samples were in close agreement (within ± 0.05 mg/l) with concentrations determined for the corresponding naturally-colored samples. Since one of these samples contained approximately 0.2 mg/l NH_3-N and the other contained approximately 4.4 mg/l NH_3-N, apparently the ion exchange resin did not alter the NH_3 concentrations of the samples. Thus it was concluded that color interference in the AutoAnalyzer determination of NH_3-N is negligible.

Dissolved Gas Analyses

The procedure used for the dissolved gas analyses was a modification of that presented by Swinnerton, Linnenbom, and Cheek (106). (A discussion of the fundamental principles of this method was presented in the preceding chapter.) Several functional tests were performed in Madison to determine the feasability of using this analytical method to measure dissolved gases. Varying the size of the gas-stripping chamber was employed to determine the optimum size for the gas concentration ranges in Lake Mary. It was hoped that the use of a 15-20 cm long x 1 cm diameter chamber would contain a sufficiently large volume of water such that a small, 5 mv recorder could be used for data quantitation instead of the 1 mv recorder. However, a sample chamber approximately 15 cm x 1 cm and containing 7.3 ml of sample gave less than twice the recorder response of a 5 cm x 1 cm chamber containing 2.2 ml of sample. In addition, the gas-stripping efficiency of the larger cell was less than that of the smaller one. This inefficiency was shown by the broader readout peaks obtained. As the sample volume increased, it became evident that the stripping of the dissolved gases from the sample was not an instantaneous process. The finite amount of time required was evidenced by a broadening and overlapping of peaks. In spite of this inefficiency, the final gas-stripping chamber employed held a sample volume of 10.0 ml. This enabled the use of a lower sensitivity setting on the gas partitioner, which allowed more stable operation than did the higher sensitivity settings.

In attempting to increase the efficiency of the gas-stripping process, various materials were added to the inside of the sample chamber to produce smaller bubbles. These materials included broken glass, 1-2 mm diameter glass beads, and boiling chips. None of these materials produced the desired results; instead of creating smaller bubbles, they collected the small bubbles and released them as larger ones, thereby decreasing the efficiency of the gas-stripping process.

The linearity of the response to a range of concentrations of N_2 and CH_4 was checked by two separate methods. The first involved the introduction of a gas sample into the gas partitioner by the use of a syringe. The instrumental response on the two percent and the ten percent sensitivity ranges was determined to be linear for CH_4 concentrations of 0-35 mg/l and for N_2 concentrations of 10-60 mg/l. However, this type of gas analysis procedure differed from analysis of lake samples since the N_2 and CH_4 were introduced as gas samples. Therefore, tests were run with distilled water samples saturated with air and CH_4. Gas-saturated water samples were produced by bubbling the pure gases through diffusor stones into the water in 1-l flasks for from 5-15 minutes. A sample of this water was then placed into the gas-stripping chamber and analyzed. Samples partially saturated (eg., $\frac{1}{2}$ saturated, $\frac{1}{4}$ saturated) were produced by diluting the saturated water with proper aliquots of He-purged distilled water. These samples were also placed into the gas-stripping chamber and analyzed. Instrumental response was verified to be linear for this procedure also. Although saturation of the water with air was possible, saturation with CH_4 was never achieved. The CH_4 saturation was always 67-73 percent of the saturation values. This inability to attain 100 percent saturation with CH_4 had no effect upon the measured linearity of response since the dilution was with CH_4-free water.

The first dissolved gas analyses for lakes Mary and Rose were performed on site with the gas partitioner set up in the Water Chemistry field truck. This arrangement was attempted in both winter and summer and proved unsuccessful. Although the Fischer 25 gas partitioner is a simply designed and constructed instrument, there are certain environmental conditions necessary for its satisfactory operation. The most important of these conditions is that the instrument remain at a constant temperature throughout the entire period of operation. If the instrument temperature fluctuates, this causes erratic response and wide instrumental baseline drift. Although an accessory for maintaining a constant temperature is provided for the gas partitioner, this is totally inadequate if the ambient temperature varies more than a few degrees. Due to the sporadic nature of outdoor temperatures, all analyses were performed in the laboratory at the Kemp Biological Station.

Analysis of samples away from Lake Mary required that all samples be collected simultaneously and that some samples would not be analyzed until up to ten hours after collection. Although these samples were kept in the tightly-closed gas-sampling bottles previously described (preceding chapter) and were maintained at as low a temperature as was possible, there was a chance that the dissolved gas concentrations might change during the time from collection until analysis. Thus, during the first use of the dissolved gas sampling bottles, some samples were analyzed at Kemp and again upon return to Madison two days after collection. Table 4.4 presents the data from these analyses. Although the data is scant, it does show that there is no significant loss of CH_4 or loss or gain of N_2 from the sample bottles over a two-day period. These samples represented a range of <u>in situ</u> temperatures comparable to those normally present in Lake Mary. The samples from cold waters (which warm during transport) showed no more change than did the samples from the warm water layers. It appeared safe to assume that once the water samples were in the sample bottles the dissolved gas concentrations were held constant until analysis two to ten hours later. Therefore, if any change in dissolved gas concentrations in the samples did occur, this alteration must have been during the transfer of the sample from the water sampler to the dissolved gas sampling bottle. Although there is no way to determine whether or not loss or gain occurred at this time, dissolved gas concentration changes appeared to be minor.

Two studies were performed to determine the precision of the sampling procedure and the precision of the overall analytical technique. It was hoped to determine whether or not there was greater variation between replicate analyses of different samples taken from the same depth than between replicate analyses of the same sample. To determine the precision of the sampling method, the following steps were taken. Three separate casts with the modified Van Dorn water sampler were made at the 5- and 16-m

TABLE 4.4

EFFECT OF STORAGE UPON DISSOLVED GAS CONCENTRATIONS

Lake Mary Depth-m	Dissolved Gas Concentrations-cc/l			
	9-23-67		9-25-67	
	N_2	CH_4	N_2	CH_4
1	16.1	-	18.2	-
2	16.5	-	17.1	-
4	18.4	-	17.0	-
7	19.4	-	18.7	-
9	19.6	3.7	19.6	4.1
17	16.0	15.4	18.5	15.5

All concentration values are the average of three or four analyses.

depths in Lake Mary. From each of these casts, water samples were drawn into two or three gas-sampling bottles. The concentrations of dissolved gases in each of these sample bottles were determined in either triplicate or quadruplicate. It was felt that this study might show if it were possible to measure the inability to identically sample the same water mass.

Table 4.5 presents a summary of the data for this study. (The data is representative of the precision of all the dissolved gas analyses.) This data points out several significant points concerning the dissolved gas analyses. In the 5-m samples it is possible to note some microstratification of the water column. The elemental statistical "t-test" (Huntsborger, 47) showed that the mean N_2 concentration determined for Van Dorn cast number one was statistically higher (at the 95 percent confidence interval) than those mean values determined for casts two and three. Microstratification at the 16-m depth was not noted. This data may indicate that monimolimnetic waters of a given depth are more homogenous than are the waters at a given depth in the mixolimnion. For waters above the chemocline, sampling discrepancies may be greater than N_2 measurement errors; however, for monimolimnetic waters microstratification and sampling dissimilarities cannot be separated from measurement errors.

Data for the CH_4 analyses indicates that there is slightly more scattering of concentrations for these analyses than for the N_2 analyses, with the overall range and standard deviation being greater than the corresponding values for the N_2 analyses. This lesser precision may result from small amounts of CH_4 gas transfer out of the sample water during the filling of the gas-sampling bottles. If such transfer does occur, however, it does not appear to be a major cause for concern.

From the above discussion it is apparent that, taking into account

TABLE 4.5

PRECISION OF DISSOLVED GAS ANALYSES

Van Dorn Cast Number	Depth-m	Sample Bottle	Individual Values (mg/1) For Sample Bottle N2 Mean	Sample Bottle N2 Range	Sample Bottle CH4 Mean	Sample Bottle CH4 Range	Van Dorn Cast N2 Mean	Van Dorn Cast N2 Range	Van Dorn Cast CH4 Mean	Van Dorn Cast CH4 Range	Sample Depth N2 Mean	Sample Depth N2 Range	Sample Depth CH4 Mean	Sample Depth CH4 Range
1	5	2	24.4±0.3	0.6	-	-								
1	5	3	23.7±0.6	1.3	-	-	24.0±0.6	1.7	-	-				
2	5	4	23.2±1.1	1.8	-	-								
2	5	5	22.2±0.2	0.4	-	-	22.5±0.7	1.8	-	-	22.9±0.9	3.0	-	-
2	5	6	22.2±0.2	0.4	-	-								
3	5	7	22.7±1.1	2.2	-	-	22.6±0.7	2.2	-	-				
3	5	8	22.6±0.4	0.5	-	-								
4	16	9	22.2±1.1	1.8	22.4±0.3	1.6	22.1±0.5	1.8	22.3±0.3	1.9				
4	16	10	22.0±0.5	1.1	22.9±0.9	1.9								
5	16	12	22.8±1.4	2.6	23.4±0.3	0.6					22.2±0.8	3.5	22.0±1.1	[illegible]
5	16	13	21.6±0.1	0.2	21.9±0.6	1.1	22.1±1.1	3.5	22.1±1.2	4.1				
5	16	14	21.9±1.1	2.2	21.0±1.0	2.3								
6	16	15	22.3±0.5	0.9	22.4±0.6	1.1								
6	16	16	22.4±0.3	0.7	22.1±1.4	2.7	22.2±0.4	0.9	22.2±1.0	2.7				

[illegible] deviation values and the ranges are for all of the individual determinations.

TABLE 4.5

PRECISION OF DISSOLVED GAS ANALYSES

			Individual Values (mg/l) For											
Van Dorn Cast Number	Depth-m	Sample Bottle	Sample Bottle				Van Dorn Cast				Sample Depth			
			N_2		CH_4		N_2		CH_4		N_2		CH_4	
			Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
1	5	2	24.4±0.3	0.6	-	-								
1	5	3	23.7±0.6	1.3	-	-	24.0±0.6	1.7	-	-				
2	5	4	23.2±1.1	1.8	-	-								
2	5	5	22.2±0.2	0.4	-	-	22.5±0.7	1.8	-	-	22.9±0.9	3.0	-	-
2	5	6	22.2±0.2	0.4	-	-								
3	5	7	22.7±1.1	2.2	-	-	22.6±0.7	2.2	-	-				
3	5	8	22.6±0.4	0.5	-	-								
4	16	9	22.2±1.1	1.8	22.4±0.3	1.6	22.1±0.5	1.8	22.2±0.8	1.9				
4	16	10	22.0±0.5	1.1	22.9±0.9	1.9								
5	16	12	22.8±1.4	2.6	23.4±0.3	0.6					22.2±0.8	3.5	22.2±1.1	1.1
5	16	13	21.6±0.1	0.2	21.9±0.6	1.1	22.1±1.1	3.5	22.1±1.2	4.1				
5	16	14	21.9±1.1	2.2	21.0±1.0	2.3								
6	16	15	22.3±0.5	0.9	22.4±0.6	1.1								
6	16	16	22.4±0.3	0.7	22.1±1.4	2.7	22.2±0.4	0.9	22.2±1.0	2.7				

The standard deviation values and the ranges are for all of the individual determinations.

both sampling dissimilarities and measurement errors, the average concentrations presented are precise to within approximately ten percent. Any type of analytical analysis involves a measure of uncertainty concerning the accuracy of the results, particularly those analyses involving gas chromatography. Quantitation of gas chromatographic data often requires the use of the discression of the analyst. Due to the harsh treatment that the gas chromatographic columns received during transport to and from the Kemp Biological Station, the operating characteristics of the columns and peak resolution ability varied from one sampling date to the next. Incomplete resolution of some peaks required that certain assumptions be made concerning the contributions of different components to peak overlap. Since the degree of overlap was different at each time of sampling, slightly different methods of quantitation were used for each set of data. Also, slightly different methods of calibration were used. For these reasons, comparisons of sets of data from different sampling dates may be difficult.

PHYSICAL AND CHEMICAL CHARACTERISTICS OF LAKES

The Lake Mary-Lake Rose system provides an opportunity for the close study of the limnology of environmentally-similar but physically-different lakes. Because of their close proximity, both lakes drain quite similar territory of forested land covered mainly by sugar maples, birch, black spruce, balsam, white cedar, and tamarack. The same environmental conditions affect both lakes and there is opportunity for logical comparison of a dimictic and a meromictic lake. Although this discussion centers upon the limnological aspects of Lake Mary, it also considers the chemical limnology of Lake Rose, particularly as it affects Lake Mary.

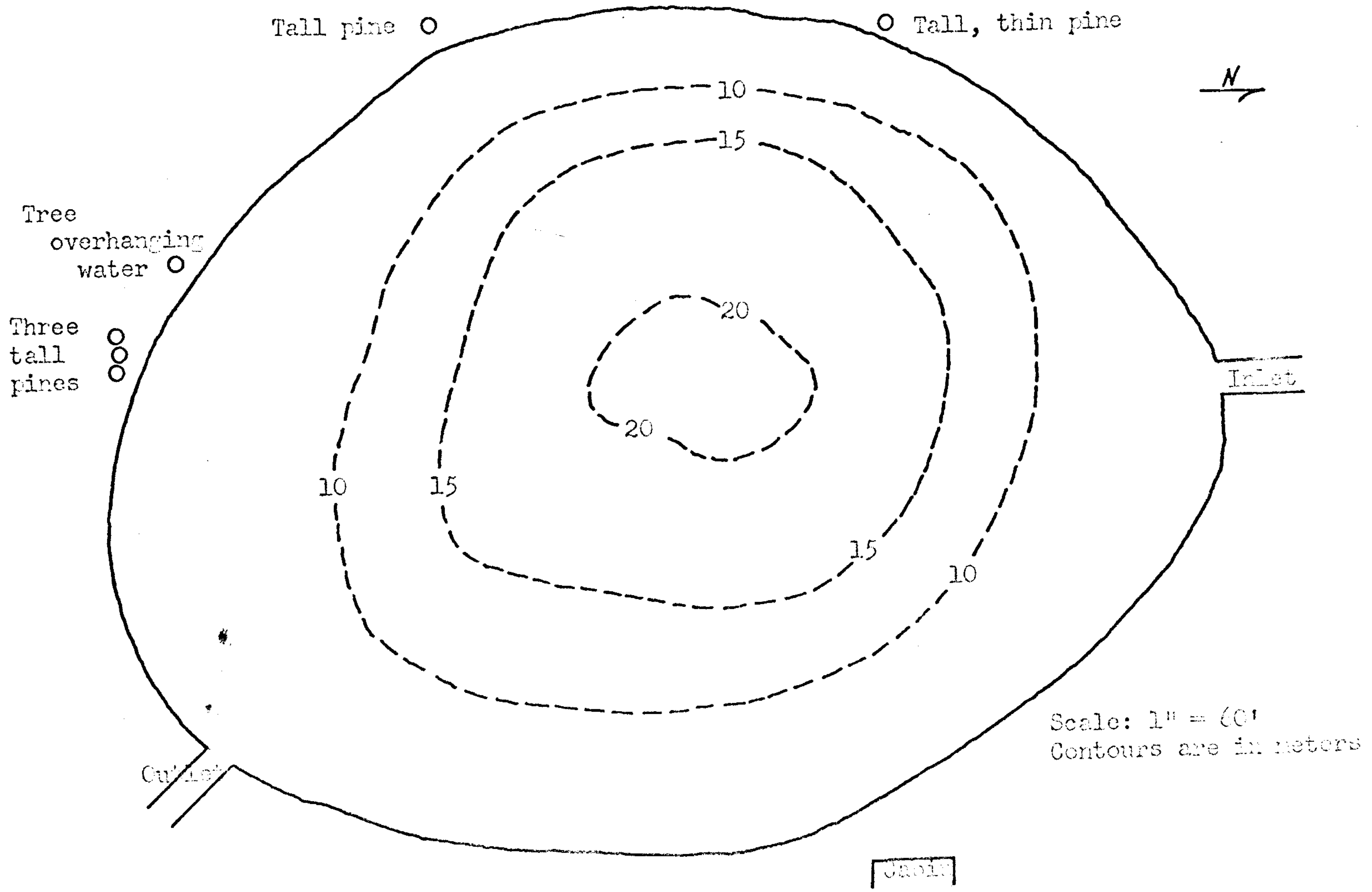
Lake Mary Physical Data

Temperature

The continued existence of the Lake Mary meromixis centers around the nearly cone-shaped basin of the lake. Figure 4.1 presents a bathymetric profile of Lake Mary. The contours shown here were determined from 23 depth measurements made through ice cover on 3-18-68. The symmetrical descent of the basin is evident in this fugure. The 10-m contour represents roughly the boundary between mixolimnetic and monimolimnetic waters of the lake. The 9-11 m water layer is the chemocline of Lake Mary, the 0-8 m water mass having the same chemical characteristics throughout and the 12-20.5 m water mass being quite homogenous.

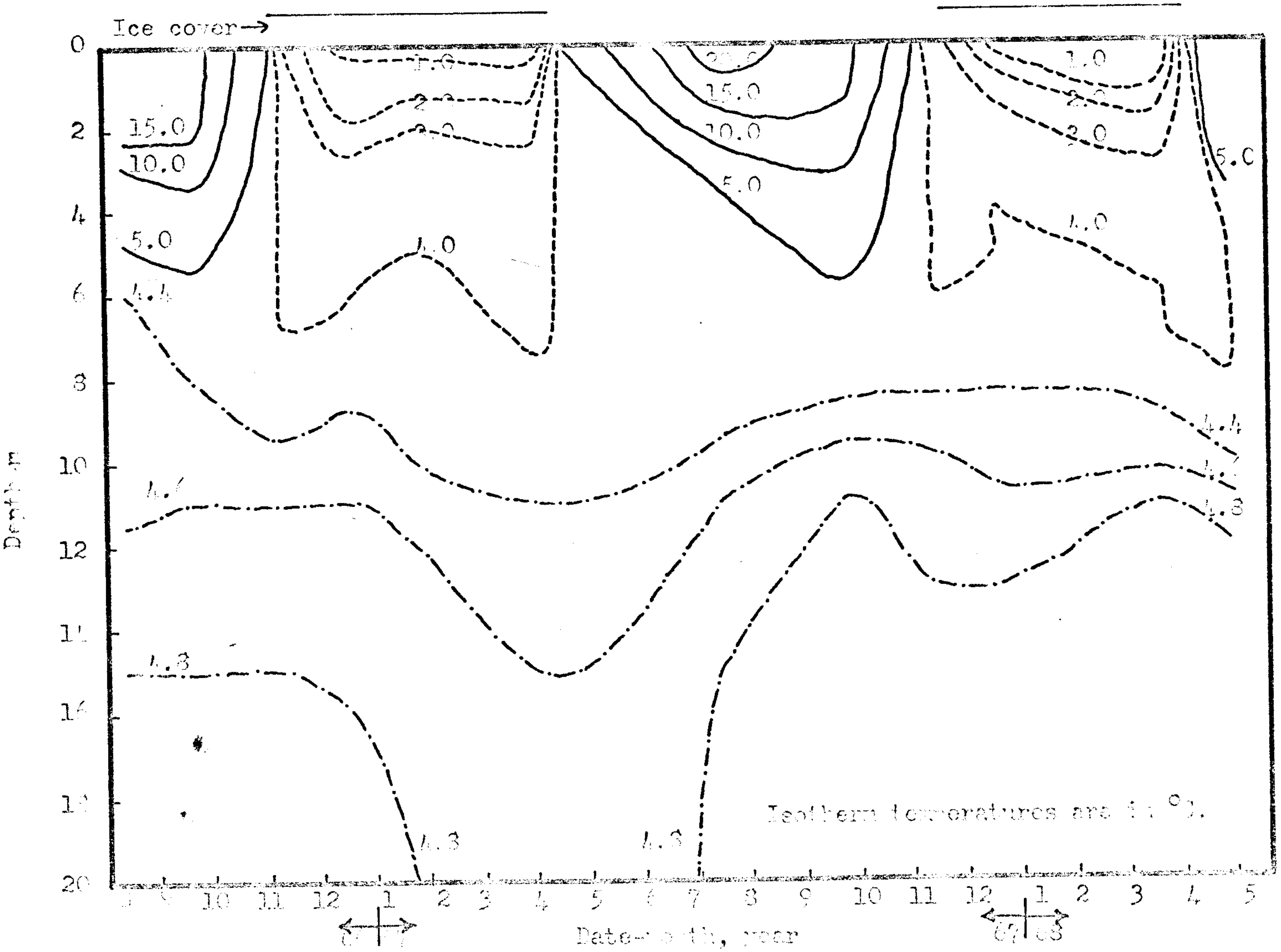
Figure 4.2 presents the seasonal distribution of some representative isotherms for Lake Mary. Figures of this type are constructed both by connecting data points of equal temperature and by interpolation. The interpolation technique assumes that the temperature change between two points of known temperature is linearly distributed with depth and/or time. This method of interpolation was generally employed to determine the isotherms in the upper mixolimnetic waters. Because of this method of isotherm construction, it is not possible to determine from this figure the exact temperature at a given depth of the lake on a given day. Variance from the exact temperature value should be minor, however.

Figure 4.2 furnishes a seasonal commentary upon the limnology of this meromictic lake. The temperature profiles shown here verify that mixing does not reach the 9-m depth. The temperature of 4.4°C appears to be closely related to the boundary between the chemically-stratified waters and the mixolimnetic waters; it is not the defining limit of the monimolimnion but fluctuates both above and below the center of the chemocline. With the exception of the temperature profile for 3-31-67, the 4.4°C isotherm never penetrated to a depth of greater than ten m. There is for this sampling time an apparent cooling of the bottom waters that was not noted at any other time during the study. This temperature lowering could



LAKE MARY BATHYMETRIC CONTOURS

FIGURE 4.1



LAKE MARY TEMPERATURE-DEPTH PROFILE

FIGURE 4.2

possibly be the result of an extremely harsh winter. More likely, it is due to an instrumental error in the precision of the thermometer.

During the two periods of ice cover, the oxygenated waters warmed and cooled again, as is seen in the periods of 11-66 to 4-67 and 11-67 to 5-68. Maximum mixing of the lake caused the 4.0°C water to penetrate to nearly the 7-m level in 11-66 and to 6 m in 11-67. After ice covered the lake, heat from the monimolimnetic waters warmed the lower mixolimnetic waters. As winter continued, however, these waters again cooled and the 4.0°C isotherm descended to a depth of nearly 8 m during both winters of study. It seems unlikely that the rate of heat influx from the monimolimnion decreased during the time period. Isotherms indicate that the total mixolimnetic water mass was depressed.

During the summer of 1967, warming from both the sun's rays and heat transfer from the meromictic layer was evident. The warming and cooling actions centered around the 9-11 m layer of water; this layer had a nearly-constant temperature throughout the year. Warming and cooling of the surface waters caused only slight variations in the temperature of the 9-11 m layer. The temperature of the monimolimnion does not appear to remain absolutely constant, but may show slight seasonal fluctuations. If this occurs, then these lower waters of the lake may simply be responding to the larger heat sink supplied by the mixolimnetic waters in the winter.

Color

The color of the waters of Lake Mary fluctuates erratically, being undoubtedly somewhat dependent upon the observer. Table 4.6 presents all of the color values determined for Lake Mary. It is interesting to note that the highest color values for both the surface and the monimolimnetic waters were observed during the periods of winter ice cover.

TABLE 4.6

LAKE MARY - COLOR

(expressed as mg/l Chloroplatinate-pt)

Sampling Date Depth-m	11-6-66	12-17-66	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67	12-17-67	3-18-68
1	80	80	120	80	120	120	100	160	160
2					120	100			
3					100	100	100	90	120
4					100	100			
5	60		120	85	100		100	100	100
6				85		80			100
7							120	120	120
8		80	105	85			120	110	
9					140	120	120	100	
10	100	100	120	130			140	140	140
11				140					
12						160	160	160	160
13		100	150	150	160				
14		100	210				200	160	160
15	100	120	210	150		160			
16	80	100	190				160	160	200
17	100	100	210	140	160	160			
18	140	100	210				160	210	200
19	140	120	175	170					
20	100	120	240	170	160	160	160	210	240

Slack (95) and Slack and Feltz (96) reported on the high color found in West Virginia and Virginia streams in the autumn. Beginning in September, leaf fall from deciduous trees produced highly-colored waters, particularly in a pooled area of the stream that received little surface flow through it. The maximum color of the stream water corresponded to the time of peak leaf fall. Hoak (45) added 180 gm of hand-picked oak leaves to 18.1 l of sterile, distilled water to study the water-soluble compounds contained within the leaves. After a five-day period of contact with the leaves, the water had a color of 1600 mg/l of chloroplatinate-Pt. This color increased to 2600 mg/l after 12 days, and then dropped to 2200 at 15 days. The color remained at this level for 75 days.

It seems likely that runoff from the Lake Mary drainage basin would both carry leaves into the lake for settling to the bottom waters and bring some highly-colored leaf leachate to the surface waters. Observations of the flocculant bottom material have shown partially-degraded leaf fragments to be present. The leaves of the deciduous trees surrounding Lake Mary probably contribute a large amount of the water's color.

