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A Description of the Temperature, Nutrient Major Ion and Trace Metal Conditions in Lake Superior 1968-1971

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by C.H. Chan

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A DESCRIPTION OF THE TEMPERATURE, NUTRIENT MAJOR ION AND TRACE METAL CONDITIONS IN LAKE SUPERIOR 1968-1971

# . by

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March, 1974.

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#### INTRODUCTION

The chemical limnology of Lake Superior is the least studied and the least understood among the Great Lakes. Much of the current studies have been directed toward the lower lakes where excessive eutrophication has caused progressive deterioration of water quality and undesirable changes of species in the biotic communities. Lake Superior has remained relatively free of the problems which the Lower Great Lakes have encountered, and measures are now being undertaken to preserve Lake Superior in its present state. il.

Historical data are few and widely scattered. Moreover, much of the chemical analyses were reported at a time when modern methods of analysis were not available, thus complicating assessment of long term trends in chemical composition.

Between 1968-1971, CCIW carried out seven limnological surveys across Lake Superior collecting physical, chemical and biological data. This is a report on the chemistry of nutrients, inorganic ions and minor trace elements in Lake Superior providing a data summary, spatial and temporal distribution maps and seasonal variation of these constituents. Results can also serve as a "baseline" reference for evaluating future changes and planning of future limnological studies of Lake Superior. A comparison is also made between CCIW data and past data.

## DATA ANALYSIS

Statistics of the data are unweighted. Any kind of weighting scheme is quite subjective and since good uniformity exists for most of the chemical parameters in Lake Superior, it is assumed that unweighted

statistics adequately describe the chemistry in Lake Superior.

Mean values for the whole lake were computed by a simple averaging process. Mean values for each sampling station, computed in a similar manner, were subsequently used in a computer plotting routine to produce spatial distribution maps. For interpolation between observations, the plotting routine interpolates from the nearest 3 data points whose weights are inversely proportional to the distance square. Distribution maps were plotted for parameters with more than fifty sampling locations. Because of the great depth of Lake Superior, sampling depths were widely spaced. To facilitate data analysis, 25 meter was arbitrarily chosen as the dividing line between surface and bottom layer measurements. For major inorganic ions and trace metals, which were fairly uniform with depth, no differentiation between surface and bottom water was made unless there were significant variations with depth.

The seven synoptic surveys were carried out within a period of four years, each in a different month. If the survey or surveys taken within each year were taken to be representative of that year, then data interpretation could be based on yearly comparison. However, a more valid assumption would be that Lake Superior with a huge volume is likely to undergo extremely slow response to any external changes. With this assumption, differences observed between each survey will be interpreted as seasonal variation rather than yearly changes.

#### ANALYTICAL METHODS

The chemical analyses were carried out by Water Quality Division, and the methods are described in "Methods for Chemical Analysis of Waters

and Wastewaters," W. J. Traversy (1971).

# SAMPLING PROGRAMS

Sampling locations for each year are shown in Figure 1. Basically the network was the same for the four years but sampling programs differed from survey to survey. Sampling programs for each survey are listed in Table 1.

#### TEMPERATURE (Fig. 11 and Fig. 12)

Water temperature is one of the prime factors controlling the rate of photosynthetic growth of primary producers. An abundance of these organisms has a dominant effect on the species population in the higher levels of the food chain. In addition, population dynamics can alter the cycle and kinetics of chemical nutrients.

Lake Superior is the coldest of the Great Lakes chiefly because of its latitude and its great depth. The annual temperature cycle of Lake Superior shows four seasonal periods. Spring warming (April to June) summer stratification (July to September), autumn cooling (October to December) and winter stratification (January to March).

The annual water temperature cycle for surface and bottom water are shown in Fig. 2 and their mean temperatures are listed in Table 2.

In April, mean bottom water temperature was  $0.9^{\circ}$ C higher than the mean surface water temperature indicating that reverse thermal stratification had occurred during the winter stationary period. Average water temperature in April was between 1 - 2°C.

Spring convection began in May, when the mean lake water temperature was raised by about 1<sup>o</sup>C. Thermal bar formation began along the shallow shore off Duluth and Thunder Bay, while isothermal conditions prevailed in the off-shore water.

By early July, warm water was found at the surface in the shallow waters. Thermal bars were well developed along the north and south shore. Signs of thermal stratification appeared in nearshore waters where

surface and bottom temperatures differed by 6°C. By mid-August, thermal bars had disappeared and the lake was well stratified. Thermal stratification extended into October when the lake water was at its warmest. The maximum may have occurred during September but was not detected due to survey schedules.

Autumn convection began in early November and consequent mixing of surface and bottom water produced isothermal conditions in the nearshore zones. By late November, the entire lake was once again near isothermal between  $5^{\circ}$  and  $6^{\circ}$ C. Through the whole annual cycle, the deepest part of Lake Superior in the Eastern Basin remained below  $5^{\circ}$ C.

#### Dissolved Oxygen and Oxygen Percent Saturation (Fig. 13 & Fig. 14)

Surface lake waters are always well saturated with oxygen because of constant exchanges with atmosphere. However, during periods of stagnant thermal stratification in summer when there is little exchange between top and bottom layers of water, the lower layer of water can be depleted of oxygen. Because of the large oxygen reserve in the hypolimnion of Lake Superior, significant oxygen depletion was never observed.

Oxygen solubility in water decreases with increasing water temperature. Fig. 3 shows that this relationship is closely followed in that surface dissolved oxygens are high in spring and winter and lower in summer and fall. Vertically warmer surface waters are lower in dissolved oxygen than the deeper cold water. (Table 3). Horizontally, warmer nearshore waters have lower dissolved oxygen. During spring and fall convection dissolved oxygen values for the upper 25 meters and those

below 25 meters are nearly the same, indicating thorough mixing in the lake.

Percent saturation of oxygen is a better indicator for oxygen conditions in water since the differences in water temperature has been taken into account. Oxygen percent saturation should remain around 100% under normal conditions. In Lake Superior, percent oxygen saturation is slightly above 100% in summer and just below 100% in spring and winter (Fig. 3, Table 4). During spring and fall circulation periods, oxygen saturation is close to 100%. The observed seasonal variation in oxygen percent saturation is probably caused by the non-equilibration of dissolved oxygen with changing water temperature.

Biological productivity in Lake Superior is low. Since Lake Superior is a huge body of cold water, dissolved oxygen is unlikely to reach very low levels.

#### **Phosphorus**

Phosphorus enrichment in lake waters has been reported to be the cause of increased biological productivity, undesirable biotic change and deterioration of water quality (Vollenweider, 1968). In an undisturbed ecosystem, phosphorus compounds in water are scarce since the only natural sources are weathering of phosphate (apatite) minerals and atmospheric precipitation. Major cultural sources of phosphorus include inputs from urban centers and agriculture run-off.

Phosphorus in Lake Superior has been analyzed in three fractions: total phosphorus, total dissolved phosphorus and orthophosphate. From these three analyses, the difference between total phosphorus and total dissolved phosphorus gives particulate phosphorus, and the difference between total dissolved phosphorus and orthophosphate is laballed soluble organic phosphorus. The mean concentrations of total phosphorus, total dissolved phosphorus, particulate phosphorus, orthophosphate and soluble organic phosphorus are found in table 5. Table 6 shows total dissolved phosphorus, particulate phosphorus, orthophosphate and soluble organic phosphorus are found in table 5. Table 6 shows total dissolved phosphorus, particulate phosphorus, orthophosphate and soluble organic phosphorus are found in table 5. Table 6 shows total dissolved

Total phosphorus and orthophosphate were sampled more frequently than total filtered phosphorus. Therefore, the sums of the fractions of soluble organic phosphorus and orthophosphate may not equal the fraction of total dissolved phosphorus (Table 6).

# Total Phosphorus (Fig. 15)

Natural variation of 80% are observed in total phosphorus measurements. Therefore, such a large variation is not uncommon in particle sampling. Other phosphorus parameters which are related to the total quantity of phosphorus or are calculated from these measurements also are subject to the same variation. Regions of consistently high total phosphorus concentrations are regarded as source area of this nutrient.

Measurements from twenty sampling locations in Lake Superior in 1968 and 1970 showed that the average total phosphorus concentration

varied from 9.3 ppb to 18.0 ppb as PO4. With fifty six sampling stations in 1971, mean total phosphorus from three synoptic surveys ranged from 9.0 - 12.0 ppb. Both surface and bottom phosphorus distribution maps (Fig.15 ) indicate Western Superior and Thunder Bay high in total phosphorus. Phosphorus level in the open lake remained between 6 -9 ppb. 8Ł

#### Total Dissolved Phosphorus (Fig.16)

Total dissolved phosphorus contains all the dissolved and soluble compounds which pass through a .45 micron filter paper. Rigler (1964) has demonstrated that the amount of total dissolved phosphorus varies with the pore size of filter paper and with the location from where the water sample was taken. A further discussion on total dissolved phosphorus is provided under orthophosphate and soluble organic phosphorus section.

Results obtained in 1970 showed that the mean total dissolved phosphorus was 3 - 4 ppb, and that the mean total dissolved phosphorus in 1971 was between 5 - 7 ppb. Spatial distribution maps in June 1971 showed high total dissolved phosphorus in the Duluth and Thunder Bay regions. Total dissolved phosphorus in October was uniformly distributed.

The percentage of total dissolved phosphorus ranged from 1-100% (Table 6) within any single survey and showed no simple relationship to total phosphorus concentration. The lake wide average fraction of total dissolved phosphorus in 1970 was between 30 - 40% and in 1971 the

lake wide average fraction was between 55 - 70%. The significance of this difference is not known.

Areal distribution maps of the percentage of total dissolved phosphorus (Fig. 17) do not show any identifiable pattern.

### Orthophosphate (Fig. 18)

Orthophosphate is continually being recycled by plankton, thus its equilibrium concentration is low and fairly constant.

The orthophosphate content of Lake Superior is low 0 - 3 ppb and close to the detection limit of the analytical method. Orthophosphate maxima for all the three surveys in 1971 were all recorded at station 69, at the exit of Duluth Harbour. Individual percentage of orthophosphate ranges from 0 - 60% and shows much larger variation than orthophosphate concentrations. Lake wide average percentage of orthophosphate remains between 10 - 20%. Fig. 19 shows the areal distribution of the percentages of orthophosphate. It is interesting to note that the nearshore waters have a lower percentage concentration of orthophosphate.

## Particulate Phosphorus (Fig. 20)

All particulate phosphorus material which is retained on a .45 micron filter paper is included in this fraction. It is composed of both organic and inorganic phosphorus compounds, the organic component can further be subdivided into living and non-living matter. The relative proportion of each individual component is highly dependent upon the

sample location. A biologically active body of water will increase the proportion of organic component at the expense of inorganic fraction while land runoff will favor the inorganic phosphorus component.

Average particulate phosphorus in Lake Superior was found to range from 4 - 9 ppb. Maximum values were recorded in Western Superior and Thunder Bay where phosphorus loading and productivity are expected to be high. It is not possible to attribute these higher particulate phosphorus concentration to any single factor.

The proportions of particulate phosphorus ranges from 0-90% of total phosphorus (Table 6). Western Superior and Thunder Bay where particulate phosphorus concentrations already are high also have higher percentages of particulate phosphorus. (Fig. 21).

On a lake wide basis, particulate phosphorus represents 60 - 70% of the total phosphorus in 1970. In 1971, the percentage of particulate is reduced to 30 - 45%.

#### Soluble Organic Phosphorus (Fig. 22)

Dissolved phosphorus compounds which do not readily react with acidified molybdate have been labelled "soluble organic phosphorus" by Hutchinson (1957), and "soluble in reactive phosphorus" by Strickland and Parson (1960). To avoid confusion with orthophosphate, the term "soluble organic phosphorus" is used here. While these "soluble organic phosphorus" compounds are also utilized for plant growth, their availabilities and turnover times are not as well studied as orthophosphate (Fogg 1973).

Lake wide average soluble organic phosphorus concentration in 1970 was found to be around 2.5 ppb (See Table 5). The 1971 average soluble organic phosphorus concentration was 3 - 7 ppb. The higher soluble organic phosphorus concentration in 1971 was the result of higher total dissolved phosphorus. Spatial distribution maps (Fig. 22) for soluble organic phosphorus show little regional disparity.

The calculated percentage of soluble organic phosphorus ranges from 0 - 89%. Lake wide average percentage of soluble organic phosphorus ranged between 20 - 25% in 1970 and 40 - 60% in 1971. Areal distribution maps of the percentage of soluble organic phosphorus (Fig. 23) resemble those of percentage of total dissolved phosphorus and show no sample identifiable pattern. The observed complicated pattern for soluble organic phosphorus is not unexpected considering the many types of phosphorus compounds which can come under this heading.

#### Soluble Silicate (Fig. 24)

Silicate in natural waters is primarily derived from weathering of silicate minerals. Man-made sources of silicate are mainly from mineral refining industries which are located along the shore of Minnesota. The silica cycle in natural waters is closely associated with diatoms whose cell walls are composed of silica materials. The dominance of the less desirable blue green algae which is considered a by-product of excessive eutrophication over diatoms in the Great Lakes have been attributed to limited available silica in surface water (Schelske & Stoermer 1971).

Soluble silicate measurements are summarized in Table 7 and Fig. 6 shows the annual cycle of soluble silicate in surface and bottom water. These values are low compared to those reported by "Cisco" in 1951, whose mean soluble silicate concentration was 5.0 ppm, and 3.6 ppm in St. Mary's River in 1957 and 1958 by Thomas and Gale (1965). More recent results by Putnam and Olson (1970), Schelske and Callender (1970) reported soluble silicate to be around 20 - 25 ppm which agreed well with CCIW measurements. The reason for this discrepancy in soluble silicate results is probably analytical.

The annual cycle of soluble silicate (Fig. 6 ) suggests two pulses of silicate uptake by diatoms in summer and fall. Lowest soluble silicate concentration found in surface water is 1.70 ppm. Vertical distributions of silicate clearly indicate that silicate is lower in surface water than deeper bottom water. It could be the combined effect of silicate uptake by diatoms in surface water and decaying of settling silicate diatom skeletons. Differences between surface and bottom water soluble silicate becomes larger as the lake becomes more stratified.

Areal distribution maps (Fig 24 ) of soluble silicate for June and July show Western Superior, where most of the mining industries are located, and Thunder Bay, to be .20 ppm higher than the rest of the lake. In October the lake is fairly homogeneous in soluble silicate.

### Nitrate (Fig. 25)

Nitrate, nitrite and ammonia are the preferred forms of nitrogen available for growth by phytoplankton and bacteria. Nitrate uptake is commonly observed in the euphotic zone. Within the Great Lakes basin, the external nitrate sources are primarily surface influence and atmospheric precipitation.

