

CITY OF THORNTON, COLORADO
CITY OF WESTMINSTER, COLORADO

STANDLEY LAKE WATER QUALITY PROGRAM
TECHNICAL MEMORANDUM NO. 2

EVALUATION OF IMPACT OF METALS
ON STANDLEY LAKE

U.S. ENVIRONMENTAL
PROTECTION AGENCY
91 NSV 21 PH12 51

October 1984

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ADMIN RECORD

A-DU03-000520

**STANDLEY LAKE WATER QUALITY PROGRAM
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ON STANDLEY LAKE**

SCOPE

The objective of this technical memorandum is to describe the impacts of metals on drinking water quality in Standley Lake. Concerns include those for specific adverse health impacts and nuisance problems.

The main body of the text presents the data from the study and develops a conceptual framework for evaluating existing and future observations of metal trends in Standley Lake. Recommendations and a summary of observations are presented in the Conclusions at the end of the text. A glossary of less commonly used technical terms is provided as an appendix.

INTRODUCTION

Metals in drinking water quality are presented regulated by the USEPA under two classifications in accordance with the types of concerns: primary drinking water standards that are for metals of concern from a specific health standpoint and secondary drinking water standards for metals of concern because of aesthetic impacts. This study assesses the potential for health impacts in Standley Lake through monitoring of the eight metals included in the primary drinking water standards: arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. Four metals are included in the secondary drinking water standards: iron, manganese, copper, and zinc. Of these, iron and manganese are commonly involved in nuisance problems (staining, color, and turbidity) in water supplies. As a consequence, a substantial data base has already been developed for iron and manganese levels in Standley Lake, and these two metals were also assessed in the study.

CHEMISTRY OF METALS IN AQUATIC SYSTEMS

General

Metals are chemically defined as a broad class of elements which act as electron pair acceptors in chemical reactions. To a large extent, the fate of metals is determined by properties which are specific to each metal. Principle aqueous species of the eight metals included in the primary drinking water standards are listed in Table 1. Of these, barium is an alkaline earth metal and does not exhibit a pattern similar to the other metals. It is generally present as a simple divalent cation (+II oxidation) which does not form an array of hydroxide or oxide species over the pH range normally encountered in water. It can react with carbonates and sulfates to form precipitates.

Arsenic and selenium fall in a borderline category of elements which have properties between metallic and non-metallic elements, and generally are found as oxyanions in aquatic systems. Arsenic is found in two oxidation states: the arsenate form (As V) and the arsenite form (As III). The arsenate form tends to predominate in oxygenated water and the arsenite form tends to occur under mild reducing conditions (Faust and Aly, 1981). In the arsenate form, AsO_4^{3-} , it behaves in a manner somewhat similar to phosphate. It is the more reactive oxidation state and is more likely to be adsorbed to sediment materials. In the arsenite form, AsO_3^{3-} , undissociated H_3AsO_3 predominates at normal pH levels. This tends to be less reactive than the arsenate form and is less readily adsorbed on the sediments. Nonetheless, arsenite has been reported to adsorb onto amorphous iron and aluminum hydroxides (Pierce and Moore, February 1980). Therefore, a degree of arsenic incorporation within sediments is possible regardless of oxidation state.

Although it can occur in the elemental form, selenium is commonly found in the selenite form (Se IV) or the selenate form (Se VI). Both forms are present in solution as the oxyanions that may adsorb to metal oxide surfaces. These oxyanions, SeO_3^{-2} and SeO_4^{-2} , correspond to selenite and selenate respectively. The selenite form tends to predominate under the moderately oxidizing conditions found in waters that contain oxygen, and the selenate form tends to be favored by more alkaline or more oxidizing conditions (Faust and Aly, 1981).

TABLE 1
SPECIATION OF METALS REGULATED AS
PRIMARY DRINKING WATER STANDARDS
 (adapted from O'Connor, 1974)

<u>Metal</u>	<u>Principal Aqueous Forms</u>
Arsenic	AsO_3^{-3} (As III), arsenite AsO_4^{-3} (As V), arsenate
Barium	Ba^{+2} (Ba II)
Cadmium	Cd^{+2} (Cd II)
Chromium	Cr^{+3} (Cr III) CrO_4^{-2} (CrVI), chromate $\text{Cr}_2\text{O}_7^{-2}$ (Cr VI), dichromate
Lead	Pb^{+2} (Pb II)
Mercury	Hg^{+2} (Hg II), mercuric Hg_2^{+2} (Hg I), mercurous CH_3Hg^+ , (HgII) methyl mercury $(\text{CH}_3)_2\text{Hg}$, (HgII) dimethyl mercury Hg (0), elemental mercury
Selenium	SeO_3^{-2} (Se IV), selenite SeO_4^{-2} (Se VI), selenate
Silver	Ag^+ (Ag I)

Two transition metals, cadmium and silver, and a non-transition metal, lead, are typically found in only one oxidation state. Lead and cadmium generally occur as divalent cations (+II oxidation state) and silver as a monovalent cation (+I oxidation state). These metal species can react with a variety of organic and inorganic ligands to form soluble complexes. In addition, they can precipitate as hydroxides, oxides, or carbonates over a wide range of conditions and can precipitate as sulfides under reducing conditions.

Mercury is a transition metal that can exist in a variety of oxidation states. Depending on the oxidizing conditions, mercury can occur in the mercuric form (+II oxidation state), the mercurous form (+I oxidation state), or in the elemental form. The solubility of mercury is generally governed by precipitation of the mercuric form or reduction to the elemental state. The mercuric form can precipitate as hydroxides or oxides under alkaline conditions and can precipitate as a sulfide under reducing conditions (Faust and Aly, 1981). In addition, biological methylation processes can result in the formation of methyl and dimethyl mercury. Although these forms can be absorbed by aquatic organisms and accumulate through the food chain to levels of concern, they are typically not stable in the water column and represent only a small fraction of the mercury compounds found in water (NAS, 1977). Although not as widely studied, it should be noted that bacterial methylation reactions can also occur for other metals, including arsenic, lead, and selenium (Forstner and Wittmann, 1983).

Chromium is a transition metal that can be found in the +III and +VI oxidation states in natural waters. Under reducing conditions, the +III oxidation state can be formed and precipitates as a hydroxide. Under more oxidized conditions, chromium can occur in the +VI oxidation state as either chromate (CrO_4^{-2}) or dichromate ($\text{Cr}_2\text{O}_7^{-2}$) and behaves as an anion. As such, chromate tends to behave as a ligand that exhibits adsorption behavior similar to other tetraoxo anions such as phosphate, and is capable of adsorption onto metal oxide surfaces (Mayer and Schick, 1981). Evaluations of trace metal contents of iron and manganese oxide coatings in stream sediments have demonstrated that chromium can be associated with these surfaces (Forstner and Wittmann, 1983).

Chemical Mechanisms that Influence the Fate of Metals in Lakes and Reservoirs

Cycling of metals within a reservoir can be significantly affected by a variety of chemical reactions. Chemical conditions determine whether metals will be removed from solution by formation of precipitates or adsorption to particulate matter, or be mobilized into the water column by solubilization reactions. A number of mechanisms are involved in these general chemical phenomena.

- 1 Adsorption to Iron/Manganese Oxide Surfaces within the Sediments - Iron and manganese oxides form coatings on clay particles that are highly reactive with respect to metals. These coatings can play an important role in determining the metal fluxes within an aquatic system. Under oxic conditions, iron and manganese exist in the more oxidized Fe (III) and Mn (IV) oxidation states. These oxidation states are relatively insoluble and form precipitates which coat clay particles. Under these conditions, it is possible for metals to be adsorbed by these surfaces. In many aquatic systems, a subsequent change to anoxic conditions as a result of depletion of dissolved oxygen concentrations within a hypolimnion layer can occur as biological productivity increases within a lake. This condition results in reduction of the iron and manganese species to the less soluble Fe (II) and Mn (II) oxidation states, resulting in a dissolution of the coatings. Under such conditions, it is possible to release the adsorbed metals to the overlying water column (Forstner and Wittmann, 1983)
- 2 Association with Organic Material within the Sediments - Organic material can play a significant role in binding of metals to sediment materials through sorption processes. In general, it is the less soluble humic materials that are associated with sediments. Degradation of humic materials results in the formation of progressively lower molecular weight fulvic acids which are highly soluble. This degradation may have the effect of increasing mobilization of metals from the sediment as a result of reactions which can subsequently occur between this soluble fulvic fraction and metals (Forstner and Wittmann, 1983)

Another mechanism whereby metals can become associated with organic material in the sediments is through incorporation into biological materials

which subsequently deposit in the sediment (Forstner and Wittmann, 1983) In the case of these materials, it is possible that the release of metals may be encouraged by oxidizing conditions. As an example, Lu and Chen (1977) investigated a sediment that was polluted by wastewater discharges into Los Angeles Harbor They concluded that metals release under aerobic conditions was partially attributed to oxidation of the organic material

3. Precipitation or Co-Precipitation with Carbonates - Most metal cations react with carbonate to form a precipitate under proper conditions Even where conditions do not favor formation of a specific metal carbonate precipitate, co-precipitation with calcium carbonate has been demonstrated (Forstner and Wittmann, 1983) Dissolution and mobilization of these metals is favored by conditions of decreasing pH

4. Precipitation and Co-Precipitation with Metal Sulfides - Under sufficiently anoxic conditions, sulfide is the predominant sulfur species When present, sulfide precipitates and co-precipitates can have a significant impact on the incorporation of metals into the sediments Sulfide precipitates tend to be stable over a relatively wide range of pH, with some tendency for release as pH is diminished Release of metals to the water column can be effected by the onset of oxic conditions which result in the oxidation of sulfides and a subsequent dissolution of the precipitate (Lu and Chen, 1977)

5. Other Mechanisms - Other mechanisms include the formation of precipitates and co-precipitates with anions other than carbonate and sulfide These include the formation of oxides, hydroxides, silicates, and phosphates Ion exchange or adsorption directly onto clay particles represents another possible means for incorporation of metals into the sediments However, this is not thought to be a significant mechanism relative to adsorption on organic or iron/manganese oxide surface coatings. The primary function of the clay materials relative to adsorption of metals is thought to be as a substrate for surface coatings which tend to be more active in immobilizing metals (Forstner and Wittmann, 1983)

Release of Metals from Sediments

Release of metals from sediments into the water column can represent an important component of the overall input of metals within a lake. These releases involve two separate arrays of processes: (1) release of metals to sediment pore water, and, (2) transport from pore water to the water column.

1 Mechanisms for Release of Metals to Sediment Pore Water

Conditions which result in the release of a metal into sediment pore water depend on the mechanism whereby it is associated with the sediment. For example, in the case of metal sulfides, a change from anoxic to oxic conditions results in the release of metals through the oxidation of sulfides. On the other hand, metals associated with iron/manganese oxide coatings will be released into solution through a change from oxic to anoxic conditions as a result of formation of more soluble, reduced forms of iron and manganese. In general, mobilization of metals from sediments into pore waters have been associated with the following factors (Forstner and Wittmann, 1983)

- a. Changes in Redox Conditions - These can occur as a result of increased biological productivity in a lake, a condition which results in shifts to less oxic conditions in the hypolimnion layer of lakes. The subsequent reduction of iron and manganese oxides and hydroxides can result in the release of associated metals into the pore water.
- b. Decrease in Hypolimnetic pH - This decrease is generally associated with the biological degradation of organic material in the sediments and is related to increased biological productivity within a lake. This activity results in the release of carbonic acid (carbon dioxide) into the hypolimnion, thereby decreasing the pH. As the pH is decreased, metals tend to desorb from metal oxide surfaces and metal precipitates such as carbonates and hydroxides tend to dissolve.
- c. Increases in Complexing Agents - These can include synthetic materials, which might be introduced by wastewater discharges, and

naturally occurring materials such as fulvic acids. The formation of complexing agents as a result of intensive decomposition of organic matter has been cited as a potential cause for increased mobilization of metals from some sediments.

- d. Biological Transformation Processes - Metals may be transferred from sediment to plant or animal organisms and ultimately find their way into the water column as a result of subsequent biological degradation processes
- e. Reduction by Organic Humic Materials - Naturally occurring organic substances, especially those containing hydroxyl and carboxylic functional groups, are capable of reducing Fe (III) and Mn (IV)

2. Transport from Pore Water to the Water Column

Following mobilization into the pore waters, the actual process of release from the sediments to the overlying water column usually involves a number of steps. The metals must be transported from the pore water to the surface of the sediment to be released. In many cases, concentration gradients and layers will develop within a sediment as a result of variations in chemical conditions. If the overlying water contains oxygen, degradation of detrital material and chemical oxidation reactions deplete oxygen with depth into the sediment. A gradient of decreasing redox potential with depth is a result. Under these conditions, iron and manganese may be released under the reducing conditions found deeper within the sediments and migrate upwards until they reach a redox boundary where oxidation occurs and the formation of solid hydroxide precipitates takes place. Because manganese is more difficult to oxidize, it tends to migrate closer to sediment surface than does iron (Forstner and Wittmann, 1983)

Other metals can be released as a result of the dissolution of manganese and iron oxide films within the deeper portions of the sediment. These may migrate upward and subsequently be immobilized through adsorption to the iron and manganese oxide layers which re-form at the respective redox boundaries

Immobilization through other processes is also possible. For example, calculations of the solubility of a number of metals in the presence of sulfide ions suggest that precipitation as metal sulfides can occur under anoxic conditions even in the presence of very small quantities of sulfide. However, this seems to contradict many observations relative to metal concentrations in pore solutions where large divergences from sulfide solubility relationships have been observed. It has been suggested that the formation of complexes, including organometal complexes, may play a role in maintaining these metals in solution under these conditions (Forstner and Wittmann, 1983).

Under conditions of decreased oxygen concentration in the overlying water, migration of metals may progress closer to the surface of the sediment layer thereby increasing the likelihood of release. Within a high porosity sediment layer, a characteristic typical of the upper part of a freshly deposited sediment, diffusion of dissolved materials readily occurs. Exchange with the water column leads to transport of dissolved species vertically through the sediment over a distance which can extend for approximately 30 centimeters into the sediment layer. Factors which contribute to exchange with the overlying water include diffusion, turbulent exchange, release of gases by microcrobial activity, and activity of higher order biota. Diffusion is less important than the other factors in shallow waters and gains in importance as water depth over the sediment increases. With respect to turbulent exchange, suspension of sediment by intense storms and by boating activity can have a significant impact (Forstner and Wittmann, 1983).

The extent of release to the overlying water column is frequently controlled by conditions within the interface region or microzone at the surface of the sediment. This microzone is a region in which a transition occurs between conditions in the water column and conditions within the sediments. Because a large concentration of detrital material and active biota tend to occur at this interface, it typically is a highly active region where changes in chemical environment occur rapidly with depth. Of particular significance is the depth of oxygen penetration into the microzone. This is governed by the activity within the microzone and the oxygen content of the overlying water. Even when the oxygen content is relatively high, penetration is generally limited to a few centimeters. However, this may be sufficient to provide an oxidized barrier to

the transport of reduced compounds which migrate upward from lower in the sediments, and a difference in penetration of a few millimeters may be sufficient to impact the degree to which release to overlying water will be restricted (Wetzel, 1983)

Although redox potential is relatively insensitive to changes in oxygen content as long as some oxygen is present (Stumm and Morgan, 1981), it is important to note that the redox conditions within a sediment can be significantly impacted by changes in dissolved oxygen concentrations in the overlying water. The major significance of oxygen content of the overlying water is its impact on the penetration of oxygen into the microzone. Once the depth of oxygen depletion within the sediment is reached, more severe reducing conditions can then be established at the corresponding depth. As this depth of penetration approaches the surface, there is an increased likelihood for the introduction of reduced species and associated compounds into the water column. Although some species are re-oxidized within the water column when oxygen is present, others may exist for extended periods of time in a reduced condition.