Turbidity

Turbidity data is shown in Table 4.7. From these turbidity values it can be seen that, generally, the waters of Lake Mary are quite clear. There was some evidence of increased turbidity in the fall or winter which could be an indicator of some mixing processes occurring within the monimolimnetic waters. However, the amounts of turbidity were not large enough to be due to a phenomenon such as a density current flowing down the sides of the lake basin. At no time throughout the study was any large sestonic material noted in any water samples.

Solids

Dissolved and suspended solids analyses were not routine, but were

TABLE 4.7

LAKE MARY - PHYSICAL DETERMINATIONS

Sampling Date	Turbidity (expressed as mg/1 SiO_2)					Dissolved Solids (expressed in mg/l)	Suspended Solids (expressed in mg/l)
	1-21-67	7-10-67	9-23-67	11-11-67	12-17-67	3-31-67	3-31-67
Depth-m							
1	6	2	3	14	5	20	9
2		2	3				
3		2	3	5	3		
4		2	3				
5	6	3		10	3	38	0
6			3			32	0
7				3	3		
8	3			10	3	31	0
9		4	4	20	3		
10	17		15	13		17	33
11						20	39
12			9	24	12		
13	23	8				61	15
14	17			26	9		
15	28		13			54	49
16	22			22	14		
17	28	5	6			60	39
18	22			42	11		
19	17					39	25
20	17	5	14	38	8	46	33

determined for one profile of water samples. The data shown in Table 4.7 was obtained mainly to see if there were any chemical species present in the lake waters for which no analyses were being performed. The average dissolved solids content of the upper waters was 25-30 mg/l; that of the monimolimnetic waters was 45-50 mg/l. Later data (a summation of the concentrations of all the dissolved species determined) showed that analyses of all major chemical components were performed.

pH

pH data is tabulated in Table 4.8. A typical pH profile is presented in Figure 4.3. No specific correlations between pH and any other chemical parameters were seen. It was noted that the pH of the chemically-stratified waters was relatively constant throughout the monimolimnetic depths at each time of sampling. There were two exceptions to this, in the bottom waters on 12-17-66 and on 4-21-68. At these times the pH of these water layers was 0.7-0.8 pH units higher than the pH of the layers above. This remains unexplained. It should be noted that, due to the low ionic strength of the waters of lakes Mary and Rose and their low buffer capacities, there was often difficulty in obtaining stable pH measurements. Possibly this problem of low ionic strength could be eliminated by adding a measured amount of KCl or similar strong electrolyte to each sample before pH determination. This procedure might provide more stable readings and eliminate apparent pH differences that are not real.

Lake Mary Chemical Data

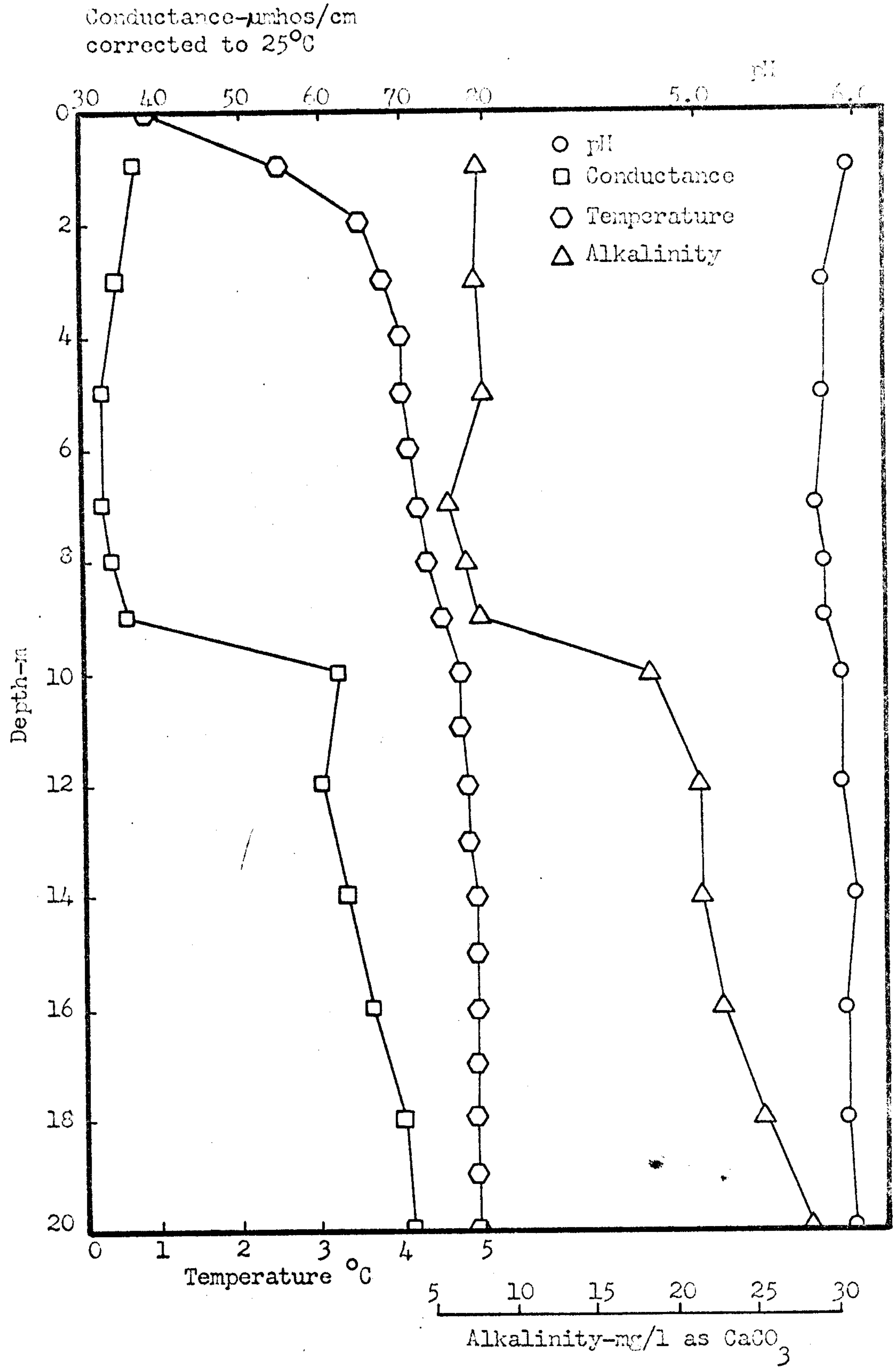
Dissolved Oxygen and Specific Conductance

The dissolved oxygen and specific conductance profiles help define the limits of the chemocline of Lake Mary. Figure 4.4 shows the oxygen concentrations in the mixolimnion. All conductivity values are given in Table 4.9. The specific conductance profiles are some of the best physical

TABLE 4.8

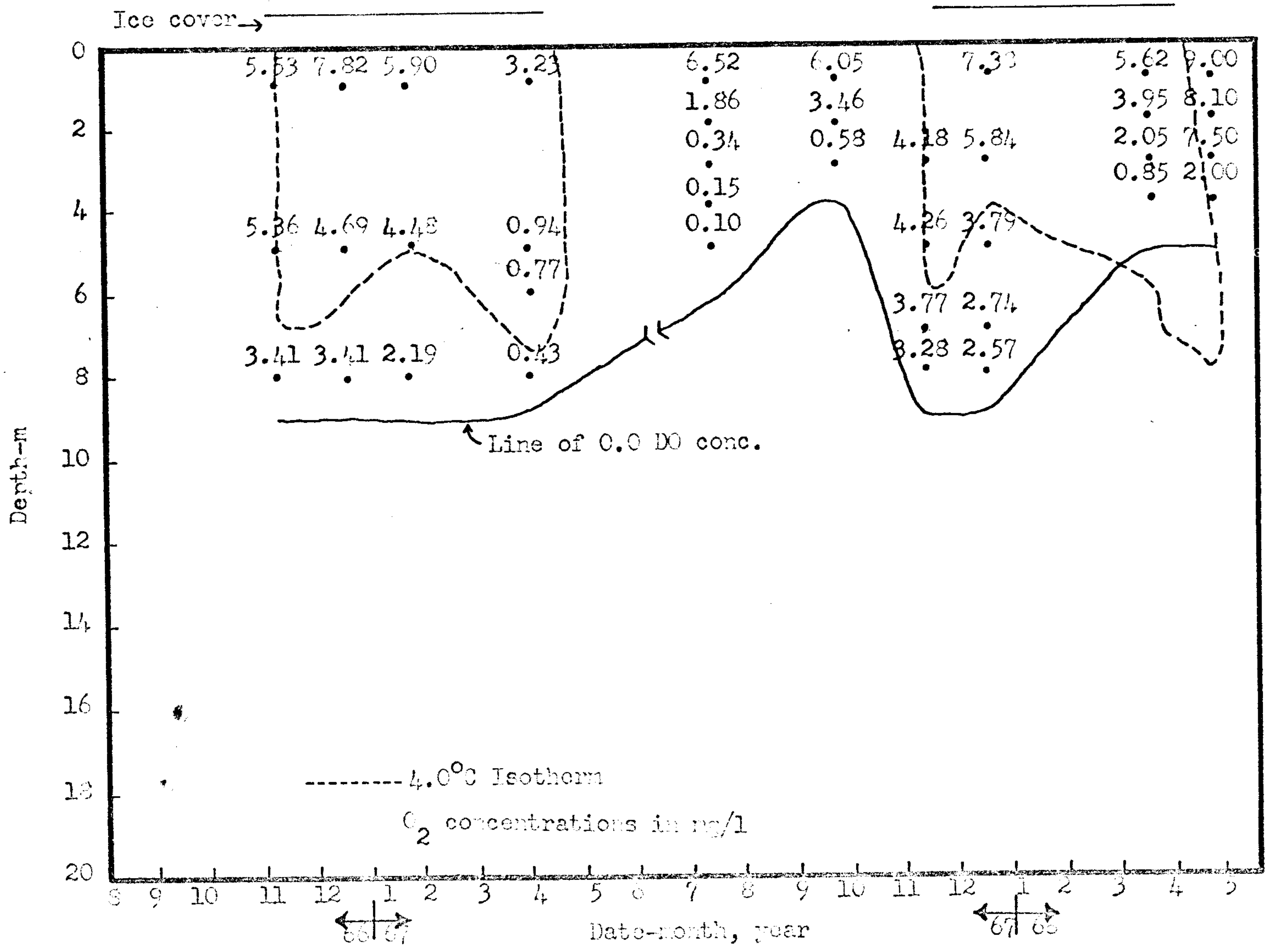
LAKE MARY - pH

Sampling Date Depth-m	9-18-66	11-6-66	12-17-66	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67	12-17-67	3-18-68	4-21-68
.1	6.1	5.9	5.8	6.6	5.75	5.6	5.7	5.6	5.95	5.75	5.4
2						5.7	5.4				
3						5.65	5.4	5.7	5.8	5.65	5.4
4						5.7	5.4				
5	5.3	5.2	5.8	6.1	5.6	5.75		5.55	5.8	5.65	5.1
6					5.55		5.4			5.7	5.1
7								5.55	5.75	5.55	
8			5.8	5.8	5.6			5.5	5.8		5.3
9						6.05	5.7	5.6	5.8		
10	5.55	6.2	5.75	6.0	5.95			5.7	5.9	5.7	5.55
11					5.9						
12							5.7	5.7	5.9	5.7	
13			5.8	6.1	5.85	6.0					5.7
14			5.8	6.1				5.7	6.0	5.7	
15	5.7	6.15	5.7	6.1	5.85		5.7				
16		6.1	5.6	6.1				5.7	5.95	5.7	5.7
17	5.7	6.15	5.75	6.0	5.9	5.9	5.7				
18		6.2	5.8	6.1				5.7	5.95	5.75	6.5
19		6.15	5.7	6.0	5.9						
20		6.0	6.4	6.0	5.75	5.9	5.7	5.7	6.0	5.75	6.5



LAKE MARY pH, TEMPERATURE, CONDUCTIVITY, AND
ALKALINITY PROFILES, 12-17-67

FIGURE 4.3



LAKE MARY DISSOLVED OXYGEN CONCENTRATIONS

FIGURE 4.4

TABLE 4.9

LAKE MARY - SPECIFIC CONDUCTANCE

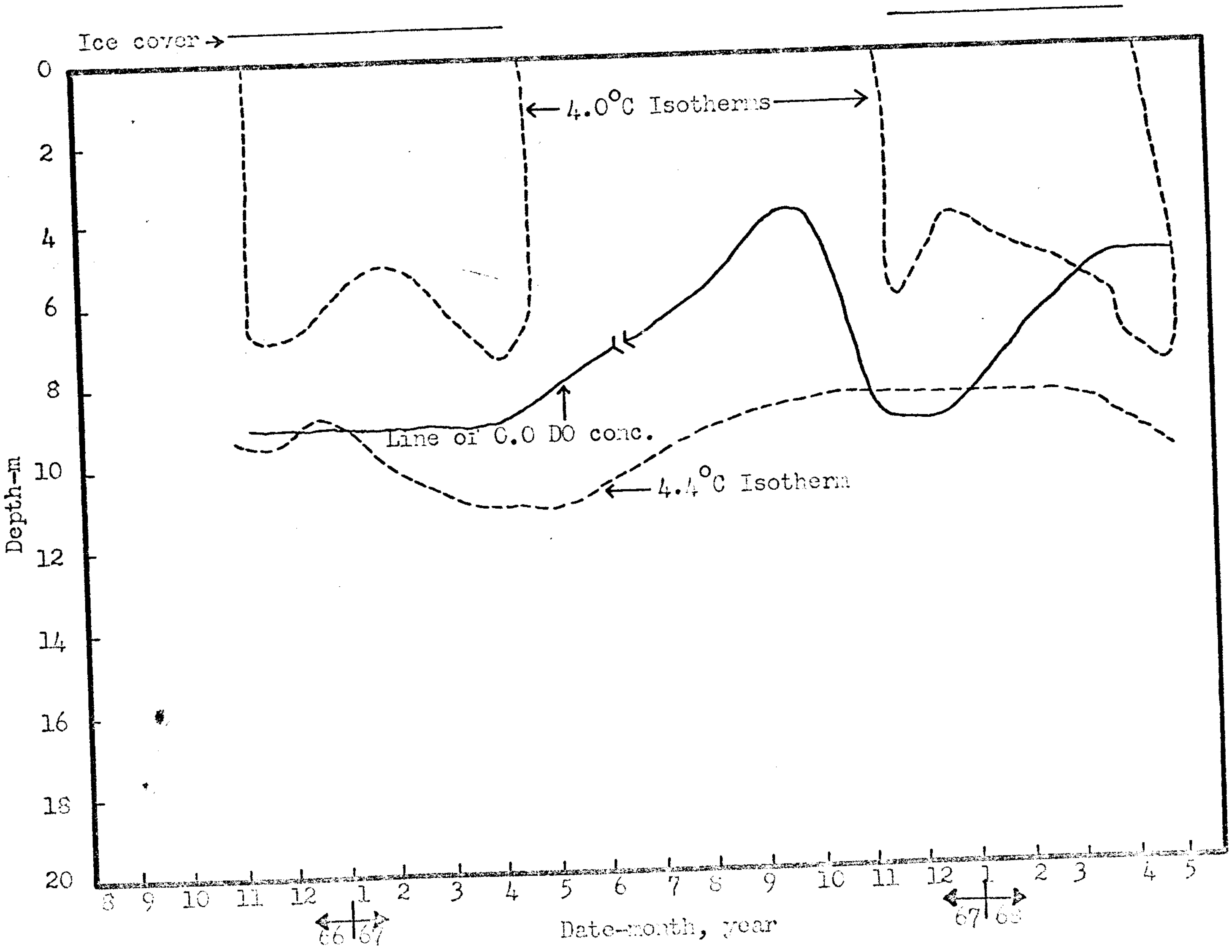
(expressed in µmhos/cm and corrected to 25°C)

Sampling Date	8-11-66	9-18-66	11-6-66	12-17-66	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67	12-17-67	3-18-68	4-27-68
Depth-m												
1	34	30	32	31	34	41	30	37	47	37	44	
2							33	32				
3							34	36	39	35	42	
4							36	-38-				44
5	31	34	30	30	33	37	46		40	33	-39-	-43-
6						36		35			37	41
7							--		39	33	36	
8				30	31	38			46	34		40
9			--	--	--	--	66	51	-57-	-36-		
10	53	54	43	40	41	54			56	62	42	50
11						54						
12								73	72	60	63	
13				56	60	68	75					64
14				55	64				79	63	63	
15	71	70	59	59	62	69		75				
16			59	59	63				87	66	63	71
17		70	59	61	65	70	76	88				
18	72		61	61	63				83	70	69	68
19			61	63	65	72						
20			61	66	66	71	76	74	85	71	71	66

Dotted lines represent shallowest depth of water layers of 0.0 mg/l dissolved oxygen content.

evidences for the presence of the chemocline. A typical profile is shown in Figure 4.3. For dates when sampling at the chemocline was at one-m intervals, the conductivity values showed the results of the increasing concentrations of the dissolved chemical species with increasing depth. The chemocline did fluctuate in depth slightly from season to season, the uppermost waters of it ranging in depth from 5-9 m. As the upper limit of the chemocline varied, so did the thickness of this layer. In July, 1967, the thickness was 4-5 m, whereas in December, 1967, it was only 1 m. There apparently is no simple explanation for this phenomenon, but it is likely a function mainly of the lake's thermal characteristics. As the chemocline was heated by both the mixolimnetic and monimolimnetic waters, its temperature reached that of the upper monimolimnetic waters. At equivalent temperatures, these two water masses may mix and transfer some of the dissolved chemical species from the upper part of the monimolimnion more easily than while the lake is more rigidly stratified. In the wintertime the chemocline cooled from above, but still warmed from below. This process diminished the thickness of the chemocline and further restricted mixing of the water layers.

The line connecting depths of zero dissolved oxygen concentrations in Figure 4.4 follows the pattern of seasonal mixing of the lake's upper waters, with oxygen reaching deeper mixolimnetic depths during the periods of maximum mixing and decreasing during periods of stagnation, due to chemical oxidation of reduced species that diffuse upwards. During stagnation the oxygen levels were independent of the temperatures of the water masses; that is, a rise in the depth of the zero DO layer was not always accompanied by a warming of the waters from lower depths. Figure 4.5 shows the zero DO contour and two isotherms, indicating the times of seasonal mixing and the approximate depth of the chemocline. At no time



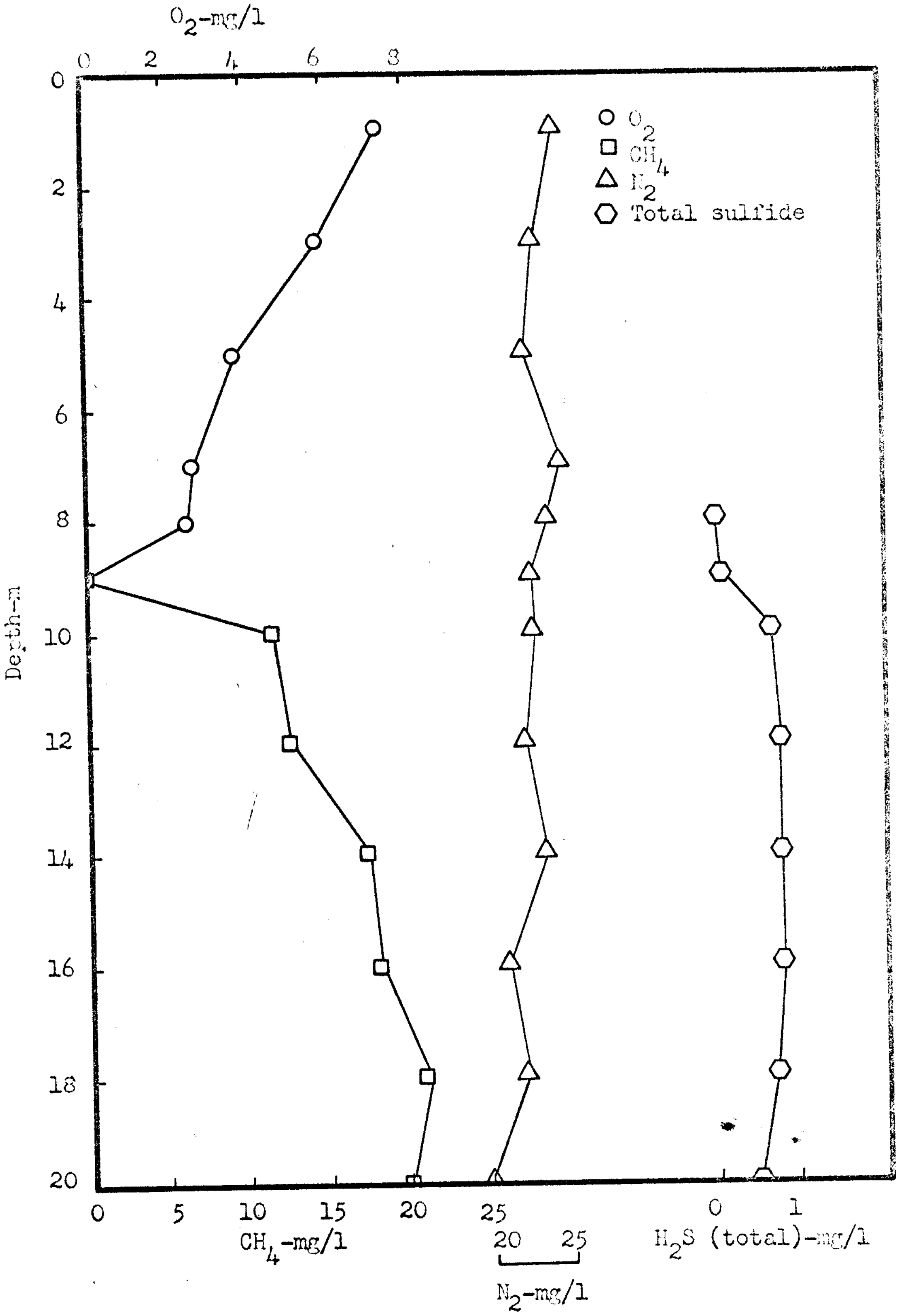
LAKE MARY TEMPERATURE-DISSOLVED OXYGEN RELATIONSHIPS

FIGURE 4.5

during the 21-month period of study of Lake Mary did any oxygenated waters reach the 9-m depth. Therefore, from lake volume data (Juday and Birge, 58) approximately 23,300 m^3, or 26 percent, of the total volume of Lake Mary is permanently devoid of oxygen.

The dissolved oxygen profiles of Lake Mary look much as those of an 8-m dimictic lake might under similar meteorological conditions. A typical oxygen profile for Lake Mary is shown in Figure 4.6. At this time the DO content decreased from 7.4 mg/l at a depth of 1 m to 0.0 mg/l at the 10-m depth. Although no oxygen sample was taken at the 9-m depth, it is likely that there was no DO present since a trace (0.04 mg/l) of total sulfide was found at that depth.

There are several factors contributing to the removal of dissolved oxygen from the Lake Mary water column. Oxidation of organic matter that enters the lake from the surrounding basin or is produced in the littoral area of the lake itself is expected. Respiration of organisms, both macro- and micro-, may consume a large amount of oxygen. The decay of falling seston particles also consumes oxygen. Reduced chemical species that are released from the sediments or that diffuse upward through the chemocline most probably exhibit the largest oxygen demand. Finally, Hutchinson (49) theorized that the colored matter in lakes undergoes some easy oxidation in the presence of oxygen and, thus, causes a decrease in the percent of oxygen saturation in lakes with large concentrations of organic material (color greater than 50 mg/l) in comparison with lakes of low color. However, the contribution of dissolved organic materials to an oxygen deficit has yet to be proven. Likely, the decay of easily-degradable organic matter is responsible for the DO decrease, but most of the colored organic materials in the water (largely decay products) are quite resistant to oxidation (Hall, 42).



LAKE MARY DISSOLVED GASES, 12-17-67

FIGURE 4.6

Alkali and Alkaline Earth Metals

The concentrations of the alkali and alkaline earth metals are tabulated in Tables 4.10 and 4.11. Typical profile concentrations are shown in Figure 4.7. Only a single profile for K^+ was determined. The concentrations of Na^+, Mg^{+2}, and Ca^{+2} ions were observed during at least three seasons.

The concentration of Na^+ ranged from 0.8-1.5 mg/l with one exception. The 2.1 mg/l concentration at the 15-m depth on 12-17-66 was not considered to be an important deviation from the other Na^+ concentrations. The Na^+ content of the water apparently does not vary with either depth or season. The average Na^+ content from all the analyses was 1.2 mg/l. The one set of K^+ data indicated that this ion does not change in concentration with depth and was present at an average concentration of 0.9 mg/l. A limited amount of previous work by Lohuis, Meloche, and Juday (71) indicated that Lake Mary water contained 4.0 mg/l Na^+ and 1.3 mg/l K^+. The Na^+ concentration seen by these workers is unexplainably higher than that presently found. The present K^+/Na^+ ratio, by mg/l, was approximately 0.75. Hem (44) stated that in waters of a low dissolved solids content the proportion of K^+ to Na^+ may be approximately 1:1. This condition is most commonly found in waters that are associated with igneous rocks. According to Martin (76), the glacial drift in the Northern Highland area of Wisconsin in which Lake Mary is located contains 65-70 percent igneous rocks. Thus, the K^+/Na^+ ratio and the concentrations indicate that the only source of these two ions is the weathering of the materials in the lake's drainage basin.