Average nitrate concentrations for surface and bottom water are given in table 8 and the annual nitrate cycle is shown in Fig. 7. Nitrate is higher in spring and winter and lower in summer and fall. Largest decrease in nitrate occurs between June and July. Uptake of nitrate in surface water is evident in that mean surface nitrate concentrations are less than those of the deeper water. Differences in nitrate concentration between surface and deeper water increase with increasing thermal stratification. Mean nitrate concentrations below 25 M remain unchanged during the stratified period. Spring and fall mixing bring mean surface and bottom nitrate concentrations to be the same.

Areal nitrate distribution maps show that nitrate uptake start from nearshore water. Surface influence of nitrate may not be detected if nitrate uptake is fast.

### Ammonia (Fig. 26)

Ammonia is a major end product of decomposition of nitrogeneous organic matters, and under aerobic conditions, it is rapidly converted to nitrate by nitrifying bacteria. Therefore, in natural waters, ammonia nitrogen is a small percentage of nitrate nitrogen, and exhibits large variations. Generally, accumulation of ammonia indicates organic decay and sewage discharge in nearshore and bay waters.

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Average ammonia concentrations are found to be in the range of 5 - 20 ppb. (Table 9). Surface water has a higher ammonia content than bottom water. The highest ammonia concentration is found in the Western Superior close to the Duluth Harbour.

#### MAJOR IONS

In the following discussion, major ions refer to some of the common natural occurring cations and anions in all natural waters (sodium, potassium, calcium, magnesium, chloride, sulphate, bicarbonate). Concentrations of these inorganic ions within a body of natural water are governed by the buffering reactions of the carbonate system and solubility limitations. These ions remain fairly constant at their equilibrium concentrations. Therefore, the concentration of these inorganic ions within a lake can serve as an index for monitoring the progress of lake aging. However, unnatural sources for these ions such as industrial, municipal and rural waste discharges have greatly raised the major ion concentrations in some lakes which have dense population and heavy industries within their drainage basin. At low concentrations, these ions are seldom considered as contaminants, but at higher concentrations water can become unsuitable for domestic and industrial usage.

Several workers have investigated dissolved ions in the Great Lakes (Beeton 1965), Kramer (1964), Weiler and Chawla (1969). Results indicate a progressive increase in the concentration of various major ions and total solids in all of the Great Lakes except in Lake Superior where there appears to be a slight decrease (Table 11). This downward trend in Lake Superior is not considered as significant.

The average concentrations of major ions in the Great Lakes compiled by some of the earlier workers are shown in Table 10.

Data compiled by the earlier workers include data from various sources where different sampling and analytical procedures were employed. The results represent four years of intensive surveys over the whole of Lake Superior. The average concentration of various major ions between 1968-1971 are summarized in Table 11. In general, the results and conclusions drawn are compatible with previously reported work.

#### pH (Fig. 27)

pH is a measure of hydrogen ion concentration which is closely regulated by the carbonate system in natural waters. It is primarily used in determining reaction paths in other systems that are pH dependent. Adams Jr. (1972) observed that pH in Western Superior in 1969 was high in summer and low in spring and fall. This was attributed to the increase in photosynthetic uptake of  $CO_2$  in summer time, thus lowering the bicarbonate and hydrogen ion concentrations.

The pH values in Lake Superior ranged from 7.4 - 8.6. Maxima and minima values recorded during each survey occurred mostly at the nearshore stations along the north shore from Thunder Bay to Marathon and along the south shore from the Apostle Islands to Keweenaw Peninsula. The mean values when interpreted on a yearly basis suggested a progressive increase of pH from 7.75 to 7.95. However, when the same set of results was plotted versus season, Fig. 8, it was more likely that pH varied with season. In June, during the thermal stratification

pH was slightly higher in surface water than in bottom water. CONDUCTIVITY (Fig. 18)

Conductivity is an indicator of areas having high concentrations of dissolved ions although this measurement is insensitive to organic chemical compounds. Specific conductance in each of the Great Lakes is changing with time on a long term basis. The upper lakes are increasing at a slower rate in relation to the input and volume while the lower lakes are increasing much more rapidly due to increasing cultural inputs and continued enrichment as the water moves through the Great Lakes.

Average specific conductance in Lake Superior remains around 95-97 micromhos at 25<sup>o</sup>C. (Fig. 9) with no apparent seasonal fluctuation. Conductivity measurements between surface and bottom show no differences even in the summer months when the lake is thermally stratified. Compared to the value of 78.7 (Beeton 1965) the increase is significantly high. The average specific conductance for 1969 was 106 which is substantially higher than the other numbers obtained in 1970 and 1971. It is unlikely that this value is real but due to differences in the calibration of conductivity meters, conductivity distribution maps show consistently high conductivity in areas of population centers and industries. Duluth Harbour, Silver Bay, Ashland, Thunder Bay, Nipigon Bay, Keweenaw Bay and Whitefish Bay are consistently higher in conductivities.

POTASSIUM (Fig. 29)

Potassium is a micronutrient required for plant and animal

growth. It is derived from weathering of minerals, chemical wastes in drainage basin, atmospheric precipitation and runoff.

Lake Superior is fairly uniform in potassium. Between 1968-1971, mean concentration ranged from 0.42 - 0.53 ppm, and the maximum and minimum recorded were 0.67 and 0.39 ppm respectively.

#### SODIUM (Fig. 29)

Sodium in lake water has origins similar to potassium. It is also introduced into the lake water as brine waste of industries and street salting.

Sodium concentration in Lake Superior remained fairly constant from 1968-1971 with averaged value between 1.2 - 1.3 ppm. Spatial distribution maps for the months of May and October show that Western Superior is about .05 ppm higher in sodium than the rest of the lake. CALCIUM (Fig. 30)

Calcium and magnesium are responsible for the hardness of water. Sources of calcium and magnesium in the Great Lakes are chemical weathering of mineral calcite  $(CaCO_3)$  and dolomite  $(CaMg(CO_3)_2)$ . Bedrock and overlying sediment in the Great Lakes region compose a high proportion of calcite and dolomite. Other major source of calcium and magnesium is from agricultural runoff.

The mean concentration for calcium between 1968-1971 was at 13.2 ppm. Most of the higher values were obtained in nearshore zone. The overall calcium concentration of Lake Superior was rather uniform.

#### MAGNESIUM (Fig. 30)

The mean concentration of magnesium remained fairly constant in the period of study. It ranged from 2.5 to 2.7 ppm with high concentrations in the western part of Superior. 1

# CHLORIDE (Fig. 31)

Because of the conservative nature of this ion, chloride has been extensively used as an indices of chemical loadings in comparison with the non-conservative constituents in the lower lakes. Tiffany and Winchester (1969), Ownkey and Kee (1967). Among the Great Lakes, Ontario and Erie have shown great increases, Michigan and Huron have shown slight increases and Superior has shown no historical buildup in chloride.

Chloride spatial distribution map for the month of May showed higher chloride levels in Duluth, the Silver Bay region and in Thunder Bay. This pattern of distribution was not apparent in October which could have been due to the influx of chloride in spring runoff from the use of road salt in winter.

#### SULPHATE (Fig. 31)

In addition to the usual sources for sulphate as described for the other major ions, sulphate is also the end product of most bacterial oxidation of sulphur compounds. The sulphur cycle in natural waters involves both chemical and biological components within the

system, which in turn may affect the sulphate concentration. Therefore, it is likely that sulphate will be more variable than the other major ions. 11

Averaged sulphate concentrations between 1968-1971 showed some large discrepancies: 3.44 ppm (1968), 2.61 ppm (1969), 1.89 ppm (1970) and 2.71 - 2.79 ppm (1971). It is probable that such data variation was the results of the change in analytical methods and not due to biological processes. In 1968 and 1969, the titrimetric method using Thorin was employed for sulphate analysis. Later in 1970 and 1971, the colormetric methyl thymol blue method was used.

Sulphate spatial distribution maps for May show that the lake was homogeneous in sulphate ion, but less homogeneous in October. <u>ALKALINITY (Fig.31)</u>

Alkalinity in water is basically a measure of carbonate, bicarbonate and hydroxide ions. The lower great lakes are shown to be saturated with calcite but Lake Superior and Huron are not (Kramer 1964). In Lake Superior, changes in pH due to photosynthetic assimilation of carbon dioxide were reported to lower the carbonate concentration. (C.E. Adams Jr. 1972).

Figure 31 shows that the nearshore waters are lower in alkalinity than open lake water. There is no observable vertical variations in alkalinity. In October, lower alkalinity is recorded near Keweenaw Peninsula, and surface water samples are lower in alkalinity than deeper water samples. Alkalinity is high in Nipigon Bay.

A plot of alkalinity versus seasons strongly indicates a seasonal relationship (Fig. 10). In general, alkalinity shows a gradual decrease from spring to fall and returns to spring level in December.

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#### TRACE METALS

One of the major problems when interpreting trace element data or data on any other micro-contaminants in the environment for the Great Lakes, is a lack of historical data with which to establish a reliable baseline for the purpose of trend comparison. Interests in water quality and levels of toxic substances are fairly recent. Lake Superior has a small population in its drainage basin and a large volume receives loads that are mostly natural in origin, could reach a steady state concentration with little change in chemical composition over a period of a century. Given a new cultural load, the size of Lake Superior will cause the instantaneous concentration of a constituent to lag behind a steady state concentration. Beeton (1965) has studied historical data on chemical concentrations in the Great Lakes and concludes that there is little change in Lake Superior chemistry over the last hundred years. Therefore, it is valid to assume that the present data are close to "natural background" concentrations. The other problem is more a laboratory one. Existing levels of trace elements in the waters of Lake Superior are low and near the detection limits of most analytical methods. Such low concentrations are also easily susceptible to contamination during sample preparation, thus making it difficult to detect values above the background level. Furthermore, much of the observed results will depend largely on the localities of the sampling network and sampling frequency. This is seen in the case of copper, iron and zinc where natural variabilities are high. Therefore, the following discussion on trace metals on Lake Superior should be treated with regard to these

reservations.

A summary of trace metal concentrations for Lake Superior 1970-1971 is tabulated in Table 12 showing the mean, the median and the range. The loss of a significant figure in the 1970 result was due to the rounding off in coding procedure and not because of the increased sensitivity in the 1971 analytical procedures. Table 13 shows the average, median and ranges of some of these trace metals in the Great Lakes compiled by Weiler & Chawla (1969). The trace metal sampling networks was denser in 1971 with 56 stations compared to 19 in 1970.

#### Cadmium (Fig. 32)

The survey conducted in May showed higher cadmium concentration (0.45 ppb) than in October (0.23 ppb). Higher cadmium values were found near the Apostle Islands and Silver Bay in the western Section and Thunder Bay on the North shore and Whitefish Bay near St. Mary's River. Overall lake wide mean Cadmium concentration was lower with a large portion of the lake showing no detectable cadmium.

#### Chromium (Fig. 32)

Similar to Cadmium, lake wide variations in chromium were observed in May with higher chromium concentrations in Western Superior. The rest of the lake was fairly homogeneous with 0.0 - 0.5 ppb of chromium in both May and October.

#### Cobalt (Fig. 32)

Mean concentration of cobalt in October was .58 ppb compared to .28 ppb in May, although both surveys showed the same ranges. Western

Superior again showed higher levels of cobalt from Silver Harbour to the Apostle Islands. While Eastern Superior concentrations were generally lower, the lake wide mean high cobalt concentration in October was due to the high readings obtained in Eastern Superior where the range of cobalt increased from 0.0 - 0.5 ppb in May to 0.05 - 1.1 ppb in October. The reasons behind such an increase are not clear.

#### Copper (Fig. 33)

Statistics for copper were similar within one year, but results obtained from 1971 showed a significantly higher copper content than 1970. The spatial distribution map for May showed a gradual decrease in copper moving from West to East. Higher readings were recorded near Silver Harbour and Thunder Bay. Some vertical variation existed at stations near the Keweenaw Peninsula, but no apparent depth relationship was found.

In October, the May distribution pattern was reversed with higher concentration found in the East. However, within Western Superior, high copper levels were still recorded from four stations on a transect from Grand Marais, Michigan to Marathon, Ontario. High values were obtained both from surface and deep water samples, and showed no apparent correlation with depth.

#### Iron (Fig. 33)

High concentrations of iron were found near Thunder Bay, Duluth Harbour and Whitefish Bay where concentrations ranged from 10-66 ppb in May and 11-29 ppb in October. Open Lake water ranged from 1-5 ppb.

The differences in ranges caused the differences in average concentrations. Results obtained from 1971 were consistent with values collected in 1970.

#### Lead (Fig. 33)

Agreement was good between 1970 and 1971 results. Mean lead concentration was low around 1.5 ppb with a narrow range of 0.0 - 8.0 ppb. Lake wide variation was small but slightly higher lead concentrations were usually found in the surface water.

#### Manganese (Fig. 34)

Lake Superior had a homogeneous manganese concentration of 0.5 ppb. Slightly higher values were recorded in Western Superior and Whitefish Bay, but their significance was not known.

#### MERCURY (Fig. 34)

Average concentration for Mercury was 0.3 ppb. The highest mercury level was found near Silver Harbour. Overall, Western Superior had a higher mercury content than the rest of the lake.

#### Molybdenum (Fig. 34)

The average concentration of molybdenum was 0.2 ppb with a range of 0.0 - 0.6 ppb.

#### Vanadium (Fig. 34)

Vanadium in Lake Superior was present in minute traces and was mostly undetectable.

# <u>Nickel (Fig. 35)</u>

Nickel distribution maps show similarities with other heavy metals such as iron and copper. Western Superior, Thunder Bay and Whitefish Bay were areas of high nickel concentrations with values as high as 10 ppb. Lake wide average concentration was 1.0 - 1.5 ppb. In October, the range was narrowed to 0.0 - 3.0 ppb, and the distribution map showed a more homogeneous uniform nickel concentration.

#### Zinc (Fig. 35)

Among the list of trace metal measured, Zinc has the highest values having mean concentrations of 15.9 ppb in May and 9.6 ppb in October 1971. Table 14 shows that zinc is the largest component in trace metal loadings from atmospheric source in the Superior Basin (Shiomi and Kuntz 1974).

Patches of high Zinc concentrations were found across the lake. A prominent feature was that the open lake water of Eastern Superior and the Keweenaw Bay were generally high in zinc concentration while Western Superior was low in May and high in October. Correlation between zinc and cultural input was less evident than with the other trace metals. In May, the zinc concentration in the top 25 M of water was significantly higher than those below 25.0 M. The same observation was observed in October with the exception of Thunder Bay and the Central region of Western Superior.