As the dissolved oxygen concentration within the water column is reduced, a continuum of changes takes place with a progressive increase in the number of compounds that are reduced and released into the water column. In the case of metals, manganese is reduced first and is followed by iron (Forstner and Wittmann, 1983)

Because phosphate can be bound iron precipitates, iron release can be accompanied by a release of phosphate into the hypolimnetic water (Wetzel, 1983). The importance of this release relative to internal nutrient loading to the lake as a whole is dependent on the extent to which phosphorus re-precipitates with iron when the lower portion of a lake is re-oxygenated during turnover. If phosphate is rapidly re-precipitated upon iron oxidation following turnover, its impact on the trophic conditions may be attenuated. However, under severely reducing conditions, sulfate is reduced to sulfide, a species that can bind the reduced ferrous form of iron in the sediments, making it unavailable for precipitation reactions in the water column and a long-term phosphate release can occur. It is also possible for iron to be made unavailable for re-precipitation of phosphate as a result of the formation of complexes with a variety of

RESULTS FROM THE STANDLEY LAKE WATER QUALITY PROGRAM

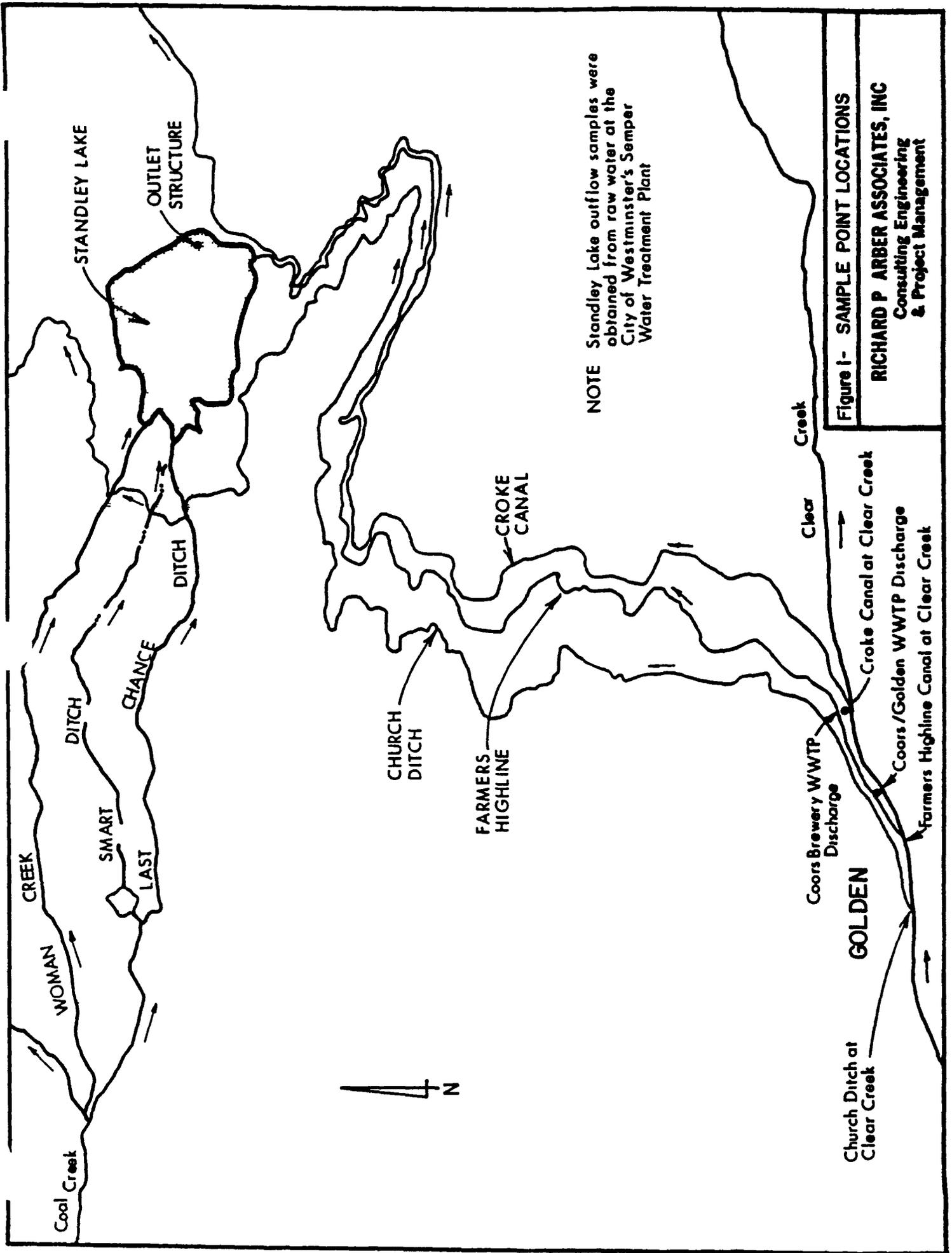
Sampling and Analytical Program

Analyses were performed to determine acid extractable metals in the lake inflow and outflow, and soluble metal concentrations were analyzed for samples in the outflow from the lake. The soluble metal data are intended to provide a measure of metals that are solubilized within the lake and also give an indication of the fraction of the total metal that has the greatest potential for passing through the water treatment processes. The data for acid extraction provides an estimate of the total quantity of the metal being analyzed. This method was selected over more extensive approaches for digestion because of simplicity.

A significant consideration in the evaluation of metal cycles within the lake is the access to a relatively large historical data base for acid extractable iron and manganese in the raw water to the Semper Water Treatment Plant of the City of Westminster. Because iron and manganese cycles are important features with respect to the fate of other metals, this data base can be used to provide a general characterization of metal chemistry within the lake. The data base for the other metals considered in this study is smaller and the concentrations are closer to detection limits. In this regard, the iron and manganese cycles provide useful information which can be used as supplemental information for assessing the significance of trends observed for the other metals.

Metals data from the Standley Lake water quality study were obtained from sample locations as shown on Figure 1. Sample locations can be categorized as follows:

1. Clear Creek Sample Points - These sample points are located in Clear Creek at the headgates of the respective diversion points from Clear Creek to Standley Lake. Locations were selected to provide a basis for assessing potential inflow quality to Standley Lake.
 - a. Church Ditch - This point is located west and upstream of the City of Golden.



NOTE Standley Lake outflow samples were obtained from raw water at the City of Westminster's Semper Water Treatment Plant

Figure 1- SAMPLE POINT LOCATIONS
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Church Ditch at Clear Creek
GOLDEN
 Coors Brewery WWTP Discharge
 Coors/Golden WWTP Discharge
 Farmers Highline Canal at Clear Creek
 Croke Canal at Clear Creek
 Clear Creek

Coal Creek
 Woman Creek
 Smart Last
 Chance Ditch
 Church Ditch
 Farmers Highline
 Croke Canal
 Standley Lake
 Outlet Structure



- b Farmers Highline Canal - This point is located within the City of Golden and is upstream of the discharge from the Coors/Golden Wastewater Treatment Plant
 - c Croke Canal - This point is located on the eastern periphery of the City of Golden. It is downstream of the discharge from the Coors/Golden Wastewater Treatment Plant and is susceptible to impacts from this discharge
2. Wastewater Effluents - Because of concerns for potential impacts arising from different options for diversion to Standley Lake, the discharge from the Coors/Golden Wastewater Treatment Plant was sampled. As presently stipulated under the existing NPDES permit, the Coors/Golden Wastewater Treatment Plant is allowed to discharge up to 7 mgd of combined industrial and municipal wastewater to Clear Creek at a point upstream of the headgate to the Croke Canal. At present, the average flow rate for this discharge is generally in the range of 3.6 mgd.
- The Coors Brewery Wastewater Treatment Plant can discharge at two locations: directly to the Croke Canal, and to Clear Creek at a point downstream from the headgate to the Croke Canal. Generally, the discharge to the Croke Canal has occurred from November to March in order to satisfy water rights. This discharge was substantially reduced in 1982 and did not occur at all during 1983. Therefore, no direct influence on Standley Lake occurred during the study period. At present, the average flow rate for the discharge is approximately 4.6 mgd, and a flow of 7.2 mgd is allowed under the present permit.
- 3 Standley Lake Outflow Sample Point - This sample point is located in the raw water pipeline at the City of Westminster's Semper Water Treatment Plant. The raw water is withdrawn directly from Standley Lake at the outlet structure, with ports located at levels varying from 10.0 to 20.5 feet from the bottom of the lake. Because the maximum water depth of the lake is 96.0 feet, water quality in the outflow correlates to quality within the lower strata of the lake. Finished water samples are also collected at the plant to give an indication of the extent of metal removal during water treatment.

General Water Quality Trends

Like many lakes and reservoirs, Standley Lake undergoes seasonal cycles that have a significant impact on the overall water quality. In addition, the lake appears to be impacted by a short-circuit condition that can result in a relatively rapid response of outflow characteristics to lake inflow conditions. This is suggested by the case of turbidity in Figure 2 for a condition where a high turbidity inflow was admitted to the lake on June 21 and a relatively direct response was observed in the outflow 20 days later. Short-circuiting is further suggested by the relatively close proximity of the major portion of the lake inflow to the outflow, and by the fact that such occurrences are common in reservoirs where outflow is withdrawn near the reservoir bottom (Sartoris et al, 1981)

In general, seasonal cycles are characterized by periods of stratification during the summer. A possibility also exists for stratification during periods of ice cover in the winter. These periods are separated by intervening periods of mixing during the spring and fall. During stratification in the summer, a warmer, less dense upper strata or epilimnion (defined as the upper level in a stratified lake) overlies a colder hypolimnion (defined as the lower level of a stratified lake). These are separated by a thermocline region where temperature changes rapidly with depth. As will be discussed further in this memorandum, under some conditions, a degree of instability appears to occur relative to the thermocline during periods of stratification.

As air temperatures and solar radiation begin to decrease during the late summer and into the fall, the temperature of the epilimnion drops and begins to approach the temperature of the hypolimnion. The decrease in the difference in the densities of the two layers results in a less stable degree of stratification, and the input of energy from water currents and wind forces ultimately becomes adequate to mix the two strata. This results in a "turnover" condition which marks the beginning of a period during the fall when the lake is vertically mixed and water quality is generally uniform with depth.

Due to a characteristic that is unique to water, the highest density occurs at 4° C, and water at colder temperatures becomes progressively less dense until it freezes at 0° C. Under winter conditions, the overall density gradient is frequently limited to a temperature range of 0° C to 4° C, with warmer water tending to be located on the

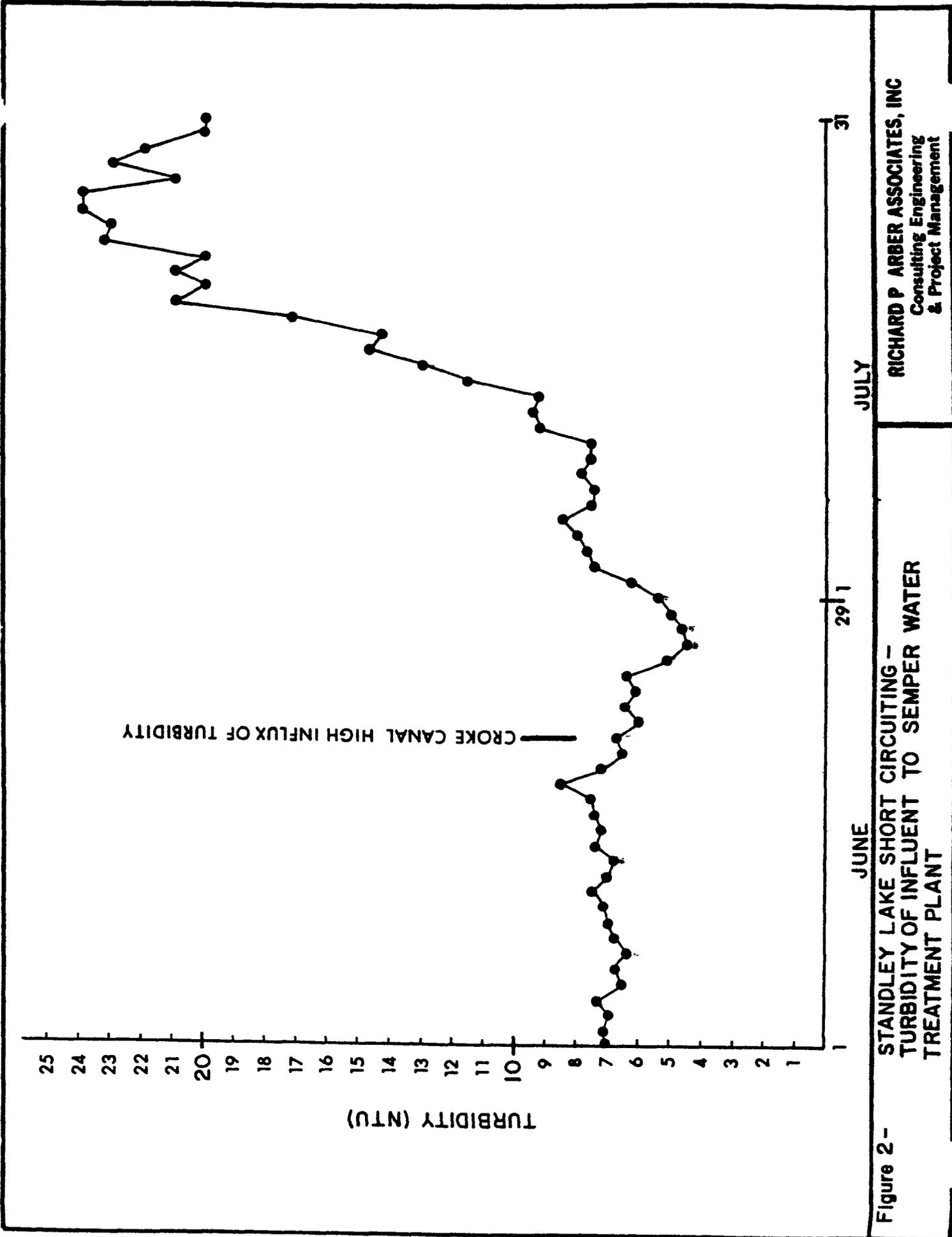


Figure 2-

STANDLEY LAKE SHORT CIRCUITING -
TURBIDITY OF INFLUENT TO SEMPER WATER
TREATMENT PLANT

JUNE

29 | 1

JULY

31

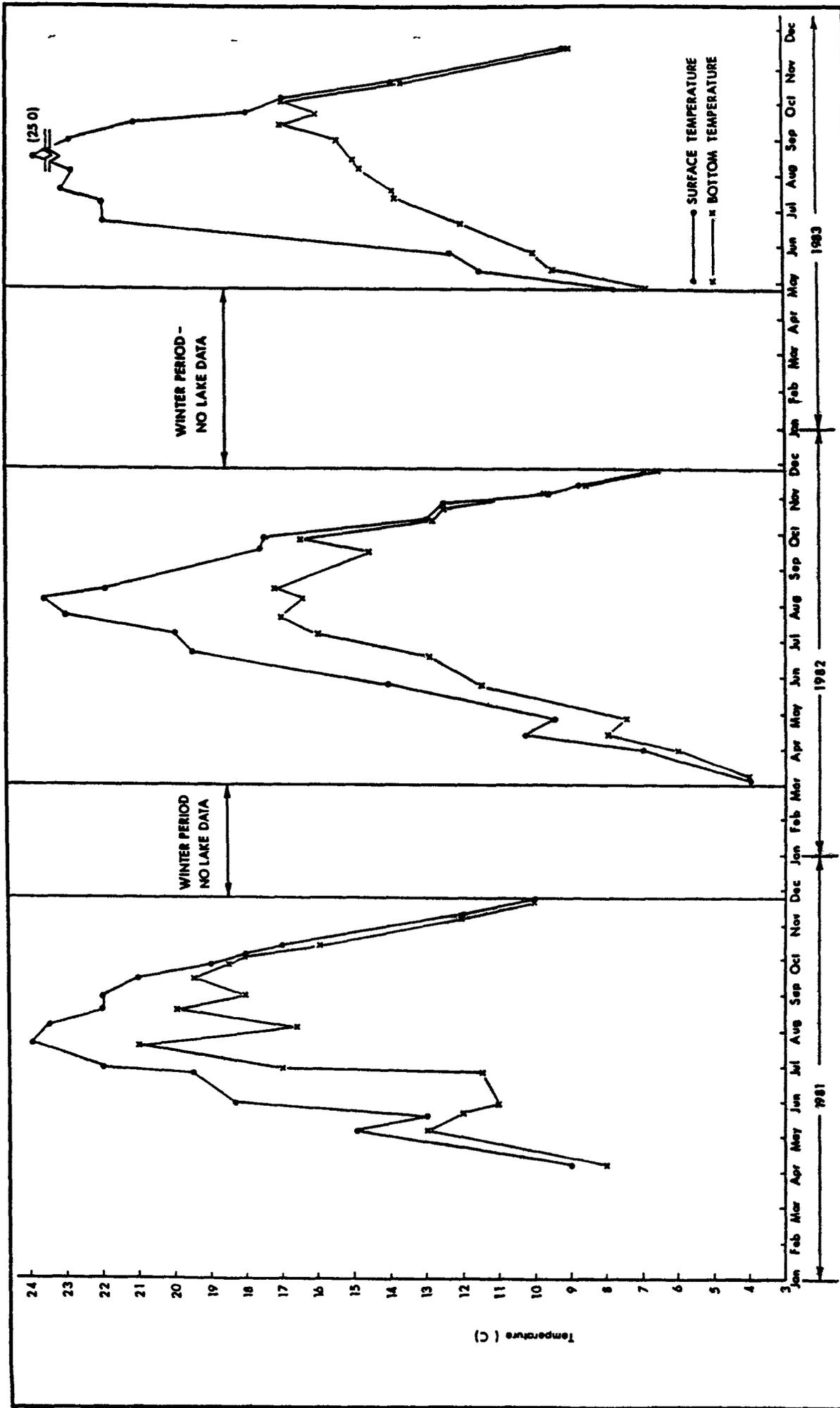
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bottom when the lake is stratified. Because of the limited range of density differential, any condition of stratification is of necessity less stable than is possible during the summer. When it occurs, stratification is generally restricted to periods of ice-cover when the lake would be insulated from wind forces. Turnover generally occurs when the ice-cover begins to break up in the late winter, and a mixed condition continues until the beginning of the summer period of stratification in late spring or early summer.