Mg^{+2} concentrations ranged from 0.8-2.5 mg/l for the 60 analyses performed. Data indicated that the Mg^{+2} distribution remained unchanged throughout the lake at all times of the year and had an average concentration

TABLE 4.10

LAKE MARY - SODIUM AND CALCIUM

(expressed in mg/l)

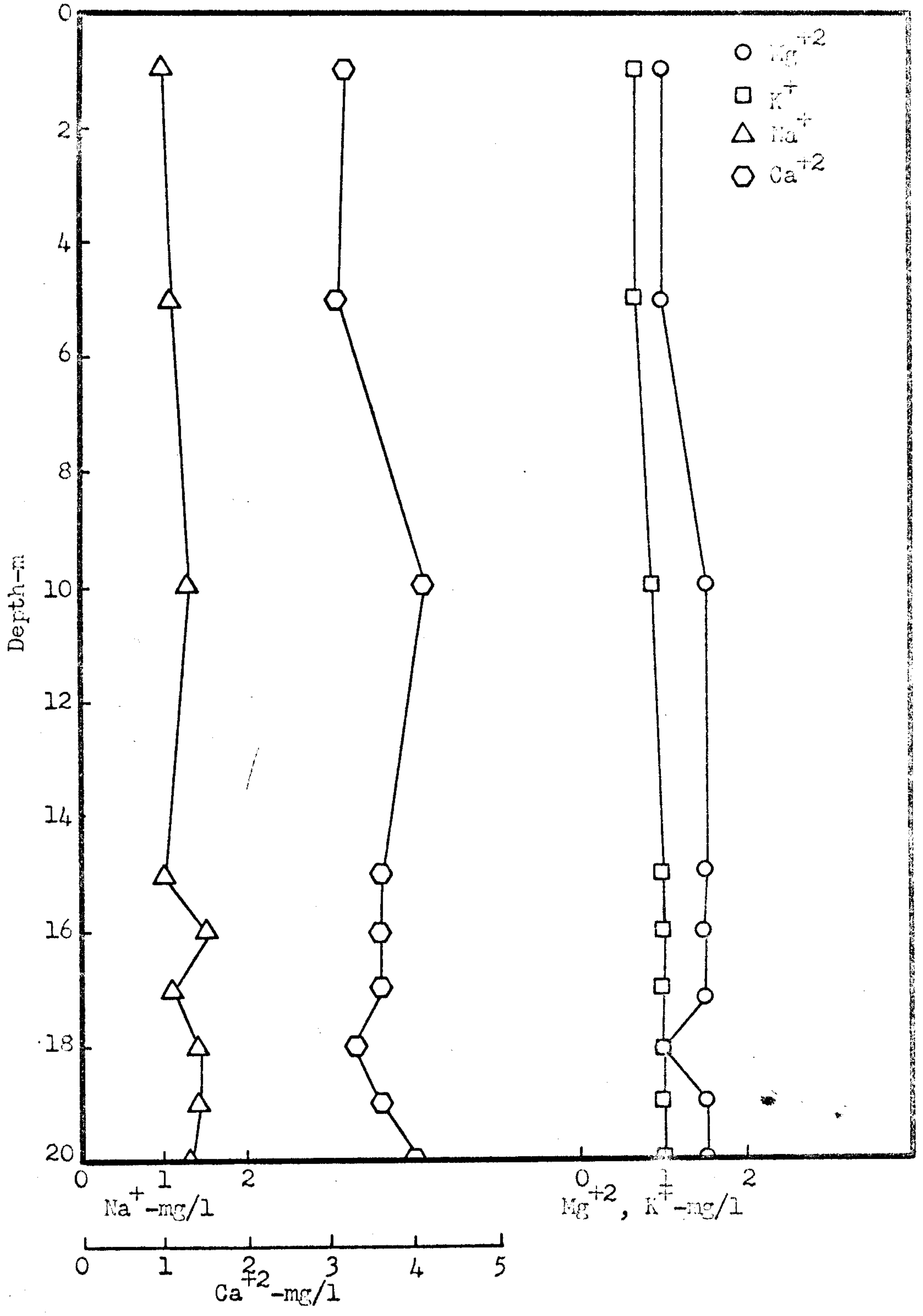
	Na^+			Ca^{+2}					
Sampling	11-6-66	12-17-66	3-31-67	11-6-66	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67
Depth-m									
1	1.0	0.8	1.2	3.2	5.7	3.9	3.9	5.2	3.1
2									
3							3.7		
4								3.8	
5	1.1	0.8		3.1		3.4	4.2		4.8
6						3.5		3.2	
7									
8		0.9			3.7	6.7			3.1
9							3.9	3.6	3.2
10	1.3	1.0	0.9	4.1		4.0			
11						4.1			
12								3.6	3.3
13		1.0			3.5	3.8	3.9		
14		1.2							3.5
15	0.9	2.1		3.6		3.9		3.6	
16	1.5	1.1		3.6					3.5
17	1.1	1.3		3.6	3.7	3.8	3.9	3.5	
18	1.4	1.0		3.3					3.8
19	1.5	1.2		3.6		4.2			
20	1.4	1.1	1.0	4.0	3.7	4.0	3.7	3.6	3.6

TABLE 4.11

LAKE MARY - POTASSIUM AND MAGNESIUM

(expressed in mg/1)

	K^+	Mg^{+2}						
Sampling Date	11-6-66	11-6-66	12-17-66	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67
Depth-m								
1	0.7	1.0	1.0	1.6	1.3	1.5	1.1	1.0
2								
3						1.5		
4							1.1	
5	0.7	1.0	1.0		1.1	1.5		1.1
6					1.1		1.1	
7								
8			0.8	1.5	1.3			1.0
9						1.7	1.1	1.1
10	0.9	1.5	1.0		1.2			
11					1.3			
12							1.2	1.2
13			1.0	1.6	1.2	1.7		
14			2.5					1.2
15	1.0	1.5	2.0		1.2		1.2	
16	1.0	1.5	1.0			1.6		1.2
17	1.0	1.5	1.0	1.8	1.2		1.2	
18	1.0	1.0	1.0					1.2
19	1.0	1.5	1.0		1.3			
20	1.0	1.5	1.3	1.0		1.6	1.2	1.2



LAKE MARY-ALKALI AND ALKALINE EARTH METALS, 11-6-66

FIGURE 4.7

of 1.3 mg/l. Generally, the Ca^{+2} concentrations in Lake Mary ranged between 3.1-4.2 mg/l. Of 49 analyses performed over a one-year period only three fell outside this range. Ca^{+2} concentrations remained approximately constant throughout the water mass and throughout the year, with an average concentration of 3.8 mg/l. Juday and Birge (58) reported one analytical value for Ca^{+2} of 1.8 mg/l and a trace amount of Mg^{+2} as being present in the waters. This data would, therefore, indicate that there has been an increase in the Ca^{+2} and Mg^{+2} concentrations in Lake Mary during the last 25-30 years and that the Ca^{+2} concentration has approximately doubled. Verification of this increase is impossible. If the increase is real, then the present-day homogenous distribution of Ca^{+2} indicates that the increase has affected both lake layers simultaneously. During the period of study, however, there was no noticeable alteration of either the Ca^{+2} or Mg^{+2} concentrations.

Scattered studies of Helmet Lake, a highly-colored, bog lake also located in Vilas County, performed by the University of Wisconsin Water Chemistry Program students showed that this lake has concentrations of alkali and alkaline earth metals comparable to those found in Lake Mary. The range of Na^{+} concentrations was 0.7-1.1 mg/l; for K^{+}, 0.8-1.1 mg/l; for Mg^{+2}, 0.7-1.5 mg/l; and for Ca^{+2}, 1.1-2.3 mg/l. Only the Ca^{+2} content was lower than that found in Lake Mary and was approximately that reported by Birge and Juday (58) for Lake Mary.

Hutchinson (49) reported that in all open-water systems there is a tendency for the concentrations of the alkali and alkaline earth metals to follow the relationship $Ca^{+2} > Mg^{+2} > Na^{+} > K^{+}$. The data for Lake Mary corresponds well with the relative distribution noted by Hutchinson.

The alkali and alkaline earth ionic concentrations were monitored and were found to remain approximately constant at all times. These ions served as conservative tracers for the water systems and indicated that no large, unpredicted influxes occurred. The inflow and outflow of these substances is presently constant in Lake Mary.

Chemical Oxygen Demand

Chemical oxygen demand was determined for one set of water samples to obtain an indication of the distribution of oxidizable species in the water column. The results are given in Table 4.12. The COD of the monimolimnetic waters was approximately constant at 70 mg/l. There was, however, much variation in the COD of the mixolimnetic waters, indicating the presence of possible currents and non-homogenous mixing. The organic carbon content of Lake Mary waters averages approximately 30 mg/l in waters from all depths (Hall, 42). COD is theoretically 2.5 x organic carbon content of a sample. The average value of 68 mg/l COD is a close approximation of 2.5 x 30 mg/l organic carbon. It would be expected for the COD distribution within Lake Mary to be approximately constant throughout the monimolimnetic waters and also constant throughout the mixolimnetic waters. The COD of the chemically-stratified waters should be slightly higher than that of the mixed, surface waters. However, in addition to the incompletely-oxidized organic materials within the water, there are relatively few chemical species that would be subject to this dichromate oxidation. Such species should ideally be equally distributed in the monimolimnetic waters; this is, evidently, the case. Non-homogenous COD concentrations observed in the mixolimnion may have been due to spring runoff entering the lake beneath the ice and forming layers of water.

Chloride

Chloride concentrations were monitored to determine if they were approximately seasonally constant. Table 4.12 shows that the Cl^- concentrations were approximately constant and averaged 1.5 mg/l. This

TABLE 4.12

LAKE MARY - CHLORIDE, TOTAL IRON, AND CHEMICAL OXYGEN DEMAND

(expressed in mg/1)

	Cl^-			Total Fe					COD
Sampling Date	1-21-67	3-31-67	7-10-67	8-11-66	9-18-66	11-6-66	12-17-66	1-21-67	3-31-67
Depth-m									
1	1.5	1.7	1.4	0.22	0.30	0.33	0.40	0.35	94
2			1.4						
3			1.4						
4			1.6						
5	1.4	2.0	1.4	0.40	0.40	0.39		0.39	32
6		1.1							85
7									
8	1.4	1.4					0.44	0.45	49
9			1.3						
10	1.3	2.0			0.73	0.73	0.79	0.68	76
11		1.5							67
12									
13	1.5	1.3	1.7				0.79	0.79	71
14	1.5						0.92	0.76	
15	1.4	1.8		0.86	0.74	0.88	0.86	0.75	71
16	1.5					0.76	0.87	0.70	
17	1.5	1.7	2.4		0.87	0.90	0.94	0.71	
18	1.4			0.74		0.86	0.90	0.79	
19	1.7	1.4				0.74	0.94	0.79	
20	1.4	1.7	1.8			0.77	0.85	0.88	

concentration was quite close to that found by Nussmann (79), 1.9 mg/l, and by Leverin (67), 1.5 mg/l, in the waters of Lake Superior. The waters of Lake Mary contain concentrations of Cl^- ion that are common to the environment of northern Wisconsin and show no contamination by Cl^--containing waters.

Total Iron

Several profiles of total iron concentrations were determined. Table 4.12 presents this data. Iron concentrations in the aerated surface waters were high in comparison to those Hutchinson (49) presents for many holomictic lakes. Plumb (85) attributed the presence of this large amount of iron to selective complexation with some of the dissolved organic materials in the lake waters. He postulated that the iron-retaining ability of the organic matter may be due to the presence of acidic functional groups on the organic molecules. In the monimolimnion, he found that approximately 90 percent of the total iron present was Fe^{+2}. This is in marked contrast to Hutchinson's (49) statement that there is no Fe^{+2} in the chemically-stratified waters of Lake Mary. Hutchinson does not state the source of this information. Present knowledge of the iron cycle in lake systems would indicate that Fe^{+2} should be the dominant iron species present in an environment such as the monimolimnion of Lake Mary. The data presented here shows only that the total iron concentrations at a given depth were approximately constant for the five times of analysis and that the concentrations were two to three times as great in the monimolimnetic waters as in the mixolimnetic waters.

Sulfur Species

The data concerning the distribution of sulfur species in Lake Mary is both limited and questionable. The reason for this situation is the lack of accurate and precise analytical techniques for the determination of (1) low concentrations of sulfide species and (2) low concentrations of sulfate in highly-colored waters containing organic materials. Simple and reliable methods for these procedures are not available.

Table 4.13 presents the sulfur data for this study. Sulfide nearly always penetrated up to the oxygenated waters, indicating the vertical mobility of the sulfide species in Lake Mary. Concentrations of the total sulfide in the water layer just below oxygenated waters ranged from 0.1-1.1 mg/l total S. The lower concentrations were generally present when the level of zero DO advanced to shallow depths. Thus, transport of sulfide to the newly anoxic waters did not occur immediately upon loss of DO since concentrations of 1.0 mg/l S or greater were never present at a depth of less than 10 m. In the monimolimnion the range of total sulfide concentrations at each sampling period was small, generally 0.5 mg/l or less, but the concentration range varied from sampling period to sampling period. (This observed temporal variation may have been a function of the analytical procedure.) Allgeier, Hafford, and Juday (2) reported that H_2S concentrations increased from 0.6 mg/l at 3 m to 2.1 mg/l at the bottom of Lake Mary, indicating incomplete mixing in the monimolimnion. In the present study H_2S concentrations were within the range reported by Allgeier _et_ _al_., but evidence of incomplete mixing was not seen.

Sulfate data is such that no positive conclusions can be made. Postulations concerning the observed sulfate distribution are possible, however. The surface water SO_4^{-2} content was determined to be 5.3 mg/l. Analytical data for the monimolimnion indicated a concentration from 0.2-0.8 mg/l. However, there was a 2.2 mg/l blank reading; differentiation between the normal blank reading and a concentration of 0.8 mg/l was difficult. Therefore, this apparent presence of sulfate ions in the Lake Mary monimolimnetic waters is highly suspect. If there is truly sulfate

TABLE 4.13

LAKE MARY-SULFUR SPECIES

(expressed in mg/1)

	Total Sulfide								SO_4^{-2}
Sampling Date	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67	12-17-67	3-18-68	4-27-68	4-27-68
Depth-m									
1									5.3
2									
3									
4				--					
5							-0.1-	--	
6			--	0.1					
7			0.2						
8								0.1	
9	--	-0.9-		0.9	-0.1-	-0.4-			
10	1.1	1.4			0.3	0.7	0.9	1.5	0.5
11		1.1	1.2						
12				1.2	0.4	0.8			
13	1.6	1.4						2.0	
14	0.9				0.6	0.8	1.4		
15	1.2	1.4	1.0	1.7					
16	1.3				0.5	0.8		1.7	0.2
17	0.9	1.3		1.9					
18	1.0				0.6	0.7	1.5	1.7	0.8
19	1.0	0.8	1.0						
20	1.2	0.6		1.8		0.5	1.5	1.8	0.7

Dotted lines represent shallowest depth of water layers of 0.0 mg/1 dissolved oxygen content.

in the monimolimnion, then it is likely brought there by ground water flow.

There did not appear to be any increase in the total sulfur concentration in the monimolimnetic waters. Indeed, there was less total sulfur in this chemically-stratified water mass than there was in the mixolimnetic waters. Sulfur may enter the monimolimnion of Lake Mary in ground water, in dead organic materials that fall from the mixolimnetic waters, or from the sediments. The major sulfur source for these waters is anticipated to be decaying organic materials containing the S in a reduced state, being bound mainly in amino acids. If there is ground water contribution of sulfur species, the net contribution should be small since the ground water leaving the lake could remove as much sulfur as it brought in. There are three possible sinks for sulfur species that have entered the monimolimnion. An unknown amount of sulfur may be permanently deposited in the sediments in organic compounds resistent to anaerobic degradation. Also, reduced sulfur species released within the monimolimnion may precipitate as heavy metal sulfides. Kjensmo (60) sites precipitation of FeS as being a factor reducing the meromictic stability of some Norwegian soft water lakes. FeS precipitation is not a likely possibility in Lake Mary. The solubility product of FeS is not exceeded by a total sulfide content of 1.5 mg/l, a total Fe^{+2} content of 0.8 mg/l, and the highest pH measured in the monimolimnetic waters, 6.5.

The previously-mentioned vertical diffusion of the sulfide species is likely a large sink for reduced sulfur species. After removal from the monimolimnetic waters, H_2S is oxidized ultimately to SO_4^{-2}. Sorokin (97) reported that for two, meromictic, Russian lakes the oxidation of H_2S occurred mainly in the contact layer at the boundary of the aerobic and the anaerobic lake zones. This layer should correspond to the upper part of the chemocline. In this zone both bacterial and chemical oxidation of sulfide were found to be important. Sorokin found that chemical oxidation was responsible for the conversion of S^{-2} to $S_2O_3^{-2}$. Biological oxidation of the intermediate product $S_2O_3^{-2}$ by Thiobacillus thioparus formed SO_4^{-2}. For instances where both chemical and biological action occurred, 5 mg/l of Na_2S was completely oxidized to SO_4^{-2} in 3-5 days. It is unknown whether or not such a rapid oxidation of S^{-2} is possible in Lake Mary due to a lack of bacteriological information. Bowers (19,20) has suggested, however, that perhaps many dystrophic, meromictic lakes provide the environments for the unique presence of both sulfate-reducers and sulfide-oxidizers within the same body of water. If sulfide-oxidizing bacteria were present just at or above the chemocline of Lake Mary, their presence might be noted by some slight increase in the SO_4^{-2} concentration at this depth. Such a situation could occur if there were rapid supply of H_2S and rapid oxidation of this, but a slow mixing into the rest of the mixolimnetic water mass. Present sulfate analytical methods would be unable to detect this, however.

The sulfate ions found in the mixolimnetic waters enter this water mass in land runoff, inflow from Lake Rose, or by the oxidation of H_2S produced within the monimolimnion. The contributions of each of these possible sources to the total SO_4^{-2} content is unknown. Some of the sulfate in these waters may be taken up by organisms which can recycle it to the monimolimnion as reduced sulfur species upon their death.

Since small concentrations of sulfate are reported present in the monimolimnion, postulations concerning these possible concentrations are necessary. Ground water flow is possible, but unconfirmed. Stuiver (105) reported on the loss of SO_4^{-2} from the anaerobic hypolimnion of Linsley Pond. During a four and one half month period approximately 65 percent of the $^{35}SO_4^{-2}$ that he released was removed from the hypolimnetic waters. From this information it is seen that sulfate reduction may occur slowly.

Lake Mary is a dystrophic lake, and observations have shown it to have both a low nutrient content and low algal and plankton populations. It is quite likely that other members of the food chain are present in low abundance. Therefore, the population of sulfate-reducing bacteria may be relatively small, and the complete reduction of sulfate ions might take several months in the monimolimnion of Lake Mary. If we assume that there is ground water inflow to the lake and that this water has the same sulfate content as does the surface waters of Lake Mary (5.3 mg/l), then the monimolimnetic waters contain only about ten percent as much SO_4^{-2} as do the mixolimnetic waters. The presence of high SO_4^{-2} concentrations in the chemically-stratified water mass would indicate ground water flow of possibly major proportions. If the flow were slow or of minor amount, most of the SO_4^{-2} would be reduced to H_2S. Possibly a small SO_4^{-2} concentration was found in the monimolimnetic waters. If ground water contributes to these waters, the contribution is small.

Although a small concentration of sulfate is reported as possibly being present in the monimolimnion of Lake Mary and the possible presence of ground water inflow discussed, likely there are no sulfate ions present in the monimolimnion. Most probably the apparent sulfate content of these waters is a result of analytical inability to determine zero sulfate content in the Lake Mary waters. Ground water flow, if it occurs at all, is likely quite small.

Alkalinity

The predominant anion in the monimolimnetic waters of Lake Mary is the HCO_3^- ion. The concentrations of alkalinity in Lake Mary for four sampling dates are given in Table 4.14. Figure 4.3 presents a plot of the

TABLE 4.14

LAKE MARY - ALKALINITY AND NITRITE + NITRATE NITROGEN

	Alkalinity (expressed as mg/l $CaCO_3$)				$NO_2^- + NO_3^-$-N (expressed in mg/l-N)						
Sampling Date	11-11-67	12-17-67	3-13-68	4-27-68	9-18-66	11-6-66	12-17-66	1-21-66	3-31-67	7-10-67	9-23-67
Depth-m											
1	6.2	7.8	6.8	7.9	0.03	<0.01	0.03	0.02	0.09	0.03	0.01
2										0.02	0.01
3	7.6	7.7	8.0							0.03	<0.01
4				6.6						0.02	0.02
5	11.0	8.2	8.8	8.5	0.01	<0.01	0.03	0.05	0.19	0.02	
6			8.2	7.9					0.20		< 0.01
7	7.9	6.0	8.9								
8	8.1	7.1		11.7			0.02	0.07	0.11		
9	11.7	7.8								0.03	< 0.01
10	12.1	18.5	14.4	17.4	0.06	0.03	0.04	0.05	0.04		
11									0.01		
12	17.8	21.4	23.8								0.02
13				23.4			0.06	0.01	0.01	0.03	
14	22.9	21.6	24.4				0.06	0.03			
15					0.06	0.01		0.03	0.01		0.02
16	21.4	22.8	26.6	24.9		0.02	0.03	0.01			
17				22.5		0.04	0.03	0.01	0.01	0.07	0.01
18	27.0	25.4	23.0	25.9				0.01			
19						0.04	0.05	0.01	0.01		
20	23.6	23.4	29.9	24.2		0.03		0.01	0.07	0.12	0.02

alkalinity distribution with depth. From an average alkalinity of 7.7 mg/l (as $CaCO_3$) in the mixolimnetic waters, the concentration increased by a factor of approximately three to a maximum of nearly 30 mg/l. This large increase was attributed entirely to the decay of organic materials that had settled into the monimolimnion. These processes of anaerobic decay (described by McCarty, 73,74) release CO_2 as one of the principle end products. However, the addition of CO_2 to a water does not alter its alkalinity, by definition. Alkalinity is defined as the sum of all the titratable bases in a water sample. It is commonly expressed by the equation

$$\begin{aligned}\text{Alkalinity} = 2\left[CO_3^{-2}\right] + \left[HCO_3^{-}\right] + \left[OH^{-}\right] + \\ \left[\text{other bases}\right] - \left[H^{+}\right].\end{aligned} \tag{4.1}$$

The addition of CO_2 to a water will not alter its total alkalinity because dissociation of H_2CO_3 releases both HCO_3^- and H^+ ions. This fundamental rule applies when the addition of CO_2 is unaccompanied by the co-addition of a species that can consume the H^+ released during the H_2CO_3 dissociation. In the monimolimnion of Lake Mary there is at least one such species, the NH_3 produced during the fermentative decay of proteinaceous material. The pK_a of the NH_4^+ species is 9.25 at 25°C (46). Therefore, at the pH values found in the waters of Lake Mary nearly all of the NH_3 produced will exist as the NH_4^+ species. (The pK_a of the N increases during the conversion of protein-N to NH_3-N.)

Recent work by Stewart, Malueg, and Sager (102) found the Lake Mary alkalinity (as $CaCO_3$) to increase from 6 mg/l in the surface waters to 30 mg/l in the bottom waters. In the current study, the highest alkalinity values found in the monimolimnetic waters were nearly 30 mg/l, or approximately a 22 mg/l (2.2×10^{-4} eq/l) increase over the average surface-water concentration. This compared with an NH_3-N (see Table 4.15) increase in average concentration of 4.18 mg/l (2.99×10^{-4} eq/l). It is evident that the increase in NH_3 equivalents is more than sufficient to account for all of the H^+ ions released during H_2CO_3 dissociation. (At the pH values of Lake Mary water, HCO_3^- is the predominant carbonate species present.) In addition to NH_3 production, oxidation-reduction reactions may contribute to the increase in alkalinity of the bottom waters as compared to the surface waters of Lake Mary. For example, the reduction of the SO_4^{-2} ion to S^{-2} consumes H^+ ions according to the equation

$$8\ H^+ + SO_4^{-2} + 8\ e^- \longrightarrow S^{-2} + 4\ H_2O. \qquad (4.2)$$

If sulfate reduction occurred, then the 4.9×10^{-5} eq/l of SO_4^{-2} reduced in the stagnant water layer would have some effect upon the water's pH. (This calculation of equivalents released is based upon a possible decrease in SO_4^{-2} concentration in the monimolimnetic waters from 5.3 mg/l to 0.5 mg/l.) It is important to note that to increase the alkalinity of the monimolimnetic waters the H^+-consuming species involved must be produced within the monimolimnion of the lake itself unless they are added from an external source more alkaline than the monimolimnion.