		May	1971	October 1971			
	X	М	R	X	M	Ŕ	
0-25	16.8	14.0	1.0 - 71.0	9.9	8.3	0.0 - 41.0	
Below 25 M	14.8	12.0	1.0 - 54.0	9.2	6.8	0.0 - 42.0	

#### SUMMARY

On a eutrophication scale, Dobson (1972) has classified Lake Superior as oligotrophic based on estimation of biomass from particulate phosphorus and nitrate, silicate uptakes in the surface water of Lake Superior.

Stoichiometric relationship (Stumm & Stumm Zollinger 1968) from photosynthesis reaction suggests that phosphorus is the most likely nutrient to become limiting. The extremely low phosphorus concentration observed and studies carried out by Schelske (1970) certainly seem to support the phosphorus limiting theory. In view of the other essential parameters controlling primary production, i.e. light and temperature, the high latitude of Lake Superior may be another significant factor in determining biomass production.

Lake Superior water quality has undergone very little change over the years and reasons for this are primarily huge volume of the lake thinly populated drainage basin. Presumably most of the material loads are natural in origin. Estimation of loadings from natural weathering are not available. Shiomi and Kuntz (1973) have demonstrated that nutrient loadings from atmospheric source represent a net and significant portion in the total loadings in the Lake Ontario Basin. Preliminary data on atmospheric material inputs in the Superior Basin from Schreiber and Thunder Bay are shown in Table 14. (Shiomi and Kuntz 1974). Results indicate that concentrations of nutrients and trace metals in the rain are

higher than those in the water. <u>Cultural loads in Lake Superior appear</u> to center around Western Lake Superior and Thunder Bay and are distributed over the entire lake.

A large body of water such as Lake Superior can absorb a large material load without any immediate observable changes in water quality. The estimated water retention time of Lake Superior is 189 years and the recovery time is over 500 years (Rainey 1967).

The present water quality of Lake Superior ranks best among the Great Lakes. Lake Superior water is also a major feeder for the Great Lakes. Any impairment of water quality in the waters of Lake Superior may have far reaching effects on the lower Great Lakes. Therefore, it is imperative that water quality in Lake Superior be maintained in its present state. Attention should be focused on embayments and loadings from human source should be closely monitored.

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TABLE 1				•
NUMBER OF SAMPLIN	G STATIONS FO	R LAKE SUPERIOR	1968 - 1971	
DATE	PHYSICAL	NUTRIENTS	MAJOR IONS	TRACE ELEMENTS
18/8-28/8 1968	85	16	21	-
15/11-23/11 1969	86	-	22	-
15/4-23/4 1970	87	19	19	19
28/10-6/11 1970	87	20	20	15
25/5-2/6 1971	70	56	56	56
30/6-7/7 1971	70	56	-	3
5/10-13/10 1971	<b>70</b> ***	56	56	56
physical	temperatú	re, dissolved ox	ygen, pH, cou	nductivity

physical	temperature, dissolved oxygen, pH, conductivity
nutrients	phosphorus, nitrate, ammonia, silicate
major ions	sodium, potassium, calcium, magnesium, chloride,
	sulphate, alkalinity
trace elements	cadium, cobalt, copper, chromium, iron, lead,
	mercury, maganese, molybdenum, nickel, vanadium,
	zinc

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WATER TEMPERATURE IN (°C) LAKE SUPERIOR 1968 - 1971

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DATE	DEPTH	MEAN	MAX	MIN	S.D.
APRIL 1970	0-25M	0.93	2.65	0.18	0.50
BELOW	I 25M	1.66	3.57	0.17	1.13
MAY 1971	0-25M	2.88	9.20	1.60	1.06
BELOW	25M	2.68	4.38	1.60	0.57
JULY 1971	0-25M	6.24	17.40	3.02	3.67
BELOW	1 25M	3.81	10.02	3.02	0.66
AUGUST 1968	0-25M	10.51	16.90	10.51	3.09
BELOW	25M	4.66	11.49	3.56	1.37
OCTOBER 1971	0-25M	11.15	14.35	4.95	1.74
BELOW	25M	6.14	14.25	3.64	2.99
NÖVEMBER 1970	0-25M	7.91	11.62	4.82	1.53
BELOW	25M	6.17	11.61	3.68	2.08
NOVEMBER 1969	0-25M	5.45	8.32	5.45	1.18
BELOW	25M	4.99	8.33	3.64	2.59
	•				

## DISSOLVED OXYGEN (MG/L) IN LAKE SUPERIOR

	·		1968-1	971	• ·	
DATE		DEPTH	MEAN	MAX	MIN	S.D.
APRIL	1970	0-25M	13.72	14.84	12.41	0.30
		BELOW 25M	13.28	14.84	12.32	0.57
MAY	1971	0-25M	13.44	14.18	11.38	0.35
		BELOW 25M	13.41	14.26	12.31	0.35
JULY	1971	0-25M	12.85	14.44	9.41	0.95
		BELOW 25M	13.35	14.44	11.79	0.31
AUG	1968	0-25M	11.54	13.46	9.45	0.95
		BELOW 25M	12.94	13.54	10.25	0.42
ОСТ	1971	0-25M	10.81	13.35	9.80	0.56
		BELOW 25M	12.23	13.78	10.00	0.86
NOV	1970	0-25M	11.58	12.80	10.39	0.51
		BELOW 25M	12.16	13.35	10.04	0.74
NOV	1969	0-25M	12.07	12.89	11.08	0.45
		BELOW 25M	12.33	13.06	11.09	0.48

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OXYGEN PERCENT SATURATION IN LAKE SUPERIOR 1968-1971

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DATE		DEPTH	MEAN	MAX	MIN	S.D.
APRIL	1970	0-25M	97.9	105.2	87.9	1.82
	BEI	LOW 25M	96.7	105.2	86.7	2.10
MAY	1971	0-25M	101.3	109.5	97.6	1.80
•	BEI	LOW 25M	100.4	109.5	88.9	2.45
JULY	1971	0-25M	105.3	124.2	91.6	3.96
. 1	BE	LOW 25M	103.0	111.7	91.6	2.33
AUGUST	1968	0-25M	105.0	110.7	97.0	3.12
•	BE	LOW 25M	102.2	107.4	85.6	2.58
OCTOBEI	r 1971	0-25M	100.3	117.0	90.7	2.55
	BE	LOW 25M	100.0	109.7	84.5	2.40
NOVEMBI	ER 1970	0-25M	99.4	105.7	92.0	1.58
	BE	LOW 25M	99.6	112.4	81.9	3.95
NOVEMBL	ER 1969	0-25M	97.5	104.5	91.0 ´	1.49
	BE	LOW 25M	98.3	102.2	91.1	1.50

S.D. Standard Deviation.

## AVERAGE MINIMUM AND MAXIMUM PHOSPHORUS (PPB PO<sub>4</sub>) CONCENTRATIONS IN LAKE SUPERIOR 1968-1971

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DATE	DEPTH	Τ.Ρ.	<b>T.</b> D.P.	ORTHO P	P.P.	S.O.P.
68	0-25M BELOW 25M	18 (2-60) 14 (2-41)		1.3 (0-12) 1.3 (0-5)		•
70	0-25M	13.2 (7-27)	4.2 (1-16)	2.9 (0-15)	9.3 (4-25)	2.6 (0-12)
, }	BELOW 25M	13.2 (7-18)	5.2 (1-16)	(0-13) 2.7 (0-8)	(1-13) (1-13)	(0-12) 2.3 (0-12)
70	0-25M	9.3 (5-27)	3.0 (11-7)	0.7 (0-3)	6.3 (0-23)	2.2 (0-5)
	BELOW 25	(3-27) 9.0 (4-27)	3.1 (1-7)	(0-3) 1.0 (0-3)	(0-23) 6.0 (0-23)	(0-5) 2.1 (0-5)
71	0-25M	9.9	7.8	1.3	3.7	6.8
	BELOW 25	(6-32) 10.0 (5-55)	(3-14) 6.9 (1-13)	(0-11) 1.3 (0-6)	(0-19) 4.6 (0-29)	(0-13) 5.7 (0-11)
71	0-25M	12.2 (3-81)	6.4 (1-33)	1.5 (0-10)	5.8 (0-49)	<b>4.9</b> (0-24)
	BELOW 25M	(2-69)	5.8 (1-14)	(0-10) 1.4 (0-12)	(0-49) 6.4 (1-62)	(0=24) 4.5 (0=12)
71	0-25M	9.3 2-27	4.8 (1-15)	1.2 (0-8)	4.4 (0-22)	3.6 (0-14)
	BELOW 25	7.8 (3-39)	4.4 (1-15)	1.2 (0-4)	3.3 (0-28)	3.2 (0-28)
() T.P.	Range Total phosp	phorus				

	nunge
<b>T.P.</b>	Total phosphorus
T.D.P.	Total dissolved phosphorus
Ortho P	Orthophosphate
Ρ.Ρ.	Particulate phosphorus
COD	Soluble encanic photobate

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DATE	DEPTH	TOTAL DIS. PHOSPHORUS	PARTICULATE PHOSPHORUS	ORTHO- Phosphate	SOLUBLE ORG. PHOSPHORUS
APRIL	70 0-25M > 25M	0.32 (.0772) 0.39 (.0892)	0.70 (.2792) 0.63 (.0892)	0.24 (.0066) 0.21 (.0066)	0.19 (.0086) 0.24 (.0092)
NOVEMBER	70 0-25M > 25M	0.35 (.00-1.00) 0.39 (.01-1.00)	0.64 (.0089) 0.63 (.0087)	.08 (.0040) 0.13 (.0060)	0.26 (.0060) 0.25 (.0069)
MAY	71 0-25M > 25M	0.70 (.37-1.00) 0.65 (.02-1.00)	0.29 (.0062) 0.36 (.0098)	0.12 (.0060) 0.14 (.0071)	0.53
JULY	71 0-25M > 25M	0.55 (.08-1.00) 0.55 (.0893)	0.45 (.0091) 0.46 (.0692)	0.14 (.0066) 0.13 (.0050)	0.42
OCTOBER	71 0-25M > 25M	0.53 (.09-1.00) 0.59 (.10-1.00)	0:47 (.0092) 0.40 (.0089)	0.14 (.0060) 0.18 (.00-1.0)	0.38 (.0093) 0.41 (.0093 <u>)</u>

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PHOSPHORUS FRACTIONS IN LAKE SUPERIOR

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Range

	SOLUBLE SILICATE (PPM SIO2) IN LAKE					
	SUPERIOR					
DATE	DEPTH	MEAN	MAX	MIN	S.D.	
APRIL 70	0-25M	2.21	2.44	1.76	0.14	
	> 25M	2.25	2.52	1.98	0.13	
MAY 71	0-25M	2.33	3.35	2.10	0.13	
	> 25M	2.33	2.00	2.16	0.08	
JULY 71	0-25M	2.18	2.75	1.84	0.12	
	> 25M	2.20	2.41	1.99	0.08	
AUGUST 68	0-25M	2.23	2.66	1.80	0.16	
	> 25M	2.34	2.90	1.84	0.20	
OCTOBER 71	0-25M	2.04	2.34	1.70	0.10	
	> 25M	2.18	2.56	1.86	0.12	
NOVEMBER 70	0-25M > 25M	2.18 2.27	2.45 2.50	1.92 1.92	0.12	

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TABLE 7

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NITRATE CONCENTRATIONS (PPM N) IN LAKE SUPERIOR

DATE	DEPTH.	MEAN	MAX	MIN	S.D.
APRIL 70	0-25M	.264	.332	.240	.016
	> 25M	.260	.285	.225	.011
MAY 71	0-25M > 25M	. 279 . 280	.350	.170 .230	.022 .018
JULY 71	0-25M	. 247	.290	.158	.025
	> 25M	. 252	.290	.210	.016
AUGUST 68	0-25M > 25M	. 235 . 257	.560 .440	.130	.066 .067
OCTOBER 71	0-25M	. 225	.290	.180	.016
	> 25M	. 261	.295	.180	.023
NOVEMBER 70	0-25M	• 257	.288	.210	.016
	> 25M	• 262	.320	.190	.026

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AMMONIA (PPB N) IN LAKE SUPERIOR (1970-1971)

DATE	DEPTH	MEAN	MAX	MIN	S.D.
APRIL 70	0-25M	11	61	2	10
	> 25M	8	18	2	3
MAY 71	0-25M	18	41	2	6
	> 25M	10	86	2	7
JULY 71	0-25M	5	36	0	4
	> 25M	4	18	1	3
OCTOBER 71	0-25M > 25M	9 6	46 52	1	6 5
NOVEMBER 70	0-25M	5	17	0	4
	> 25M	5	17	0	5

AS REPORTED BY EARLIER AUTHORS							
^	ONTARIO	ERIE	HURON	MICHIGAN <sup>2</sup>	SUPERIOR		
Ca	40.3	37.4	28.1	32	13.2		
Mg	8.1	8.3	6.7	10	2.7		
Na	12.6	11.5	3.2	3.4	1.3		
К	1.35	1.23	.84	.9	. 54		
so <sub>4</sub>	2.94	25.7	17.2	15.5	3.9		
C1	27.5	24.6	6.3	6.2	1.3		
F	.116	.110	.074	0.1	0.32		
Aklalinity	92.8	92.4	78.6	113	51.8		
Dissolved Solids	194	198	118	150	52		
pH	7.9	8.1	8.0	8.0	7.8		

AVERAGE MAJOR IONS CONCENTRATIONS (MG/L) IN THE GREAT LAKES

Decore -

Weiler and Chawla 1969

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TABLE 10

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Kramer 1964

MEAN, MAXIMUM, MINIMUM CONCENTRATIONS OF MAJOR IONS IN LAKE SUPERIOR FOUND IN CCIW DATA

	0CT 68	NOV 69	APR 70	MAY 71	OCT 71
рН	7.75 7.50-7.90	· · · ·	7.84 7.45-8.01	8.02 7.68 -8.32	7.95 7.62-8.57
CONDUCTIVITY	95	108	97	99	97
	81-108	103-121	90-113	85-116	88-111
• <b>К</b> •	0.54 0.50-0.67	0.47 0:40-0.61	0.42 0.39-0.60	0.53 0.50-0.60	0.49 0.40-0.50
Nà	1.32	1.23	1.27	1.20	1.20
	1.20-1.80	1.10-1.45	1.20-1.50	1.20-1.30	1.10-1.40
Ca	13.17	13.26	13.23	13.13	13.44
	12.8-13.8	12.4-14.0	12.5-16.0	12.0-14.8	10.8-18.4
Mg	2.72	<b>2.</b> 69	2.49	2.56	<b>2.65</b>
	2.60-2.90	<b>2.50-2.</b> 85	2.10-2.80	2.30-3.00	2.50-2.90
Cl	1.29	1.16	1.28	1.23	1.14
	1.00-1.90	1.10-1.40	1.00-1.70	0.90-2.30	1.00-1.40
so <sub>4</sub>	3.94	2.61	1.89	2.71	<b>2.79</b>
	1.90-6.7	1.90-2.90	1.50-2.50	2.00-3.80	2.00-7.40
Alkalinity	41.32	42.30	42.39	41.73	41.18
	40.6-42.6	41.5-46.0	39.5-49.0	37.0-45.5	34.1-48.3