Annual temperature variations for lake surface and bottom locations are shown in Figure 3 for a sample point located in the vicinity of the lake outlet. This sample point is located at a deep-water location that is adjacent to the dam and has a maximum depth of 70 to 75 feet. Annual temperature cycles of the surface water exhibit a trend of steady increase from late winter and early spring to a maximum temperature of 23 to 25° C in the period from July to August. This is followed by a trend of decreasing temperature which extends through the fall and early winter. Because of concerns for safety to personnel, samples are not collected during periods of ice-cover during the winter, and no data are available for this period.

The trends for bottom temperature are generally similar to those observed in the surface water. However, during the period from May to September, the bottom temperatures are generally cooler, indicating the formation of separate thermal strata. Stratification was confirmed during the summers of 1982 and 1983 by evaluations to determine the existence of a region of rapid temperature change with depth, a condition which suggests the existence of a thermocline. Such evaluations were not performed during the summer of 1981, and other indicators such as dissolved oxygen, pH, and available temperature data must be used to assess the extent of stratification for this period.

The extent of temperature difference is observed to be more pronounced during 1982 and 1983 than in 1981. In contrast to the trends observed in 1982 and 1983, the bottom temperature approached the surface temperature during two periods during the summer of 1981: mid-July and mid-August. A possible cause for the observed differences in temperature trends derives from the variations in lake operation for the respective years. As shown in Figure 4, the lake was filled in late June for each year and remained at a relatively constant level over the summer for the years of 1982 and 1983. However, the water level was significantly drawn down over the summer of



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Figure 3
SURFACE AND BOTTOM TEMPERATURES - SAMPLE LOCATION ADJACENT TO STANDLEY LAKE OUTLET

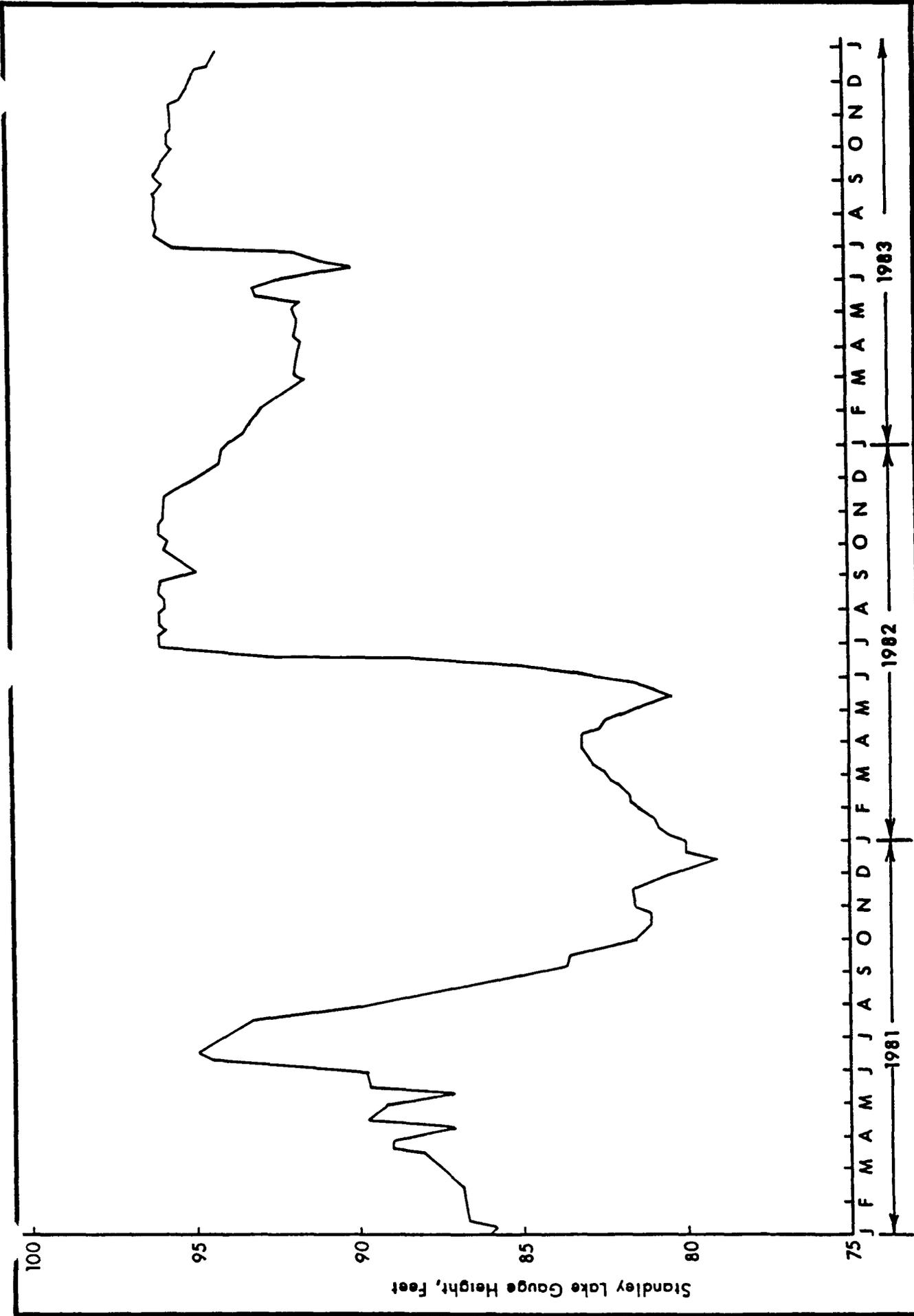


Figure 4
STANDLEY LAKE MEASURED WATER SURFACE LEVELS - 1981 - 1983

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1981 Because of the location of the outlet near the bottom, an outflow of hypolimnetic water would result. When replenishment of the hypolimnion by the influx of colder water from the lake inflows is reduced or halted, a reduction in the volume of hypolimnetic water can occur with continued outflow, resulting in less stable stratification and possible periods of upset occurring during the summer of 1981. Sartoris et al., (1981) have reported similar phenomena for reservoirs with hypolimnetic points of outflow on the upper North Platte River in Wyoming. In a similar fashion, stratification during the less stable winter condition may also be disrupted by this mode of withdrawal.

An important feature of reservoir systems with hypolimnetic withdrawal is the major advective influence that derives from "short-circuiting" associated with the resultant underflow pattern. This advection results in somewhat greater hypolimnetic temperature than observed in other bodies of water and can create conditions of varying stability relative to stratification. As such, conditions can vary significantly over different annual cycles depending on the mode of reservoir operation relative to inflows and outflows.

Under conditions of stratification, the hypolimnion is insulated to a degree from inputs of chemical constituents from the epilimnion. As a consequence of this insulation, dissolved oxygen is not readily replenished within the hypolimnion and accumulations of detrital material can undergo biological degradation processes that deplete the hypolimnetic dissolved oxygen. These processes also result in the release of carbonic acid which lowers the hypolimnetic pH. Impacts from these processes vary depending on the duration of stratification, the extent of flushing of hypolimnetic water, and the quantity of biodegradable material in the bottom detritus. Because much of the organic matter that enters lakes from external sources are generally not readily biodegradable (Wetzel, 1983), loadings of biodegradable material and associated hypolimnetic decreases in pH and dissolved oxygen can be strongly influenced by productivity within a lake. However, the influx of BOD, ammonia and other compounds subject to oxidation can have a significant impact in some cases.

The in-lake annual cycles for dissolved oxygen and pH at the sample location in the vicinity of the outlet from the lake are shown in Figures 5 and 6. The trends for dissolved oxygen concentration at the surface exhibit a pattern of progressive decrease as water temperature warms over the period from winter to summer,

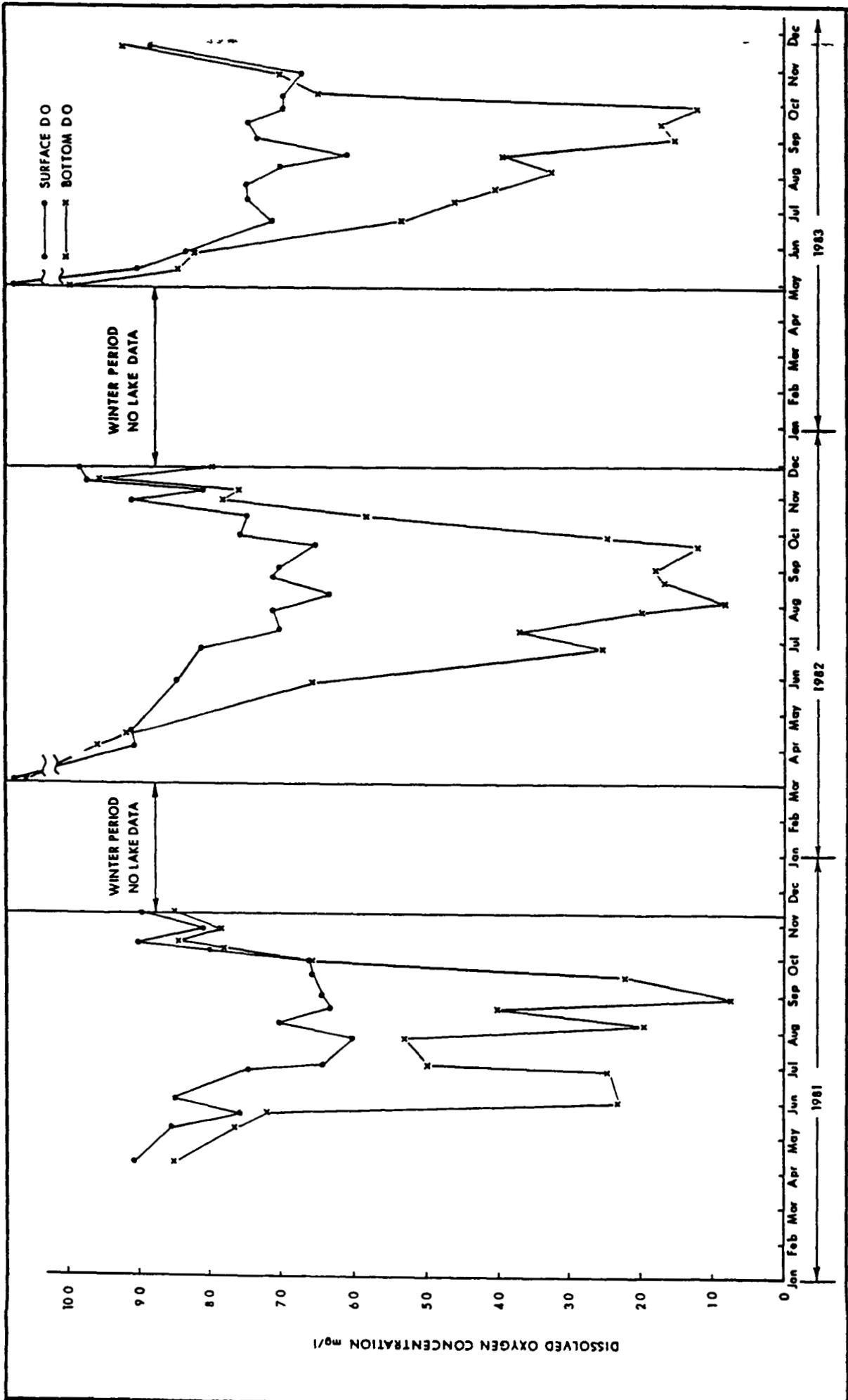
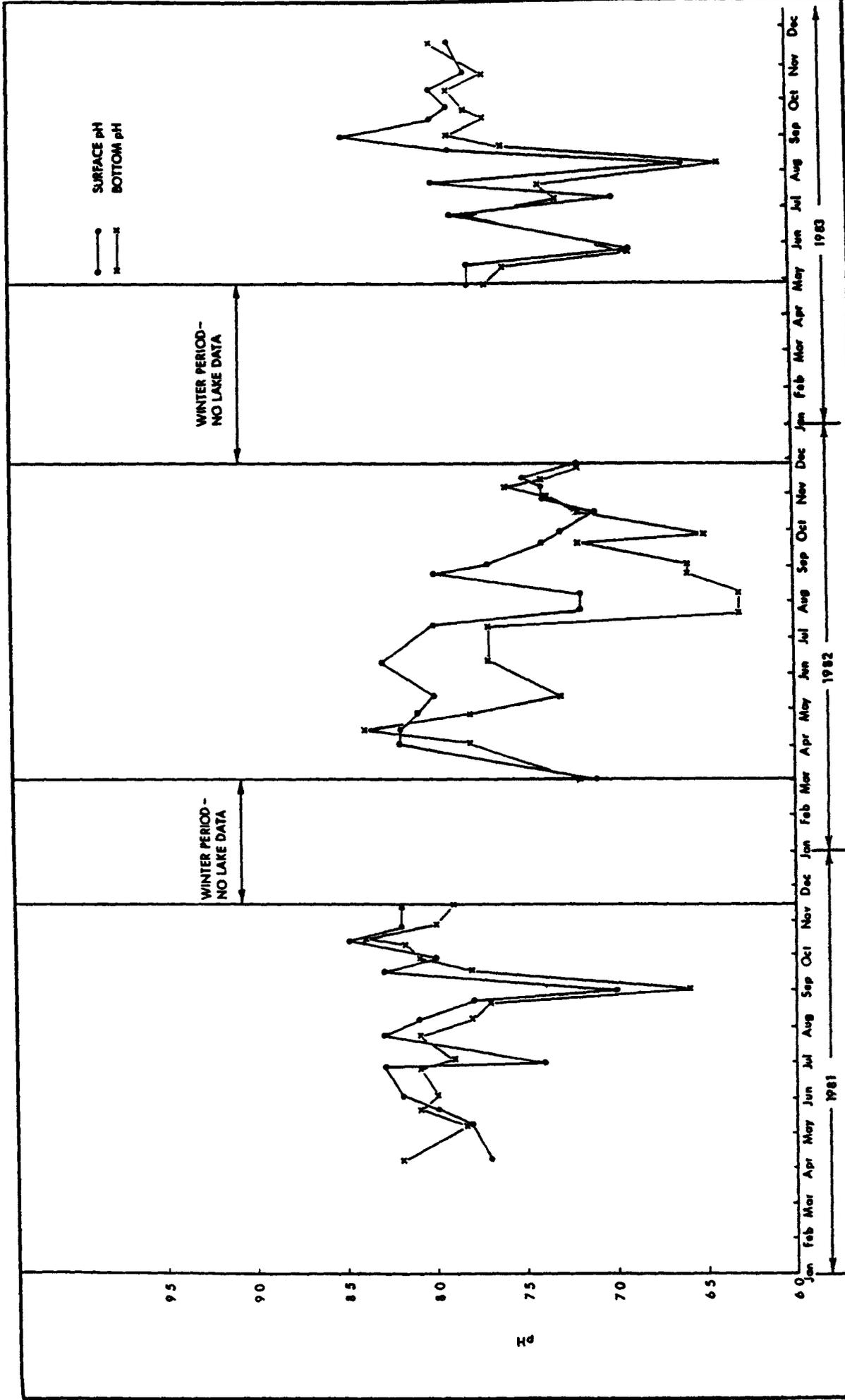


Figure 5
 SURFACE AND BOTTOM DISSOLVED OXYGEN CONCENTRATIONS - SAMPLE LOCATION ADJACENT TO STANDLEY LAKE OUTLET

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Figure 6
 SURFACE AND BOTTOM pH --SAMPLE LOCATION ADJACENT TO STANDLEY LAKE OUTLET

followed by a subsequent increase with cooling temperatures during the late summer and fall. This pattern tends to follow the trend of increased solubility of dissolved oxygen in water with decreased temperature and is characteristic of lakes of moderate productivity (Wetzel, 1983)

The dissolved oxygen concentration at the lake bottom tends to approach the concentration at the surface during the periods of destratification in the spring and fall. However, during the period of stratification over the summer, the dissolved oxygen is significantly depleted. Although this general trend occurs in each year of study, some specific differences are noted for the respective years. During the summer of 1981, two episodes of sudden increase in bottom dissolved oxygen concentration are observed. These episodes occurred during periods of increase in hypolimnetic water temperature during July and August as has been previously discussed (see Figure 3), and give further indication of a possible intrusion of epilimnetic water into the lower level of the lake at these times.