For alkalinity titrations in Lake Mary water there is the possibility of titrating some weak organic acids and H_2S in addition to the titration of the carbonate species. Since both the organic carbon content of the lake and the pH of the waters (see Table 4.8) are approximately constant through the entire depth, then any contribution that the organic species make to the apparent alkalinity may be approximately constant. At the pH values found in Lake Mary, nearly all of the sulfide species are present as H_2S and, hence, not subject to titration with a mineral acid. The observed increase in alkalinity with increasing depth is attributed mainly to the addition of the NH_3 species, which is titrated indirectly in the titration of HCO_3^-.

The alkalinity values were generally highest at or near the 20-m depth. From this depth upward the values decreased nearly consistently, indicating that major ammonification reactions and production of CO_2 occur within the lake sediments. Although alkalinity distribution with depth indicates that diffusion is the main vertical transport mechanism, the NH_3 distribution pattern does not show this (see following section).

Nitrogen Species

The data for the analyses for the nitrogen species are presented in Tables 4.14 and 4.15. Typical vertical distributions of these species are shown in Figure 4.8. The organic-N concentrations were quite variable, ranging randomly from 0.0-1.74 mg/l N. Much of this variability may have been the result of the analytical procedure. Previous data for organic-N reported by Birge and Juday (15) showed concentrations increasing from 0.67 mg/l N in the surface waters of Lake Mary to 1.31 mg/l N at a depth of 20 m. Present values generally fall into the lower range of concentrations and do not increase with increasing depth. Because of the uncertainty of the accuracy of the analytical method, there is no discussion of the distribution of the organic-N species.

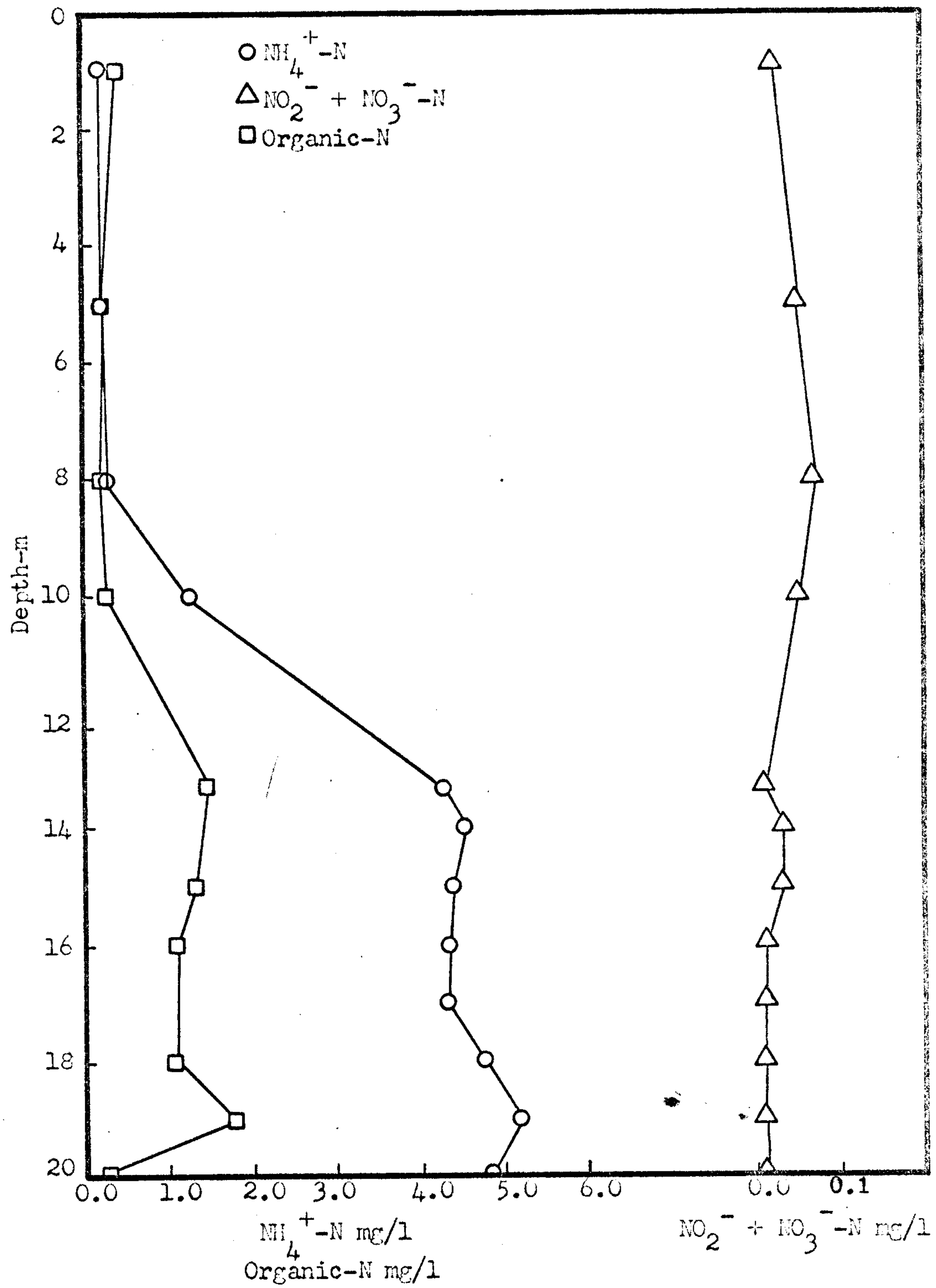
Juday, Birge, and Meloche (57) determined the distributions of NH_3 and $NO_2^- + NO_3^-$ in Lake Mary. They found no NO_2^- at any depth in the lake; NO_3^--N concentrations varied from 0.04-0.06 mg/l, the highest concentrations being in the 20-m water. The data for $NO_2^- + NO_3^-$ in Table 4.14 shows that these concentrations remain fairly constant throughout the year and with depth. With four exceptions, all concentrations were less than 0.1 mg/l N. In the mixolimnetic waters the highest concentrations were on 3-31-67. At this time the oxic water of Lake Rose contained rather high concentrations, from 0.23-0.31 mg/l $NO_2^- + NO_3^-$-N. The large $NO_2^- + NO_3^-$ concentration in Lake Rose was likely due to nitrification of

TABLE 4.15

LAKE MARY - AMMONIUM AND ORGANIC NITROGEN

(expressed in mg/1-N)

	NH_4^+-N								Organic N		
Sampling Date	9-18-66	11-6-66	12-17-66	1-21-67	3-31-67	7-10-67	9-23-67	4-27-68	1-21-67	3-31-67	7-10-67
Depth-m											
1	0.05	0.70	0.40	0.21	0.10	0.11	0.12	0.06	0.39	0.65	0.95
2						0.15	0.17				1.05
3						0.05	0.10				0.60
4						0.08	0.10	0.16			0.57
5	0.00	0.51	0.50	0.23	0.06	0.13		0.20	0.24	0.39	0.57
6					0.04		0.25	0.06			
7											
8			0.36	0.25				0.25	0.20		
9						0.70	0.91				0.70
10	1.95		2.48	1.25	2.25			2.45	0.28	0.05	
11					2.17					0.43	
12							4.13				
13			4.40	4.26	3.20	3.63		4.25	1.44	0.25	
14				4.50							
15	3.42			4.38			5.00		1.32		
16			4.02	4.32				4.60	1.03		
17		3.60	4.00	4.30	4.00		4.68				
18		4.14	5.72	4.74				5.10	1.08		
19		4.41	3.85	5.16	4.50				1.74	0.00	
20		4.05	4.25	4.81	4.20	4.20	4.55	4.97	0.29	0.40	0.30



LAKE MARY NITROGEN SPECIES
DISTRIBUTIONS, 1-21-67

FIGURE 4.8

NH_3 produced by ammonification reactions. The relatively high NH_3-N concentrations (0.25-0.30 mg/l N) seen in Lake Rose on 1-21-67 had decreased to 0.05-0.07 mg/l N by 3-31-67 and the NO_2^- + NO_3^- concentrations had increased in both lakes Rose and Mary.

There were always approximately the same concentrations of NO_2^- + NO_3^- in the monimolimnetic waters of Lake Mary as were present in the mixolimnetic waters. This could be due to a slow downward diffusion of these ions across the chemocline and then homogenous distribution throughout the monimolimnion. During this slow process, however, denitrification reactions in the chemically-stratified waters could reduce the NO_2^- + NO_3^- concentrations. There is no concentration decrease noted. Another possible source of these oxidized nitrogen species could be ground water inflow, previously mentioned as a possible explanation for the presence of oxidized sulfur species within these waters. It is impossible to speculate concerning the amount of NO_2^- + NO_3^- added through ground water influx because denitrification rates are not known. As with the apparent sulfate content of the monimolimnetic waters, the apparent presence of oxidized nitrogen forms in these waters may be strictly an artifact of the analytical procedure. Interfering substances may have been responsible for the apparent NO_2^- + NO_3^- concentrations found in the chemically-stratified waters.

Juday, Birge, and Meloche (57) found that NH_3-N concentrations increased from 0.0 mg/l at the surface to 4.00 mg/l at a depth of 20 m. They found no NH_3 above 10 m, this depth probably corresponding to the upper edge of the monimolimnion. Their data for NH_3 at the 20-m depth determined on three occassions during the summers of 1927 and 1928 showed concentrations ranging from 1.30-4.00 mg/l N. These authors theorized that the low NH_3 concentrations could be due to NH_3 utilization by a large bacterial population. Present data (Table 4.15) indicated no such trend for the NH_3 concentrations. The NH_3-N concentration was fairly constant (random variation within a range of 2.5 mg/l N) below the 11-m depth. The chemocline (9-11 m) was a layer of decreasing NH_3 content with decreasing depth, the NH_3-N decreasing from greater than 2.00 mg/l to less than 1.00 mg/l. At depths of 8 m or less, the NH_3-N concentrations were, with only one exception, less than 0.50 mg/l, averaging 0.19 mg/l.

NH_3 concentrations in the mixolimnetic waters were generally highest in the winter under ice cover; for example, the highest values recorded were on 11-6-66 and 12-17-66. Possible sources of this NH_3 were excretion by organisms, transport from Lake Rose, transport into the lake with land runoff, release from sediments, and transport from the monimolimnetic waters through mixing and diffusion across the chemocline. The most probable sources were transport from Lake Rose and land runoff. As noted above, the oxic waters of Lake Rose contained relatively high amounts of NH_3 during the winter of 1966-1967. During the fall and winter there was on the ground much leaf material which could decay with subsequent ammonification processes occurring. Runoff during this time of the year should be slight, however. Because of the gradient in NH_3 concentrations seen through the chemocline of Lake Mary, it appears that NH_3 transfer from the monimolimnion occurred. Since this transfer occurs throughout the year at the same rate, the NH_3 concentration increase in the Lake Mary surface waters seen during the winter may not have been due to this transfer. NH_3 concentrations in the mixolimnion may be lower during periods without ice cover due to uptake and utilization by plankton, algae, and bacteria. Increased winter NH_3 concentrations in the mixolimnion of Lake Mary appear to be due mainly to a reduced biological uptake and an increase in the NH_3 entering the lake through land runoff and in the Lake Rose water.

Processes of ammonification occurring within the anaerobic sediments are evidently responsible for the higher NH_3 concentrations in the monimolimnion of Lake Mary as compared to the mixolimnion. One other possible NH_3 source has been mentioned by Brezonik and Harper (22). Their studies show that heterotrophic nitrogen fixation apparently occurs in the anaerobic waters of Lake Mary. Based upon the hypothesis that all water below 5 m is anaerobic throughout the year (an incorrect assumption), nitrogen fixation produces approximately 4.6 kg of NH_3-N in a year in the monimolimnetic waters. Considering the volume of these waters, this fixation amounts to a 0.1 mg/l/yr increase in NH_3-N concentration. If this concentration increase were to continue without some removal process, the NH_3 concentration in the monimolimnion of Lake Mary would be large. Since the NH_3 concentrations may not have changed markedly from previous data of 25-30 years ago, there is either a removal process, or the nitrification reaction does not occur at the postulated rate. Of course, removal at the chemocline is apparent. Currently (summer, 1969) the University of Wisconsin Biochemistry Department is performing experiments to determine the rates of possible nitrogen fixation within the Lake Mary waters. None of these results are presently available.

Unlike alkalinity values, NH_3 concentrations did not decrease with decreasing depth from the sediments. It may be worthwhile to note that there are no alkalinity values available for the same days as when NH_3 concentrations are known. However, since alkalinity values and NH_3 concentrations varied little, this lack of coincident data may be unimportant. There are at least three possible reasons that alkalinity distribution is apparently controlled by diffusion whereas the NH_3 distribution is not. CO_2 produced within the sediments may be released as small bubbles that dissolve as they pass through the water column. Much of this bubble absorption could occur in the waters immediately above the lake sediments. Also, NH_3 released from the decaying organic materials within the sediments may be rapidly taken up by microbial populations present there. Most of the organic materials subject to degradation in the Lake Mary sediments likely have a high C/N ratio. Because of this, much of the small amount of nitrogen that is present may be rapidly removed from solution by microorganisms. Removal of NH_3 from solution near the sediment-water interface could mask any apparent diffusion-controlled transport of this species. Finally, as discussed in the preceding section, some oxidation-reduction reactions may contribute to the titratable alkalinity values. If these reactions occurred within the lake sediments, their effects might be controlled by diffusion. The analytical determinations made in this study would not have noted this final effect.

In summary, it appears that in Lake Mary the dominant reactions involving nitrogen species occur within the monimolimnion and are ammonification of proteinaceous material and possible nitrogen fixation. Within the chemocline of the lake any nitrification occurring is not measurable; there is no $NO_2^- + NO_3^-$ increase accompanying the decrease in NH_3 concentration. The monimolimnion is not a trap for nitrogen species, except for those organic nitrogen compounds that will not undergo ammonification. Diffusion and mixing transfer NH_3 from the monimolimnion at such a rate that the NH_3 concentration remains essentially constant. The surface water NH_3 concentrations are generally low, due to both flushing by water from runoff and from Lake Rose and nitrification of NH_3. Algal uptake of NH_3 and then death cycle some of the nitrogen back into the monimolimnetic water mass. Any nitrogen fixation that occurs in the surface waters may be minor.

Phosphorus Species

The distribution of phosphorus species within Lake Mary shows the presence of two distinct layers, one in which phosphorus concentrations are quite low and the other containing high phosphorus concentrations. This data is presented in Tables 4.16 and 4.17. Typical vertical distributions of these species are shown in Figure 4.9. Total phosphorus concentrations within the mixolimnetic waters were consistently lower than 0.05 mg/l P, averaging 0.03 mg/l. Essentially, all of this phosphorus was present as soluble, orthophosphate (average concentration, 0.02 mg/l P). As with the NH_3 species, there was an increasing concentration of phosphorus in the chemocline of the lake; this phosphorus was also nearly all soluble, orthophosphate. Apparently, the higher concentration of phosphorus in the lake's monimolimnion as compared to the mixolimnion is caused mainly by mineralization of the organic detritus that settles into the lower waters. In this water the average total phosphorus concentration was 0.43 mg/l P of which 0.34 mg/l was soluble, orthophosphate.

Phosphorus data collected by Juday, Birge, Kemmerer, and Robinson (55) and by Birge and Juday (16) showed distributions of phosphorus species and concentrations nearly the same as those in the present study. These workers determined concentrations of total phosphorus within the mixolimnetic waters to be 0.05 mg/l P or less. In these surface waters, nearly all of the total phosphorus was some form of organic phosphorus compound. Samples were collected during the summer; organism uptake of all soluble, orthophosphate could have explained these results. In the monimolimnetic waters, they found that total phosphorus concentrations ranged from 0.40-0.75 mg/l P. Of this, approximately 0.1 mg/l was organic phosphorus. One point of interest shown by the phosphorus data of these two reports is that sampling at the 5-m depth showed a total phosphorus concentration of 0.1-0.15 mg/l P, the concentration levels found at the chemocline depth during the present study. This could indicate that the chemocline has in

TABLE 4.16

LAKE MARY-TOTAL PHOSPHORUS

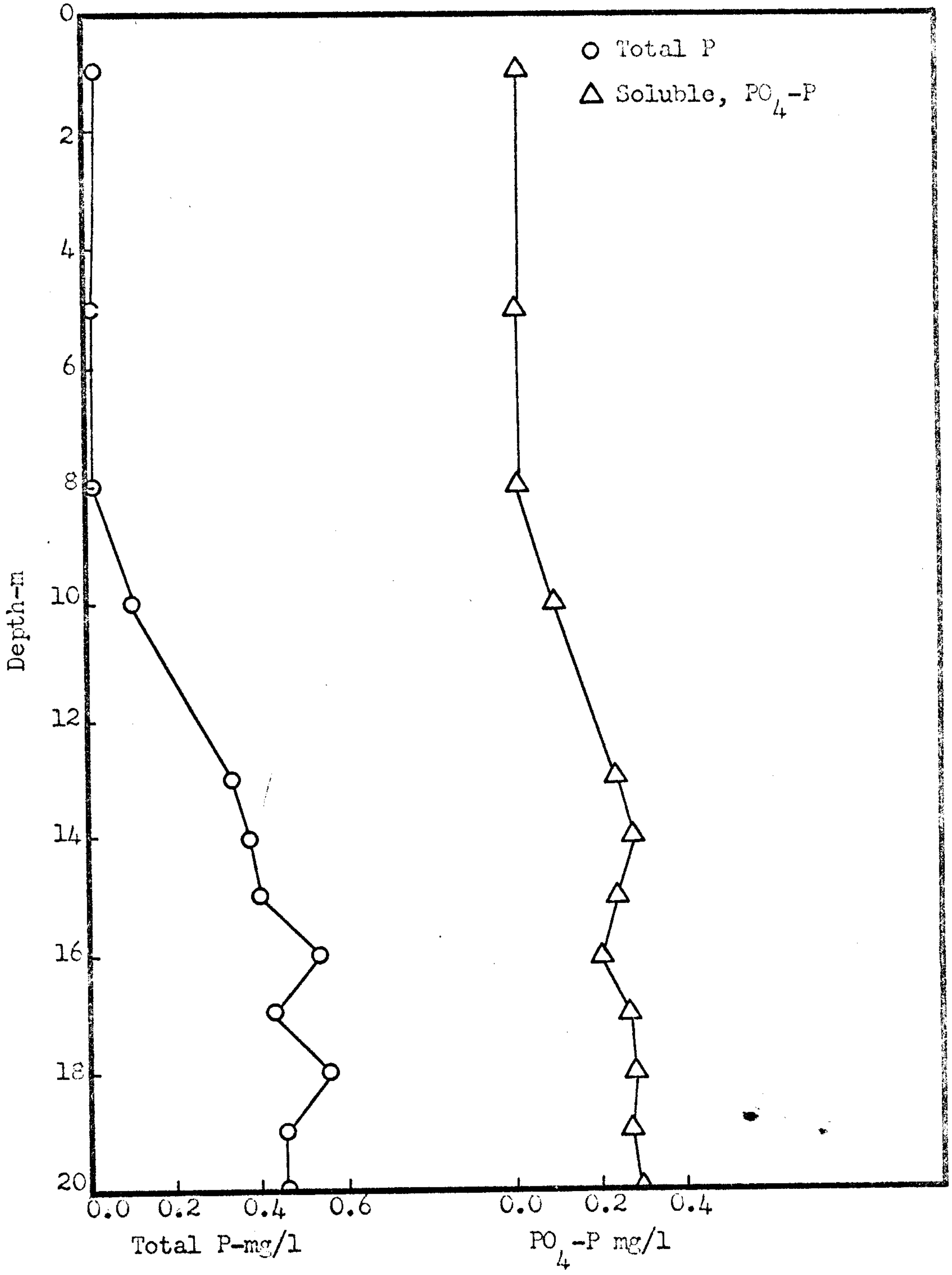
(expressed in mg/1-P)

Sampling Date	9-18-66	11-6-66	12-17-66	1-21-67	3-31-67	7-10-67	9-23-67
Depth-m							
1	0.02	0.02	0.04	0.03	0.04	0.02	0.02
2						0.03	0.02
3						0.02	0.01
4						0.02	0.03
5	0.02	0.02	0.03	0.02	0.02	0.02	
6					0.04		0.02
7							
8			0.04	0.02	0.04		
9						0.18	0.09
10	0.23	0.19	0.11	0.11	0.19		
11					0.19		
12							0.36
13			0.49	0.34	0.38	0.48	
14			0.37	0.33			
15	0.44	0.45	0.30	0.40	0.42		0.43
16		0.47	0.41	0.54			
17	0.48	0.46	0.42	0.43	0.46	0.52	0.41
18		0.45	0.43	0.56			
19		0.53	0.46	0.46	0.50		
20		0.53	0.31	0.46	0.50	0.72	0.50

TABLE 4.17

LAKE MARY - SOLUBLE, ORTHOPHOSPHATE
(expressed in mg/1-P)

Sampling Date	9-18-66	11-6-66	12-17-66	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67	12-17-67
Depth-m									
1	0.02	0.01	0.04	0.02	0.04	0.02	0.02	0.02	
2						0.03	0.01		
3						0.02	0.01	0.02	0.04
4						0.02	0.03		
5	0.02	0.02	0.03	0.01	0.02	0.01		0.03	0.02
6					0.04		0.02		
7								0.03	0.04
8			0.03	0.01	0.04			0.03	0.02
9							0.09	0.09	0.05
10	0.18	0.15	0.07	0.10	0.17			0.09	0.17
11					0.19				
12							0.22	0.23	0.19
13			0.27	0.24	0.38	0.48			
14			0.22	0.28				0.17	0.34
15	0.32	0.38	0.24	0.24	0.39		0.34		
16		0.42	0.36	0.20				0.36	0.36
17	0.40	0.40	0.31	0.27	0.46	0.52	0.41		
18		0.38	0.33	0.28				0.20	0.29
19		0.40	0.34	0.27	0.50				
20		0.44	0.13	0.30	0.50	0.72	0.36	0.33	0.28



LAKE MARY PHOSPHORUS SPECIES DISTRIBUTION, 1-21-67

FIGURE 4.9

the past been at a shallower depth than it presently is.

The orthophosphate in the waters of Lake Mary may be free or may exist in complexes such as those that Schnitzer (92) reported. He found that up to 11 percent of the inorganic phosphorus added to a fulvic acid-iron complex would form a fulvic acid-iron-phosphate complex. Although Schnitzer was working with large concentrations of phosphorus and fulvic acids and both Fe^{+2} and Fe^{+3}, interaction similar to this certainly is possible within the Lake Mary monimolimnion. There is an indication (Plumb, 85) that some of the iron found within the chemically-stratified waters of the lake may be in a form other than Fe^{+2}. Thus, the existence of both Fe^{+2}-fulvic acid-phosphate complexes and Fe^{+3}-fulvic acid-phosphate complexes may be postulated for these waters. Perhaps some of the higher phosphorus concentration found in the monimolimnion may be due to phosphate associated with such an iron-fulvic acid complex since the iron concentration increases approximately threefold from the mixolimnion to the monimolimnion.

Discussion of Lake Mary Physical and Chemical Data

The main species of chemical interest in the monimolimnion of Lake Mary are the NH_4^+ and HCO_3^- ions. There is an average increase in the NH_4^+ concentration of 299 μeq/l in the lower as compared to the upper water masses; the corresponding increase in alkalinity is 332 μeq/l. That these increases are approximately equal may be coincidence, for there is no *a priori* reason to anticipate that in a system of biological fermentation such as this the NH_4^+ increase would be equivalent to the alkalinity increase.

The water chemistry of Lake Mary approximates that of two separate bodies of water, one aerobic and one anaerobic, that are separated by a semi-permeable membrane, the lake's chemocline, which appears to be permeable in one direction only. This chemocline layer acts as a membrane permeable to dissolved species and as an insulator for heat transfer. That dissolved species go through this layer is shown by the concentration gradient of species whose concentrations are relatively low in the surface waters and higher in monimolimnetic waters. Such species are NH_4^+, orthophosphate, total phosphorus, total sulfide, and alkalinity; also, there is a specific conductance gradient within this 9-11 m water layer. Upon reaching the mixolimnetic waters, these species are chemically and/or biologically oxidized and flushed out of the lake by inflowing waters or recycled to the monimolimnetic waters.

The monimolimnion of Lake Mary is quite effectively sealed from any downward disturbance by the mixolimnetic waters. The apparent presence of SO_4^{-2} and NO_3^- ions in these monimolimnetic waters indicates that possibly either the lake has circulated at some recent time or that there is some ground water flow into the lake. Observations of the thermal and chemical data indicate that any recent period of complete circulation is highly unlikely. If there is ground water inflow into the monimolimnion of Lake Mary, it is evidently of minor importance. Most likely the apparent presence of $NO_2^- + NO_3^-$ and SO_4^{-2} ions in the monimolimnetic waters of Lake Mary are artifacts of the analytical techniques used for these analyses.