					•	TABL	<u>E 12</u>					
	•			TRACE ME	TALS (PP	B) IN LA	(E SUPERI	OR 1970-19	71			
		April 1	<u>970</u>		Nov 1	970		May	1971		<u>Oct 1971</u>	
	X	M	R	X	м	R	X	M	R	<del>к</del> м	R	
CD	0.0	0	0-1	0.0	0	0-1	.45	0.4	0.0-3.3 .23	3 0.0	0.0-1.3	
CR	0.0	0	0	0.0	0	0	.35	0.0	0.0-6.2 0.3	0.2	0.0-1.5	•
CO	0.5	1	0-1	0.0	0	0	.28	0.0	0.0-2.2 .58	<b>0.5</b>	0.0-2.8	
CU	2.5	2	1-17	1.9	2	1-5	7.67	7.0	1.0-34.0 7.80	5 5.2	1.2-50.0	
FE	6.9	S. <b>5</b>	0-48	5.5	4	1-31	<b>4.86</b> • •	2.0	. 0.0-66.0 2.5	7. 1.1.1.2	0.2-38.0	n 1997 - Standard Barry, Standard Barry, Standard Barry, Standard Barry, Standard Barry, Standard Barry, Standard 1998 - Standard Barry, Standard Barry, Standard Barry, Standard Barry, Standard Barry, Standard Barry, Standard
РВ	1.8	1	0-8	2.1	2	1-7	1.53	1.0	0.0-8.0 1.20	5 1.2	0.0-3.2	
MN	0.5	0	0-12	.1	0	0-2	. 54	0.2	0.0-23.0 .47	7 0.4	0.1-6.7	
HG HG	0.0	0		Ó.O	0	Ö	.30	.21	.05-1.50 .34	3	.06-1.30	
MO	0.0	0	0	0.0	Ŏ	0	.19	.21	0.0-0.6 .24	0.2	0.0-1.0	
Ni	0.3	0	0-2	0.0	0	0	1.4	1.0	0.0-10.0 .92	2 0.8	0.0-3.0	
V	0.0	0	0	0.0	0	.0	.02	0.0	0.0-0.3 0.03	0.0	0.0-0.7	•
ZN	4.8	4	2-16	-	-	-	15.96	13.0	1.0-71.0 9.57	8.0	0.0-42.0	
· ·	<del>x</del> -	mea	n									

M - median

R – range

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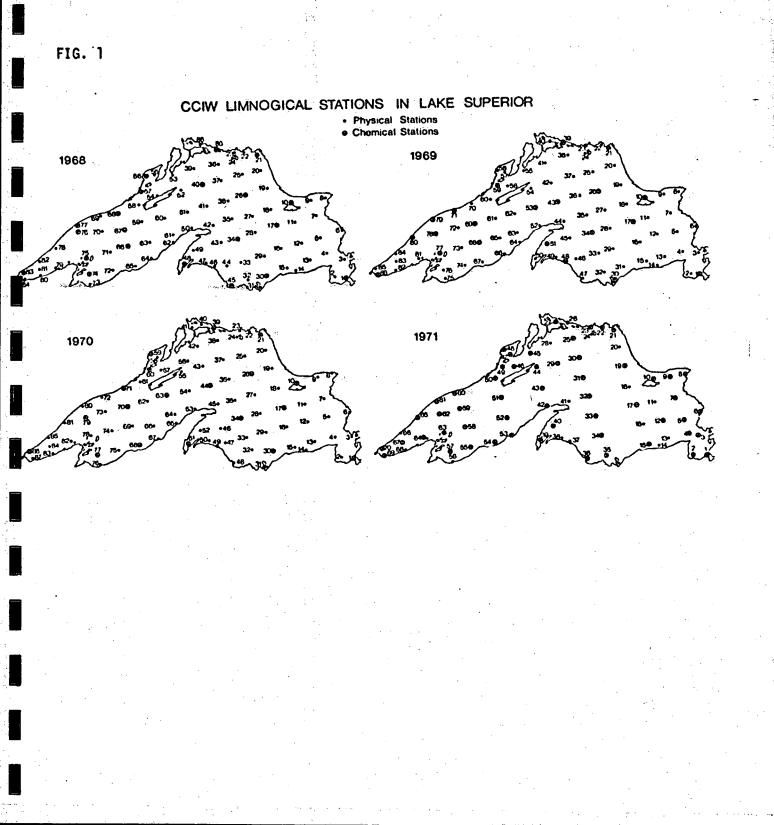
## TRACE METALS IN THE GREAT LAKES

(WEILER AND CHAWLA, 1969)

	SUPERIOR		H	HURON		ERIE		ONTARIO		
. *	MEAN	RANGE	MEAN	RANGE	MEAN	RANGE	MEAN	RANGE		
CD			· ·	λ. τη της τους τους τους τους τους τους τους του	* 2		•	•		
CR	1,	0-18	1.6,	0-19	1.6,	07-14	0.7,	0-12		
CO	1997 <u>-</u> 1997					· .				
CU	12,	4-230	3,	2-13	7,	4-58	60,	5-175		
FE	8	3-230	22,	3-400	48,	3-460	8,	4-500		
PB	2.2,	1-7	2.7	2-7	2.8,	1-12	3.3,	2-7		
MN	< 1,	0-1	< 1,	0-100	্ব,	0-20	< ],	0-44		
KG			•					• • •		
Mo		· ·		•		•.				
Ni	2,	0-9	4,	2-15	3,	2-30	5.6,	2-16		
¥.	· · · ·					•				
ZN	27	9-80	33,	10-110	11,	0-290	71,	18-115		
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	MEAN	MEDIAN	MEAN	MEAN
рН	6.12	6.30	6.56	6.50
Total phosphorus	61.0	52.0	90.3	85.5
Nitrate	447	438	619	467
Ammonia	329	275	872	309
Silicate	1540	1220	332	1700
Sodium	593	67.5	3178	1675
Potassium	193	130	648	435
Magnesium	300	250	550	250
Calcium	1983	1150	2466	2000
Chloride	633	400	1100	650
Sulphate	5385	3500	7433	4450
Lead	11.5	7.0	12.0	6.0
Copper	9.0	6.0	5.8	5.0
Iron	26.8	22.0	65.5	26.5
Zinc	47.3	53.0	41.2	40.0
Cadmium	1.8	2.0	1.8	2.0
Nickel	1.5	1.5	1.0	1.0

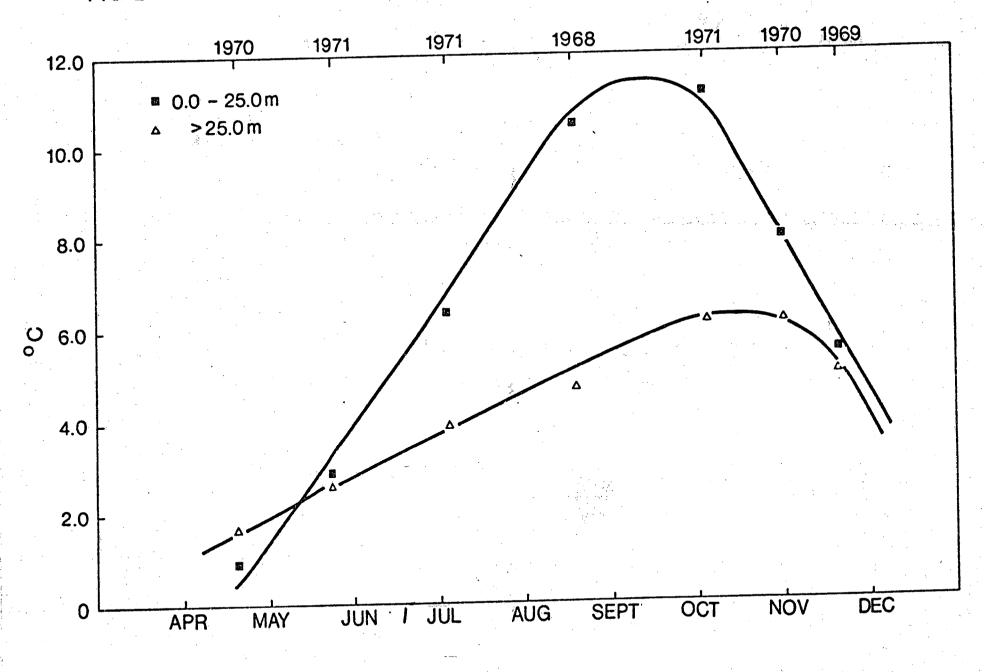
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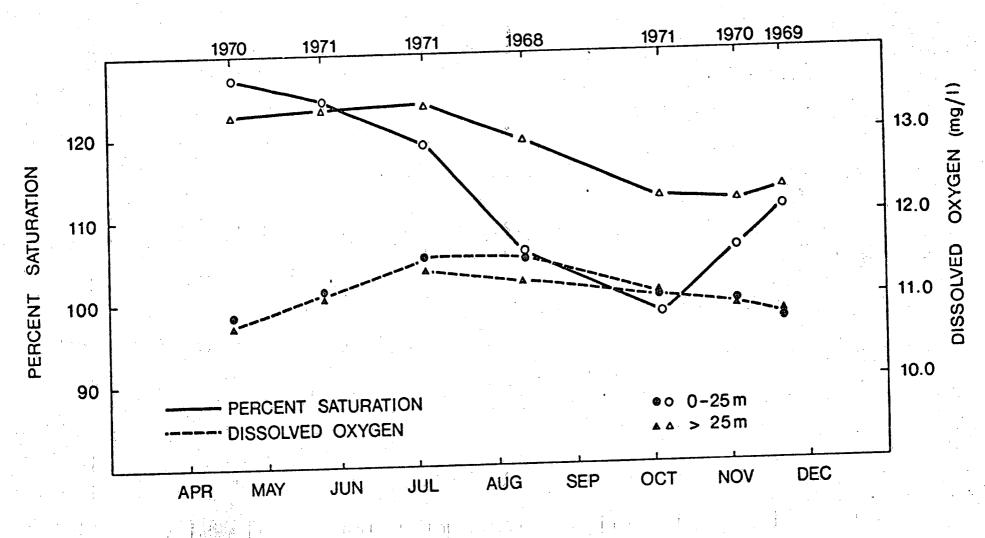
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FIG.2 LAKE SUPERIOR MEAN WATER TEMPERATURE



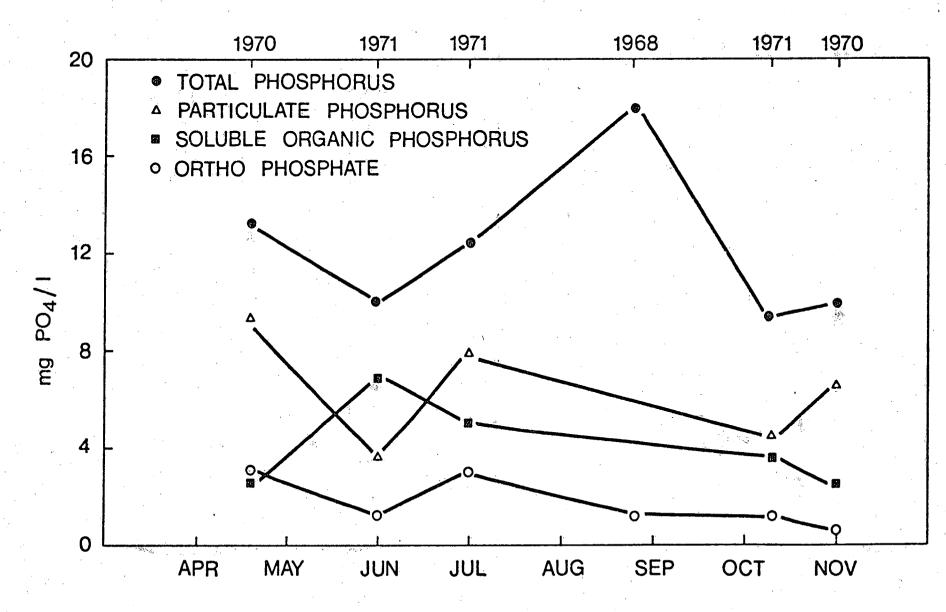
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FIG.3 DISSOLVED OXYGEN (mg/I) AND OXYGEN PERCENT SATURATION IN LAKE SUPERIOR



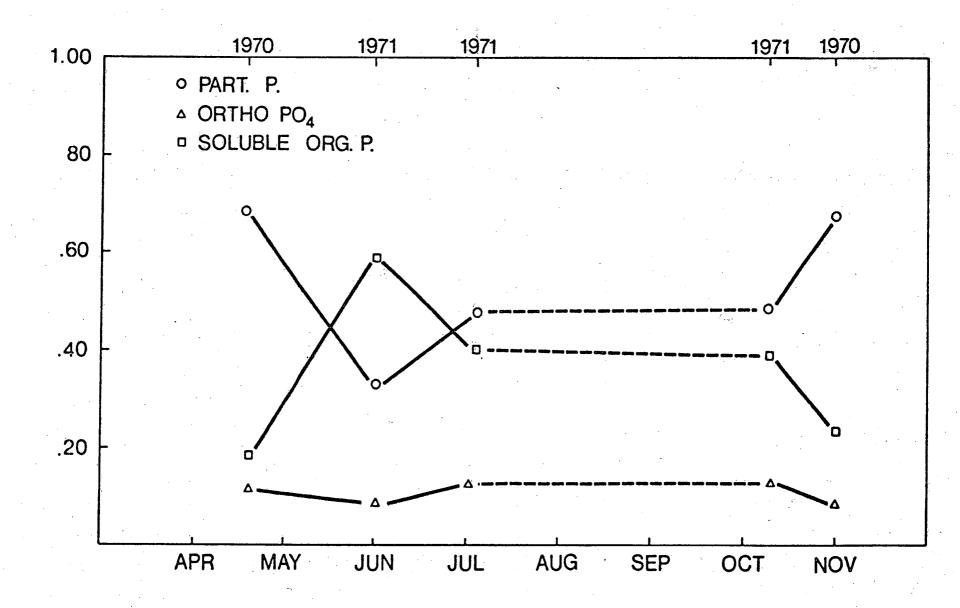
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# FIG.4 PHOSPHORUS (mg $PO_4/I$ ) IN LAKE SUPERIOR