Although the dissolved oxygen trends for the summers of 1982 and 1983 suggest a more stable condition of stratification for both years, the extent of depletion of bottom dissolved oxygen in 1983 is reduced compared to 1982. An explanation for this difference derives from changes in lake inflow patterns observed for the respective years as shown in Tables 2 through 4. The maximum monthly inflow occurred during June in 1981 and 1982 as contrasted to the pattern in 1983, when the largest inflow occurred in July. Because water temperatures in the inflows are generally less than the lake surface temperatures during the summer, this inflow pattern is likely to have resulted in a relatively high influx of water into the hypolimnion during this period. This would have resulted in a comparatively lower hypolimnetic temperature observed during the summer of 1983 (see Figure 3), and would have provided a potential for an advective source of dissolved oxygen to the hypolimnion. Similar conditions have been noted by La Bounty, et al (December, 1980) for extended summer periods of inflow from high snowmelt for Twin Lakes located on the upper Arkansas River watershed in Colorado.

The trends for surface and bottom pH are shown in Figure 6. A lowering of bottom pH is observed with the extensive reduction occurring only during the summer of 1982. These results indicate that a significant difference between surface and bottom pH also occurs only during the summer of 1982. Although the differences noted in these

TABLE 2

1981
STANDLEY LAKE INFLOW, ACRE-FEET

<u>Month</u>	<u>Croke Canal</u>	<u>Farmers Highline Canal</u>	<u>Woman Creek & Church Ditch</u>	<u>Last Chance Ditch & Church Ditch</u>	<u>Total</u>
January	1865	—	—	—	1865
February	1956	—	—	—	1956
March	2293	—	—	—	2293
April	751	877	248	—	1882
May	359	1606	273	25	2263
June	3876	3954	693	608	9131
July	526	949	164	242	1881
August	214	472	—	—	686
September	113	648	—	—	761
October	119	446	—	—	565
November	126	390	—	—	516
December	989	—	—	—	989
	—	—	—	—	—
TOTAL	13193	9342	1378	875	24788

TABLE 3

1982
STANDLEY LAKE INFLOW, ACRE-FEET

<u>Month</u>	<u>Croke Canal</u>	<u>Farmers Highline Canal</u>	<u>Woman Creek & Church Ditch</u>	<u>Last Chance Ditch & Church Ditch</u>	<u>Total</u>
January	1927	--	--	--	1927
February	1798	--	--	--	1798
March	1530	282	--	--	1812
April	74	1140	--	--	1214
May	173	2448	148	536	3305
June	6540	9123	289	698	16,650
July	2259	4646	566	199	7670
August	489	3014	508	364	4375
September	124	1892	628	239	2883
October	187	1014	517	77	1795
November	113	273	9	--	395
December	49	--	9	--	58
					<hr/>
					43,882

TABLE 4

1983
STANDLEY LAKE INFLOW, ACRE-FEET

<u>Month</u>	<u>Croke Canal</u>	<u>Farmers Highline Canal</u>	<u>Woman Creek & Church Ditch</u>	<u>Last Chance Ditch & Church Ditch</u>	<u>Total</u>
January	34	—	94	—	128
February	25	—	30	—	55
March	190	—	467	—	657
April	379	—	836	50	1265
May	327	1312	698	540	2877
June	2466	234	407	292	3399
July	6351	1709	577	576	9213
August	499	2624	1115	639	4877
September	441	3135	1288	0	4864
October	100	1450	665	252	2477
November	49	644	0	0	693
December	65	0	9	0	74
					<hr/>
					30,579

pH trends give further indication of the variable nature of annual reservoir cycles, there is a relatively consistent trend towards lower bottom pH during the summer of each year

Overall, the seasonal trends towards reduced levels of bottom pH and dissolved oxygen have a significant impact on chemical reactions which take place in the sediments. Depending on the severity of these conditions, a variety of chemical constituents can be released from the sediments into the water column. For example, solubilization of iron and manganese under these conditions has been widely reported and has been a phenomenon of general interest to the water industry. The associated solubilizations are attributed to conditions that result in chemical reduction reactions that convert iron (III) and manganese (IV) to less soluble iron (II) and manganese (II) respectively. The onset of reducing conditions is dependent on redox potential, a factor that is strongly influenced by the oxidizing capability of dissolved oxygen. As the oxygen concentration declines within the water column adjacent a sediment, the depth of oxygen penetration into the sediments is decreased, resulting in conditions more favorable to iron and manganese reduction reactions near the sediment surface.

As discussed in previous sections, solubilization of iron and manganese can have significant direct impacts or associations with the fate of other metals within an aquatic system. Therefore, they offer an important indicator of chemical cycles. Results from monitoring of acid extractable levels of iron and manganese are shown in Tables 5 and 6. In general, these data indicate a substantial decrease in the concentrations of both metals between the respective diversion points on Clear Creek and the outflow from Standley Lake. The magnitude of difference suggests the probability of significant accumulation within the lake.

The general trend of iron inflow concentrations shows a pronounced peak in late spring, suggesting an association with high flows during the spring runoff period (see Table 15). This may occur as a result of suspension of particulates that accumulate on the stream bottom or that are suspended during overland flow. An additional cause of increased levels may be increased leaching from areas impacted by mining. The trend for manganese is not as pronounced. However, slightly elevated levels are also noted during late spring and because of the greater quantity of streamflow during this period, this represents the period of greatest mass loading in the stream. Both iron

TABLE 5

ACID EXTRACTABLE CONCENTRATION OF IRON AT
STANDLEY LAKE INFLOWS AND OUTFLOWS, ug/l

	<u>5/23/83</u>	<u>6/20/83</u>	<u>7/18/83</u>	<u>9/12/83</u>	<u>10/3/83</u>	<u>11/1/83</u>	<u>12/5/83</u>	<u>1/3/84</u>	<u>1/30/84</u>
<u>Clear Creek</u>									
Church Ditch at Clear Creek	8,200	9,100	900	1,200	1,200	1,100	500	400	2,500
Farmers Highline Canal at Clear Creek	7,700	9,500	800	900	1,100	1,300	600	300	2,400
Croke Canal at Clear Creek	—	8,500	900	800	1,000	900	600	400	2,900
<u>Wastewater Effluents</u>									
Coors/Golden WWTP	200	100	300	300	100	137	100	100	200
Coors Brewery WWTP	200	200	200	300	200	200	600	100	600
<u>Standley Lake Outflow</u>									
Raw Water - Semper Plant	600	200	500	400	300	100	100	100	100
Finished Water - Semper Plant	—	40	—	—	94	29	72	23	19
% Removed by Water Plant	—	80%	—	—	69%	71%	28%	77%	81%

TABLE 6

ACID EXTRACTABLE CONCENTRATION OF MANGANESE AT
STANDLEY LAKE INFLOWS AND OUTFLOWS, ug/l

	<u>5/23/83</u>	<u>6/20/83</u>	<u>7/18/83</u>	<u>9/12/83</u>	<u>10/3/83</u>	<u>11/1/83</u>	<u>12/5/83</u>	<u>1/3/84</u>	<u>1/30/84</u>
<u>Clear Creek</u>									
Church Ditch at Clear Creek	2,430	1,810	490	950	1,850	1,550	1,690	1,690	1,780
Farmers Highline Canal at Clear Creek	1,720	2,060	480	910	1,120	1,800	1,680	1,500	1,530
Croke Canal at Clear Creek	--	1,900	420	770	1,050	1,370	1,690	1,390	1,710
<u>Wastewater Effluents</u>									
Coors/Golden WWTP	50	100	180	60	210	40	120	190	90
Coors Brewery WWTP	140	250	150	180	80	200	700	90	100
<u>St andley Lake Outflow</u>									
Raw Water - Semper Plant	100	100	100	670	60	36	18	50	50
Finished Water - Semper Plant	--	5	--	--	31	4	9	3	4
% Removed by Water Plant	--	95%	--	--	48%	89%	50%	94%	92%

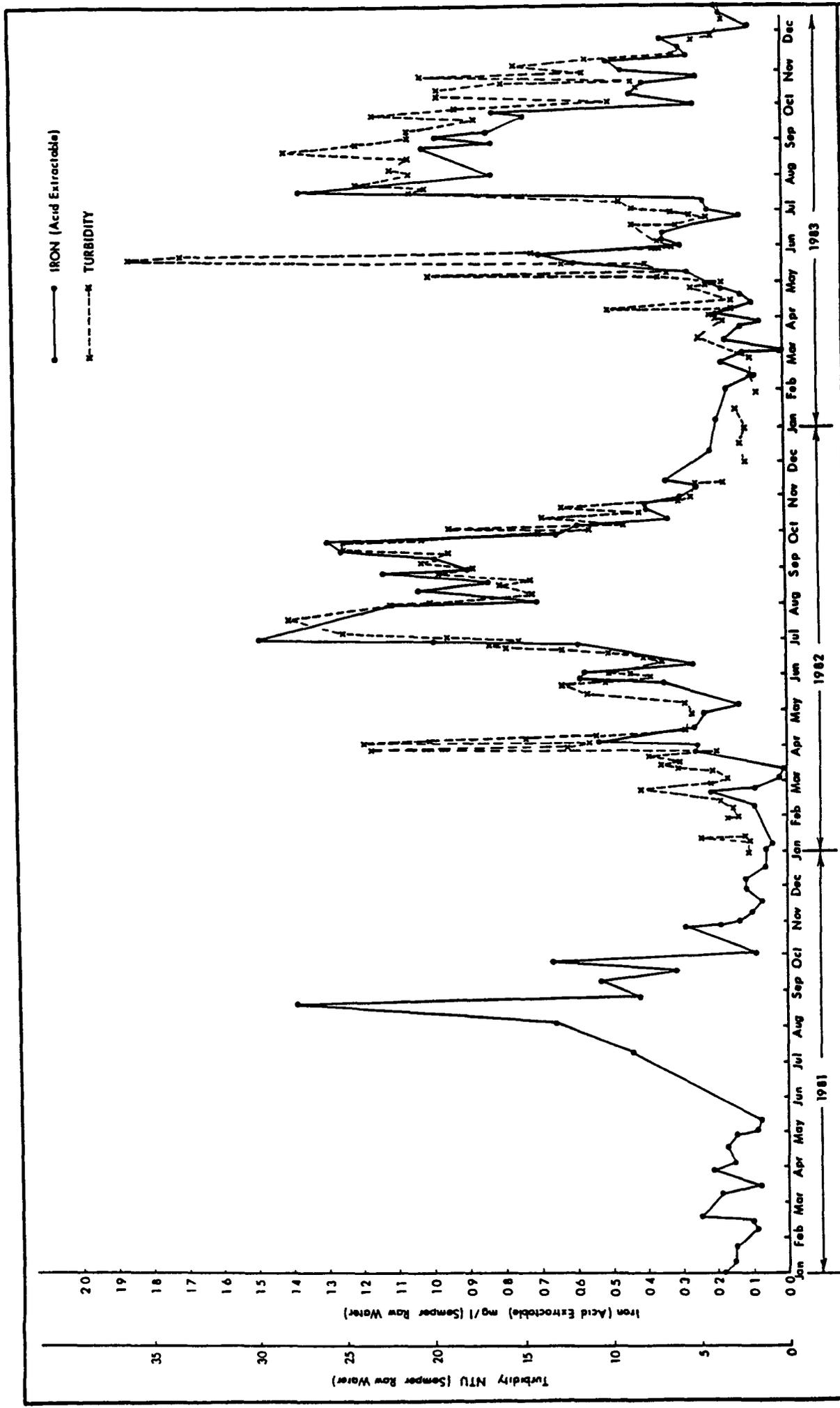
and manganese showed a trend towards highest loadings during the initial portion of the runoff period, suggesting a "first flush" type of impact followed by reduced levels

Historically, data for acid extractable iron and manganese have been obtained by personnel at the Westminster Semper Water Treatment Plant. These are data which exist in addition to those developed for this study, and which permit longer term trends to be developed that characterize concentrations in the outflow from the lake. Generally, the trends of these data, as presented in Figures 7 and 8, show elevated levels of both iron and manganese during the summer and early fall. In addition, manganese has periodically shown a tendency to become slightly elevated during the late winter months, whereas the behavior of iron over this period is somewhat erratic.

The trend for soluble manganese as determined in the water quality program is also shown in Figure 8. The trend for soluble manganese generally tends to correlate with that for total manganese over the period of study, and significant levels of increase in soluble manganese parallel those for total manganese. Conversely, the concentrations of soluble iron are extremely low (generally less than 20 ug/l), and it appears that most of the iron in the water column is present in particulate form.

Iron and manganese cycles within a lake are influenced by internal sources, as well as by loadings from lake inflows. In cases where hypolimnetic oxygen is sufficiently depleted, internal loadings of iron and manganese can result from the formation of the more soluble, reduced forms of these metals. The data for manganese strongly suggest a phenomenon of this type. There is a generally progressive increase in manganese concentration over the period of the summer that reaches a peak in early fall, followed by a precipitous decline which corresponds to a period of turnover and increased levels of oxygen and pH within the bottom water of the lake. This pattern, along with the high levels of soluble manganese observed during this period, tends to support a hypothesis of solubilization by reduction reactions.

Generally, the historical data show a large peak during the summer months and a small peak during the winter months, suggesting a much lower level of release during the period of winter stratification of the lake. Winter stratification of the lake probably occurs over a shorter duration, and cold water temperatures would tend to reduce the level of biological activity responsible for decreases of dissolved oxygen and pH. In addition, the less stable stratification typically associated with the winter period is



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Figure 7
 HISTORICAL ACID EXTRACTABLE IRON AND TURBIDITY -STANDLEY LAKE OUTFLOW

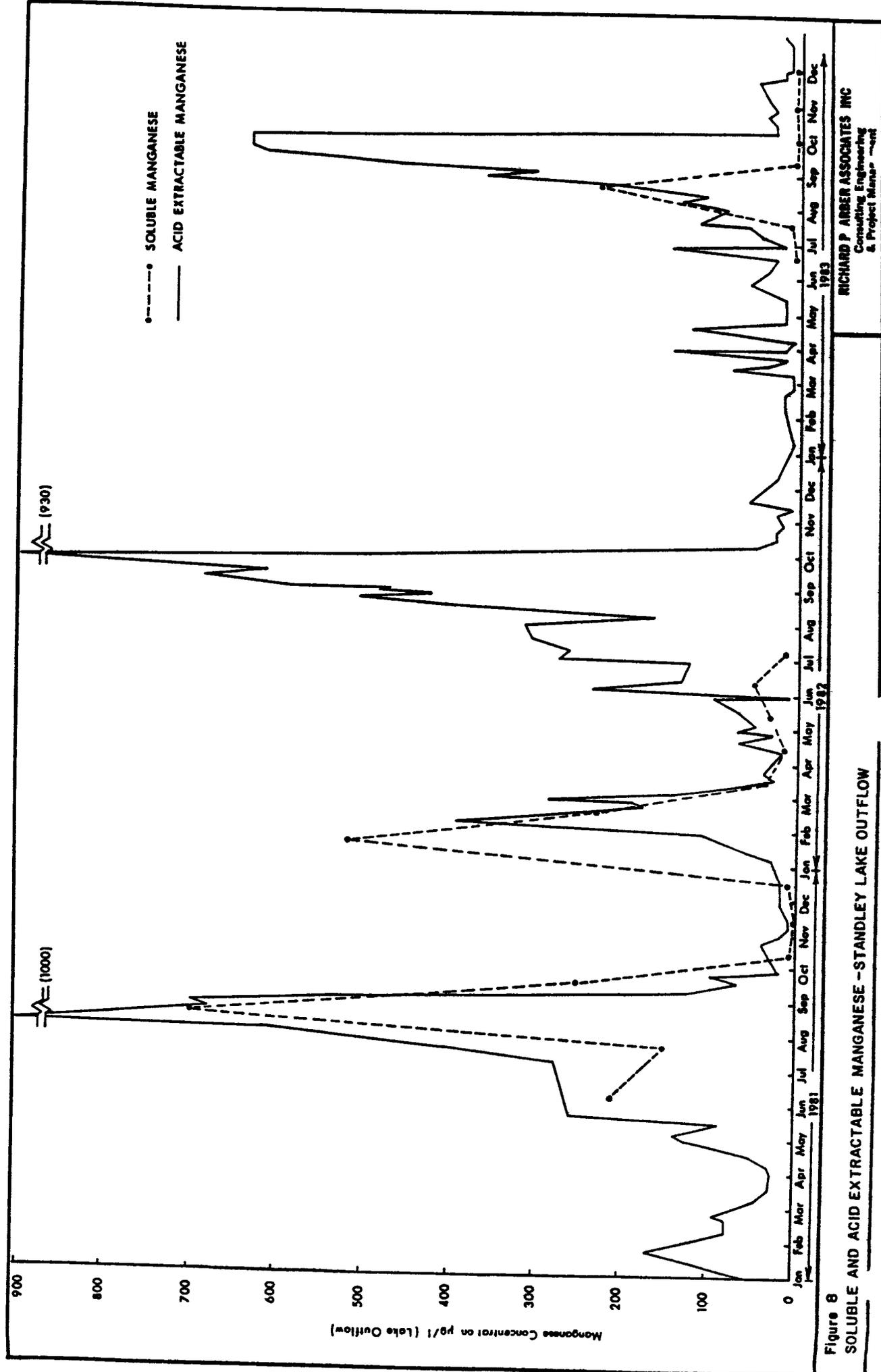


Figure 8
 SOLUBLE AND ACID EXTRACTABLE MANGANESE - STANDLEY LAKE OUTFLOW

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more easily disrupted. Because no lake sampling has been performed during the period of ice cover, the degree to which stratification is disrupted by bottom withdrawal is unknown