Lake Rose Physical Data

Lake Rose has a surface area of 1.43 ha, a maximum depth of 13 m, and a volume of 73,890 m^3 (80 percent of the volume of Lake Mary) as reported by Juday and Birge (58). The basin of Lake Rose is oval shaped with the greatest depth being in the eastern section of the lake. Sampling at this deepest portion of the lake was always attempted. However, this spot is of small area, and often the maximum depth found was 9-10 m. In its relation to Lake Mary (a small stream connects Lake Rose to Lake Mary), Lake

Rose serves mainly as an extension of the mixolimnion of Lake Mary. The purpose of studying Lake Rose was to provide a comparison between a meromictic and a dimictic lake. Lake Rose, subjected to the same environmental factors that influence Lake Mary, is an ideal example for such a comparison.

Temperature

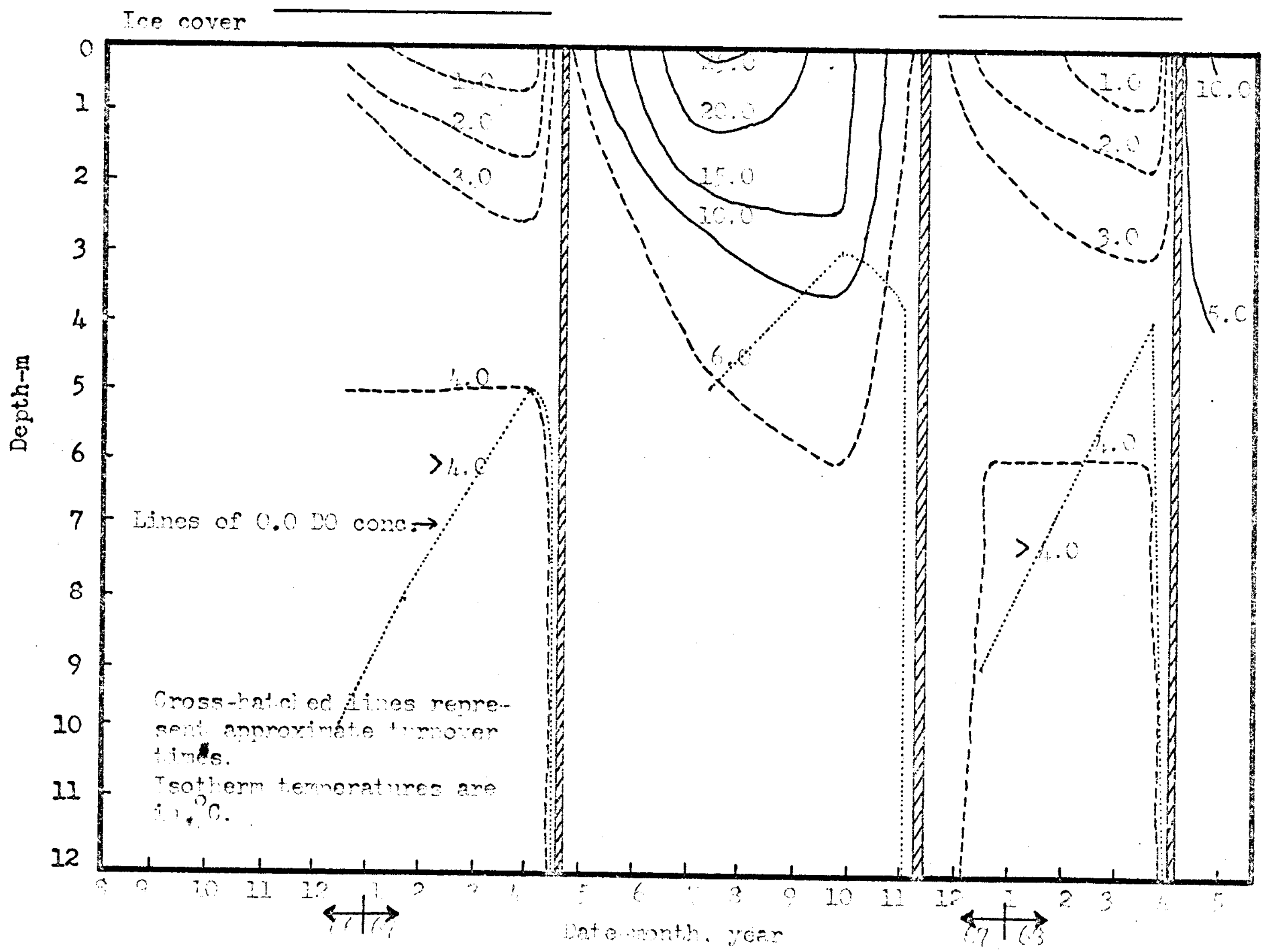
Figure 4.10 presents the temperature-time distribution in Lake Rose for the period of study. The times indicated as times of complete mixing are only approximate since the sampling dates did not correspond exactly with spring or fall overturn. Because of the larger surface/volume ratio and smaller mean depth (5.2 m for Lake Rose, 7.8 m for Lake Mary) the waters of Lake Rose heated to a greater depth during the summer than did those of Lake Mary. Under ice cover the cooling of the two lakes was approximately the same; ie., the 1°C, 2°C, and 3°C isotherms penetrated to about the same depths in both of these lakes. Also, the lower waters of Lake Rose showed the same geothermal heating from the sediments as did the Lake Mary bottom waters.

Color and Turbidity

The color values determined for Lake Rose waters are given in Table 4.18. The color nearly always ranged from 40-80 mg/l chloroplatinate-Pt. During thermal stratification in the winter of 1966-1967, the color of the deepest water did reach 170 mg/l, indicating that the processes of anaerobic decay of leaf fragments occurring in the sediments are important color release mechanisms. Table 4.18 also presents the turbidity values for Lake Rose. Turbidity was generally quite low and approximately the same as that of Lake Mary.

pH

The pH values for all of the waters of Lake Rose were always significantly higher than those found in Lake Mary. Table 4.19 lists all of the



Cross-hatched lines represent approximate turnover times.
Isotherm temperatures are in °C.

LAKE ROSE TEMPERATURE-TIME PROFILE

FIGURE 4.10

TABLE 4.18

LAKE ROSE - COLOR AND TURBIDITY

Color (expressed as mg/l Chloroplatinate-pt)

Sampling Date		12-17-66	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67	12-17-67	3-18-68
Depth-m	1	50	60	60	80		80	80	
	2				80	60			60
	3		70		70		80	70	
	4	50		55		60			60
	5		70	60	70		80		
	6					60		60	
	7		80						80
	8	50							
	9		90	70		80	80	100	
	10	55							80
	11		150	165					
	12			170					

Turbidity (expressed as mg/l SiO_2)

Sampling Date		12-17-66	1-21-67	7-10-67	9-23-67	11-11-67
Depth-m	1	8	13	3		8
	2			2	3	
	3		9	2		8
	4	10			3	
	5		5	3		8
	6				12	
	7		5			
	8	8				
	9		13		13	7
	10	13				
	11		34			
	12					

TABLE 4.19

LAKE ROSE - pH AND SPECIFIC CONDUCTANCE

pH

Sampling Date		12-17-66	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67	12-17-67	3-18-68	4-27-68
Depth-m	1	6.3	6.9	5.95	7.7		6.1	6.5		6.2
	2				8.2	6.4			5.75	
	3		7.1		8.25		6.0	6.2		
	4	6.2		5.95		5.8			5.75	6.1
	5		7.2	6.0	8.25		6.0			
	6					5.85		6.1		5.8
	7		7.2						5.75	
	8	6.0								
	9		6.8	6.15		5.8	5.9	6.2		6.1
	10	6.0							5.8	
	11		6.6	6.2						
	12			6.15						

SPECIFIC CONDUCTANCE (expressed in umhos/cm and corrected to 25°C)

Sampling Date		12-17-66	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67	12-17-67	3-18-68	4-27-68
Depth-m	1	38	39	47	36		52	45		89
	2				36	40			46	
	3		39		39	---	47	42		
	4	38		42		55			-43-	41
	5		39	-42-	-50-		46			
	6					54		42		-46-
	7		39						49	
	8	39	---							
	9		45	50		61	48	-51-		55
	10	-45-							53	
	11		64	69						
	12			73						

Dotted lines represent shallowest depth of water layers of 0.0 mg/1 dissolved oxygen content.

pH values. These generally fell in the range of 6-7 pH units, with the exception of those of 7-10-67 and 3-18-68. The higher values for 7-10-67 may be attributed to the presence of an active photosynthetic community removing CO_2 from the water. The low pH values for 3-18-68 may be due largely to reactions of acidic functional groups on partially degraded organic molecules released during the processes of decay occuring under the ice. Relatively low pH values were also measured during March, 1967, when fermentative decay processes had been active for several months under the ice cover.

Lake Rose Chemical Data

Specific Conductance

Specific conductance values are shown in Table 4.19. The average conductivity of oxygen-containing waters was 42 µmhos/cm, 16 percent higher than that of the surface waters of Lake Mary. No average conductivity values for the anaerobic waters were computed since dissolved species from the sediments were continually released into these waters. In the anaerobic waters the conductivity values increased with increasing lake depth, showing the active dissolution processes.

Dissolved Oxygen

The dotted line in Figure 4.10 is a line representing the depths of zero dissolved oxygen for Lake Rose. Table 4.20 presents all of the dissolved oxygen data collected during this study. The most striking feature of this data was the marked difference in the DO concentrations of the surface waters during March of 1967 as compared to March of 1968. On 3-31-67, there was less than 1 mg/l of DO in the 1-m water of Lake Rose. This was a winter of moderate ice cover and snow. However, on 3-18-68, there was approximately 14 mg/l of DO in the water immediately beneath the ice and 4.95 mg/l at a depth of 1 m. During this winter the snow

TABLE 4.20

LAKE ROSE - DISSOLVED OXYGEN

(expressed in mg/l)

Sampling Date	12-17-66	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67	12-17-67	3-18-68	4-27-68
Depth-m									
sfc								14.0	
1	7.04	4.42	0.68	7.81		8.24	12.76	4.95	12.00
2				6.92	4.85			2.85	10.00
3		2.52		0.40	0.00	7.30	5.60	0.55	9.51
4	4.50		0.09					0.00	1.20
5		2.07	0.00	0.00		5.00			0.00
6							3.70		
7		1.38							
8	0.50	0.00							
9						4.76	0.00		
10	0.00								
11									
12									

cover had been unusually light, allowing light penetration through the ice and, evidently, considerable photosynthetic activity.

Comparison of the Chemical Limnology of Lakes Mary and Rose

A logical approach to further description of the chemical limnology of Lake Rose is to provide a comparison between the concentrations of the major chemical components in Lake Mary and Lake Rose. Table 4.21 presents such a comparison. (The remainder of the Lake Rose data is compiled in the Appendix.) Generally, a comparison of the chemical components of the anaerobic waters of Lake Rose and the monimolimnetic waters of Lake Mary was not possible because many species were continually increasing in concentration in the anaerobic waters of Lake Rose. The concentrations of species which were released under anaerobic conditions increased during stagnation but did not reach the concentration levels found in the monimolimnion of Lake Mary. From Table 4.21 it is apparent that concentrations of Na^+, Mg^{+2}, Cl^-, and $NO_2^- + NO_3^-$ throughout Lake Rose were essentially equivalent to those found in Lake Mary. In addition, the surface water concentrations of Lake Mary and aerobic water concentrations of Lake Rose were equivalent for total phosphorus, orthophosphate, and NH_3. The aerobic waters of Lake Rose showed slightly higher alkalinity, specific conductance, and Ca^{+2} values than did the mixolimnetic waters of Lake Mary. The average chemical oxygen demand value, 57 mg/l, for Lake Rose was slightly less than that for Lake Mary, 68 mg/l. There appeared to be a definite distribution pattern of COD in the waters of Lake Rose. Concentrations in the upper waters ranged from 40-46 mg/l, with increases up to 94 mg/l seen in the deepest water samples. These increases are expected as reduced species are released from the sediments.

Changes in the concentrations of chemical species in the aerobic waters of Lake Rose were often accompanied by corresponding changes within the

TABLE 4.21

COMPARISON OF AVERAGE CONCENTRATIONS OF SELECTED CHEMICAL SPECIES IN LAKE MARY AND LAKE ROSE

	LAKE MARY		LAKE ROSE	
SPECIES	Mixolimnetic Waters	Monimolimnetic Waters	Aerobic Waters	Anaerobic Waters
Na^+	1.2	1.2	1.4	1.4
Mg^{+2}	1.3	1.3	1.5	1.5
Ca^{+2}	3.8	3.8	4.5	4.5
Cl^-	1.5	1.5	1.6	1.6
COD	68	68	57	57
$NO_2^- + NO_3^- - N$	0.04	0.04	0.06	0.06
Total Iron	0.37	0.81	0.23	0.80
Specific Conductance	36	68	42	(43-73)
Alkalinity	7.7	24.3	12.3	(19.1-21.9)
$NH_4^+ - N$	0.19	4.28	0.19	(0.75-8.43)
Soluble, orthophosphate	0.02	0.34	0.03	(0.03-0.18)
Total P	0.03	0.43	0.03	(0.05-0.19)

All values are expressed in mg/l except for specific conductance which is expressed in u mhos/cm at 25°C. The values in parentheses for the anaerobic waters of Lake Rose are the concentration ranges observed.

Lake Mary mixolimnion. High specific conductance values on 3-31-67 and 9-23-67 in Lake Rose water were also seen for the Lake Mary surface waters. High NH_3 concentrations on 12-17-66 and 1-21-67 in Lake Mary waters were accompanied by high NH_3 concentrations in Lake Rose waters on these dates. The unusually high $NO_2^- + NO_3^-$ concentrations found in Lake Mary surface waters on 3-31-67 were also seen in the aerobic waters of Lake Rose on that date. Chemically, Lake Rose is nearly just an extension of the mixolimnion of Lake Mary. Factors influencing the chemistry of the Lake Mary mixolimnetic waters effect the aerobic Lake Rose waters in a similar manner and to a similar degree. During stratification of Lake Rose, in the anoxic waters increases in the same chemical species as are of constantly high concentration in the monimolimnion of Lake Mary were seen, namely phosphorus (orthophosphate and total), color, alkalinity, NH_3, and total sulfide.

Surface waters of Lake Mary generally had lower conductivity and alkalinity values and much higher color values than did the aerobic waters of Lake Rose. The low alkalinity values in Lake Mary and generally-restricted mixing at the chemocline indicate that the color of the Lake Mary surface waters does not originate entirely in the Lake Mary monimolimnion. The lower conductivity and alkalinity values may indicate that there is a source of relatively-fresh, highly-colored water entering the mixolimnion of Lake Mary. One possible source of such water could be water percolating through the upper portion of the bog mat that surrounds Lake Mary. On 3-18-68 a small spring supplying water at the surface of Lake Mary was noted. If this is the type of water supplied to the mixolimnion of Lake Mary, then it must provide a relatively-large percentage of the total amount of water in the mixolimnion for it must dilute the higher alkalinity values supplied by the Lake Rose inflow and by water crossing the chemocline.

Both the physical and chemical characteristics of Lake Mary and Lake Rose are strikingly similar. Differences observed in the concentrations of certain species are attributed to the semi-annual complete mixing of Lake Rose. This overturn mixes chemical species released to the anaerobic waters by the fermentative processes with the surface waters. Such mixing does not occur in Lake Mary. When Lake Rose is thermally stratified, its chemistry appears similar to that of Lake Mary.

There is one cottage situated on the shore of each of the lakes Mary and Rose. The cottage on the shore of Lake Mary is occupied during only the summer, roughly from May through September. That on the shore of Lake Rose, however, is periodically occupied throughout the year. The possible affects that the sewerage systems of these homes have upon the chemistry of lakes Mary and Rose are unknown. It is known that there is no septic tank system for the home located on Lake Mary; no information concerning the sewerage system of the cottage on Lake Rose was available. Throughout the study of these two lakes, no sudden pulses of any chemical species were noted either seasonally or otherwise. Any observed changes in concentrations of chemical species in Lake Rose were attributed to phenomena associated with dissolution processes occurring within the sediments. If the sewerage systems of these two cottages effect the chemical limnology of Lake Mary and/or Lake Rose, then the effect is a constant one that apparently does not increase during cabin occupancy.

Some general observations were made concerning some physical characteristics of the sediments of lakes Mary and Rose. All of the Lake Rose sediments observed during coring operations, dredging procedures, or general samplings were seen to have a very flocculant and dispersed sediment-water interface. This interfacial layer apparently was composed of partially-degraded leaf fragments and detrital materials possibly produced within the lake. This layer was found throughout the lake and may have been up to 0.5 m thick. The bottom of the small stream connecting Lake Rose and Lake Mary was also composed of the same type of flocculant material. Some of the Lake Mary sediments were also of this type. Generally, this flocculant material was found in Lake Mary at shallow depths and on the bottom near the creek flowing from Lake Rose. However, some of the deeper sediments (from the 20-m depth) of Lake Mary showed almost no flocculant sediment-water interface. Apparently, the flocculant sediments are limited to the shallower areas of the lake, and the surface sediments become more compacted with increasing lake depth.

Dissolved Gases in Lakes Mary and Rose

Major analytical emphasis in this research project was placed upon the determination of the concentrations of two dissolved gases in Lake Mary and Lake Rose, N_2 and CH_4. A typical vertical profile of the distributions of these two gases in Lake Mary is shown in Figure 4.6. The methane determinations were undertaken to verify biological activity, and, possibly, to determine the location of the majority of this activity and to estimate the rates of such activity. Nitrogen data was collected to qualitatively determine if measurable amounts of nitrogen fixation or denitrification were occurring within the Lake Mary system.

Nitrogen

Concentrations of dissolved N_2 gas and the percent of saturation values for lakes Mary and Rose are presented in Table 4.22. The analytical data spans eight months and includes information for three seasons. The waters of both Lake Mary and Lake Rose appeared to be near saturation, or slightly undersaturated, for the three determinations made when there was no ice cover. For 9-23-67 there was a trend towards a lower percent saturation with increasing depth. The average percent saturation (for the

TABLE 4.22

LAKE MARY AND LAKE ROSE NITROGEN CONCENTRATIONS AND PERCENT SATURATION VALUES

(concentrations are expressed in mg/l)

LAKE MARY

	7-10-67			9-23-67			11-11-67			12-17-67			3-19-68		
Depth	Conc	Temp	% Sat	Conc	Temp	% Sat	Conc	Temp	% Sat	Conc	Temp	% Sat	Conc	Temp	% Sat
1 m	15.1	18.7°C	100	16.1	15.9°C	101	19.0	3.9°C	93	24.6	2.5°C	118	24.3	1.0°C	111
2	19.2	12.3	112	16.5	14.2	100									
3	21.7	7.4	113	18.8	10.2	105	20.0	4.0	93	23.4	3.8	114	23.3	3.1	111
4	19.1	4.3	96	-13.4-	6.8	96									
5	22.4	4.5	112				18.6	4.0	91	23.1	4.0	113	-22.5-	3.7	110
6													23.2	4.0	114
7	20.3	4.3	100	19.4	4.5	97	19.3	4.2	94	24.8	4.2	121	22.5	4.0	110
8							18.9	4.3	92	24.0	4.3	117			
9	-22.3-	4.3	109	19.6	4.5	98	-17.8-	4.5	89	-22.8-	4.5	114			
10							18.1	4.6	91	22.4	4.7	115	23.3	4.5	116
11															
12				17.7	4.9	89	18.2	4.7	91	22.3	4.8	112	23.0	4.9	115
13															
14							18.1	4.8	91	23.5	4.9	118	23.4	4.9	117
15				19.7	4.9	99									
16							19.7	4.9	99	21.1	4.9	106	22.8	5.0	114
17				16.0	5.0	80									
18							19.6	4.9	98	22.3	4.9	112	22.8	5.0	114
19															
20				18.3	5.0	92	17.8	4.8	89	20.0	4.9	100	23.2	5.0	116

Dotted lines represent shallowest depth at water layers of 0.0 mg/l dissolved oxygen content.

N_2 saturation values after Fox (40).

Cont'd. TABLE 4.22

LAKE ROSE

	7-10-67			9-23-67			11-11-67			12-17-67			3-18-68		
Depth	Conc	Temp	% Sat	Conc	Temp	% Sat	Conc	Temp	% Sat	Conc	Temp	% Sat	Conc	Temp	% Sat
1 m	15.9	21.2°C	108				20.5	3.5°C	100	26.0	2.5°C	124			
2	18.3	15.7	115	16.0	16.5°C	102							22.6	2.3°C	106
3	25.2	8.3	135				18.4	3.7	90	23.0	3.7	113			
4				-18.9-	8.2	101							-22.7-	3.7	111
5	-22.1-	5.9	113				18.0	3.8	88						
6				18.2	6.0	93				23.3	3.9	114			
7													23.2	4.0	114
8															
9				18.0	5.5	92				-29.4-	4.2	144			
10													24.1	4.2	116

N_2 saturation values after Fox (40).

Dotted lines represent <u>shallowest</u> depth of water layers of 0.0 mg/1 dissolved oxygen content.

total N_2 profile) on this date was 96 percent for Lake Mary and 97 percent for Lake Rose. On 11-11-67, a time soon after the complete vertical mixing of Lake Rose, N_2 percent saturation values were fairly constant throughout the depth of Lake Mary, averaging 93 percent. The average percent saturation in Lake Rose based on this data was also 93 percent.

The N_2 concentrations in December, 1967, and March, 1968, showed an apparent supersaturation of the entire water column for both lakes of approximately 15 percent. The N_2 data for Lake Rose for 12-17-67 and 3-18-68 indicated that there may have been denitrification of NO_2^- and/or NO_3^- occurring within the anaerobic waters since an increase in N_2 concentration with increasing depth was noted. This type of N_2 distribution was not seen for the Lake Mary profiles. Both of these profiles showed similar percent saturation values throughout the entire water column, and the average saturation of both water columns was 113 percent. It is unlikely that this supersaturation in Lake Mary could have been due to denitrification reactions occurring within the monimolimnion because there was no available supply of nitrogen that was subject to denitrification. However, it is probable that denitrification of NO_2^- and/or NO_3^- did occur in dimictic Lake Rose and was the source of the increased N_2 concentrations found in the bottom waters.

The apparent N_2 supersaturation of the waters of Lake Mary during a time of ice cover may have been due to an error in the calibration technique. Since the calibration procedure was varied slightly at each time of dissolved gas analysis, comparison of N_2 data from two different sampling times is difficult. However, N_2 vertical distribution data for any one sampling date is consistent and allows comparison of N_2 concentrations at different water depths.

No nitrogen fixation or denitrification reactions were seen to occur within the waters of Lake Mary. For a given sampling date the percent N_2 saturation was approximately the same throughout the entire water column. In Lake Rose there appeared to be N_2 production in the bottom waters due to denitrification occurring as these waters became anaerobic.

Methane

Methane is one of the principle end products from the anaerobic degradation of a wide variety of organic substrates. These degradable substances include not only the proteinaceous materials common to sewage sludges but also carbohydrate materials. Buswell and Neave (23) and Symons and Buswell (107) found that cellulose, starch, xylose, and several other sugars were all anaerobically fermentable and were major CH_4 producers. Anderson (3) lists the major components of wood fiber and cell walls as being cellulose (consisting of glucose polymers), hemicelluloses (consisting of polymers of other sugar units), and lignin (possibly composed of linked phenylpropane units with phenolic -OH and $-OCH_3$ groups attached as side chains). Two of these three major components of wood are classes of compounds which will undergo anaerobic degradation, with CH_4 production as a consequence.

Because of the forested nature of the land surrounding Lake Mary, much of the organic material that enters the lake is in the form of leaves, branches, or extracts from these materials. Thus, most of the allochthonous material that enters Lake Mary is a potential source of CH_4. One of the first steps in the production of CH_4 is the breakdown of the complex organic materials by acid-forming bacteria to produce short-chain, organic acids (McCarty, 73). One of the initial degradation steps is evidenced in Lake Mary by the relatively low pH of the waters (5.5-6.0). (See Table 4.8 for complete pH data.) These low pH values may be due to the reactions of the acidic functional groups on the partially-degraded organic molecules. The final step in the breakdown process is the production of CH_4 and CO_2 from two- and three-carbon acids.

Most previous work concerning CH_4 production in aquatic environments points to the sediments as the site of the major amount of production. Laboratory studies of fermenting lake sediments have generally shown CH_4 to be the main gaseous product (1,65). Koyama (62) analyzed the sedimentary pore water of some short cores from three Japanese lakes. He found that CH_4 was a major gaseous component, but not always the gas present in the greatest concentrations. In sediments from these three lakes, the greatest CH_4 concentrations were found in the water from the 15-30 cm sections of the cores, indicating that the greatest rate of production was occurring at some depth below the water-sediment interface. Richards, Cline, Broenkow, and Atkinson (87) found that the highest concentrations of CH_4 in Lake Nitinat were in the mid-water column and suggested that production occurred within the water column.

Methane produced within the sediments can be transferred throughout the anaerobic water column by molecular diffusion, mixing due to eddy currents, or bubble formation and release. Koyama (62) cited bubble formation within the mud as being a likely means of gas escape but found no evidence for this bubble formation. Conger (25) captured and analyzed bubbles escaping from the sediments of a shallow lake and found methane to be the principle component of the bubbles. Ohle (80) feels that the "so-called methane convection, produced by the ascending gas bubbles, causes a vertical current of water by which mud particles and dissolved substances will be transferred to the upper regions of the water bodies." He has verified this hypothesis through the use of sonar equipment and analytical work.