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FIG.5 PHOSPHORUS FRACTIONS IN LAKE SUPERIOR



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# FIG.6 REACTIVE SILICATE (mg/1) IN LAKE SUPERIOR

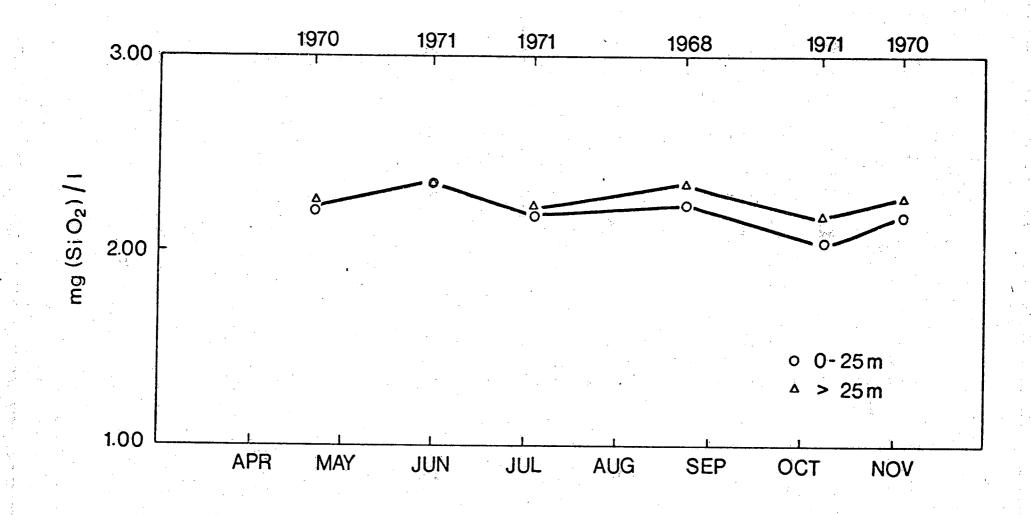
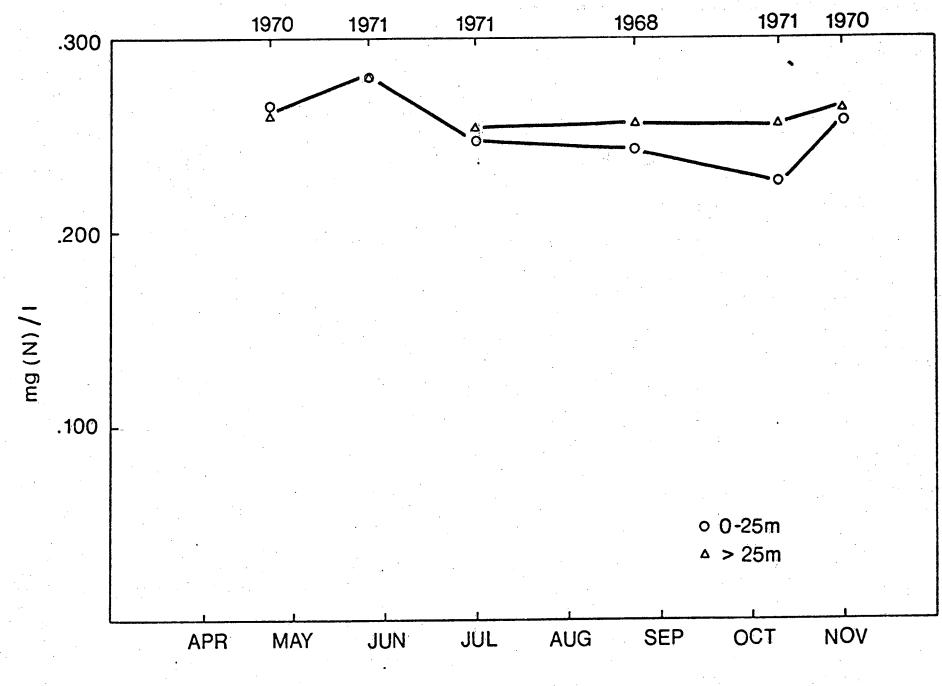


FIG.7 NITRATE + NITRITE (mg/I) IN LAKE SUPERIOR



# FIG.8 pH (-log(H+)) IN LAKE SUPERIOR

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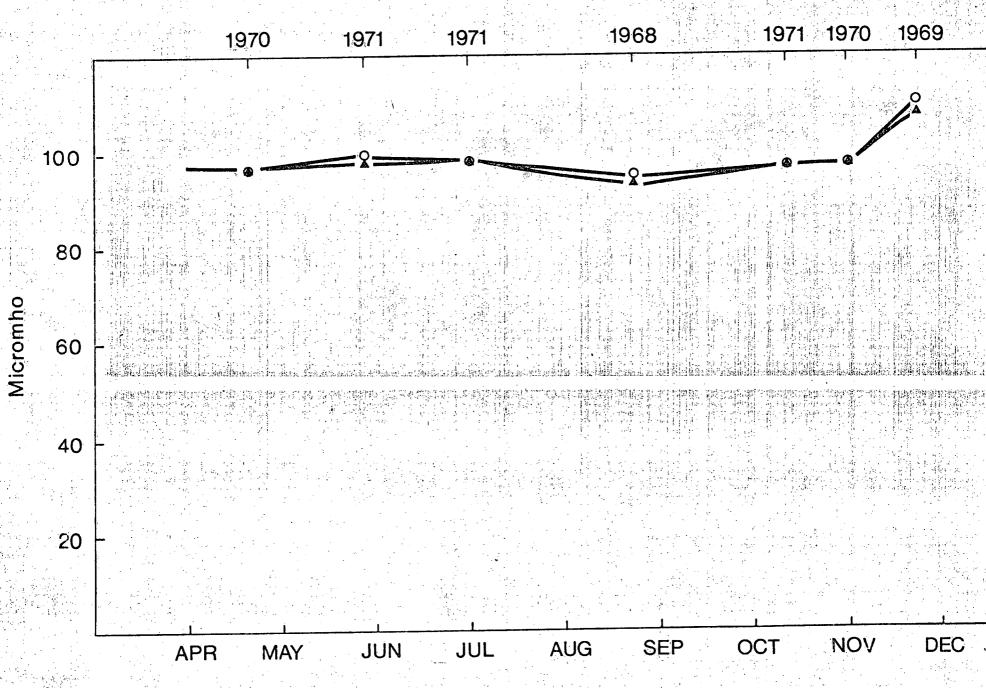
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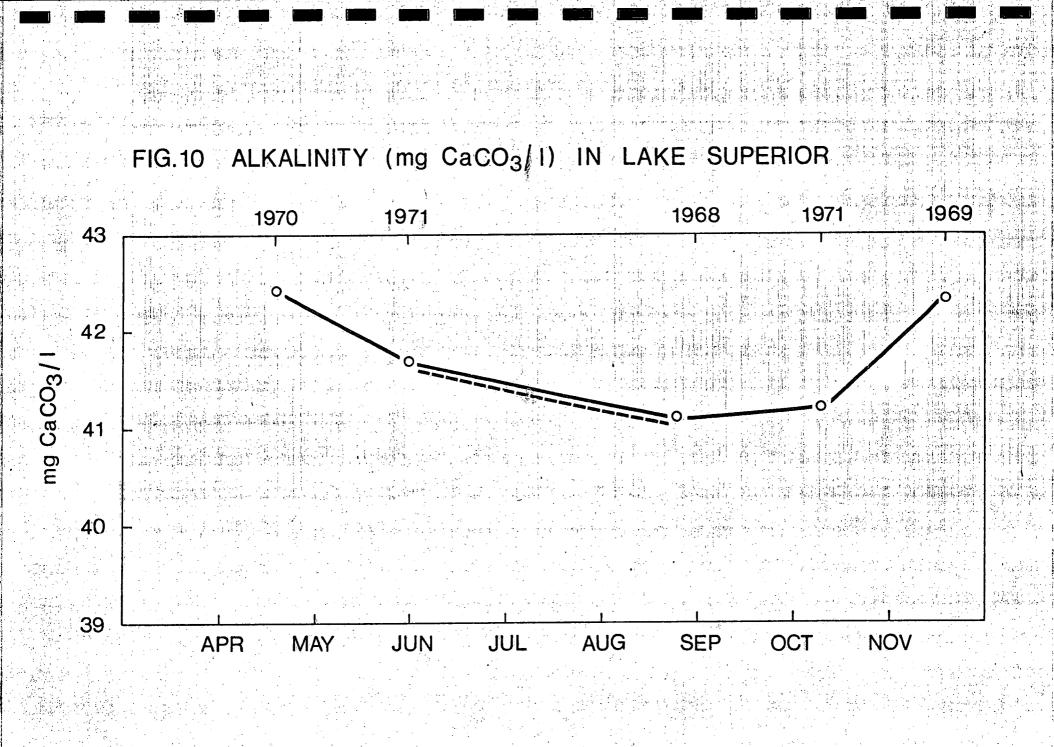
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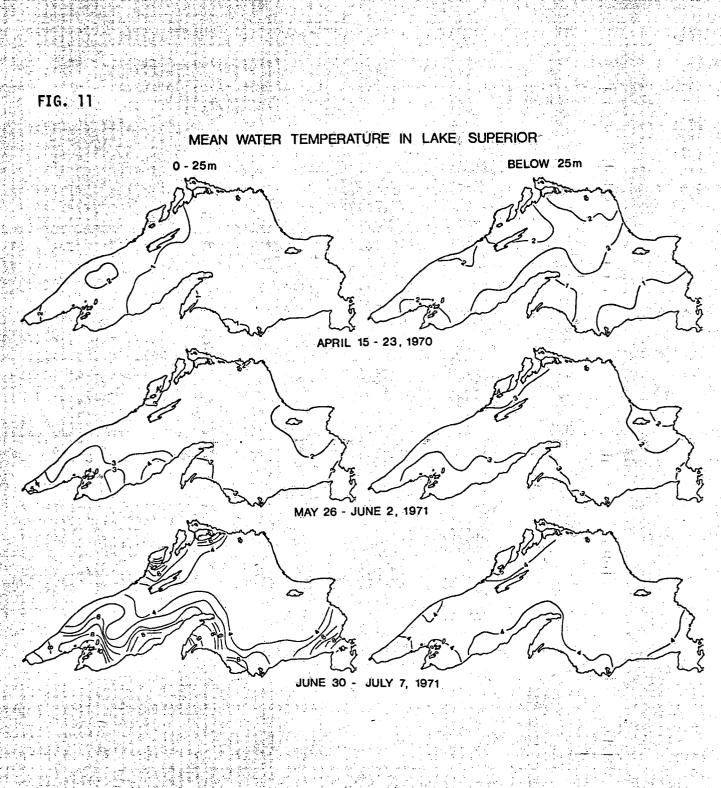
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FIG.9

CONDUCTIVITY IN LAKE SUPERIOR

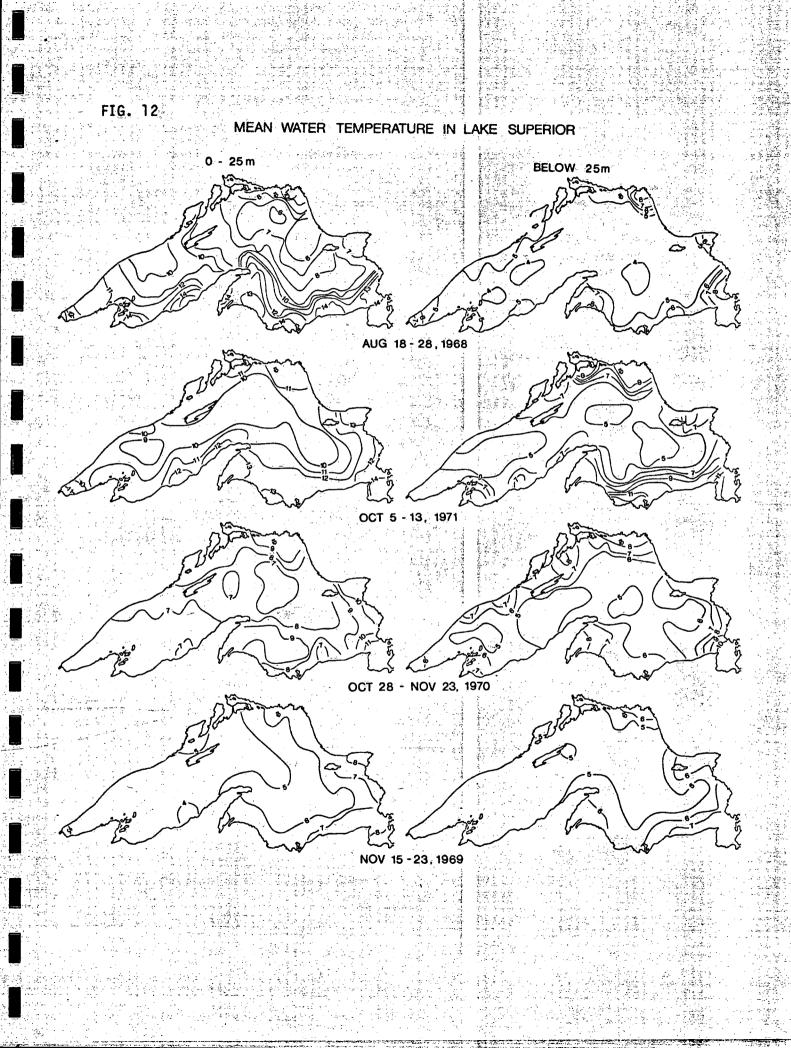




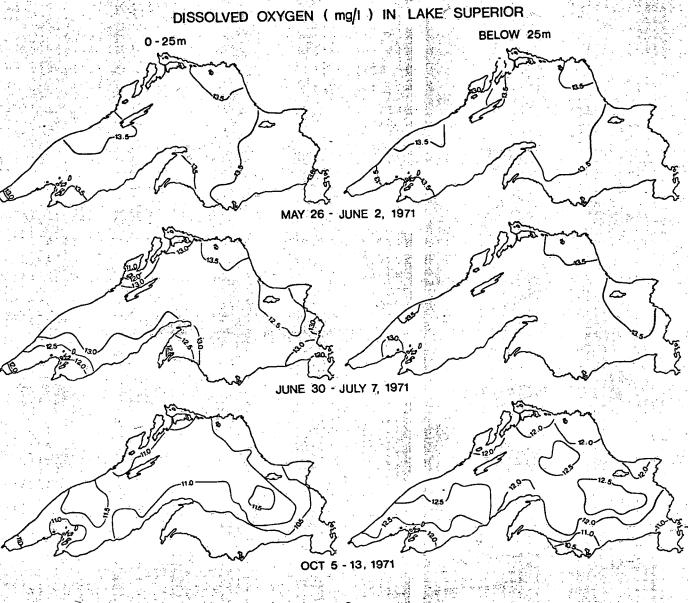


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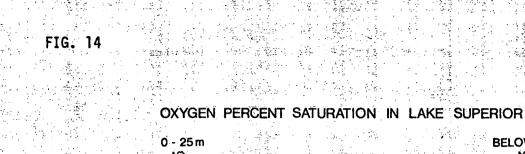
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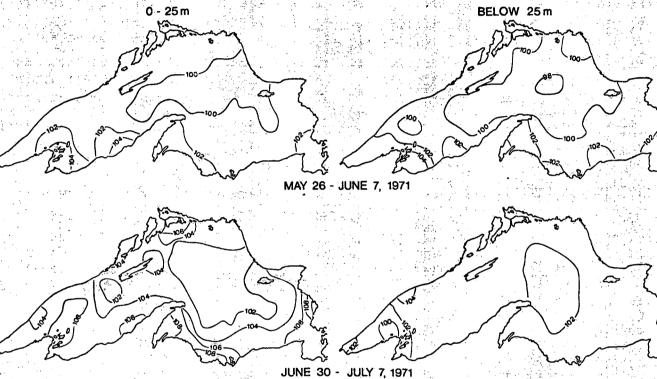