An association of manganese concentration with hypolimnetic oxygen depletion is further suggested by comparing the annual trends. As shown in Figure 8, soluble manganese exhibits much lower concentrations during the summer of 1983 than during the summer of 1981. In a similar fashion, a substantially lower level of acid extractable manganese is observed in the historical data in 1983. Comparison of the dissolved oxygen data for these two periods (Figure 5) indicates that the period of hypolimnetic oxygen depletion extended over a much greater period of time during 1981, and that the oxygen concentration decreased to a lower level. Although the peak of the soluble manganese concentration occurs prior to the minimum oxygen level for 1983, the acid extractable manganese data suggests continued release until the minimum oxygen level is reached. The possibility for release from sediments over this period followed by subsequent re-precipitation of manganese within the water column is suggested by decreased solubility that would be associated with the increase in pH within the water column prior to the occurrence of minimum oxygen levels. The formation of manganese carbonate precipitate is an example of such a pH dependent reaction that can be important to manganese chemistry (Hoffman and Eisenrich, 1981)

Although iron generally tends to elevate during the summer period, neither the pattern of its release or the finding of extremely low soluble levels support a hypothesis of significant release from the sediment. In some cases, a maximum iron concentration occurs during the early part of the summer, and no subsequent trend of progressive increase is observed. This results in a peaking of iron concentration prior to a peaking of manganese concentration. However, if solubilization from the sediments was responsible for release of both of these metals, a peak manganese concentration would be anticipated to occur first, since manganese tends to be reduced and solubilized first.

Because soluble iron does not occur at significant levels, the possibility of an association with particles within the water column was explored. To determine the extent to which patterns of iron concentrations correlate with fluxes of particulate matter within the reservoir, the trend of acid extractable iron concentration is compared to the turbidity trend for the raw water at the Semper Water Treatment

Plant in Figure 6 As shown in this figure, the pattern of iron concentration tends to closely parallel the pattern for variations in raw water turbidity The extent to which the respective trends parallel one another is clear from this plot, and a strong relationship between solids and iron fluxes can be inferred. The high iron and turbidity levels measured during the summer period are probably due to the large influx of particulate matter which occurs during the runoff period of May and June, and which can extend further into the summer as in 1983. Additional loadings may occur as a result of suspension of sediments in shallower portions of the lake due to wind action and as a result of boating activity

The patterns for acid extractable iron and manganese within the lake were further characterized by analyses performed for different lake depths. These data were obtained over the period from September to November of 1982 and 1983 at the sample point adjacent to the lake outlet (Figures 9 through 13), and provide a basis for evaluating the vertical distributions of these metals for the lake turnover period. Bottom dissolved oxygen concentration is shown on Figures 9 through 12 to generally characterize the extent to which the bottom of the lake is oxygenated The sudden increase in dissolved oxygen concentration in late September and early October indicates that as the time of lake turnover for both 1982 and 1983. The trends for both iron and manganese show higher concentrations prior to lake turnover, followed by a general trend of decrease following turnover

The general trends for iron and manganese are similar in that concentration tends to increase with depth and concentrations in the lower levels are decreased following turnover However, there are specific differences relative to the relationship between the bottom concentrations of these two metals and the bottom dissolved oxygen concentration In Figures 9 and 10, the bottom manganese concentration is observed to specifically elevate when the dissolved oxygen concentration decreases and decline as it increases No such direct relationship for the bottom iron concentration is observed in Figures 11 and 12 Therefore, the possibility of an association of iron with the vertical distribution of turbidity was examined An adequate quantity of turbidity data was available only for 1983, and these data are shown in Figure 13 As shown in this figure, the trends for vertical distribution of iron closely parallel the trends for vertical distribution of turbidity

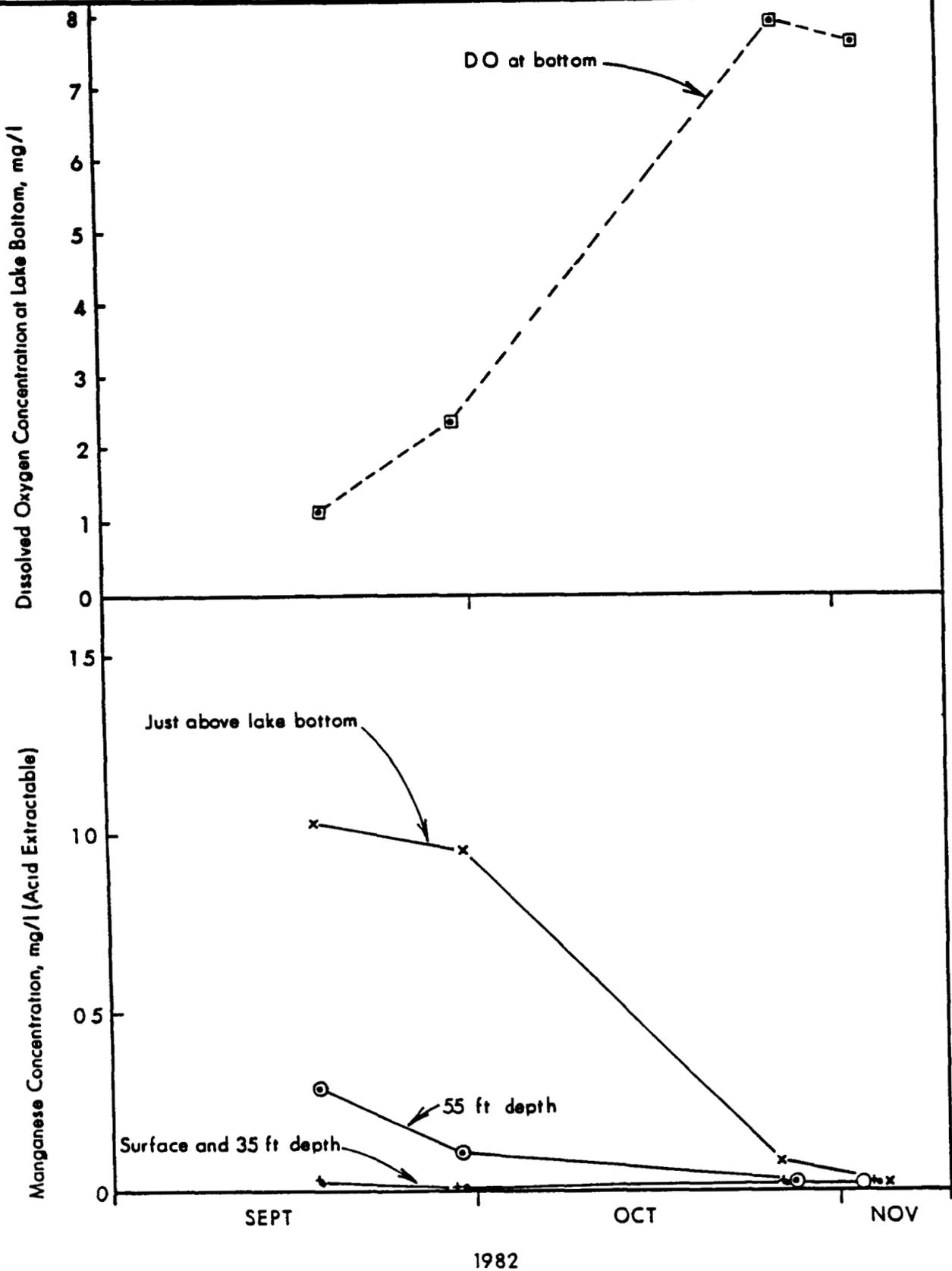


Figure 9 - TRENDS OF MANGANESE CONCENTRATION WITH DEPTH-VICINITY OF LAKE OUTLET-1982

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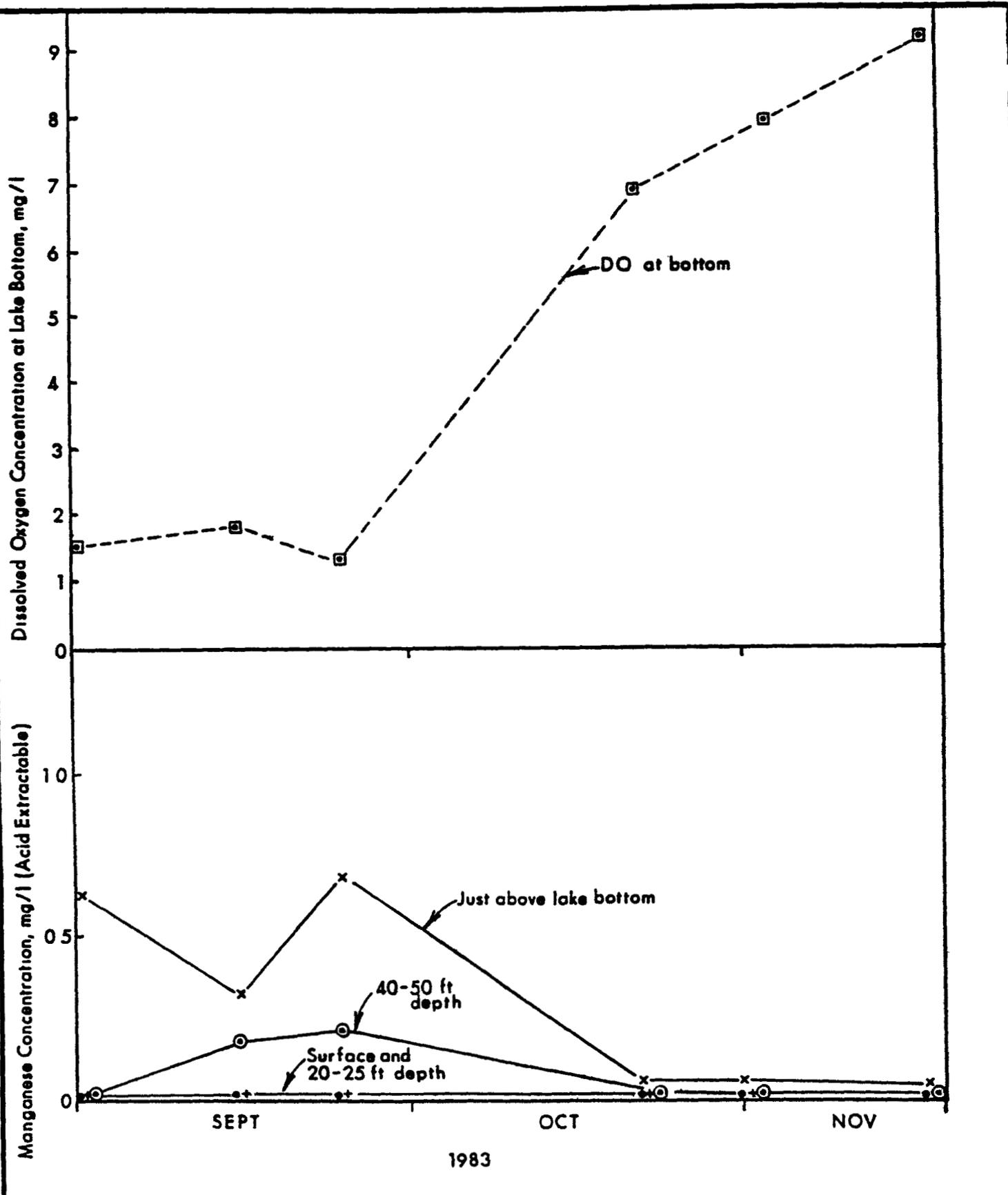


Figure 10- TRENDS OF MANGANESE CONCENTRATION WITH DEPTH- VICINITY OF LAKE OUTLET-1983

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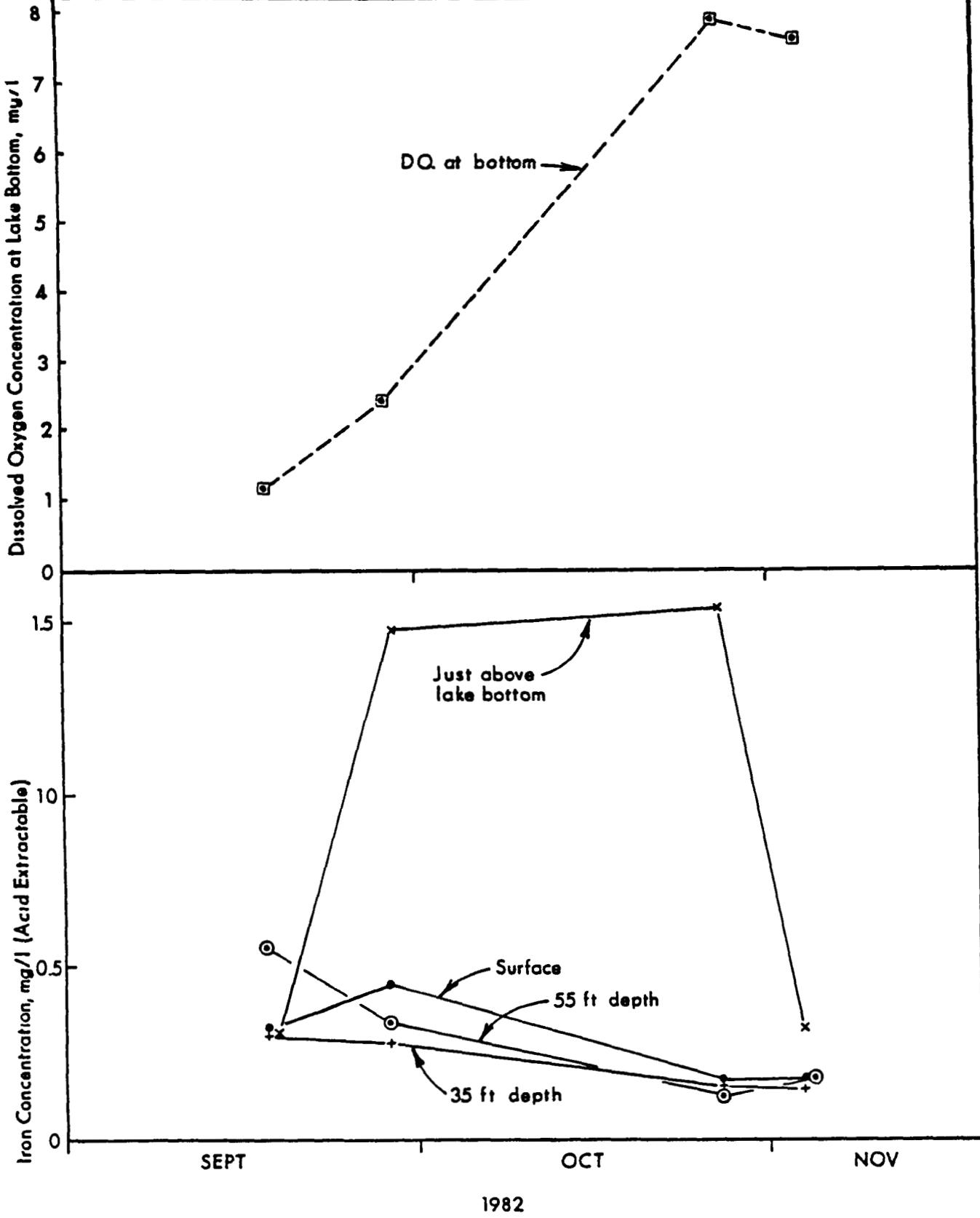