Methane produced in the sediments or lower waters of lakes is transported from the site of production to the total water column. When the CH_4 reaches the aerobic waters of a lake, it may either be diluted and flushed from the lake or oxidized. Overbeck and Ohle (81) indicated that methane-oxidizing bacteria play an important role in the removal of oxygen from the waters lying just above the anaerobic waters.

The data for CH_4 concentrations and percent saturation in lakes Mary and Rose is presented in Table 4.23. This data indicates that the dissolved CH_4 does not always penetrate all of the anaerobic waters up to the oxygenated mixolimnetic waters. Evidently, the rate of DO removal is greater than the rate of CH_4 vertical transfer. Figure 4.11 shows plots of CH_4 concentrations and percent saturation values vs depth of Lake Mary for 3-18-68. This data is representative of all of the CH_4 data and shows that the CH_4, like alkalinity, is not of equal concentration throughout the monimolimnion. Rather, the concentration decreased with decreasing depth. The distribution profile up to the 12-m depth was similar to one predicted by Fickian diffusion alone as the method of CH_4 transfer; ie., the distribution was nearly linear. This type of CH_4 distribution in Lake Mary was seen on each sampling date.

The values for the percent CH_4 saturation for Lake Mary also remained approximately the same throughout the study. Methane concentrations at the 20-m depth were 52-59 percent of the CH_4 saturation value. In the water layers nearest the aerobic zone of the lake, the CH_4 concentrations were generally 0-15 percent of saturation. The sharp decrease in the CH_4 concentrations above the 12-m depth was indicative of mixing of the monimolimnetic waters with the mixolimnetic waters. This decrease was much larger than what diffusion alone would indicate.

The CH_4 concentrations for Lake Rose were determined for only a few samples. They indicated that CH_4 production occurred in the sediments of

TABLE 4.23

LAKE MARY AND LAKE ROSE METHANE CONCENTRATIONS AND PERCENT SATURATION VALUES

(concentrations are expressed in mg/1)

LAKE MARY

	7-10-67			9-23-67			11-11-67			12-17-67			3-18-68		
Depth	Conc	Temp	% Sat	Conc	Temp	% Sat	Conc	Temp	% Sat	Conc	Temp	% Sat	Conc	Temp	% Sat
1 m															
2															
3															
4				--											
5	0.0	4.5°C	0										--		
6															
7	0.9	4.3	2	0.0	4.5°C	0							0.0	4.0°C	0
8							0.0	4.3°C	0						
9	-5.3-	4.3	15	3.7	4.5	11	-3.0-	4.5	9	-0.0-	4.5°C	0			
10							5.6	4.6	16	11.7	4.7	34	2.2	4.5	6
11															
12				15.5	4.9	45	12.3	4.7	36	12.6	4.8	37	13.6	4.9	40
13	18.2	4.7	53												
14							15.9	4.8	47	17.5	4.9	51	15.3	4.9	45
15				17.6	4.9	52									
16							18.5	4.9	54	18.2	4.9	53	16.9	5.0	50
17	19.5	4.8	57	15.4	5.0	45									
18							18.3	4.9	54	21.0	4.9	62	17.9	5.0	52
19															
20	19.1	4.9	56	17.6	5.0	52	18.5	4.8	54	20.0	4.9	59	19.1	5.0	56

CH_4 saturation values after Winkler (108).

Dotted lines represent shallowest depth of water layers of 0.0 mg/1 dissolved oxygen content.

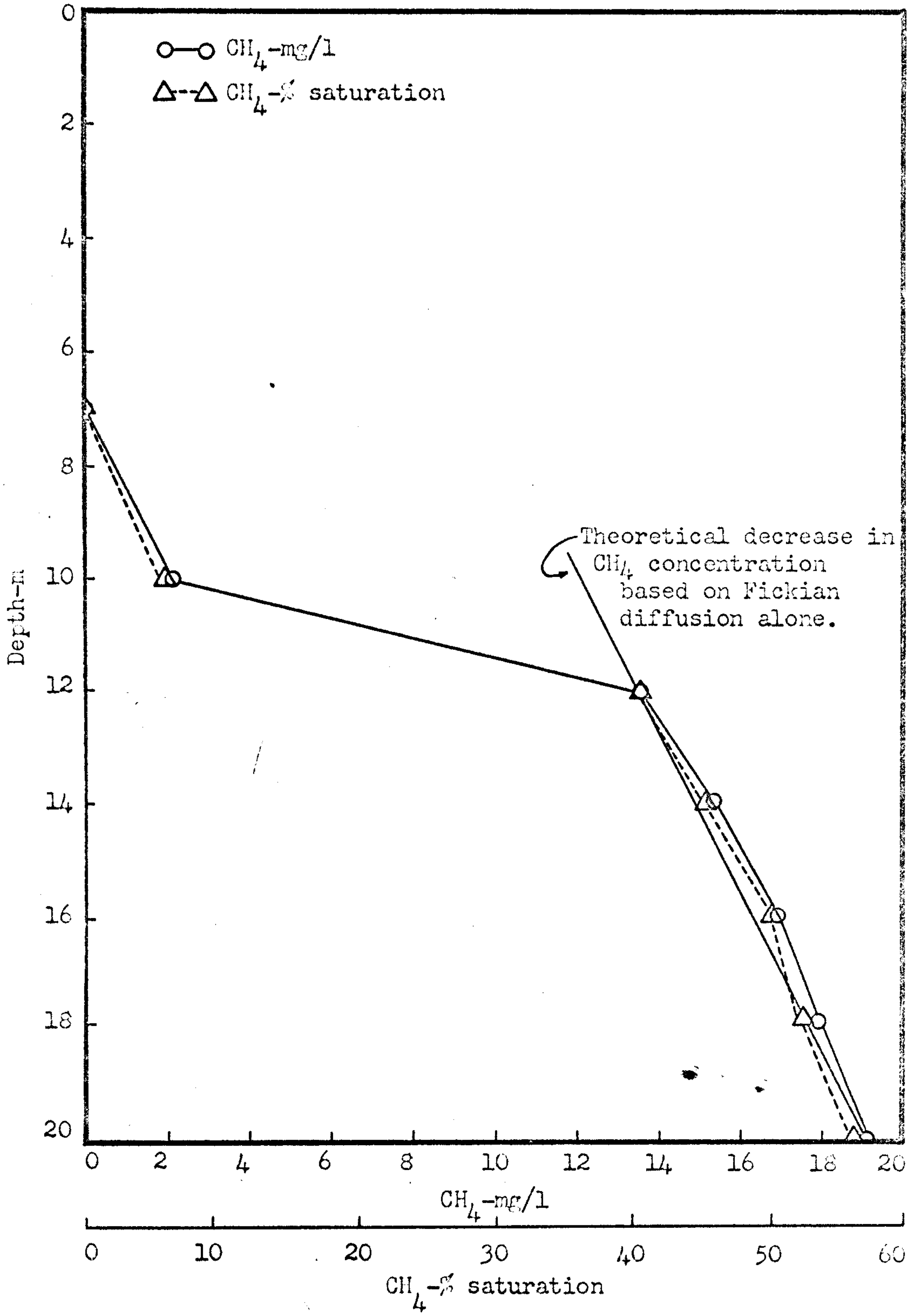
Cont'd. TABLE 4.23

LAKE ROSE

	7-10-67			9-23-67			11-11-67			12-17-67			3-18-68		
Depth	Conc	Temp	% Sat	Conc	Temp	% Sat	Conc	Temp	% Sat	Conc	Temp	% Sat	Conc	Temp	% Sat
1 m															
2				0.0	16.5°C	0									
3	0.0		0												
4				-4.0-	8.2	13							-0.0-	3.7°C	0
5	-1.8-	5.9°C	5					NO CH_4 FOUND ON THIS DATE							
6				3.9	6.0	12				0.0	3.9°C	0			
7													Tr.	4.0	+
8															
9				6.6	5.5	20				-13.7-	4.2	39			
10													2.5	4.2	7

CH_4 saturation values after Winkler (108).

Dotted lines represent shallowest depth of water layers of 0.0 mg/l dissolved oxygen content.

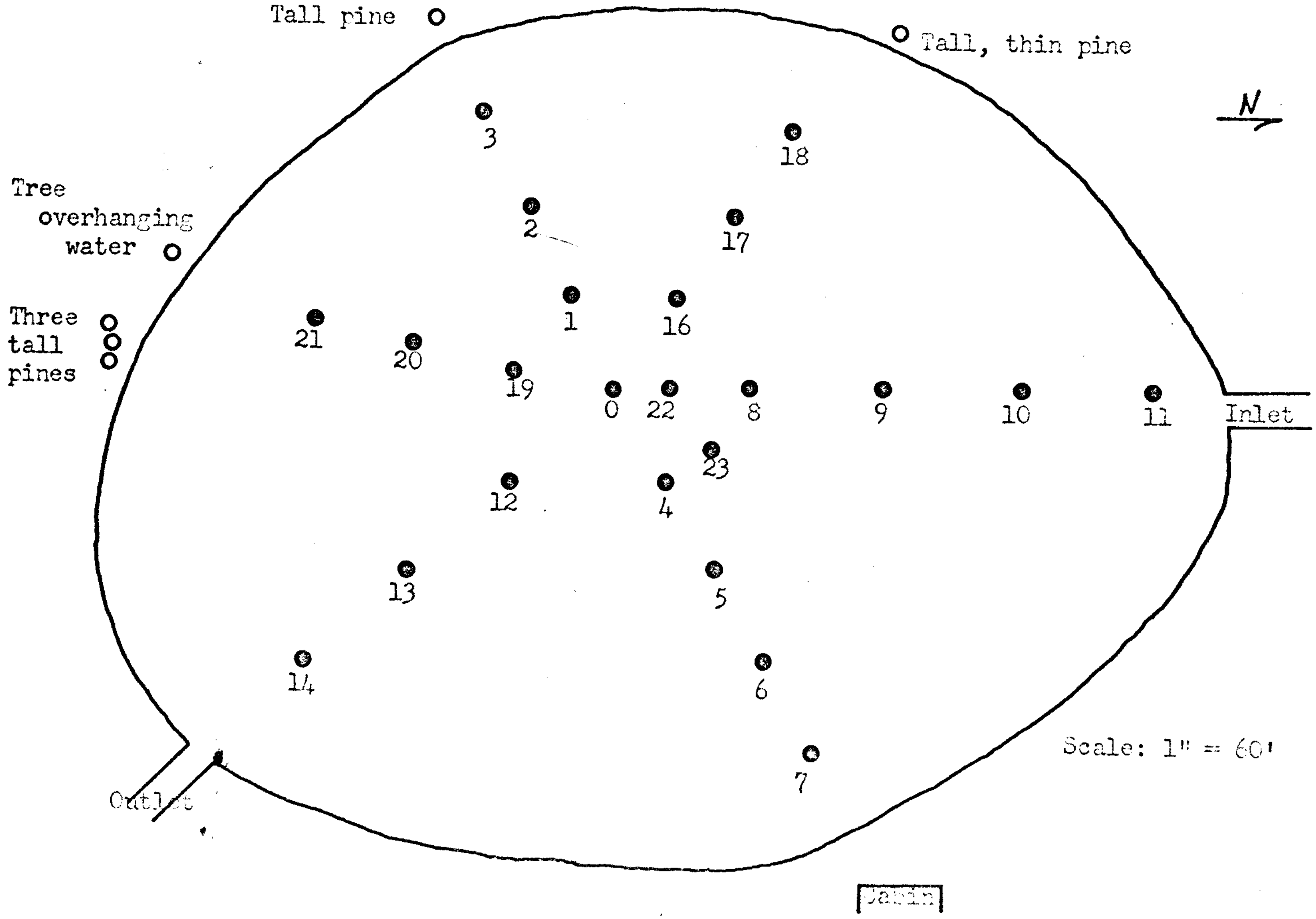


LAKE MARY METHANE DATA, 3-18-68

FIGURE 4.11

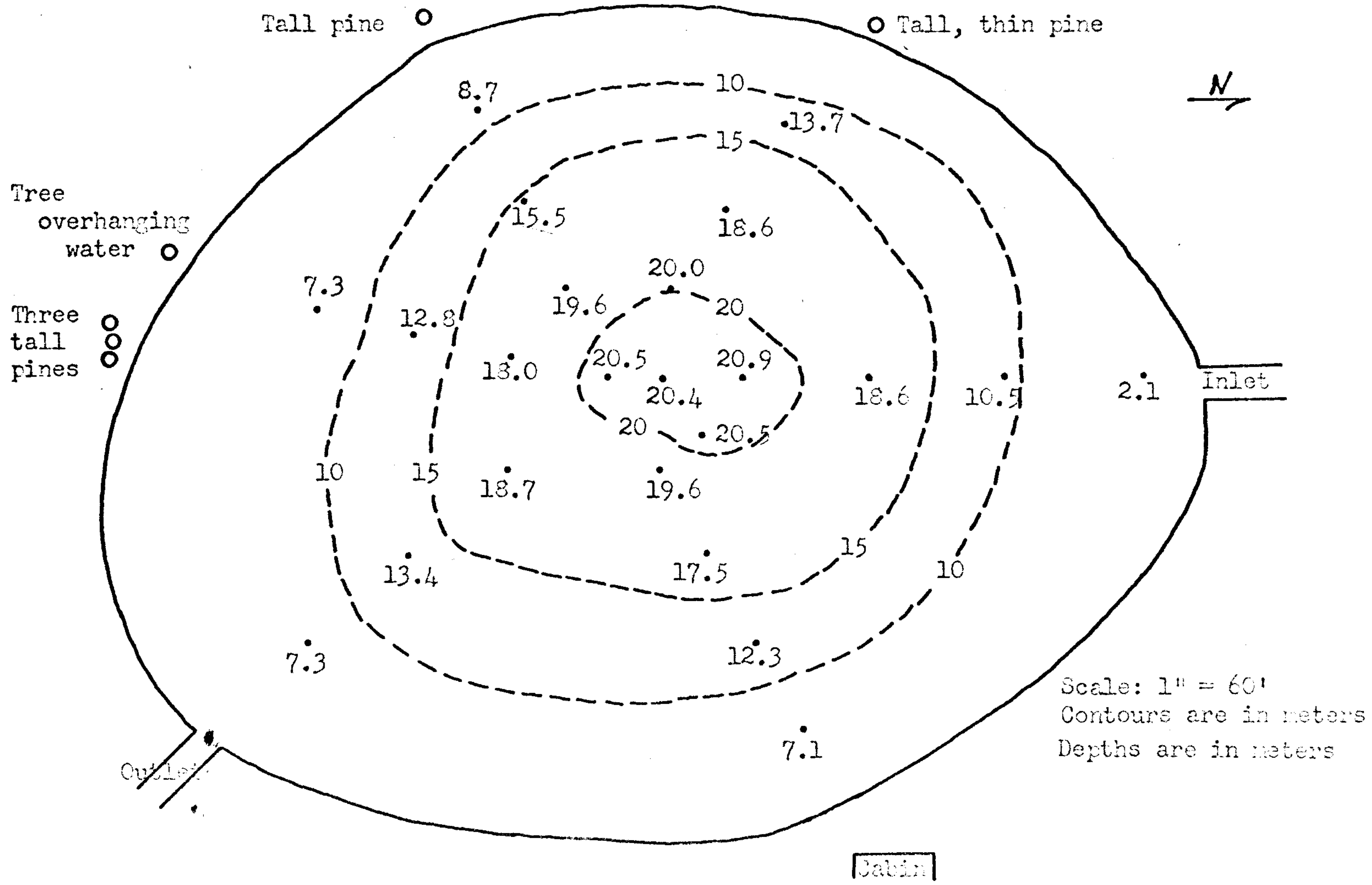
Lake Rose and that CH_4 penetrated up the water column to at least the 4-m depth. The reason for the high concentration of CH_4 found at the 9-m depth on 12-17-67 which had disappeared three months later is uncertain. Only low concentrations of CH_4 were present on 3-18-68 in the water column even though the waters were anoxic and had been under ice cover for four months.

Because the highest concentrations of CH_4 in Lake Mary were usually found in the deepest water samples, it was felt that the production of the CH_4 must be centered in the sediments, as other authors have found for many environments. As an attempt to verify this hypothesis, the CH_4 concentrations were determined at specific distances above the sediments for 22 different sampling sites. Figure 4.12 shows the sites from which these samples were collected during the period of 3-17-68 to 3-19-68 when the lake was under ice cover. Figure 4.13 shows the depths of the water columns at the sampling sites and the 10-, 15-, and 20-m contours. In Figures 4.14, 4.15, and 4.16 are presented the CH_4 concentrations at various distances above the sediments for the three transects of the lake. (The N_2 gas concentrations determined at the same time are given in parentheses.) From these figures it can be seen that CH_4 concentrations were always the greatest in the waters closest to the sediments. In addition, the concentrations were found to increase toward the center of the lake from the sides. For any given depth within the lake, the CH_4 concentration appeared to be fairly constant. Figure 4.17 presents a bathymetric map of Lake Mary and the CH_4 concentrations determined for the deepest water samples at these sites; these concentrations are for waters from 0.5-1.5 m above the sediments. This figure confirms that the CH_4 concentrations for any given water level are approximately constant. There is more fluctuation in concentrations at the shallower depths, near the



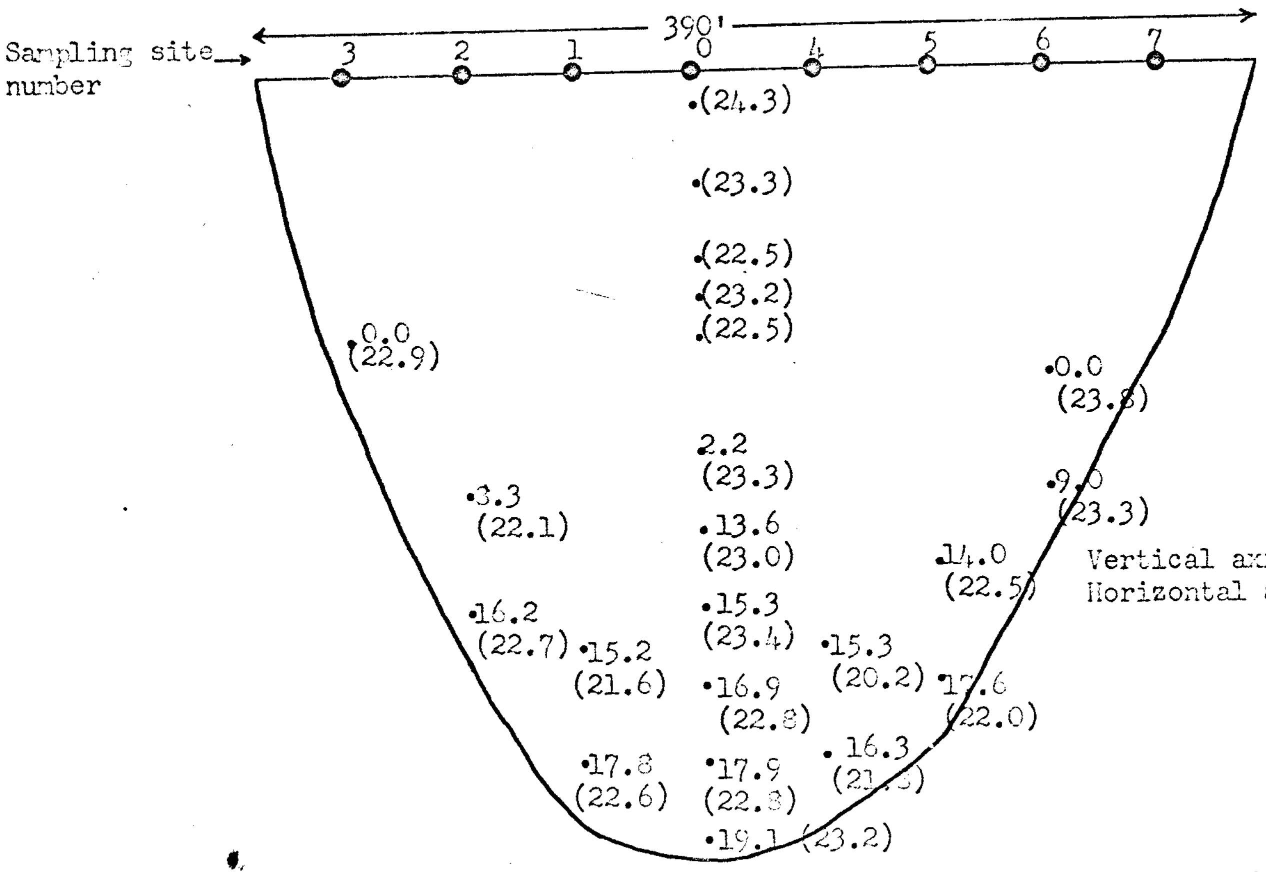
LAKE MARY CH_4 SAMPLING SITES

FIGURE 4.12



TOTAL DEPTHS OF LAKE MARY CH_4 SAMPLING SITES

FIGURE 4.13

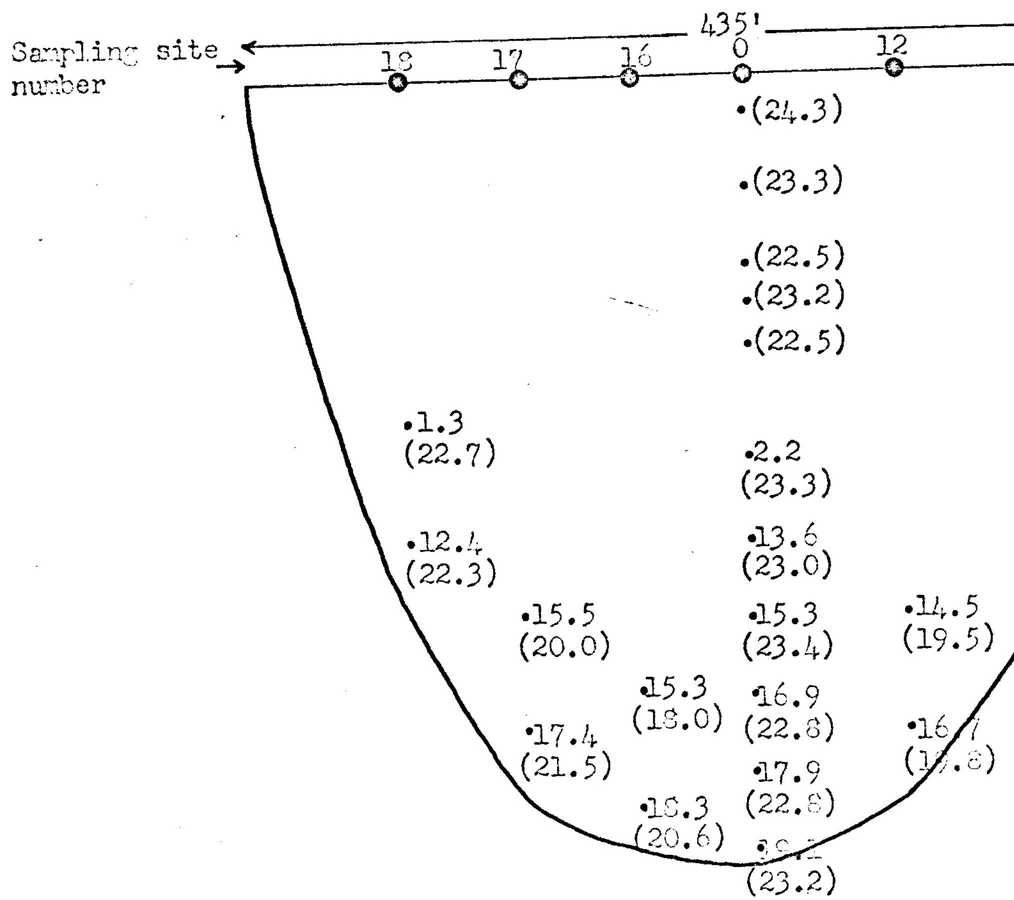


Vertical axis scale: 1" = 4 m
Horizontal axis scale: 1" = 60'

The numbers given at each point represent CH_4 and N_2 concentrations in mg/l. N_2 values are in parentheses.