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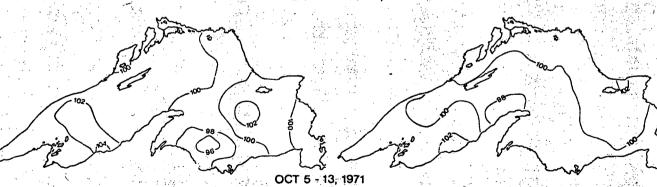
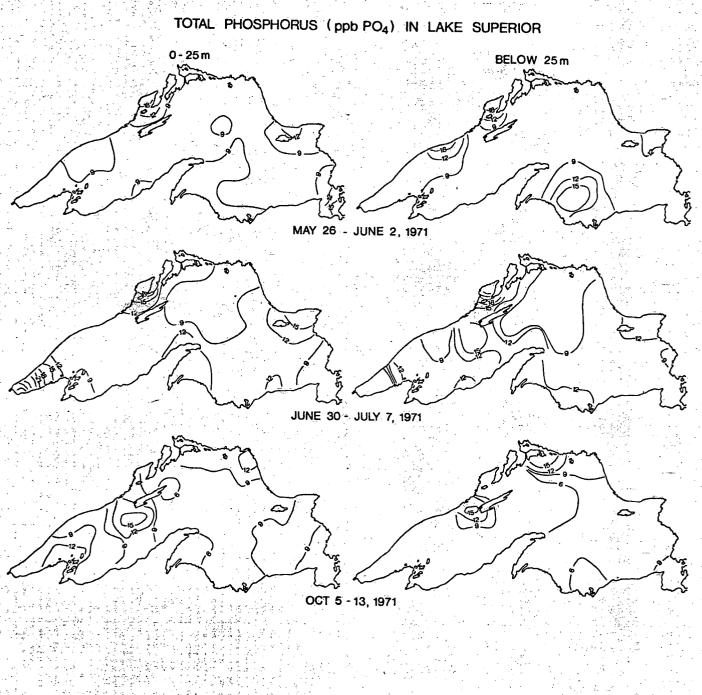
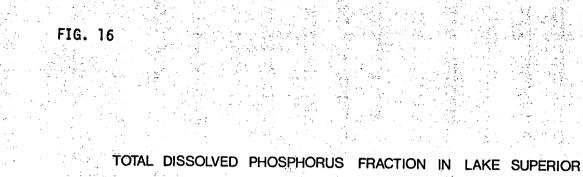


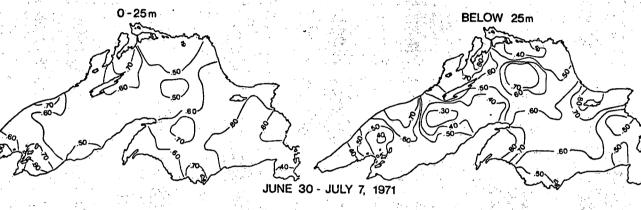
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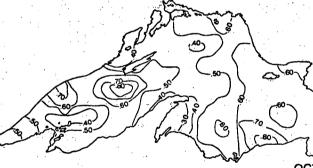


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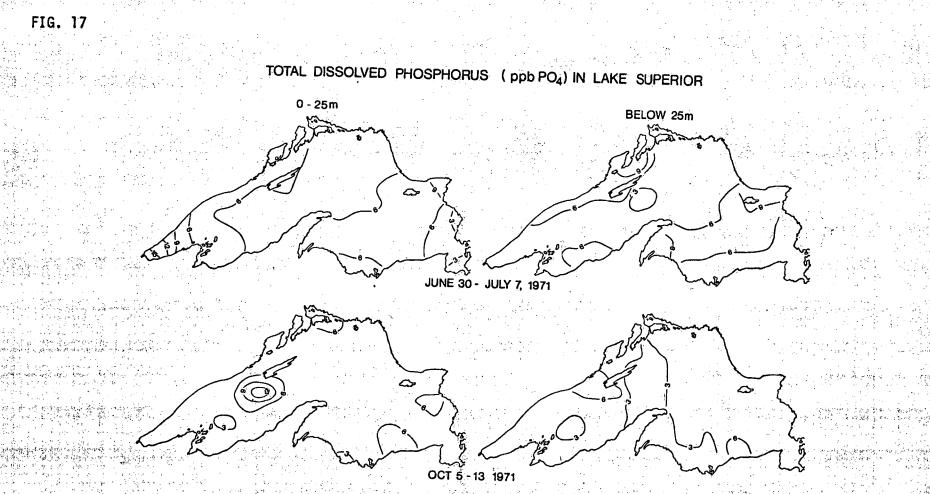
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# FIG. 18

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ORTHOPHOSPHATE ( ppb PO4) IN LAKE SUPERIOR

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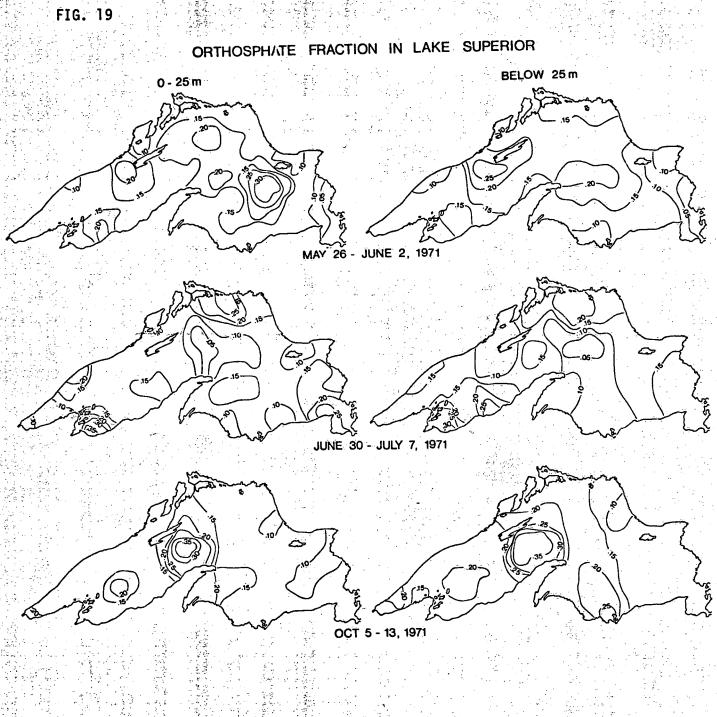
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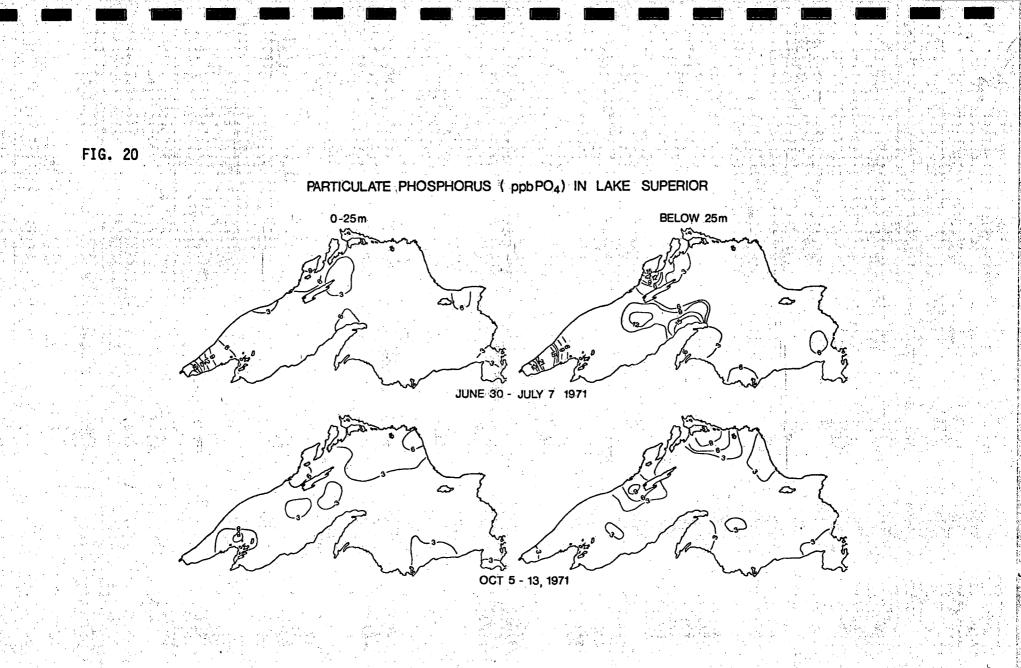
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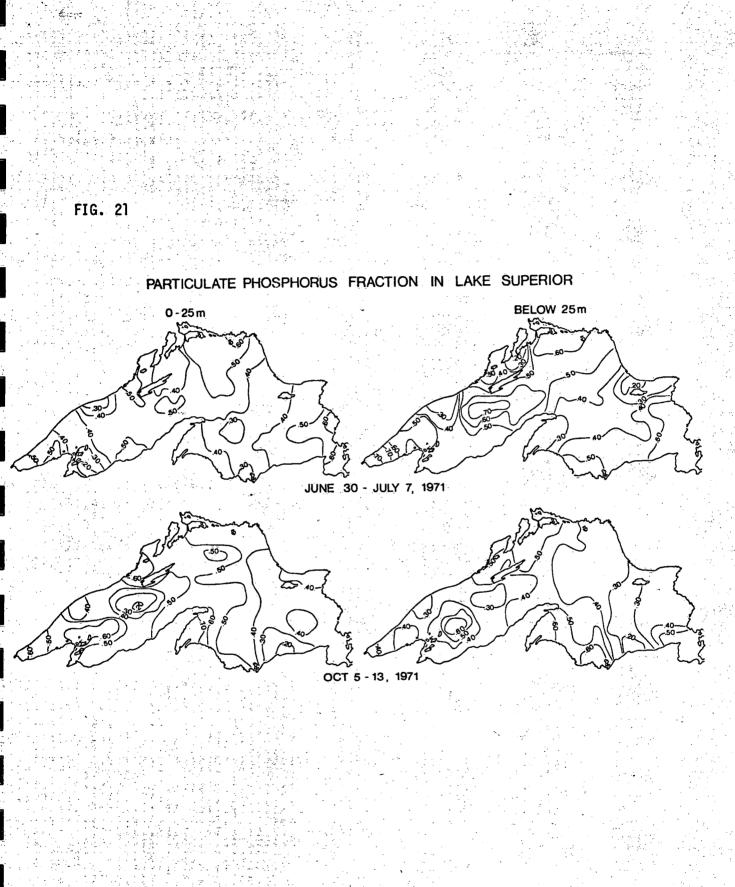
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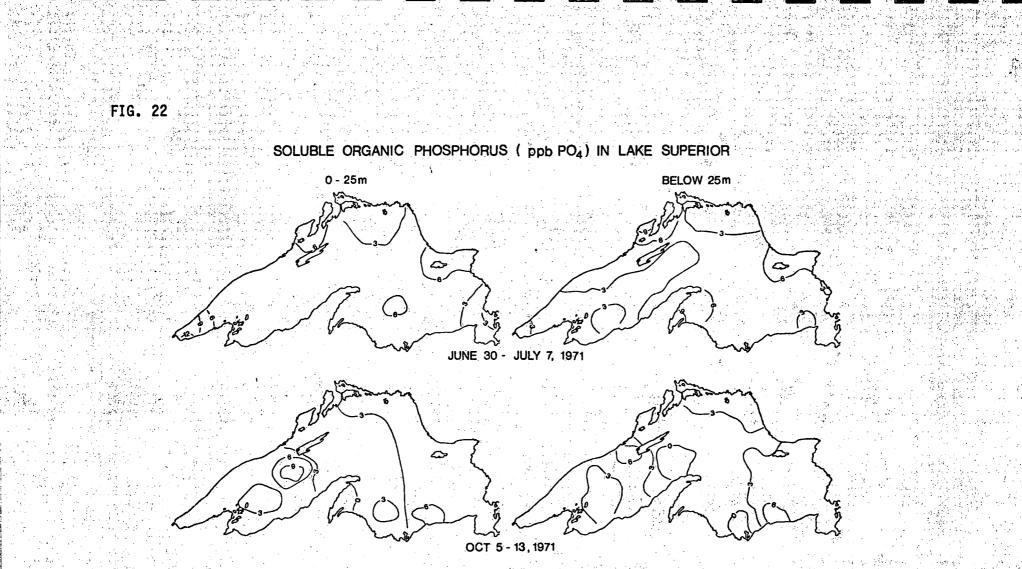
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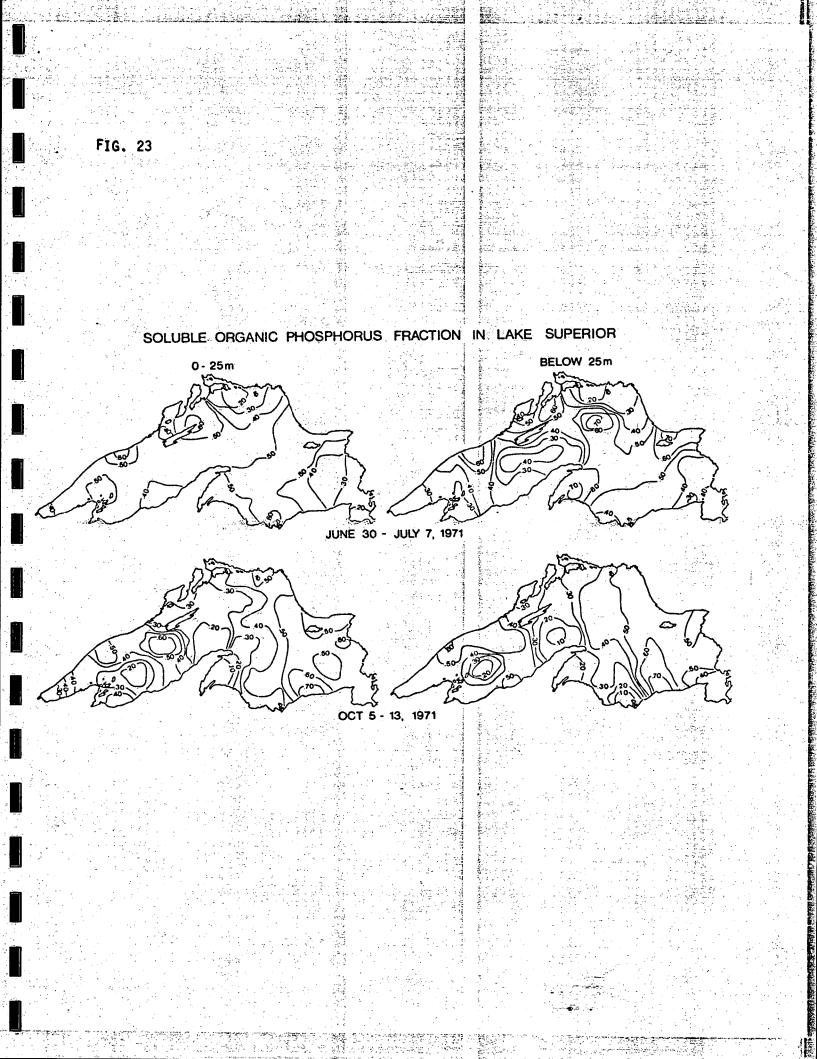