Figure II - TRENDS OF IRON CONCENTRATION WITH DEPTH-VICINITY OF LAKE OUTLET-1982

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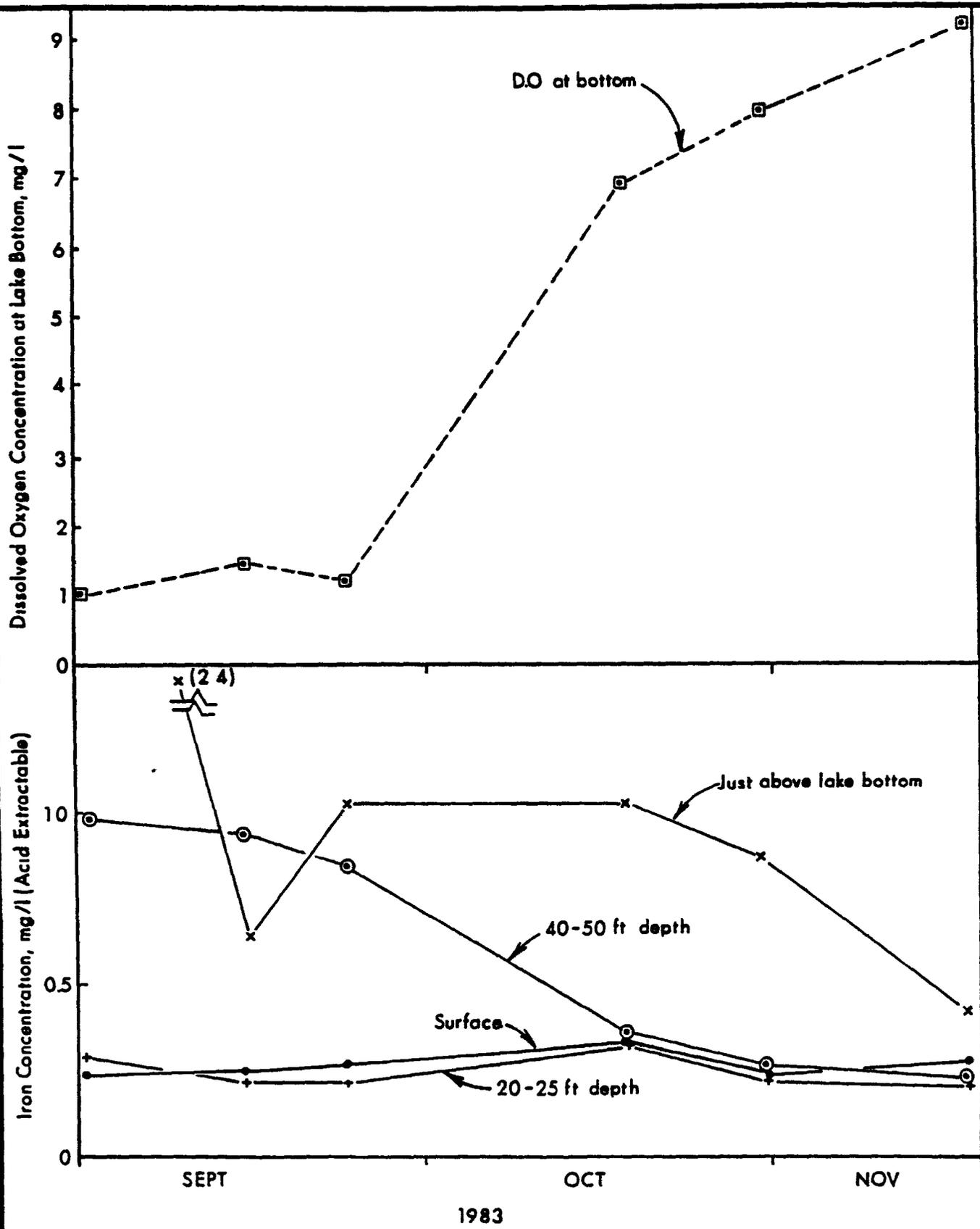


Figure 12 - TRENDS OF IRON CONCENTRATION WITH DEPTH - VICINITY OF LAKE OUTLET - 1983

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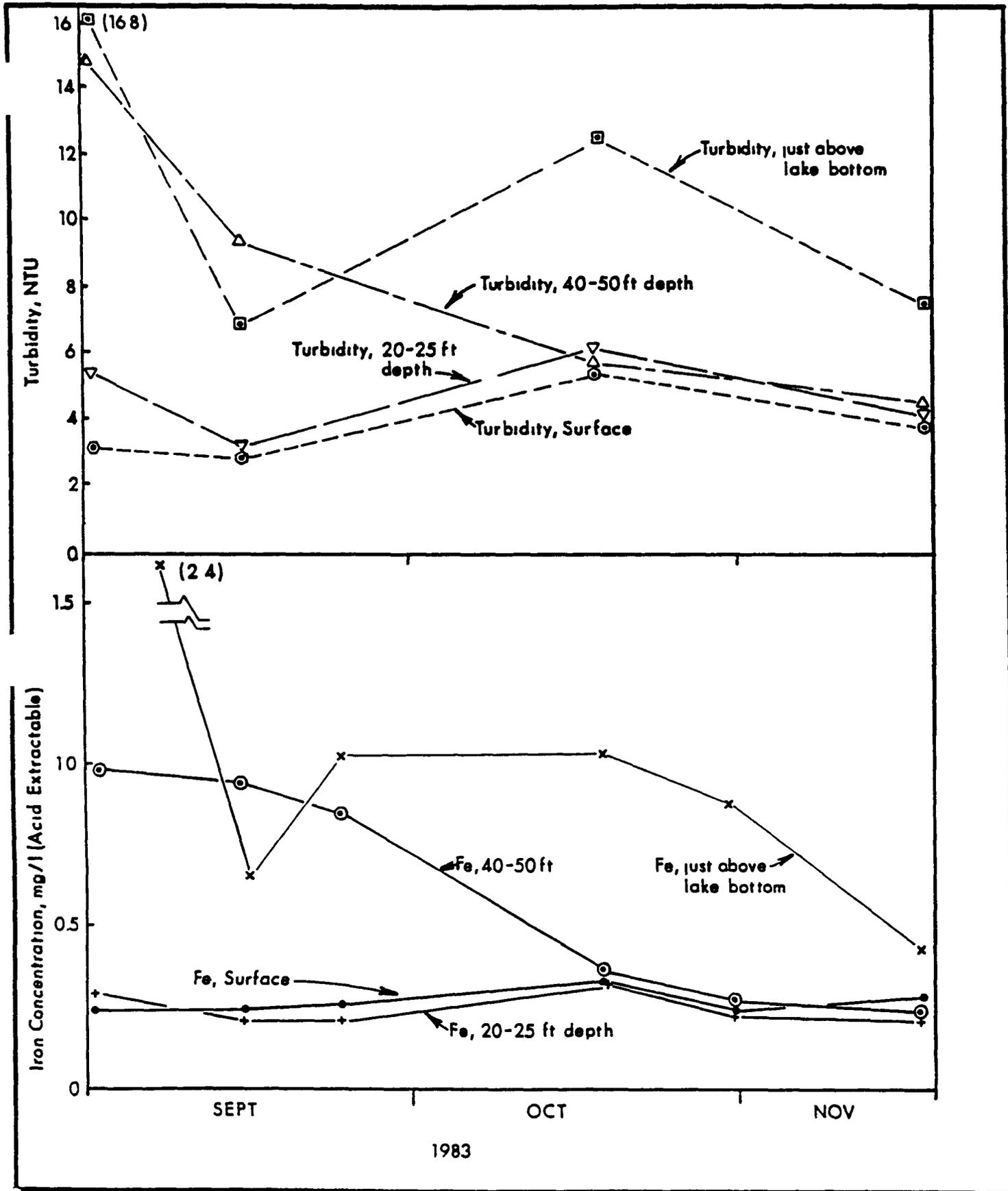


Figure 13 - TURBIDITY AND IRON CONCENTRATION WITH DEPTH - VICINITY OF LAKE OUTLET - 1983

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Overall, the observations relative to vertical distribution of iron and manganese provide additional support to arguments that iron is related to turbidity and manganese is related to bottom dissolved oxygen concentration. Based on these findings, the condition of the lake can be characterized as being moderately degraded with respect to reductions in hypolimnetic dissolved oxygen and pH. Conditions are developed that are adequate for a degree of solubilization of manganese and compounds with which it may associate. Further decreases in hypolimnetic dissolved oxygen in association with further degradation of the lake could become sufficient to cause anoxic conditions, a situation that is likely to solubilize iron and compounds with which it might be associated. Since redox potential tends to decrease with distance into the sediment, the less readily oxidized manganese tends to precipitate closer to the surface than iron as it migrates upward through the sediment. Because it occurs at a lower depth, the iron layer can act as a barrier for upward migration of a number of metals (Sartoris et al., 1977, Cole, 1979). Therefore, a potential for significant additional degradation may exist.

In summary, the solubilization of iron and manganese are of concern because of the potential for nuisance problems directly associated with these metals and the possibility for associated releases of other trace metals. Depletion of hypolimnetic dissolved oxygen is a major contributing factor to solubilization, and lowering of hypolimnetic pH may also be a factor. Both phenomena are impacted by internal lake productivity and the influx of oxygen demanding substances such as BOD and ammonia. Control of productivity through the limitation of inputs of nutrients and oxygen demanding substances should be implemented if further degrees of solubilization are to be avoided.

Results From Analyses of Metals Regulated in the Primary Drinking Water Standards

Analyses for metals included in the Primary Drinking Water Standards have been performed to assess the following: lake inflow and outflow concentrations, potential contributions from the Coors Brewery and Coors/Golden wastewater treatment plants, extent of removal by water treatment, and the trends for soluble metals in the lake outflow. Results for acid extractable metals are summarized in Tables 7 through 14 for sample locations shown on Figure 1. Sample points on Clear Creek are located at the headgates of the respective diversions. These results generally characterize the

TABLE 7

ACID EXTRACTABLE CONCENTRATION OF ARSENIC AT
STANDLEY LAKE INFLOWS AND OUTFLOWS, ug/l

	<u>5/23/83</u>	<u>6/20/83</u>	<u>7/18/83</u>	<u>9/12/83</u>	<u>10/3/83</u>	<u>11/1/83</u>	<u>12/5/83</u>	<u>1/3/84</u>	<u>1/30/84</u>
<u>Clear Creek</u>									
Church Ditch at Clear Creek	19	14	< 1	4	2	3	3	2	5
Farmers Highline Canal at Clear Creek	16	11	1	4	3	5	2	3	4
41 Croke Canal at Clear Creek	--	9	4	< 1	4	2	3	4	5
<u>Wastewater Effluents</u>									
Coors/Golden WWTP	7	12	--	8	2	7	5	3	5
Coors Brewery WWTP	10	10	--	13	4	3	6	6	5
<u>Standley Lake Outflow</u>									
Raw Water - Semper Plant	5	6	5	4	6	3	4	4	3
Finished Water - Semper Plant	--	5	--	--	2	5	4	2	3
% Removed by Water Plant	--	17%	--	--	67%	--	0%	50%	0%

TABLE 8

ACID EXTRACTABLE CONCENTRATION OF BARIUM AT
STANDLEY LAKE INFLOWS AND OUTFLOWS, ug/l

	<u>5/23/83</u>	<u>6/20/83</u>	<u>7/18/83</u>	<u>9/12/83</u>	<u>10/3/83</u>	<u>11/1/83</u>	<u>12/5/83</u>	<u>1/3/84</u>	<u>1/30/84</u>
<u>Clear Creek</u>									
Church Ditch at Clear Creek	304	248	77	106	128	9	1	13	38
Farmers Highline Canal at Clear Creek	255	291	110	149	76	15	2	18	48
Croke Canal at Clear Creek	—	262	77	96	45	103	14	5	34
<u>Wastewater Effluents</u>									
Coors/Golden WWTP	180	172	119	134	38	22	75	12	42
Coors Brewery WWTP	165	165	88	128	33	30	5	< 1	28
<u>Standley Lake Outflow</u>									
Raw Water - Semper Plant	207	198	125	122	7	16	14	16	28
Finished Water - Semper Plant	—	77	—	—	12	10	14	21	28
% Removed by Water Plant	—	61%	—	—	—	38%	0%	—	0%

TABLE 9

ACID EXTRACTABLE CONCENTRATION OF CADMIUM AT
STANDLEY LAKE INFLOWS AND OUTFLOWS, ug/l

	<u>5/23/83</u>	<u>6/20/83</u>	<u>7/18/83</u>	<u>9/12/83</u>	<u>10/3/83</u>	<u>11/1/83</u>	<u>12/5/83</u>	<u>1/3/84</u>	<u>1/30/84</u>
<u>Clear Creek</u>									
Church Ditch at Clear Creek	1	5	2	2	3	3	3	4	3
Farmers Highline Canal at Clear Creek	6	5	2	3	3	4	4	2	3
Croke Canal at Clear Creek	—	3	1	3	2	3	4	3	5
<u>Wastewater Effluents</u>									
Coors/Golden WWTP	< 1	< 1	2	< 1	< 1	< 1	< 1	< 1	< 1
Coors Brewery WWTP	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
<u>Standley Lake Outflow</u>									
Raw Water - Semper Plant	< 1	< 1	< 1	2	< 1	< 1	< 1	< 1	< 1
Finished Water - Semper Plant	—	< 1	—	—	< 1	< 1	< 1	< 1	< 1
% Removed by Water Plant	—	—	—	—	—	—	—	—	—

TABLE 10

ACID EXTRACTABLE CONCENTRATION OF CHROMIUM AT
STANDLEY LAKE INFLOWS AND OUTFLOWS, ug/l

	<u>5/23/83</u>	<u>6/20/83</u>	<u>7/18/83</u>	<u>9/12/83</u>	<u>10/3/83</u>	<u>11/1/83</u>	<u>12/5/83</u>	<u>1/3/84</u>	<u>1/30/84</u>
<u>Clear Creek</u>									
Church Ditch at Clear Creek	16	20	59*	49*	71*	3	1	3	3
Farmers Highline Canal at Clear Creek	16	18	7	26	14	3	2	3	6
Croke Canal at Clear Creek	—	23*	8	16	44*	7	3	3	5
<u>Wastewater Effluents</u>									
Coors/Golden WWTP	5	5	4	7	12	4	4	4	11
Coors Brewery WWTP	5	20	21	11	5	4	3	3	4
<u>Standley Lake Outflow</u>									
Raw Water - Semper Plant	4	53*	13	3	5	2	3	3	3
Finished Water - Semper Plant	—	4	—	—	4	2	2	2	4
% Removed by Water Plant	—	92%	—	—	20%	0%	33%	33%	—

* Out of range in initial analysis Analyzed again to confirm high concentration

TABLE 11

ACID EXTRACTABLE CONCENTRATION OF LEAD AT
STANDLEY LAKE INFLOWS AND OUTFLOWS, ug/l

	<u>5/23/83</u>	<u>6/20/83</u>	<u>7/18/83</u>	<u>9/12/83</u>	<u>10/3/83</u>	<u>11/1/83</u>	<u>12/5/83</u>	<u>1/3/84</u>	<u>1/30/84</u>
<u>Clear Creek</u>									
Church Ditch at Clear Creek	7	16	5	3	12	2	2	2	4
Farmers Highline Canal at Clear Creek	6	19	6	2	< 1	2	1	< 1	2
Croke Canal at Clear Creek	—	14	7	4	2	< 1	2	2	< 1
<u>Wastewater Effluents</u>									
Coors/Golden WWTP	5	4	5	2	10	1	2	2	1
Coors Brewery WWTP	7	5	5	2	6	4	8	1	8
<u>Standley Lake Outflow</u>									
Raw Water - Semper Plant	1	< 1	4	2	< 1	3	2	< 1	< 1
Finished Water - Semper Plant	—	1	—	—	< 1	2	2	1	< 1
% Removed by Water Plant	—	—	—	—	—	33%	—	—	—