CH_4 AND N_2 CONCENTRATIONS IN LAKE MARY, 3-18-68
CROSS SECTION #1

FIGURE 4.14

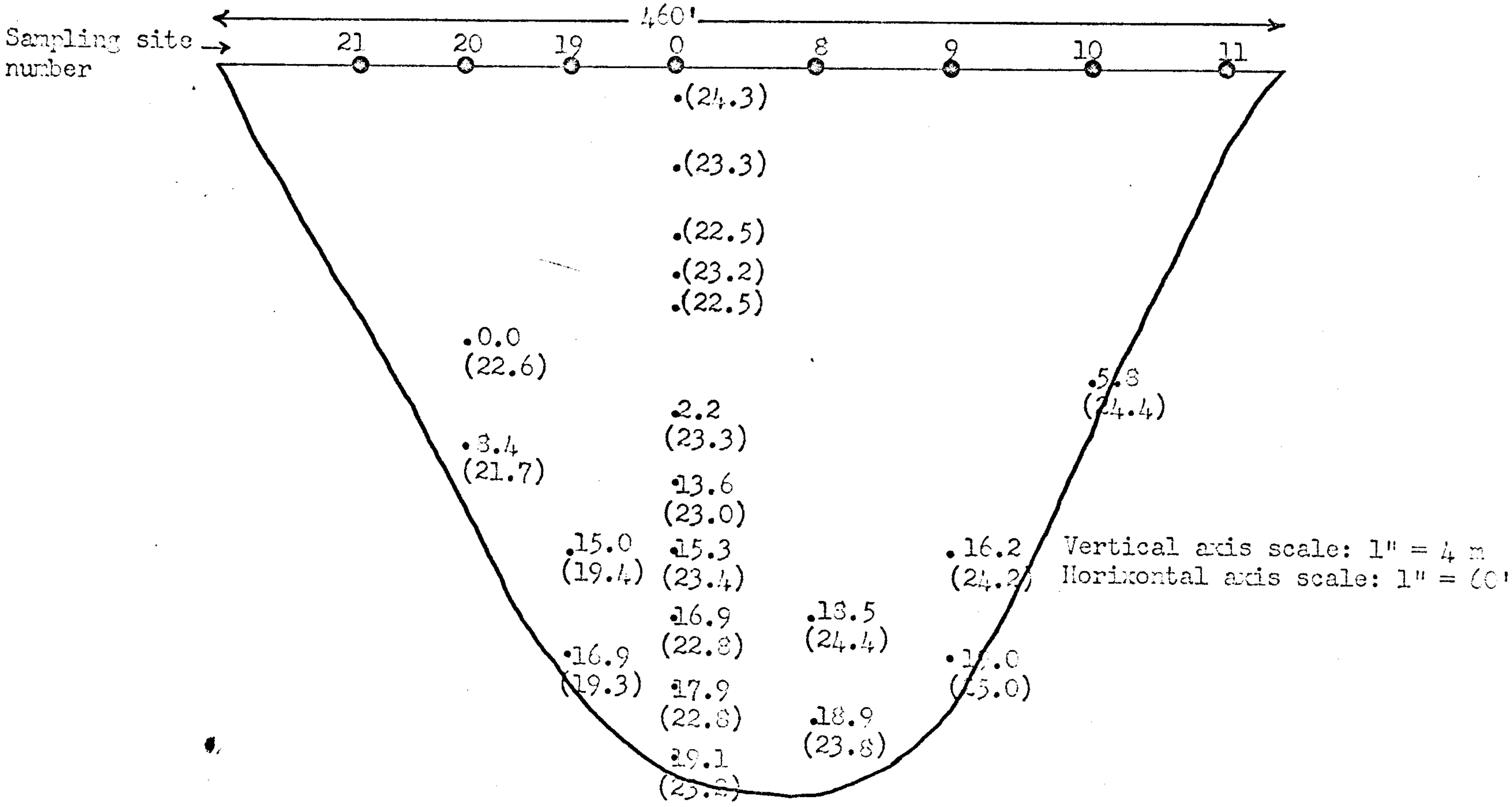


Vertical axis scale: 1" = 4 m
Horizontal axis scale: 1" = 60'

The numbers given at each point represent CH_4 and N_2 concentrations in mg/l. N_2 values are in parentheses.

CH_4 AND N_2 CONCENTRATIONS IN LAKE MARY, 3-18-68
CROSS SECTION #2

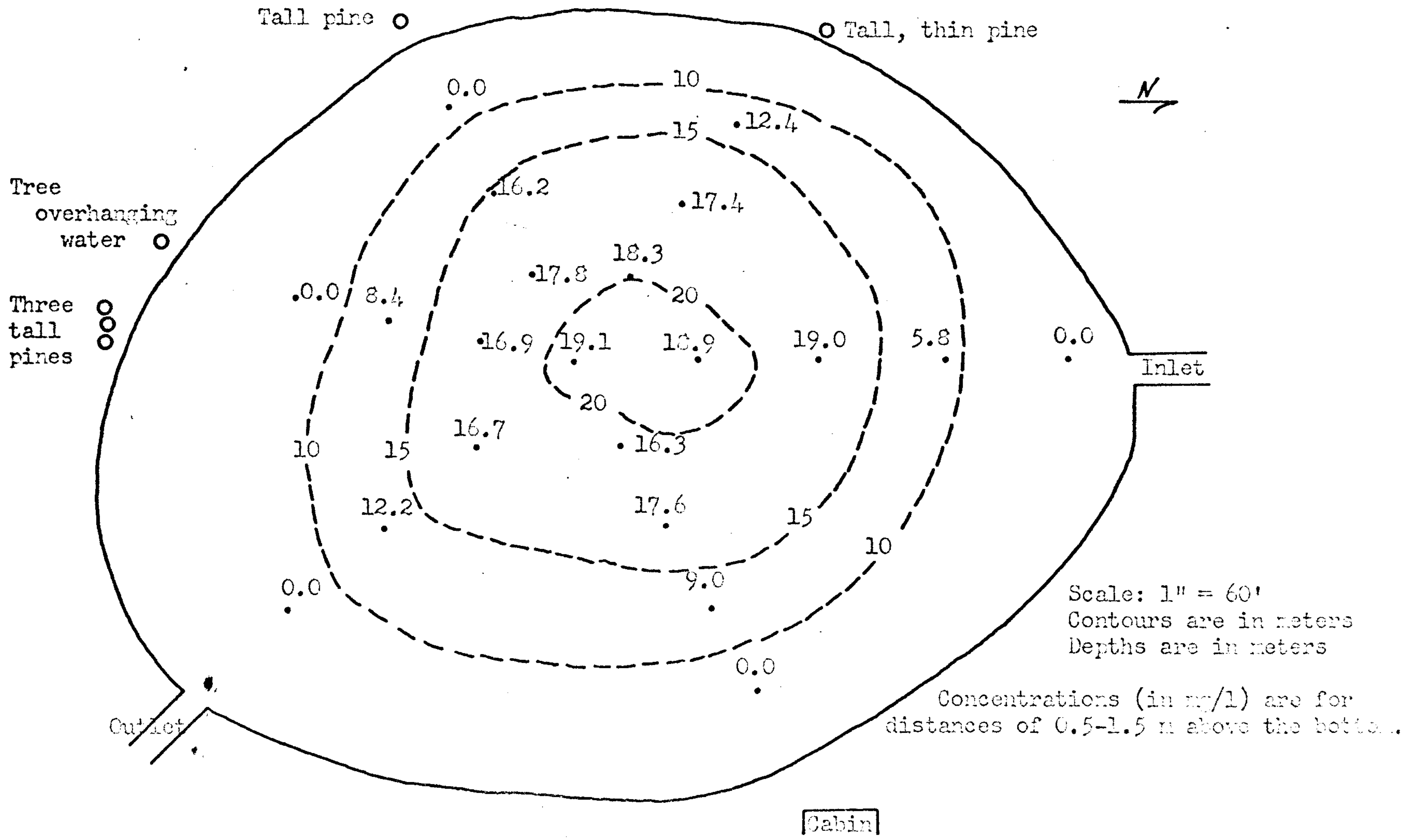
FIGURE 4.15



The numbers given at each point represent CH_4 and N_2 concentrations in mg/l. N_2 values are in parentheses.

CH_4 AND N_2 CONCENTRATIONS IN LAKE MARY, 3-18-68
CROSS SECTION #3

FIGURE 4.16



Scale: 1" = 60'
Contours are in meters
Depths are in meters

Concentrations (in mg/1) are for distances of 0.5-1.5 m above the bottom.

CH_4 CONCENTRATIONS NEAR LAKE MARY SEDIMENTS, 3-18-68

FIGURE 4.17

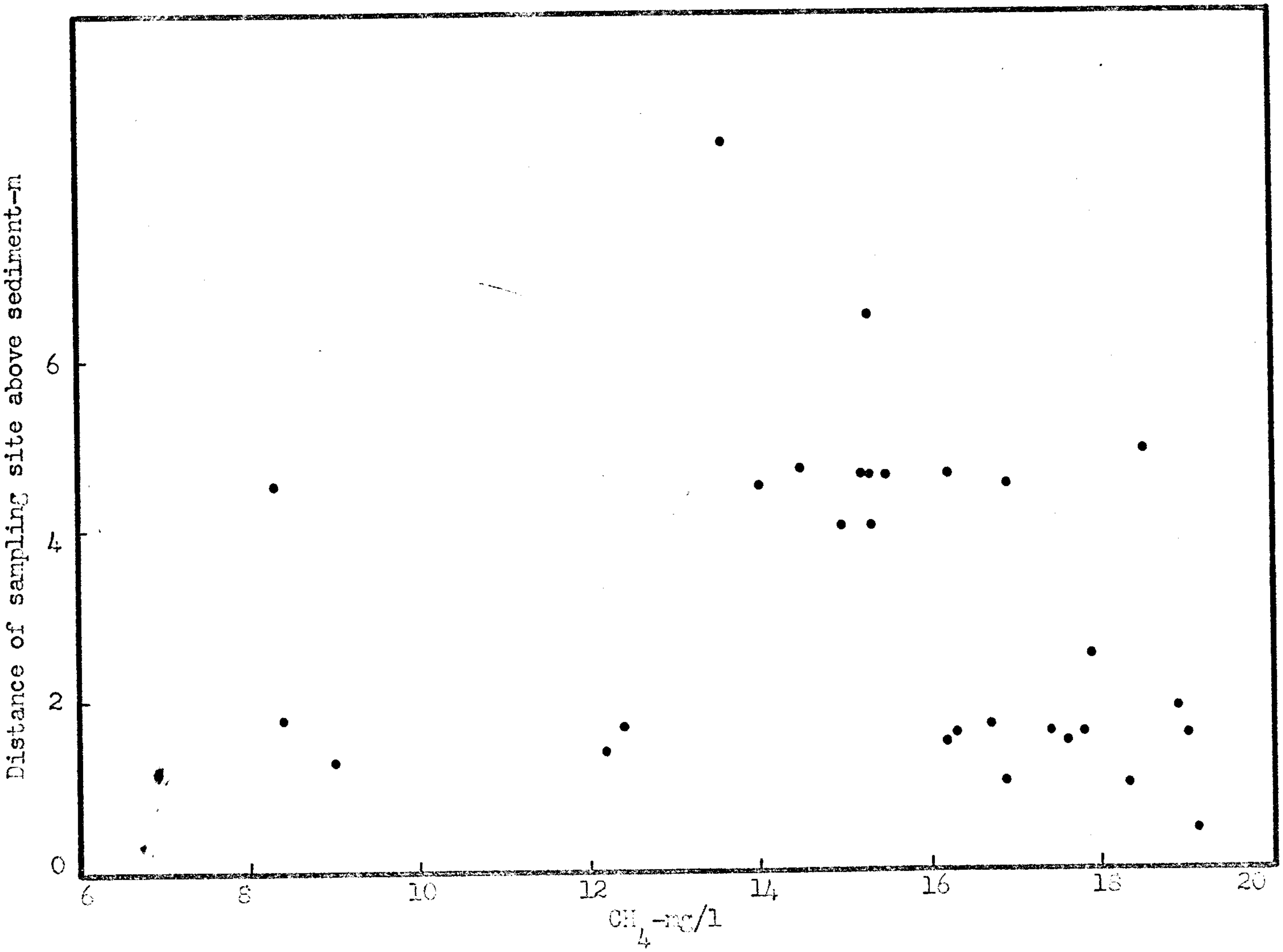
chemocline where mixing action may be occurring. Finally, Figure 4.18 presents a plot of CH_4 concentration as a function of distance above the sediments. Although this data is rather scattered, there is a definite trend. The highest concentrations were generally found closest to the sediments. The scattered values that show relatively low CH_4 concentrations at distances of less than two m above the sediments are from depths of less than 15 m. This data does not show that CH_4 production occurs only within the sediments of Lake Mary. However, no evidence of production in any layers of water has been seen. By far, the majority of CH_4 production apparently occurs within the sediments or at the sediment-water interfacial boundary.

The presence of CH_4 and its distribution pattern verify biological activity near the bottom of Lake Mary. No definite CH_4 production rates could be determined from the data. However, a later discussion section speculates concerning the rates of CH_4 production.

DATA INTERPRETATION

Anion-Cation Balance

An anion-cation balance was made for the mixolimnetic and the monimolimnetic waters of Lake Mary. This was to determine if analyses were made for all major chemical species. Table 4.24 presents this data based upon average concentration values; these concentrations were averages of all the collected data. For both the surface and anaerobic waters there were anion equivalents equal to about 80 percent of the total cation equivalents. However, calculated specific conductance values shown in Table 4.25 indicated that these average concentrations of cations and anions accounted for all of the measured conductivity. The calculated conductivity values were determined by multiplying the average concentrations in equivalents/l times the equivalent conductance of each species. The calculated specific



CH$_4$ CONCENTRATIONS VS DISTANCE ABOVE LAKE MARY SEDIMENTS, 3-18-68

FIGURE 4.18

TABLE 4.24

LAKE MARY – ANION-CATION BALANCE

MIXOLIMNETIC WATERS (0-8 m)

CATIONS			ANIONS		
	Concentration			Concentration	
Species	mg/l	µeq/l	Species	mg/l	µeq/l
NH_4^+-N	0.19	13.57	$H_2PO_4^-$-P	0.02	0.63
Na^+	1.2	52.20	$NO_2^- + NO_3^-$-N	0.04	2.90
K^+	0.9	23.02	Cl^-	1.5	42.30
Mg^{+2}	1.3	106.91	SO_4^{-2}	5.3	110.35
Ca^{+2}	3.8	189.62	Alkalinity as $CaCO_3$	7.7	154.00
		385.32			310.18

MONIMOLIMNETIC WATERS (12-20.5 m)

CATIONS			ANIONS		
	Concentration			Concentration	
Species	mg/l	µeq/l	Species	mg/l	µeq/l
NH_4^+-N	4.37	312.11	$H_2PO_4^-$-P	0.34	10.97
Na^+	1.2	52.20	$NO_2^- + NO_3^-$-N	0.04	2.90
K^+	0.9	23.02	Cl^-	1.5	42.30
Mg^{+2}	1.3	106.91	SO_4^{-2}	0.5	10.41
Ca^{+2}	3.8	189.62	Alkalinity as $CaCO_3$	24.3	486.00
		683.86			552.58

All concentrations shown above are average concentrations throughout each water mass.

TABLE 4.25

LAKE MARY - CALCULATED SPECIFIC CONDUCTANCE

MIXOLIMNETIC WATERS (0-9 m)

CATIONS			ANIONS		
Species	Conc-μeq/l	Contribution to Conductivity- μmhos/cm @ 25°C	Species	Conc-μeq/l	Contribution to Conductivity- μmhos/cm @ 25°C
NH_4^+	17.45	1.3	$H_2PO_4^-$	1.93	0.1
Na^+	52.20	2.7	NO_3^-	12.85	0.9
K^+	23.02	1.7	Cl^-	42.30	3.2
Mg^{+2}	106.91	4.1	SO_4^{-2}	110.35	8.9
Ca^{+2}	189.62	11.3	HCO_3^-	93.94	4.2

Total calculated conductivity = 38.3 μmhos/cm @ 25°C

Average actual conductivity = 36.4 μmhos/cm @ 25°C

All concentrations shown above are average concentrations throughout the water mass.

Cont'd. TABLE 4.25

LAKE MARY - CALCULATED SPECIFIC CONDUCTANCE

MONIMOLIMNETIC WATERS (12-20.5 m)

CATIONS			ANIONS		
Species	Conc-µeq/l	Contribution to Conductivity-µmhos/cm @ 25°C	Species	Conc-µeq/l	Contribution to Conductivity-µmhos/cm 25°C
NH_4^+	401.37	29.5	$H_2PO_4^-$	33.62	1.1
Na^+	52.20	2.7	NO_3^-	12.85	0.9
K^+	23.02	1.7	Cl^-	42.30	3.2
Mg^{+2}	106.91	4.1	SO_4^{-2}	10.41	0.8
Ca^{+2}	189.62	11.3	HCO_3^-	296.46	13.2

Total calculated conductivity = 68.5 µmhos/cm @ 25°C

Average actual conductivity = 67.5 µmhos/cm @ 25°C

All concentrations shown above are average concentrations throughout the water mass.

conductance of the surface waters was 9.4 percent higher than the average measured conductivity; for the monimolimnetic waters, the calculated value was 1.5 percent higher than the measured value. This close agreement between calculated and measured values indicated that all important species had been considered. Rainwater and Thatcher (86) stated that the specific conductance (in μmhos/cm) of a water sample should be roughly equal to the sum of the cations or anions-μeq/l/10. The conductivities of both the surface and the chemically-stratified waters of Lake Mary approximated closely the sum of the cationic μeq/l/10. If the anionic microequivalents were used instead, the computed specific conductance values were much less than the measured values.

There are at least two possible explanations for the apparent deficit of anionic equivalents. The sulfate analytical data could have been inaccurate as the analytical procedure was not highly reliable. In addition, whereas normally many analytical values were used to obtain an average concentration value for a given species, relatively few sulfate analyses were performed. The SO_4^{-2} concentration value for the surface waters was based on a duplicate determination of the SO_4^{-2} concentration of one sample. The SO_4^{-2} content of this sample may not have been representative of the normal SO_4^{-2} concentrations. A concentration of 8 mg/l SO_4^{-2} higher in both water masses than that measured would have accounted for nearly all of the needed anion equivalents, but this higher concentration in both water masses seems unlikely. Also, additional SO_4^{-2} ions would increase the calculated conductivity to much above the measured specific conductance.

Another possible explanation of the anion-cation balance discrepancy is that the uncounted anion equivalents are provided by the organic materials in the lake waters, which are of constant concentration throughout the lake. Dubach and Mehta (33) state that the average equivalent weight of humic acids is approximately 300. For an organic carbon concentration of 30 mg/l (52.5 mg/l organic matter, based on an average molecular formula for humic acids given by Schnitzer, 91) there is a possible maximum of 170 μeq/l of humic acids available (more than the anion deficit), if all of the organic materials were humic acids. An unknown percentage of the organic matter may be present as some dissociated form of humic acid. Because of the large size of these molecules and resulting low ionic mobility, their contribution to the conductivity of the water would be minor. Calculated specific conductance values should, therefore, correspond closely to the measured values.

In calculating the anion-cation balances, no contribution by any iron species was considered. Since much of the iron may be present in a complexed state, the extent of its participation into reactions with other charged species is unknown. Also, total sulfide was not considered as contributing to the total anionic equivalents since it exists nearly entirely as H_2S at the pH of the Lake Mary waters. There were no analytical determinations of any dissolved silica species made. However, calculations (for waters with a pH of 5-6) indicated that approximately 30,000-40,000 mg/l H_4SiO_4 would be necessary to supply the deficit anion equivalents. Thus, possible contributions of silica species were disregarded.

Mixing Processes Within the Monimolimnion

The data collected during this study does not clearly signify the main mixing processes that occur within the monimolimnion of Lake Mary. Most of the chemical data indicates that the monimolimnetic waters are quite homogenous and chemically equivalent. However, alkalinity values (Table 4.14) and the vertical distribution of CH_4 concentrations (Table 4.23) decrease with decreasing lake depth. The Lake Mary sediments are considered to be the ultimate source of those species whose concentrations are higher in the monimolimnetic waters (12-20 m depths) than they are in the mixolimnetic waters; these are specific conductance, COD, total iron, total phosphorus and orthophosphate, H_2S, and NH_3. Although these species are likely released only from the sediments, their distributions are homogenous throughout the monimolimnion. Alkalinity species and CH_4 are also probably produced only in the sediments and released from there. However, the distributions of these two chemical parameters indicate that their vertical transport is controlled by diffusion alone; ie., their distribution patterns can be adequately described by Equation 4.5.

Both molecular diffusion and eddy diffusion may transport the CH_4 and alkalinity species. There is little indication of major currents having a role in the mixing of the monimolimnetic waters. The turbidity data (see Table 4.7) on two occassions, 1-21-67 and 11-11-67, was higher in the monimolimnetic waters than in the mixolimnion and also was higher than that determined on other occassions. This increased turbidity could have been caused by water currents flushing through the chemically-stratified waters. However, such a small amount of data does not allow postulation of current-controlled mixing.

Likely the main mixing process within the monimolinmion is that caused by eddy diffusion. Temperature differences within this water layer could cause small vertical eddy currents to function as mixing mechanisms. These eddy currents need not be large to homogenously mix the monimolimnetic waters over a long period of time. One apparent reason that the alkalinity and CH_4 distribution patterns vary from those of the other chemical species of interest is that these two species are associated with gas production within the sediments. If CH_4 and CO_2 are occassionally released as bubbles, then solution of these bubbles during vertical transport may explain the observed distribution. All of the other chemical species may be only slowly released from the sediments into the overlying waters. If this release is slower than diffusion processes, then no concentration increase would be seen in the waters directly above the sediments. CO_2 and CH_4 occassionally released as bubbles from the sediments could supply these species more rapidly than diffusion alone could disperse them. Hence, their vertical distributions could appear to be diffusion controlled.

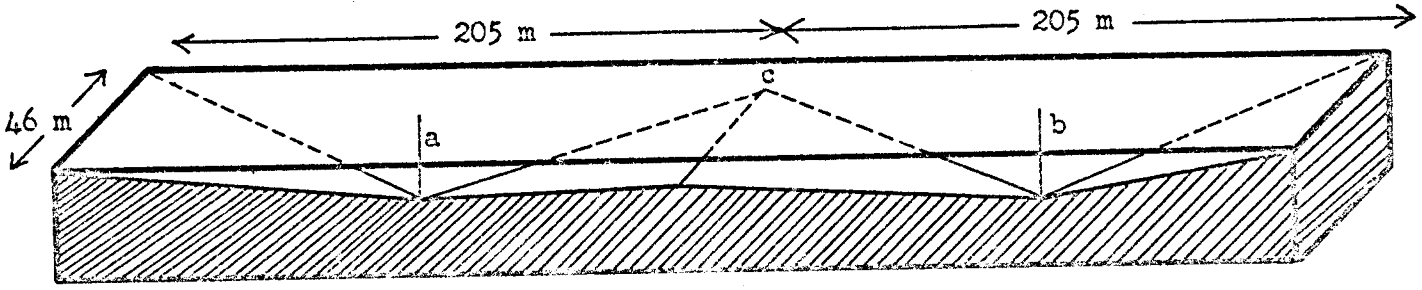
Molecular and eddy diffusion are likely the mechanisms controlling the distribution of all chemical species within the monimolimnion. CO_2 and CH_4 distribution patterns indicate this because these species are supplied from the sediments more rapidly than diffusion alone can homogenously mix them into all of the monimolimnetic waters. The release from the sediments of all other chemical species is slower than the diffusion-controlled mixing processes.

Dissolved Oxygen Demand

For the winter of 1966-1967 the rate of DO loss in Lake Rose was calculated based upon the total oxygen content in the waters on 12-17-66 and the total oxygen content on 3-31-67. The average DO decrease was 4.16 mg/l, or 4.00×10^{-2} mg/l/day. During this same time period, the DO decreased in the Lake Mary mixolimnion at a rate of 3.62×10^{-2} mg/l/day, or 90.5 percent of the rate in Lake Rose. Since there was a large snow cover during most of the winter and since DO was nearly absent from the Lake Rose waters, it was assumed that photosynthetic activity contributed a minor amount of oxygen to the total oxygen budget during this winter. The rate of oxygen disappearance from Lake Rose was believed to depend largely upon the oxidation of both species released during the dissolution of organic materials and some reduced chemical species released from the lake sediments. For Lake Mary DO loss was due to at least three processes, the oxidation of reduced chemical species that diffused through the chemocline, the oxidation of some reduced species transported from Lake Rose, and the oxidation of reduced species released from the Lake Mary sediments. Since the outlet of Lake Rose is less than 1 m deep, it seems likely that any easily-oxidized species would have been oxidized before they were transported into Lake Mary. In like manner, since the outlet of Lake Mary is less than 1 m deep, any species diffusing through the chemocline would likely be oxidized before being flushed from the lake.

It can be shown qualitatively that a large portion of the DO decrease in the Lake Mary mixolimnion was due to the oxidation of reduced species transferred from the monimolimnion, if the following assumptions are made: (1) all of the DO lost from Lake Rose is due to the oxidation of reduced species released from the sediments or oxidation of organic materials produced within the water column, (2) the oxidation of organic materials produced within Lake Mary contributes exactly the same oxygen demand as does this process in Lake Rose, (3) the sediments in Lake Mary at depths of 0-8 m release the same amount (meq) of reduced species/time period/m^2 as do the Lake Rose sediments, (4) the Lake Rose basin can be approximated by Figure 4.19, (5) the colored organic materials in both Lake Mary and Lake Rose do not undergo oxidation by O_2, and (6) the sediments of Lake Mary and Lake Rose are chemically equivalent.