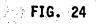
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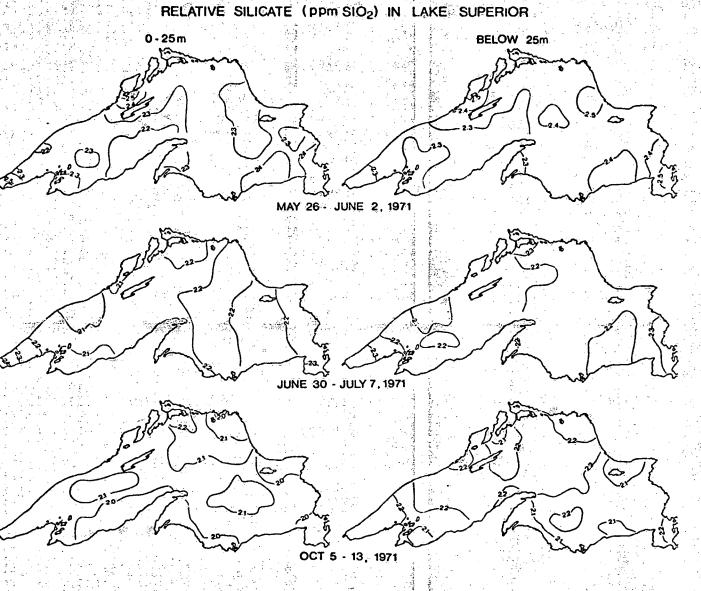
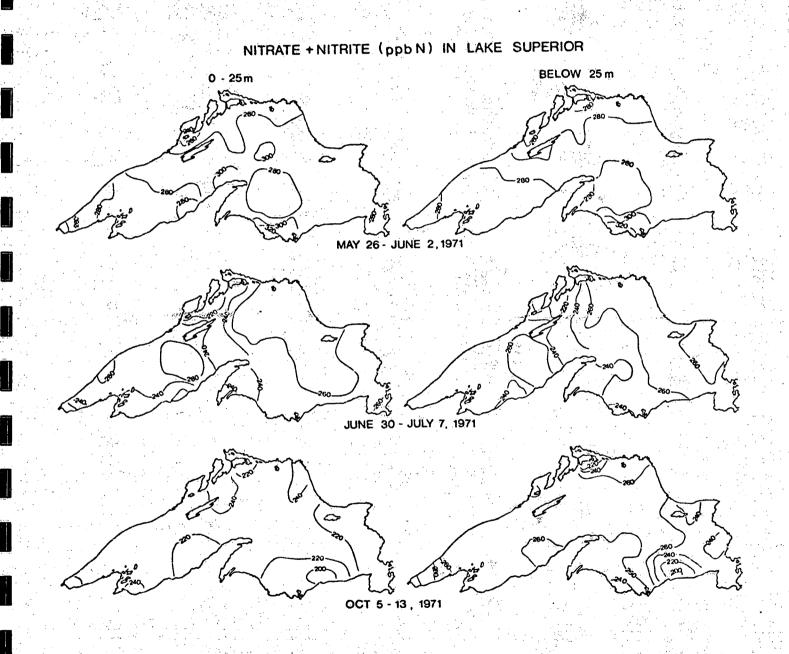


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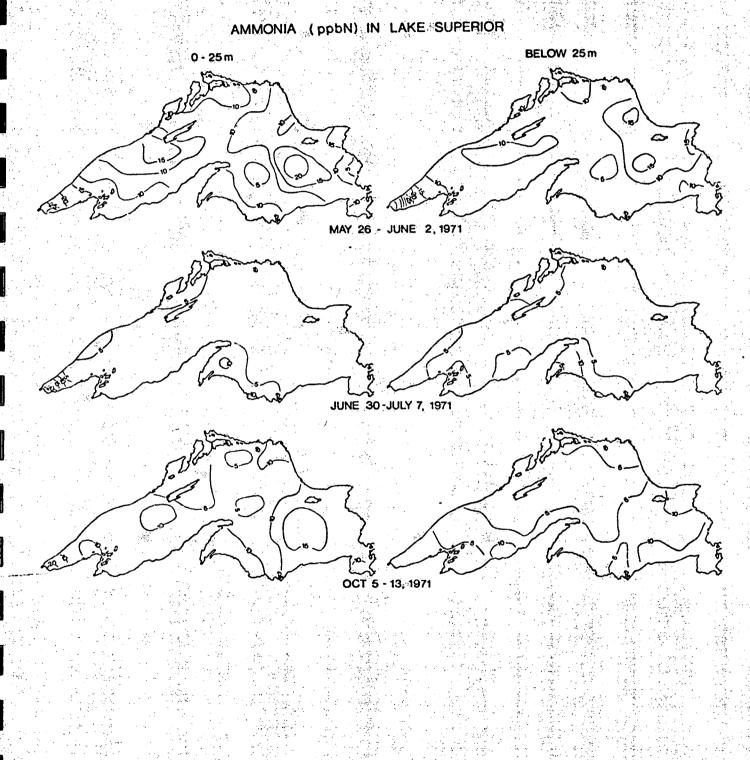


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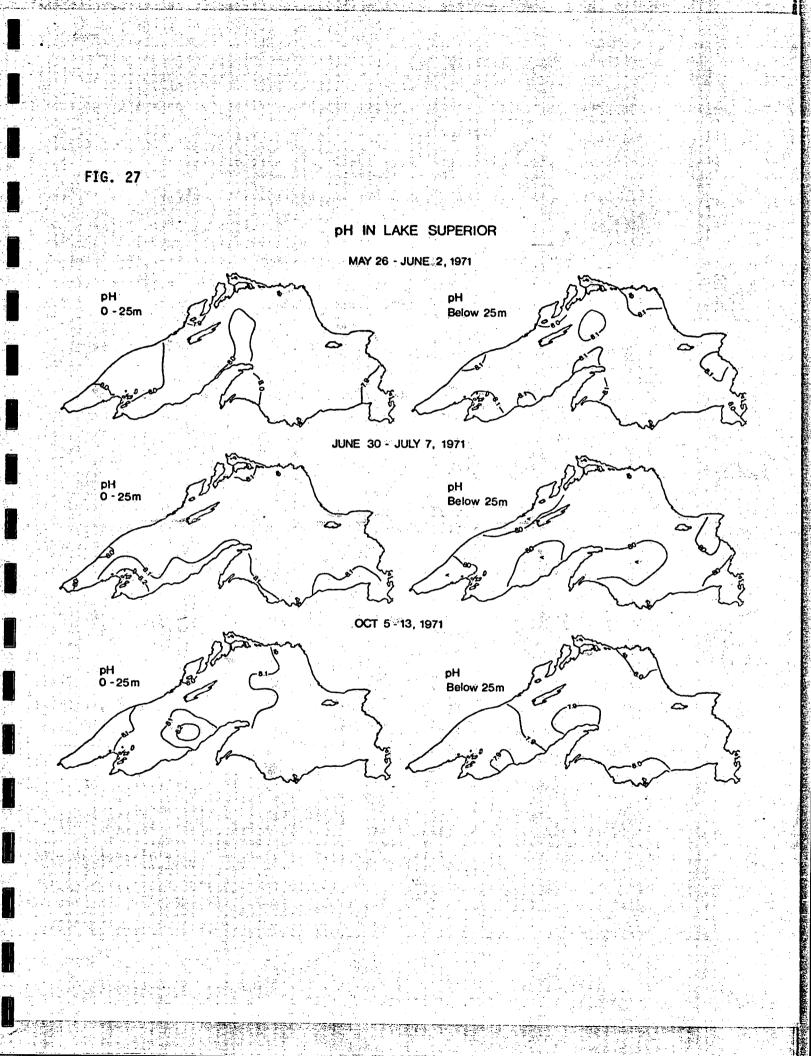
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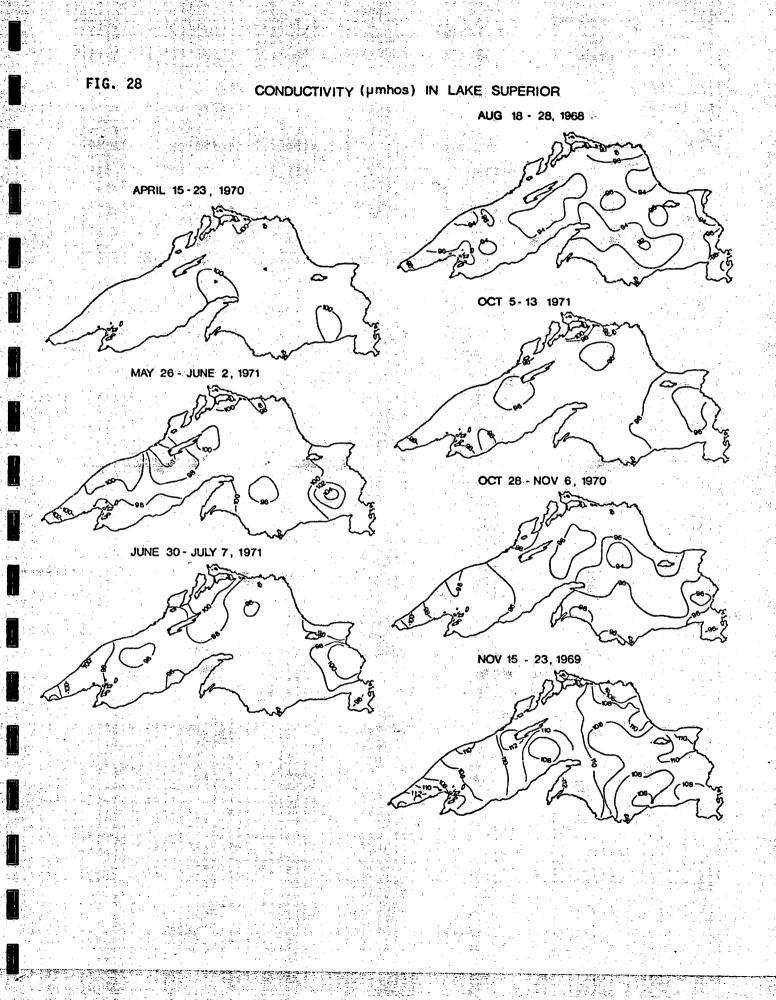