TABLE 12

ACID EXTRACTABLE CONCENTRATION OF MERCURY AT
STANDLEY LAKE INFLOWS AND OUTFLOWS, ug/l

	<u>5/23/83</u>	<u>6/20/83</u>	<u>7/18/83</u>	<u>9/12/83</u>	<u>10/3/83</u>	<u>11/1/83</u>	<u>12/5/83</u>	<u>1/3/84</u>	<u>1/30/84</u>
<u>Clear Creek</u>									
Church Ditch at Clear Creek	4	4	2	< 1	< 1	< 1	< 1	< 1	< 1
Farmers Highline Canal at Clear Creek	3	5	2	4	< 1	< 1	< 1	< 1	< 1
Croke Canal at Clear Creek	--	3	2	2	< 1	< 1	< 1	< 1	< 1
<u>Wastewater Effluents.</u>									
Coors/Golden WWTP	< 1	< 1	< 1	2	< 1	< 1	< 1	< 1	< 1
Coors Brewery WWTP	< 1	< 1	< 1	3	< 1	< 1	< 1	< 1	< 1
<u>Standley Lake Outflow</u>									
Raw Water - Semper Plant	5	6	6	< 1	< 1	< 1	< 1	< 1	< 1
Finished Water - Semper Plant	--	3	--	--	< 1	< 1	< 1	< 1	< 1
% Removed by Water Plant	--	50%	--	--	--	--	--	--	--

TABLE 13

ACID EXTRACTABLE CONCENTRATION OF SELENIUM AT
STANDLEY LAKE INFLOWS AND OUTFLOWS, ug/l

	<u>5/23/83</u>	<u>6/20/83</u>	<u>7/18/83</u>	<u>9/12/83</u>	<u>10/3/83</u>	<u>11/1/83</u>	<u>12/5/83</u>	<u>1/3/84</u>	<u>1/30/84</u>
<u>Clear Creek</u>									
Church Ditch at Clear Creek	3	2	3	2	5	6	5	8	10
Farmers Highline Canal at Clear Creek	2	4	6	2	5	6	4	8	8
Croke Canal at Clear Creek	--	3	3	2	6	5	4	5	8
<u>Wastewater Effluents</u>									
Coors/Golden WWTP	1	9	9	1	8	6	4	12	11
Coors Brewery WWTP	10	12	11	8	8	9	8	9	8
<u>Standley Lake Outflow</u>									
Raw Water - Semper Plant	5	3	5	8	7	4	7	7	8
Finished Water - Semper Plant	--	3	--	--	4	4	10	10	8
% Removed by Water Plant	--	0%	--	--	43%	0%	--	--	0%

TABLE 14

ACID EXTRACTABLE CONCENTRATION OF SILVER AT
STANDLEY LAKE INFLOWS AND OUTFLOWS, ug/l

	<u>5/23/83</u>	<u>6/20/83</u>	<u>7/18/83</u>	<u>9/12/83</u>	<u>10/3/83</u>	<u>11/1/83</u>	<u>12/5/83</u>	<u>1/3/84</u>	<u>1/30/84</u>
<u>Clear Creek</u>									
Church Ditch at Clear Creek	2	2	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Farmers Highline Canal at Clear Creek	< 1	2	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Croke Canal at Clear Creek	—	2	< 1	< 1	< 1	< 1	< 1	< 1	< 1
<u>Wastewater Effluents</u>									
Goors/Golden WWTP	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Coors Brewery WWTP	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
<u>Standley Lake Outflow</u>									
Raw Water - Semper Plant	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Finished Water - Semper Plant	—	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
% Removed by Water Plant	—	—	—	—	—	—	—	—	—

inflows to Standley Lake, however, some change in concentration may occur within the canal prior to entry into Standley Lake

Potential impacts of the wastewater effluents from the Coors Brewery and Coors/Golden wastewater treatment plants were assessed as shown in Tables 7 through 14 Based on these analyses, no significant impact would be anticipated in terms of overall loading of acid extractable metals. However, because this assessment is based on acid extractable concentrations, some differences may be observed if more extensive digestion techniques were used for evaluating total concentrations. It should also be noted that additions or changes related to industrial facilities such as those which discharge to the Coors/Golden wastewater system can effect large changes in effluent quality. These types of changes have already been observed for fluorides under other portions of the Standley Lake Water Quality Program

In general, the metal concentrations in Clear Creek exhibit seasonal trends that are characterized by elevated levels during periods of high stream flow in the spring and summer. Because the fate of metals can be influenced by patterns of sedimentation and resuspension within a stream, scouring during high stream flow can be a factor which relates to elevated concentrations. This flow condition also corresponds to increased overland runoff which results in increased levels of particulate matter that can be accumulated by overland flow, increased flushing of mining tunnels, and increased runoff from tailing piles and ponds. Therefore, flow conditions can have a major impact on metal fluxes. Monthly flow volumes for Clear Creek during the 1983 water year are shown in Table 15. These data indicate a sharp increase in flow volume during May, followed by a peak in June. Stream flow did not substantially decrease until September. Complete monthly flows from October through December 1983 had not been compiled at the time of this report. However, based on individual readings of gauge height, the stream flow was observed to generally decline towards the end of the year.

Because of a large snowpack, 1983 was an abnormal year for runoff from snowmelt and high stream flows extended further into the summer than is normal. This may have had an influence on inflow metal concentrations. Because higher flows result in dilution as well as increased suspension of particulates, the direction of influence cannot be speculated.

TABLE 15
MONTHLY FLOWS IN CLEAR CREEK ABOVE GOLDEN
(1983 Water Year)

<u>Month</u>	<u>Flow, Acre-Feet</u>
October, 1982	5,082
November, 1982	3,830
December, 1982	2,590
January, 1983	2,460
February, 1983	2,270
March, 1983	3,350
April, 1983	6,120
May, 1983	22,370
June, 1983	63,320
August, 1983	28,750
September, 1983	12,790

In the case of silver, the limited availability of data above the detection limit precludes any conclusions relative to trend. However, some general trends tend to characterize the patterns followed by other metals at the Clear Creek sample stations over the study period. With the exception of selenium, cadmium and chromium, the concentrations are greatest during May and June. This period corresponds to the beginning of runoff, and the resultant initial scouring and increased exposure to mining leachate may be responsible for the high concentrations. Barium, mercury, lead, and chromium concentrations all tend to decline in the fall as the stream flow decreased.

Chromium concentrations did not peak until the period from July to October. This suggests that chromium was not as greatly influenced by initial scouring as some of the other metals. Selenium followed an inverse pattern relative to flow and became more concentrated as flow diminished. Therefore, its inflow characteristics do not appear to be related to those for the other metals. The cadmium concentrations were near the detection limit and do not show a significant degree of variation over the study period.

Lake outflow concentrations for barium tended to directly parallel the lake inflow (Clear Creek sample locations) concentrations over the study period, suggesting that outflow barium cycles were strongly influenced by inflow patterns. The direct response of the outflow probably derives from a strong short-circuiting pattern of inflow to the outlet. Mercury cycles appeared to follow the same patterns as barium, however, concentrations were generally close or below the detection limit and firm conclusions for patterns cannot be formed. Chromium concentrations appeared to be slightly influenced by inflow patterns. However, the outflow concentrations were greatly reduced from those observed in the inflow, suggesting a high degree of accumulation within the lake. Outflow concentrations of arsenic, cadmium, and lead, all exhibit cycles that suggest little direct influence from inflow patterns. The data for lead and cadmium are generally near the detection limit. However, a consistent reduction of the concentration of these metals is observed to occur from inflow to outflow, and suggests a general trend of accumulation within the lake as a cause for the difference between inflow and outflow patterns. Although arsenic accumulation within the lake is suggested by comparison of the overall average inflow concentration to the average outflow concentration, the trends are not consistent and additional data would be desirable to provide a more extensive basis for comparison. As will be

discussed below, the difficulty associated with making this comparison may partially derive from an apparent internal lake source for arsenic during late summer

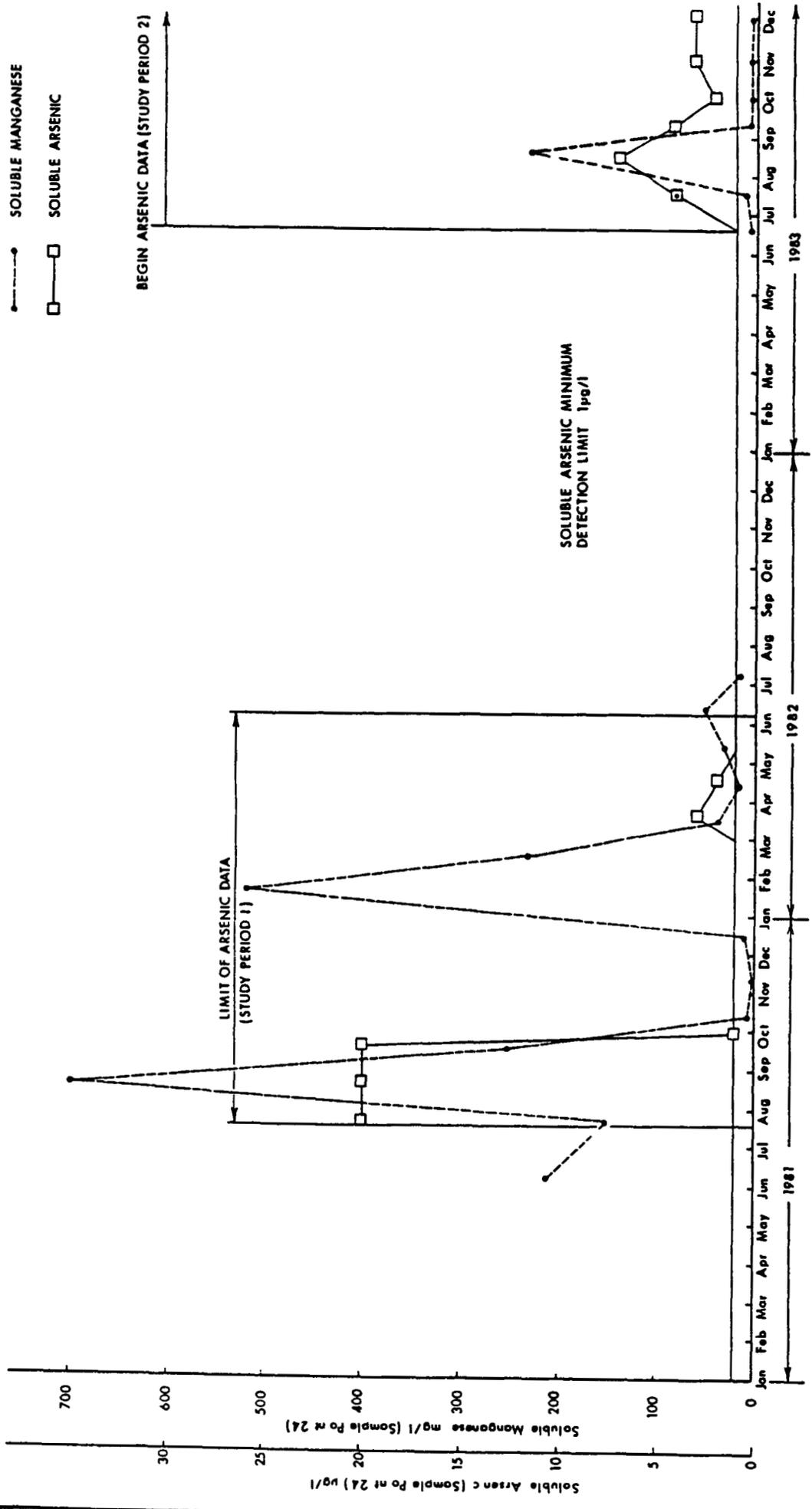
In addition to outflow samples obtained from the raw water at the Semper Water Treatment Plant, finished water samples were obtained to evaluate the extent of metal removal by water treatment and to assess the concentrations in the finished water. As can be seen from these data, the extents of removal tend to be highly variable. This is as would be expected since many factors can influence metal removals in water treatment, including pH, type of coagulant, coagulant dose, and the amount of turbidity present (U S EPA, 1977).

Potential problems relative to drinking water standards in the finished water were noted with respect to mercury and selenium. In the case of mercury (Table 12), one finished water sample exceeded the drinking water standard of 2 ug/l, and three raw water samples were sufficiently in excess of the standard to require significant removal across the water plant. This appears to be a seasonal problem which may be controllable at present. However, the condition should not be permitted to deteriorate further. Concern should be directed towards possible inflows to the lake and releases from sediments.

Selenium analyses indicate finished water concentrations which varied up to the drinking water standard of 10 ug/l. Little removal across the plant was observed for the study period, an observation which conforms to results reported by U S. EPA (1977). Based on these observations, increased selenium loadings should be avoided.

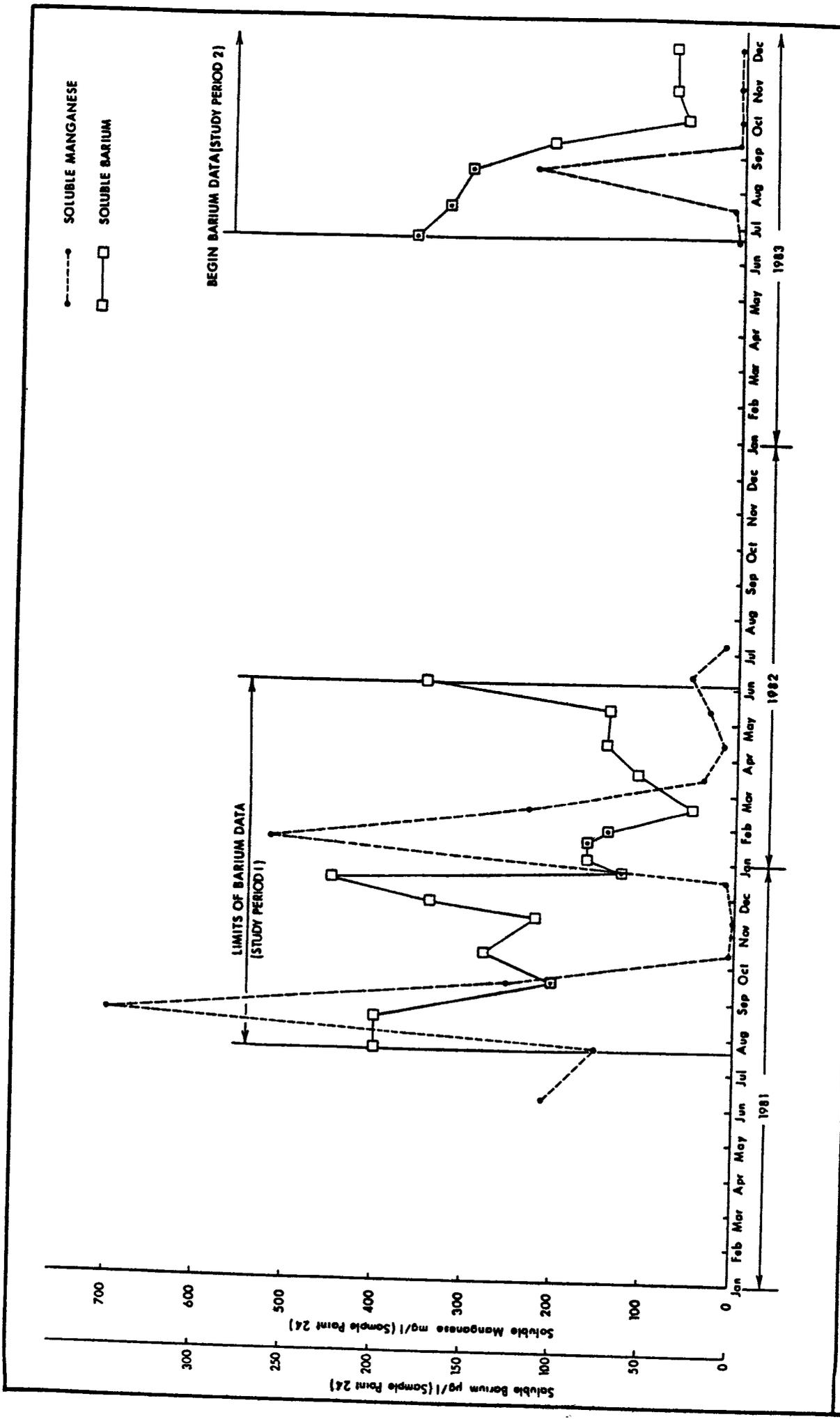
Variations in soluble concentrations in the lake outflow are shown in Figures 14 through 18 for metals for which there are sufficient data for showing some trends (arsenic, barium, chromium, lead, and mercury). Data are shown for two periods of study as indicated on these figures. Concentrations below the minimum detection limits result in a number of breaks in trends within the indicated study periods. Trends for soluble manganese are also shown on these figures to provide a basis for assessing the extent to which the respective solubilization patterns tend to be associated with manganese solubilization and associated periods of low dissolved oxygen.

