

EFFECTS OF STORAGE ON WATER TREATMENT PLANT SLUDGES

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(ABSTRACT)

The effects of in-basin storage of sludge on the iron, manganese, and TOC removal of water treatment plant (WTP) clarifiers and on the dewatering characteristics of sludge were examined. The use of chlorine dioxide as a preoxidant to retard observed detrimental effects was also investigated.

Sludge samples that were stored over a period of 120 days were found to release up to ten times the original supernatant concentration of iron and manganese from the sludge into the overlying supernatant liquor when sludge redox potential values decreased below +100 mV. Organic carbon also increased in the supernatant but to a lesser extent. Sludge dewatering characteristics as measured by specific resistance and capillary suction time were found to improve when sludge redox potential readings remained over 100 mV but varied greatly when readings were below this level.

Field monitoring and sampling of the clarifiers at Lee Hall WTP and Harwood's Mill WTP from April to July showed that the removal efficiencies of the clarifiers was not related to in-basin sludge storage. This conflicted with a later portion of the study and was thought to be due to the lack of standardized sampling techniques.

The final phase of the investigation dealt with the use of chlorine dioxide to retard the negative effects of in-basin storage of sludge. Sludge accumulation in clarifiers resulted in decreased iron and manganese removal efficiencies when chlorine dioxide was not used. Addition of chlorine dioxide improved the iron and manganese removal efficiencies of the clarifiers. Sludge dewatering characteristics were found to improve with the use of chlorine dioxide as a preoxidant.

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I. INTRODUCTION

The City of Newport News Department of Public Utilities furnishes water for one-third million customers on the lower Virginia peninsula. Its service area encompasses the Newport News-Hampton metropolitan area, as well as the more rural areas in the counties of Poquoson, York, and James City. Two water treatment plants (WTP) are operated to supply the area. The largest plant is the Lee Hall WTP with a capacity of 57 million gallons per day (MGD) building a 24 MGD facility to replace the existing Harwood's Mill facility that is to be completed in 1987.

The treatment processes at both plants are similar. Water is drawn from the reservoir and alum is added prior to flash mixing, flocculation, and sedimentation. Dual-media filtration is then provided followed by the addition of chlorine, fluoride, and polyphosphate prior to distribution. Two different types of sedimentation basins are currently in use. Half of the basins at the Lee Hall WTP are rectangular clarifiers that are equipped with rake mechanisms and pumps that continually remove sludge from the clarifiers. The remaining clarifiers at the Lee Hall plant, as well as the three clarifiers at the Harwood's Mill WTP, are similar except that they have no mechanism to remove sludge. Instead, the clarifiers are operated for four to eight weeks and then taken out of service to be drained and cleaned.

The plants receive water from different terminal reservoirs, but these reservoirs derive much of their water from the same source -- the Chickahominy River. This river passes through many low, swampy areas and

has a high total organic carbon (TOC) level. While the TOC level of the river water is often in the range of 11 to 12 mg/L, the influent to the treatment plants is somewhat lower (7-11 mg/l). The lower levels are characteristic of the Harwood's Mill reservoir. The high TOC content causes the water to have an extremely high trihalomethane formation potential (THMFP).

In 1981, Newport News was unable to comply with the primary maximum contaminant level (PMCL) of 0.10 mg/L for total THM's (TTHM'S). The State Department of Health granted a one-year exemption to the City to enable it to investigate different alternatives to solve the problem. One of the changes that enabled the City to successfully comply with the TTHM standard was to move the point of chlorination. Instead of prechlorinating, as had been done in the past, chlorination was delayed until just prior to filtration.

Although this enabled the City to meet the MCL, it had some undesirable consequences. These problems included shortened filter runs and a significant increase in macroscopic plant growth (bladderwort), and biological slime and microscopic invertebrates (Cyclops and Daphnia) in the sedimentation basins. There was also a concern that the sludge in the clarifiers that were not equipped with sludge removal-mechanisms were becoming anaerobic and releasing previously bound impurities such as iron and manganese into the water.

Another concern of the City was the effect that in-basin storage or lagooning of sludge might have on sludge dewaterability. It is possible that the City will be required to dewater the sludge in the future and the effects of lagooning on sludge dewatering and recycle of the

supernatant through the treatment plant were questions that required investigation.

The objectives of this study then were threefold:

1. to measure the effects of in-basin storage of the sludge on the quality of the clarifier effluent,
2. to determine the effects of sludge storage on the dewatering characteristics and the supernatant water quality, and
3. to investigate the effects of preoxidation of raw water with chlorine dioxide on the dewatering characteristics of the sludge and the quality of the clarifier effluent.