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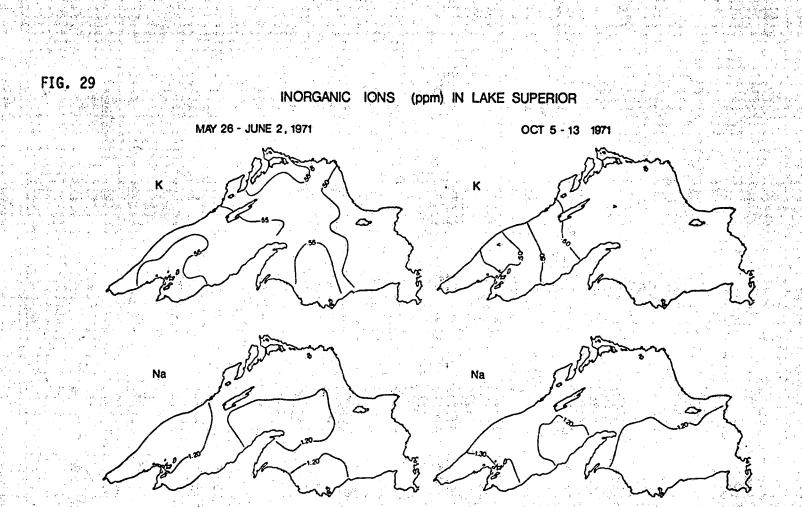
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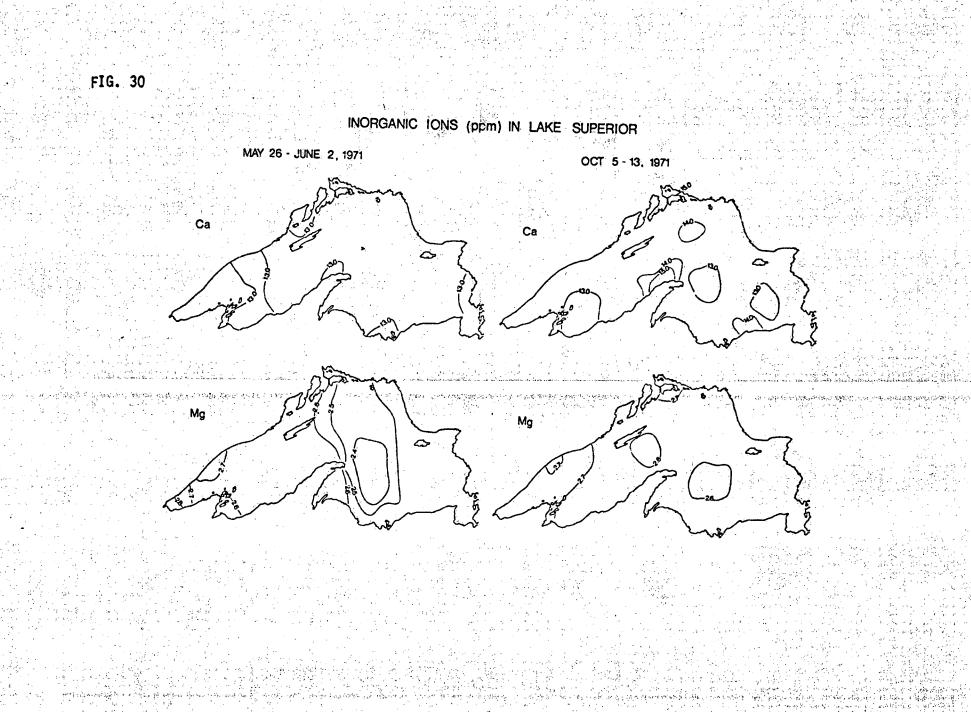
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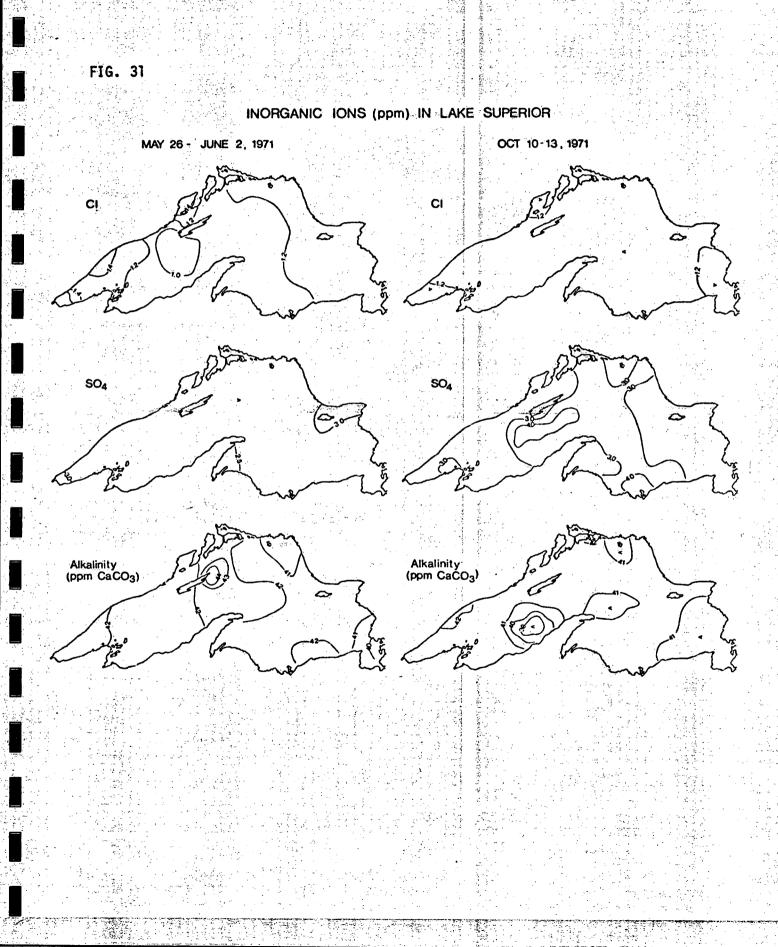
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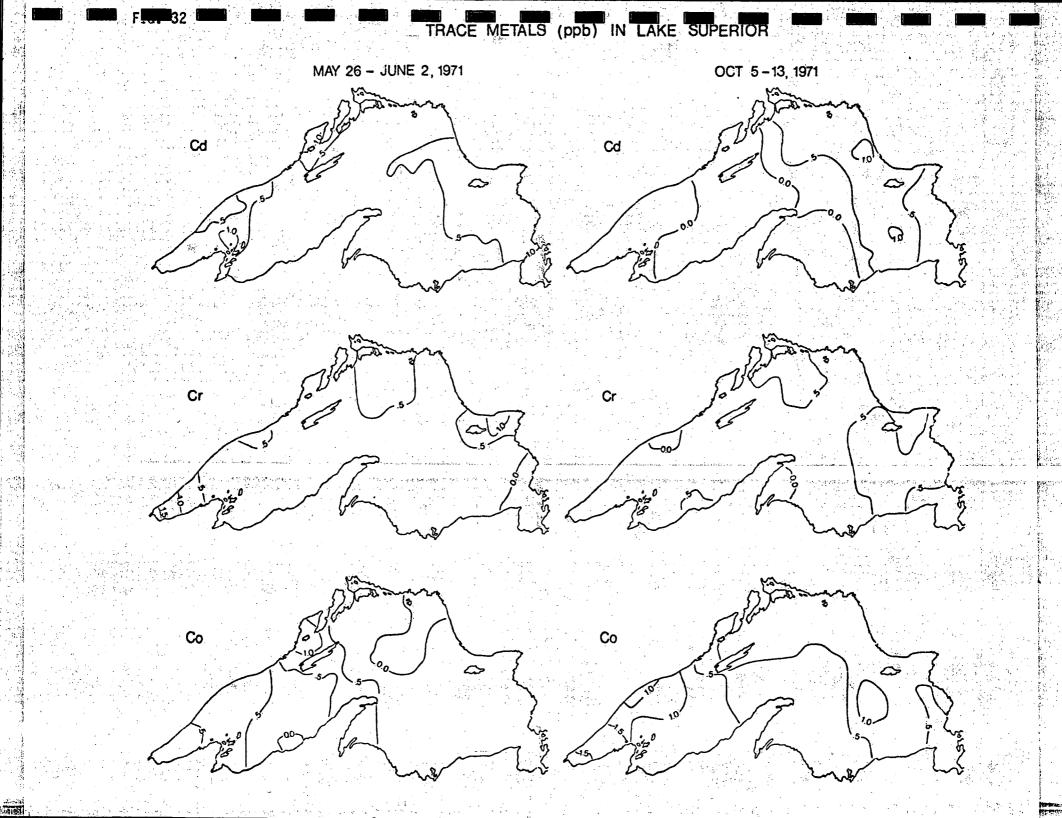
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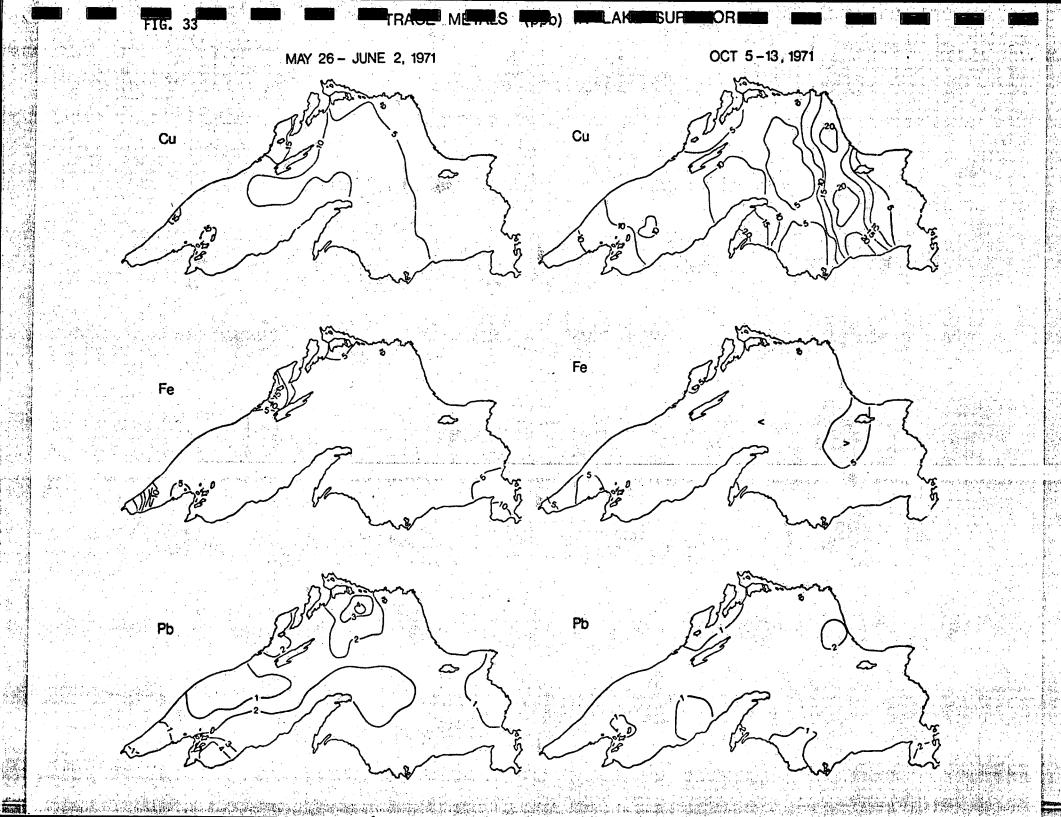
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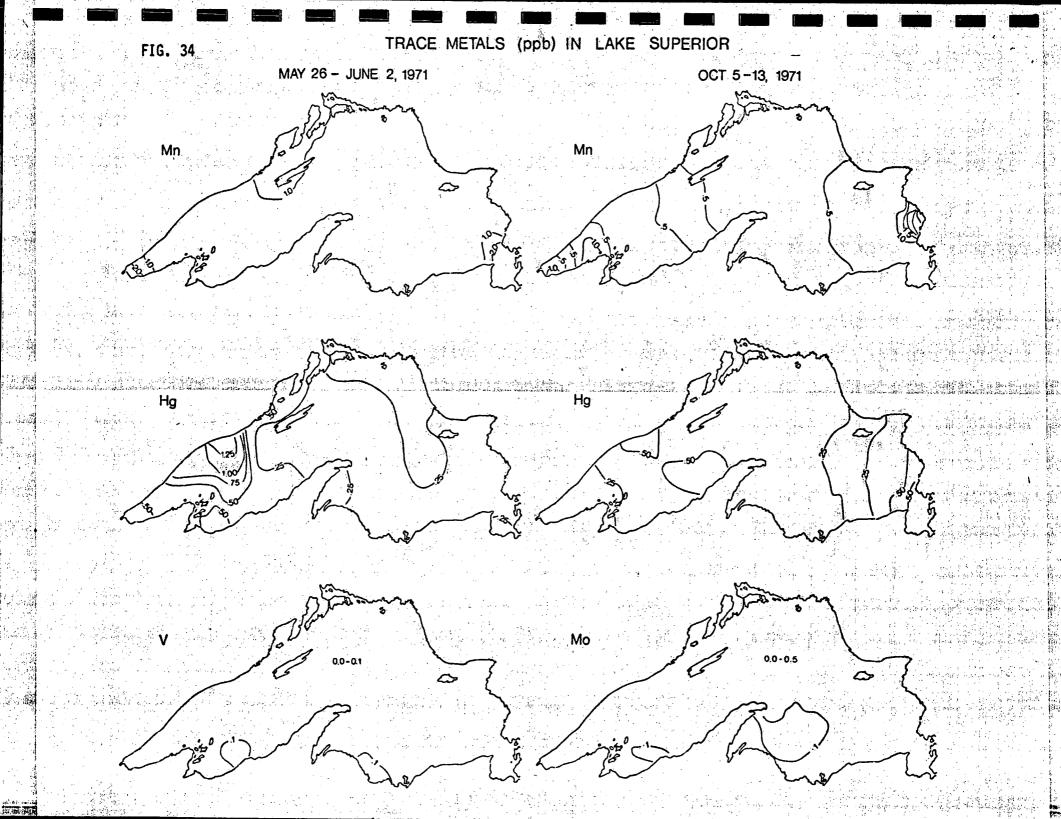


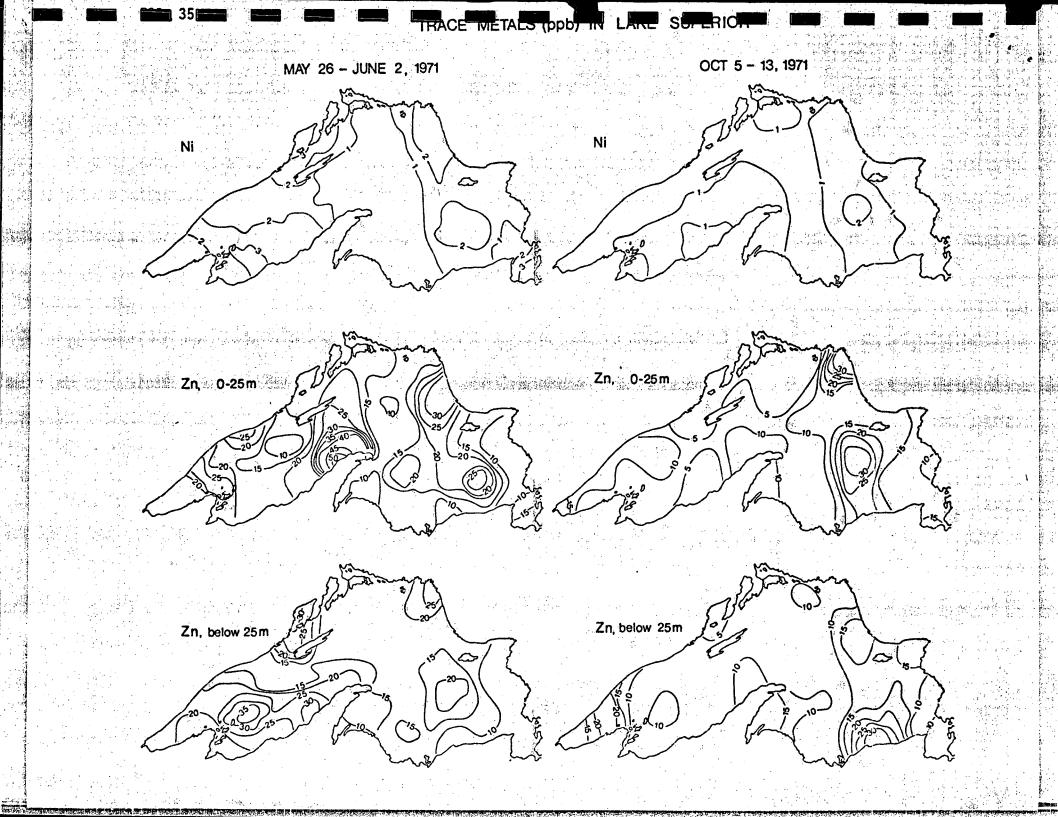
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