As previously discussed, it should be noted that the high manganese concentration shown in January, 1982 is probably not representative of the soluble manganese level.



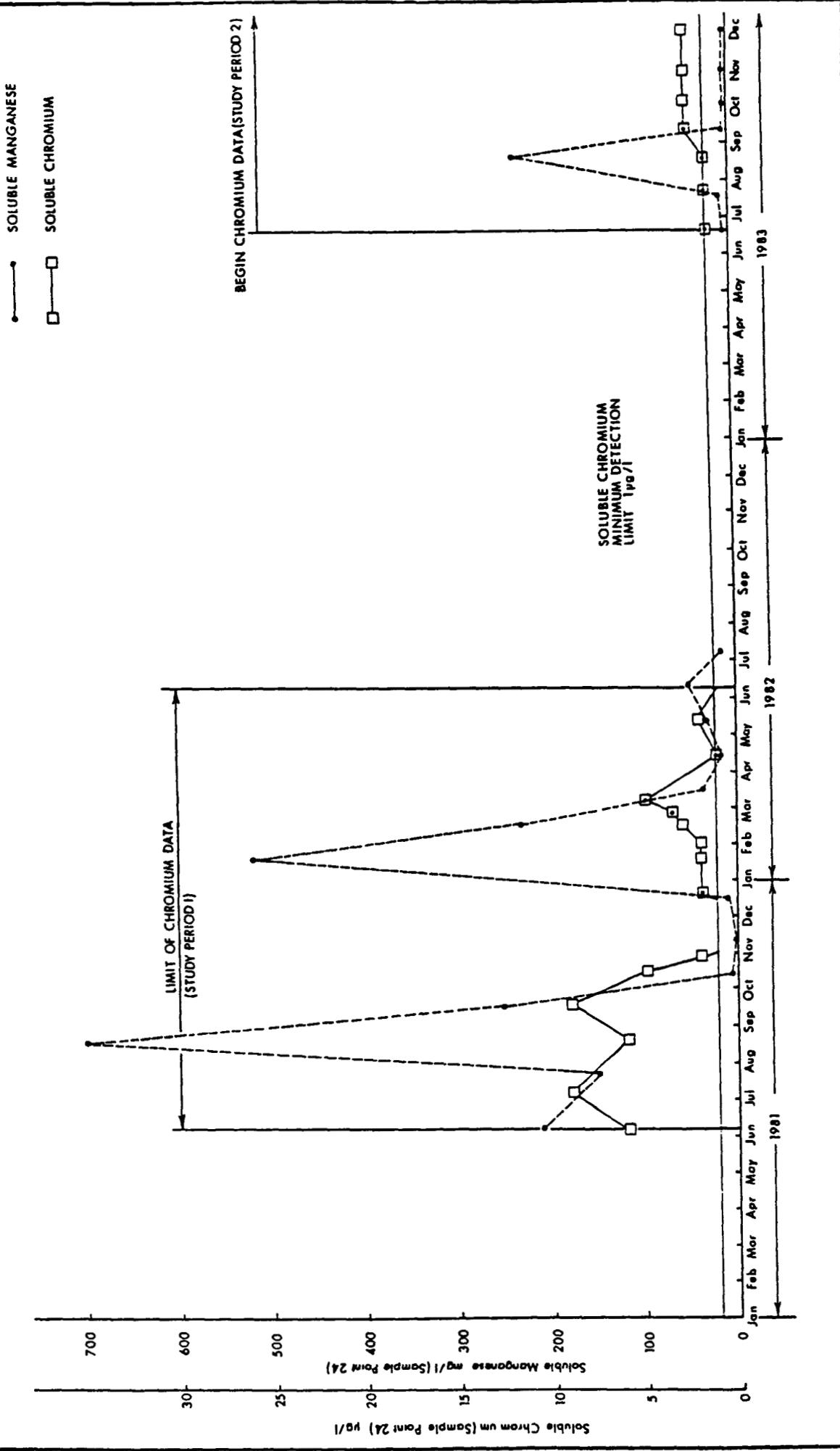
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Figure 14
SOLUBLE ARSENIC IN LAKE OUTFLOW



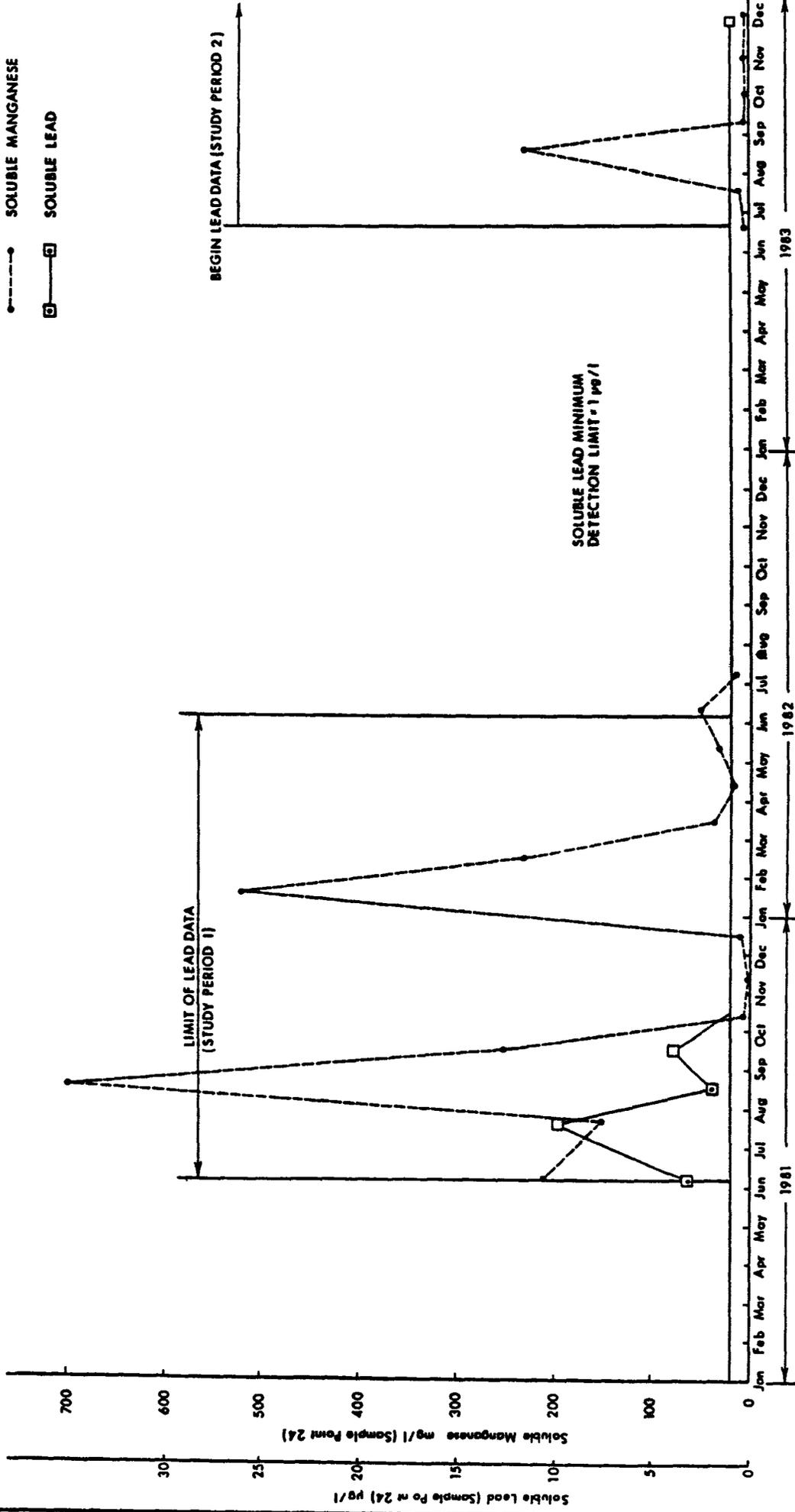
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Figure 15
SOLUBLE BARIUM IN OUTFLOW



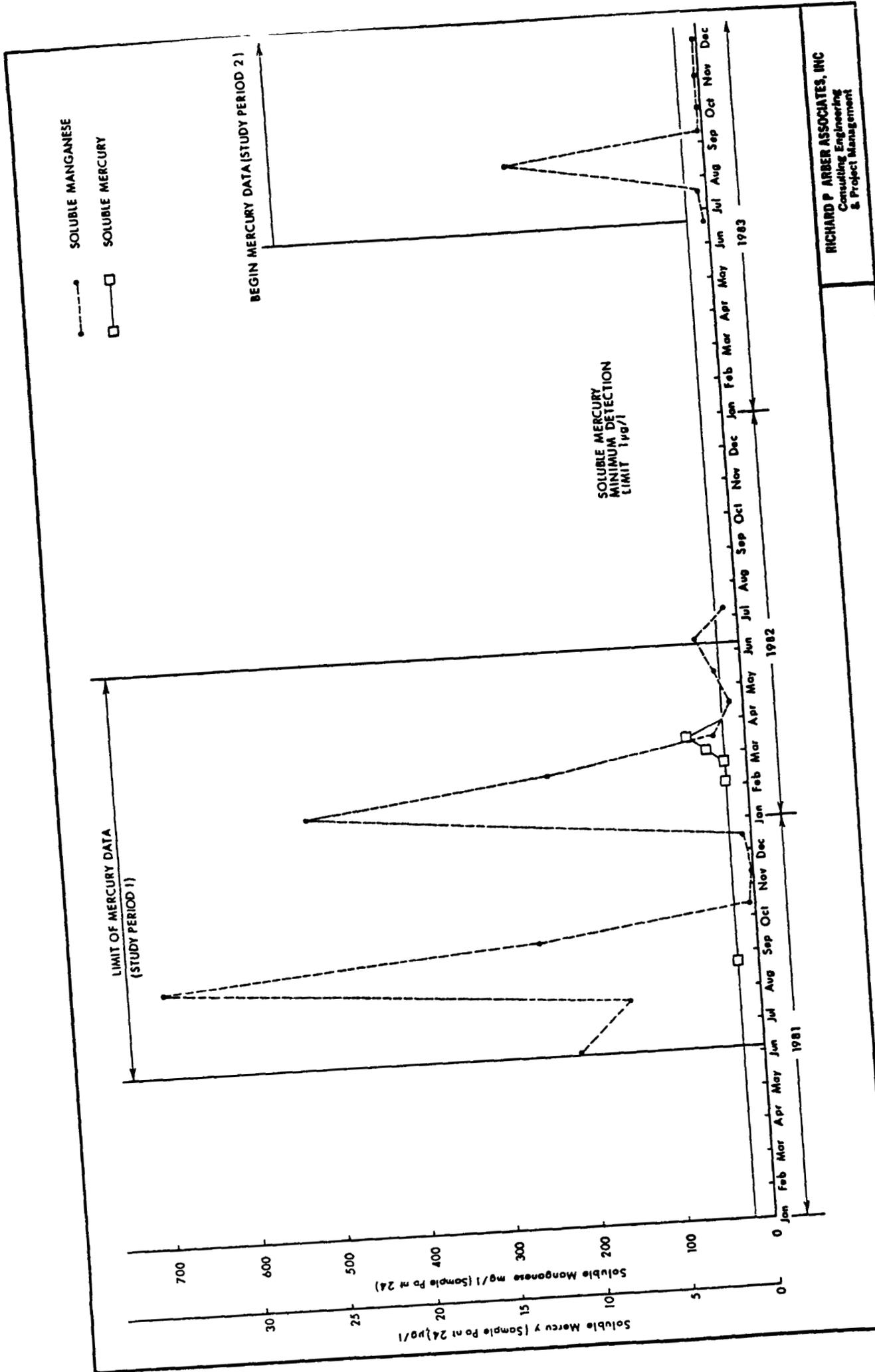
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Figure 16
SOLUBLE CHROMIUM IN LAKE OUTFLOW



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Figure 17
SOLUBLE LEAD IN LAKE OUTFLOW



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Figure 18
 SOLUBLE MERCURY IN LAKE OUTFLOW

for this period. Results for acid extractable manganese over this period yield concentrations that are generally half the soluble concentration of 500 ug/l. Therefore, a much lower extent of solubilization is likely for this period.

Of the metals shown in these figures, soluble arsenic showed a strong tendency to elevate during the summer of 1981 over the period corresponding to the greatest degree of manganese solubilization and it is noted that this period corresponded to the highest levels measured for lead and chromium. The potential association of soluble arsenic with manganese tends to be confirmed by its reappearance in the summer of 1983 at a time coincident with manganese solubilization. It is also noted that the acid extractable arsenic concentration is observed to peak at this time as opposed to the time of peak inflow, suggesting an overall loading to the lake from an internal source. No significance is attached to the failure of arsenic to elevate coincident with measured manganese during the winter of 1982 because of the suspected lower extent of manganese solubilization for this period.

Although soluble concentrations of lead and chromium never reoccur to a sufficient degree to confirm a possible association with manganese, they have been associated in the literature with iron/manganese oxides (Lion et al, 1982, Leland and Shimp, 1973, Benjamin, 1983, and Forstner and Wittmann, 1983), and a possible association in Standley Lake cannot be precluded. They were not as strongly solubilized as arsenic in 1981, and it is possible that the subsequent periods of manganese solubilization were not sufficiently extreme to result in measurable releases. It is also possible that they could be precipitated or reabsorbed by particles suspended in the water column and be incorporated within the non-soluble fraction. For example, the data for acid extractable lead in the outflow shows increased concentrations for period of late summer of 1983, a time corresponding to manganese solubilization. Conversely, the data for acid extractable chromium do not suggest any association with manganese solubilization for this period, and the extent to which more extreme conditions might be significant relative to chromium solubilization is not known.

Trends for soluble barium or mercury provide a contrast to those for arsenic, lead and chromium. They do not show any tendency to associate with manganese solubilization, and as has been discussed previously, these metals appear to cycle primarily in response to inflow patterns. However, because of present seasonal elevations of mercury and unknowns relative to the extent to which release of metals might

CONCLUSIONS

The lake presently appears to be in a moderately degraded state relative to exposure to metals regulated by the primary standards in the Safe Drinking Water Act. Inputs of metals are observed to occur, and it appears that the lake can act as sink for selected metals. At present, a release of manganese is observed to occur in association with periods of low hypolimnetic dissolved oxygen during the summer. With respect to the trace metals regulated under the USEPA primary drinking water standards, the trends observed for arsenic suggest an association with the release of manganese. Evidence for associations with chromium and lead is less firm. Nonetheless, an association appears to be possible. All of the information developed for this study suggests that iron is associated with particulate content and that conditions which would promote iron solubilization may not presently exist. This gives cause for concern relative to implication for additional release of metals associated with iron in the sediments upon further depletion of hypolimnetic dissolved oxygen within the lake. Because conditions within the hypolimnion can approach anoxia, factors which might cause further depletion of dissolved oxygen are of specific concern with respect to additional manganese release, initiation of iron release, and additional release of trace metals that may be associated with iron and manganese.

With respect to drinking water standards, analyses of finished water indicate that present problems may periodically exist relative to meeting standards for mercury and selenium. In addition, trends for soluble metals suggest a potential problem with arsenic and, to a lesser extent, lead. Depending on the extent of accumulation in the lake sediment, further degradation has the potential for increasing these problems. As a consequence of this and concern for significantly increased releases that could be associated with iron solubilization, it is recommended that further depletion of oxygen in the lower level of lake be minimized until a more definitive estimate can be made of overall impacts. To avoid further degradation, this will require control of nutrient loadings to manage in-lake productivity and limitation of the input of oxygen demanding substances. Several in-lake treatment options might be considered, however, their effectiveness and subsequent extent of exposure to other quality problems is not known. Therefore, they represent a less desirable alternative.

At present, it does not appear that either the Coors Brewery or the Coors/Golden Wastewater Treatment Plant represent a significant source of the acid extractable

fraction of metals under evaluation in this study. However, the use of more complete digestion techniques for the analytical work may result in a different conclusion of overall significance. In addition, exposure of the Coors/Golden Wastewater Treatment Plant to wastes from a large industrial complex raises concern for sudden changes in quality that can be associated with modifications or additions to facilities.