With the above assumptions, the DO decrease in Lake Rose is calculated to be



a = 12 m, depth at center of shallower basin
b = 13 m, depth at center of deeper basin
c = 4 m, depth of shelf dividing two basins

Vertical scale: 1 mm = 1 m
Horizontal scale: 4 mm = 10 m
Vertical exaggeration of 40

ASSUMED GEOMETRY OF BASIN OF LAKE ROSE:
CROSS-SECTION THROUGH CENTER OF LAKE

FIGURE 4.19

$$\frac{28.8103 \times 10^{7} \text{ mg total DO lost}}{3.8108 \times 10^{4} \text{ m}^{2} \text{ total basin area}}$$

$$= \frac{7.56 \times 10^{3} \text{ mg DO lost}}{\text{m}^{2} \text{ bottom area}} .$$

For Lake Mary these same calculations give

$$\frac{26.1846 \times 10^{7} \text{ mg total DO lost}}{7.502 \times 10^{2} \text{m}^{2} \text{ total bottom area (0-8 m depth)}}$$

$$= \frac{34.90 \times 10^{3} \text{ mg DO lost}}{\text{m}^{2} \text{ bottom area}} .$$

Thus, for all of the DO loss in Lake Mary to be due to reduced species released from the 0-8 m sediments, the rate of release would have to be 4.6 times as great as that for the Lake Rose sediments. Yet, the sediments of these two lakes are likely to be chemically quite similar since the allochthonous matter deposited in each lake arises from similar biotopes. If the DO loss/m^{2} of bottom area calculated for Lake Rose is used to calculate the DO decrease due to release of reduced species from the sediments in the 0-8 m depth of Lake Mary, then the loss expected is 5.6715×10^{7} mg DO, leaving a loss of 20.5131×10^{7} mg DO unaccounted. This is approximately 78 percent of the total amount of DO lost from Lake Mary. The major amount of this DO loss must be due to the chemical and/or biological oxidation of reduced species that are transferred across the chemocline.

The unaccounted DO decrease amounts to 2.47×10^{5} meq of DO/day consumed. There are in the monimolimnetic waters a limited number of reduced species that can exert an oxygen demand. Because it may exist in a complex, the possible reactions of Fe^{+2} are unknown. In addition to ferrous iron, the main reduced species present in the monimolimnion are H_2S and CH_4. The maximum oxygen demand that these species could exert (through biological and/or chemical reactions) may be represented by the equations

$$4\ H_2O + S^{-2} + 2\ O_2 \longrightarrow SO_4^{-2} + 8\ H^+ + 4\ O^{-2}. \qquad (4.3)$$

$$2\ O_2 + CH_4 \longrightarrow CO_2 + 2\ H_2O. \qquad (4.4)$$

The equation for mass transfer by molecular diffusion alone can be used to determine the masses of reduced species transferred. This equation is

$$\frac{dm}{dt} = DA\,\frac{c_1 - c_2}{z_1 - z_2} \qquad (4.5)$$

where

$\frac{dm}{dt}$ = mass transferred/unit time

D = coefficient of molecular diffusion
For CH_4 = 6.4×10^{-6} m^2/hr
For H_2S = 6.5×10^{-6} m^2/hr

A = surface area of transfer
For CH_4 = 3100 m^2 at 12-m depth
For H_2S = 4900 m^2 at 9-m depth

$c_1 - c_2$ = concentration gradient
For CH_4 = 6 mg/l
For H_2S = 0.9 mg/l

$z_1 - z_2$ = transfer distance = 1 m.

Based upon molecular diffusion alone, the transfer of these species across the chemocline into the mixolimnetic waters would be about 1.6×10^3 meq/day. This is considerably less than the DO decrease of 2.47×10^5 meq/day. Even if unknown sources of oxygen demand are present, their concentrations would likely be low in comparison to those of H_2S and CH_4 and, thus, their contributions to the DO demand should be less. If the Lake Mary monimolimnetic waters exerted a BOD, then this could be a significant contribution to the oxygen demand. However, this demand would also be coming across the chemocline and this movement would support the hypothesis presented here. Apparently, only enhanced mixing at the chemocline can explain the large DO decrease observed in the Lake Mary mixolimnetic waters.

Thermal Stratification of Lake Mary

Two different approaches towards a study of the thermal stratification of Lake Mary were used. The first involved calculations concerning the stability of the layered waters of Lake Mary; the second was concerned with the sources of heat for the monimolimnetic waters of Lake Mary.

Lake Mary Thermal Stability

Although the difference in density between the mixolimnetic and monimolimnetic waters of Lake Mary is not large, the extent of chemical stratification is highly significant. The number of cationic milliequivalents increased from an average value of 385 μeq/l in the surface waters to 684 μeq/l in the chemically-stratified layer, an increase in ionic concentration of 178 percent (see Table 4.24). The effect of this increase in ionic species upon the density of the water is great enough to outweigh any density decreases due to small temperature changes. At times of maximum density, when the mixolimnetic water temperature was 4.0°C, the 8-m water of Lake Mary had a density of 0.999973 gm/cm^3 + 0.000026 gm/cm^3 (dissolved solids content) = 0.999999 gm/cm^3. The chemocline had an average temperature of 4.4°C and a density of 0.999972 gm/cm^3 + 0.000039 gm/cm^3 (average dissolved solids content) = 1.000011 gm/cm^3. The density of the monimolimnetic waters at 4.8°C was 0.999968 gm/cm^3 + 0.000052 gm/cm^3 (dissolved solids content) = 1.000020 gm/cm^3. Thus, even at the times of maximum density in the mixolimnion, the chemocline was an effective barrier against mixing of the mixolimnetic and monimolimnetic water masses. The increase in ionic concentrations provided the stability required by the monimolimnetic waters to hinder mixing.

In this relation Hutchinson (49) sites the work of Schmidt (89,90) in calculating the stability of a lake. Schmidt defined the stability of a lake as the work/unit area required to mix a body of water to a uniform temperature and used the equation

$$S = \frac{1}{A_o} \int_0^{z_m} \left| z - z_g \right| A_z \, (1 - \rho_z) \, dz \qquad (4.6)$$

where

A_o = surface area of the lake

A_z = lake area at any given depth, z

z = any given depth

z_m = maximum depth

ρ_z = water density at any given depth

$$z_g = \frac{1}{V} \int_0^{z_m} z \, A_z \, dz, \qquad \text{where } V = \text{lake volume.} \qquad (4.7)$$

Evaluation of S for the Lake Mary temperature distribution observed on 7-10-67 (see Figure 4.2) provides a value of 264 gm-cm/cm^2. The value of S for a Lake Mendota summer temperature profile is 514 gm-cm/cm^2.

Hutchinson (48,49) calculated the stability values for two meromictic lakes, Hemmelsdorfersee and Big Soda Lake and estimated that to mix the monimolimnion of Hemmelsdorfersee into the mixolimnion would require 2690 gm-cm/cm^2, considerably more than that calculated as necessary to mix Lake Mary. For Big Soda Lake, the estimated work required for mixing would be 60,000 gm-cm/cm^2. From these two examples of calculated meromictic stability, Lake Mary appears to be relatively unstable in comparison to some other meromictic lakes. The sheltered characteristics of the lake basin are undoubtedly the main reasons for the lack of complete vertical mixing. The small amount of the summer heat income transferred to the deeper waters of the mixolimnion is an indication of the limited wind-induced mixing that occurs.

Heat Budget of Lake Mary Monimolimnion

The 20-m water of Lake Mary is maintained at an almost constant temperature of 4.8-5.0°C. In addition, the 9-11 m layer of water, the chemocline, maintains a constant 4.2-4.6°C temperature, only slightly subject to the heating and cooling influences of the mixolimnetic waters.

The sun's energy, therefore, apparently does not penetrate the total depth of the mixed surface waters. The sources of heat for the monimolimnetic waters may be biological activity in the mud and/or geothermal heating from the bottom sediments.

Johnson and Likens (54) and Likens and Johnson (70) have studied the sedimentary contribution to the heat budgets of two, small, Wisconsin lakes. One of these is a biogenic meromictic lake located within 150 miles of Lake Mary, namely Stewart's Dark Lake, a bog-type which has an area of 0.69 ha and a maximum depth of 8.8 m. Reportedly, because of the high color of the water, the sun's light does not penetrate greater than the 3-m depth. Because of this fact and the permanent stratification of the lake at 6 m, the "temperature gradient below this depth [6 m] is essentially an extension of the local geothermal gradient." The sediment at the sediment-water interface has a yearly temperature of 5.1-5.2°C. This temperature increases linearly down through the gelatinous sediments at a rate of 0.2 C°/m of sediment. These authors also studied the distribution of temperatures in the bog area surrounding the lake. In these adjacent sediments they found that below a depth of approximately 4 m temperatures were constant throughout the year and that the lake was surrounded by a warm basin of constant temperature. The overall contribution of the sediments was shown to be 10 percent of the total heat budget of Stewart's Dark Lake. Likens and Johnson considered biological activity within the sediments to be of negligible importance in comparison to geothermal heating.

The physical characteristics of Stewart's Dark Lake are similar to those of Lake Mary. Both lakes exhibit biogenic meromixis, are surrounded by bogs, and are located in the same area of Wisconsin. In addition, the temperature of the surface sediments of Lake Mary is 5.0-5.1°C, the same as that in Stewart's Dark Lake. The gelatinous, surface sediments of Lake Mary contain 95.2 percent water, as compared with 93-96 percent water in the sediments of Stewart's Dark Lake. It may, therefore, be possible to compute a theoretical heat inflow from the lake sediments into the waters of Lake Mary using a value for the thermal conductivity of the surface sedimentary gel given by Likens and Johnson (70) for Stewart's Dark Lake of 1.1×10^{-3} cal/cm^2-C^o-sec. The amount of heat transferred by conduction alone can be calculated using the equation

$$q = k \frac{A}{L} (t_1 - t_2) T \tag{4.8}$$

where

q = heat flow

k = thermal conductivity of the insulating layer between the heat source (sediments) and the heat sink (water)

A = transfer area

L = thickness of insulating layer

$t_1 - t_2$ = temperature differential between heat source and heat sink

T = total time of heat transfer.

To make these calculations for the sediments of Lake Mary, certain assumptions were necessary. These included assumption of (1) a uniform surface sediment temperature of 5.1^{o}C, (2) a uniform water temperature of 4.8^{o}C for the 15-20 m depths, (3) a 4.6^{o}C temperature for the 12-15 m water layer, (4) a conical basin, and (5) a thickness of 20 cm for the insulating layer between the heat source (sediments) and the heat sink (water). This thickness may be an approximation of the depth of the flocculent, well-mixed, sediment-water interfacial layer. The thickness of this layer was observed to vary throughout the basin of Lake Mary. Those sediments nearer the surface and near the inlet to the lake had a flocculent sediment-water interface much thicker than the sediments in the deeper area of the lake. Here the interfacial layer was generally only a few mm thick. The 20 cm thickness was chosen as an approximate average thickness of the sediment-water interface throughout the lake. With these assumptions, Equation 4.8 predicts a heat inflow from the sediments into the 12-m and deeper water of Lake Mary of 56.76 x 10^6 cal/day. Further calculations will assist in determining the significance of this heat flow.

If the monimolimnion of Lake Mary is considered to be a well-mixed but isolated system consisting of water at the 12-m depth and lower, and the mixolimnetic waters are considered to be a well-mixed system consisting of all waters at a depth of less than 9 m, then the 9-11 m layer of water acts as the buffer or insulating layer between these two separate systems. With conduction as the single means of heat transfer, the amount of heat transferred across this 3-m thick insulating layer can be calculated by the use of Equation 4.8 presented above. The monimolimnion is considered to provide a constant heat source of 4.6°C temperature; the mixolimnion is a constant heat sink of 4.2°C. The thermal conductivity of the insulating layer is estimated to be 1.37 x 10^{-3} cal/cm-C°-sec at 5°C (46). For these conditions a maximum of 7.71 x 10^6 cal/day can be transferred from the monimolimnion to the mixolimnion by conduction alone. The amount of heat supplied by the sediments to the monimolimnion is roughly 7.4 times this amount.

Because of the close similarities between the physical conditions of Lake Mary and Stewart's Dark Lake, it is felt that the calculations of heat transfer from the sediments to the lake waters are a good approximation of the actual heat transfer. Also, the description of Lake Mary as being two well-mixed layers with an insulating layer fits the physical data. Discrepancies arising in the amounts of heat transferred may be due to the heat transfer processes across and through the 3-m thick insulating layer. If, for instance, some heat transfer occurs through the vertical mixing of small packets of water instead of by conduction alone, much more heat transfer would occur. There is evidence for the occurrence of such water mass transfer. Chemical species other than those associated strictly with dissolved gases are seen to penetrate into the chemocline waters from the monimolimnetic waters. Such species are mainly phosphorus and nitrogen species. In addition, Likens and Johnson (70) noted that the heat added to the monimolimnion of Stewart's Dark Lake is sufficient to raise its overall temperature by 0.7 C°; yet, the temperature of the monimolimnion remains approximately constant throughout the year. They feel that both conduction and convection are important processes in the transfer of this heat from the monimolimnion to the mixolimnion.

Because of the depth of Lake Mary and the high color of the water, sunlight does not penetrate to the monimolimnetic waters. The heat source for the constantly-warm monimolimnion is apparently the lake sediments. Since the monimolimnion of Lake Mary maintains a nearly-constant temperature, heat must be transferred from the monimolimnion into the mixolimnetic waters. Evidence indicates that this heat transfer across the chemocline occurs more rapidly than can be attributed to conduction alone. Vertical mixing activity in the chemocline region may be quite important. If mixing here is important for heat transfer, then it must also contribute to the transfer of chemical species.

Estimates of Methane Production Rates

One attempt to estimate rates of CH_4 and CO_2 production from $NaC_2H_3O_2$ was made. This involved the incubation of $NaC_2H_3O_2$ (labelled with ^{14}C in both carbon atom positions) in situ at a depth of 15 m in Lake Mary for a 24-hour period. A total of 10 µc of 13.3 mc/mM of $Na^{14}C_2H_3O_2$ was added to the 2900 ml sample; this was a dosage of 27.2 µg/l of $Na^{14}C_2H_3O_2$. After incubation the water sample was filtered, preserved with $CHCl_3$, acidified, and stripped with air to remove the CO_2, which was then precipitated as $BaCO_3$. Counting the $BaCO_3$ thus produced showed no significant counts above background counts, indicating that little of the added $Na^{14}C_2H_3O_2$ had been metabolized. This was an indication that the rates of CH_4 production within the 15-m water of Lake Mary are quite low. Attempts to measure rates of $Na^{14}C_2H_3O_2$ metabolism in mud-water suspensions were unsuccessful.

Assuming that CH_4 production occurs almost exclusively in the sediments of Lake Mary, some simple computations concerning amounts of CH_4 produced can be made using production rates given by Koyama (65). Koyama studied the rates of CH_4 production by different types of paddy soils under different temperature conditions. He found the rate of CH_4 production for an average paddy soil at 5°C by extrapolating data for higher incubation temperatures and assuming no production at 0°C. The rate that he arrived at in this manner is 0.04 ml of CH_4/day/100 gm of dry soil. This is the rate used in the following calculations for Lake Mary. This rate compares with an average rate for Lake Mendota sediments found by Allgeier et al. (1), to be 0.144 ml of CH_4/day/100 gm of dry sediment at an incubation temperature of 7°C.

The amount of CH_4 production was calculated after making some basic assumptions for some of which there was no supporting evidence. However, the nature of these calculations is such that they are useful as a qualitative descripter of the Lake Mary system. These basic assumptions were (1) the rate of production in the Lake Mary sediments was uniformly 0.04 ml of CH_4/day/100 gm of dry sediment, (2) this production rate was applicable uniformly to the top 20 cm of all the Lake Mary sediment at a depth of 12 m or greater, (3) there was no CH_4 production below the 20-cm sediment depth, (4) the basin of Lake Mary is conical, and (5) 5 gm (dry weight) of Lake Mary sediment would occupy a wet volume of approximately 100 ml. Using these assumptions gave an estimated CH_4 production rate of 1.3252×10^6 ml of CH_4/day, or (based on a normal atmospheric pressure at Lake Mary of 0.944 atm.) 8.48×10^5 mg of CH_4/day.

In addition, it is possible to approximate the total amount of CH_4 in the Lake Mary water body at any given time. To do this, it must be assumed that CH_4 concentrations are homogenously distributed throughout any given water layer and that the concentration decrease with decreasing depth is linear. Both of these assumptions are justified by data previously presented. On 3-18-68 there were 211.71×10^6 mg of CH_4 below the Lake Mary Chemocline (depths of 12 m and greater). Based upon an assumed production rate of 0.04 ml of CH_4/day/100 gm of dry sediment and assuming that none of the produced CH_4 was removed, 250 days would be required to produce this much CH_4 in the Lake Mary monimolimnion.

Finally, if it is assumed that molecular diffusion alone is transporting CH_4 from the lake sediments to the mixolimnion, the time required for the total amount of CH_4 in the monimolimnion to diffuse can be calculated. This calculation does not assume that there is a constant source of CH_4 but, rather, that there are 211.71×10^6 mg of CH_4 in the 12-m water and that this amount will diffuse out of this water mass. Since the chemocline water is evidently mixing within itself and with the mixolimnetic waters, the CH_4 does not have to diffuse the total 3-m thickness but merely 1 m (from the 12-m water layer to the 11-m water layer) to get into the chemocline. Equation 4.5 is used for this calculation. Solving this equation for dt gives a total time of 208 years required for molecular diffusion alone to remove all of the CH_4 from the monimolimnetic waters. Hence, the rates of this removal are vastly less than the rates of production calculated above. Only 2860 mg of CH_4/day would diffuse. Admittedly, these calculations are rather crude. They are based upon unsubstantiated rates of production and removal of CH_4. However, they do indicate the possible importance of mixing at the chemocline. Since the concentrations of CH_4 within the monimolimnion of Lake Mary appear to be at a steady state, molecular diffusion alone cannot account for the observed CH_4 transfer, and the mixing of water packets at the chemocline must be an important process.

CHAPTER V

SUMMARY AND CONCLUSIONS

The results of the study of the chemical limnology of lakes Mary and Rose may be summarized as follows:

1) The increases in ionic concentrations in the monimolimnion of Lake Mary as compared with the mixolimnion can be attributed entirely to the processes of anaerobic degradation of organic materials. Thus, biogenic meromixis is the stabilizing influence on Lake Mary.

2) In comparison with other meromictic lakes, Lake Mary has a low meromictic stability. The sheltered characteristics of the lake basin are the main physical features assisting the state of permanent meromixis.

3) Chemically, the aerobic waters of Lake Rose function as an extension of the mixolimnion of Lake Mary. Factors effecting the chemistry of the aerobic waters of Lake Rose influence the chemistry of the Lake Mary mixolimnetic waters in similar manners and to similar extents.

4) Anion-cation balance data indicates that some of the uncharacterized organic materials in the Lake Mary waters are present in an ionized form and serve to electronically balance the cationic charged species in the waters.

5) CH_4 production in Lake Mary centers near or in the lake sediments.

6) There may be a significant amount of relatively-fresh, highly-colored water flowing into the Lake Mary mixolimnion from the surrounding bog mat.

7) Eddy diffusion is apparently the main mixing process that occurs within the monimolimnetic waters of Lake Mary.

8) There is a significant amount of heat and chemical species transfer across the chemocline beyond that which molecular diffusion and heat conduction alone would predict.

CHAPTER VI

RECOMMENDATIONS FOR FURTHER STUDY

Based upon the previous data discussion, the following recommendations for future study of the Lake Mary-Lake Rose system are proposed:

1) Develop an analytical procedure to determine low-level sulfate concentrations (0-5 mg/l) in Lake Mary water.

2) Release a radiotracer, ^{45}Ca for example, in the Lake Mary monimolimnion near the sediments and observe the horizontal and vertical dispersion of this isotope, with particular emphasis upon observing mixing at the chemocline.

3) Formulate a water budget for Lake Mary, measuring outflow and all visible sources of inflow and determining the piezometric surface of the groundwater table surrounding the lake.

4) Consider the effects that the two cottages on Lake Mary and Lake Rose may have upon the water chemistry of these two lakes.

5) Determine the natural acetate levels in the sediments of Lake Mary. Incubate selected concentrations of ^{14}C-labelled acetate in mud-water suspensions to determine what natural CH_4 production rates may be.

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APPENDIX

TABLE A.1

LAKE ROSE - PHOSPHORUS DATA
(expressed in mg/l-P)

Soluble, orthophosphate

Sampling Date		12-17-66	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67	12-17-67
Depth-m	1	0.03	0.01	0.03	0.04		0.06	0.04
	2				0.03	0.03		
	3		0.01		0.04	--	0.03	0.04
	4	0.02		0.02		0.01		
	5		0.01	-0.03-	-0.04-		0.03	
	6					0.02		0.03
	7		0.02					
	8	0.02	--					
	9		0.04	0.07		0.08	0.03	-0.03-
	10	-0.04-						
	11		0.09	0.18				
	12			0.17				

Total Phosphorus

Sampling Date		12-17-66	1-21-67	3-31-67	7-10-67	9-23-67
Depth-m	1	0.03	0.02	0.03	0.04	
	2				0.03	0.03
	3		0.02			--
	4	0.02		0.03		0.04
	5		0.02	-0.03-	-0.06-	
	6					0.04
	7		0.03			
	8	0.03	--			
	9		0.05	0.07		0.11
	10	-0.09-				
	11		0.17	0.19		
	12			0.17		

Dotted lines represent shallowest depth of water layers of 0.0 mg/l dissolved oxygen content.

TABLE A.2

LAKE ROSE - NITROGEN DATA

(expressed in mg/l-N)

		NH_4^+-N						Organic-N		
Sampling Date		12-17-66	1-21-67	3-31-67	7-10-67	9-23-67	4-27-68	1-21-67	3-31-67	7-10-67
Depth-m	1	0.30	0.27	0.07	0.07		0.06		0.43	0.48
	2				0.33	0.10				0.52
	3		0.25		0.13	--		0.25		
	4	0.23		0.05		0.65	-0.02-		0.55	
	5		0.30	-0.35-	-0.53-			0.25	-0.80-	-0.67-
	6					0.89	0.08			
	7									
	8	0.45	-S.43-							
	9		1.06	0.85		1.21	1.45	0.84	0.65	
	10	-0.75-						--		
	11		3.24	2.37				0.71	0.88	
	12			3.42					0.00	

		$NO_2^- + NO_3^-$-N				
Sampling Date		12-17-66	1-21-67	3-31-67	7-10-67	9-23-67
Depth-m	1	0.01	0.05	0.31	0.02	
	2				0.04	0.01
	3		0.07		0.05	--
	4			0.23		0.02
	5		0.06	-0.05-	-0.06-	
	6					0.01
	7		0.06			
	8	< 0.01	--			
	9		0.01	0.01		0.02
	10	< -0.01-				
	11		0.01	0.01		
	12			0.15		

Dotted lines represent shallowest depth of water layers of 0.0 mg/l dissolved oxygen content.

TABLE A.3

LAKE ROSE - MISCELLANEOUS DATA

(expressed in mg/l)

Sampling Date		Mg^{+2}						Ca^{+2}				
		12-17-66	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67	1-21-67	3-31-67	7-10-67	9-23-67	11-11-67
Depth-m	1	1.0	1.7	1.4	1.6		1.3	4.8	4.7	3.9		3.8
	2					1.3					5.2	
	3				1.6					3.9		
	4	1.2		1.3		1.4			4.0		4.3	
	5		1.7	1.4	1.7		1.3	4.0	4.0	4.4		4.0
	6											
	7											
	8	1.0										
	9			1.4		1.4	1.3		4.4		4.5	4.0
	10	1.0		1.5								
	11		1.8	1.6				5.2	6.1			
	12								5.0			

Sampling Date		Total Iron		Total Sulfide		Cl^-		
		12-17-66	1-21-67	1-21-67	3-31-67	1-21-67	3-31-67	7-10-67
Depth-m	1	0.23	0.11			1.3	1.3	1.6
	2							1.3
	3		0.09			1.6		1.2
	4	0.25					1.4	
	5		0.23		--	1.4	1.8	1.4
	6							
	7		0.35					
	8	0.38	—	-0.18-				
	9		0.78	0.34	0.46	1.4	1.4	
	10	-0.80-						
	11		0.80	0.12	1.26	1.9	1.7	
	12				0.92		3.2	

Dotted lines represent shallowest depth of water layers of 0.0 mg/l dissolved oxygen content.

TABLE A.4

LAKE ROSE - MISCELLANEOUS DATA

		Alkalinity (expressed as mg/l $CaCO_3$)				Na^+ (expressed in mg/l)	COD (expressed in mg/l)
Sampling Date		11-11-67	12-17-67	3-18-68	4-21-68	12-17-66	3-31-67
Depth-m	1	11.9	13.5		31.2	1.6	46
	2			12.4			
	3	12.3	11.7				
	4			-12.7-	12.7	1.6	41
	5	11.5			---		-44-
	6		12.6		12.3		
	7			17.8			
	8					1.2	
	9	12.7	-19.9-		19.1		42
	10			21.9		1.3	
	11						73
	12						94

Dotted lines represent shallowest depth of water layers of 0.0 mg/l dissolved oxygen content.

APPROVAL

The foregoing thesis is hereby approved as a creditable study of a water chemistry project, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it is submitted.

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