II. LITERATURE REVIEW

INTRODUCTION

The discovery in 1974 (Rook) of chloroform and other chlorinated organics in public drinking waters has since stimulated an extensive effort to develop strategies to reduce concentrations of these compounds to levels deemed safe. That same year, the drinking water in New Orleans was found to contain 66 organic compounds (Environmental Protection Agency, 1974) and was subsequently linked to an increased incidence of cancer in the residents of the City (Environmental Defense Fund, 1974; Environmental Protection Agency, 1975).

In 1975, (Symons et al.) the public drinking water supplies of 80 cities in the United States were tested to determine the levels of organics present and to determine what effects different treatments processes and diverse raw water sources play in the formation of trihalomethanes (THM's). The results indicated that THM's were present in almost all drinking water that had been chlorinated, but the levels varied greatly. The highest levels were found in systems where the raw water was a surface source, when chlorine was applied early in the treatment process, when a high residual dose of free chlorine was maintained, and when a precipitative softening process was employed. The principal THM found in almost every system was chloroform.

In 1976 the National Cancer Institute reported that chloroform had been found to cause cancer in male rats. Another study conducted in 1976

by the National Academy of Sciences reported that cancer could be a result of chronic exposure to a carcinogen and that it would be desirable to reduce exposure whenever possible. These and other studies confirming the occurrence of THM's in drinking water (Hoehn et al., 1977; Saunders et al., 1974; Scheimart et al., 1974) resulted in the EPA mandating a maximum contaminant level (MCL) of 0.10 mg/L in drinking waters (Environmental Protection Agency, 1979).

STRATEGIES TO CONTROL THM'S

Strategies to reduce THM's in drinking water have focused on modifying treatment processes, removal of THM precursors before the chlorination process, utilization of alternate disinfectants, and the removal of THM's once they have been formed. One of the most widespread control strategies has been to discontinue prechlorination of raw water in favor of chlorination at some later point. Culp (1984) reported that nine utilities that have adopted this approach have successfully reduced THM concentrations. This is also one of the control methods recommended by the EPA (1982) to reduce THM concentrations. This approach provides the opportunity to optimize the removal of THM precursors before chlorination is undertaken. There are major drawbacks to this strategy, however. One is the reduction in the disinfection capacity of the chlorine due to decreased contact time (Hoehn et al., 1978). Another problem is that biological slime (Culp, 1984) and aquatic plants tend to flourish in clarifiers that do not receive prechlorinated influent. There have been no studies published on the effect of discontinuation of prechlorination

on the removal efficiencies of clarifiers or on the characteristics of the sludges produced during treatment.

DISPOSAL OF WASTE SLUDGE

Prior to the 1960's little thought was given to the disposal of waste sludge from water treatment plants because sludges were usually returned to the receiving stream. The rationale for this procedure was that the only additional impurities added to the stream were the iron and/or aluminum hydroxides used to treat the water. Because these materials were relatively inert it was assumed that they had little impact on the receiving waters.

Increased public awareness of environmental problems resulted in the passage of the 1972 Federal Water Pollution Control Act (PL 92-500) which focused attention on any discharge into the nation's watercourses. Wastes from water treatment plants were classified as an industrial waste under this act and, therefore, will be subject to federal discharge standards in the future (Montgomery, 1985). Potential problems that such discharges could cause include sludge deposits, increases in color and/or turbidity, possible decomposition of the organic portion of the sludge, and the dissolution of iron and aluminum into the water.

Because of these problems and the probability of future regulation, many municipalities have begun to dispose of treatment plant sludge elsewhere. The most common form of treatment of such sludge is lagooning (AWWA, 1969). Lagooning is rarely a method of ultimate disposal, however, unless there is extremely inexpensive land available near the plant. More

often a lagoon is used to thicken sludges for later dewatering. Typical solids concentrations in a lagoon range from 1 to 10 percent (AWWA, 1969). One study conducted by Neubauer (1969) found that sludge in a 17 foot deep lagoon that had been in operation for three years had maximum solids concentration of no greater than 14 percent while the average solids concentration remained at 4.3 percent. It was also found in the study that the volatile content of the sludge remained high, about 27 percent.

Because Neubauer's criteria for disposal of sludge by landfilling stated that a minimum of 20 percent solids was needed, it was concluded that lagooning was not sufficient treatment by itself before landfilling. Montgomery (1985) stated that a properly designed lagoon with provision for decanting of the supernatant is capable of producing 4-6 percent solids after a month and that for design purposes a 5 percent concentration can be assumed after two to three months. Neubauer (1969) characterized the supernatant of the lagoon he studied as follows: BOD- 16 mg/L; COD- 5 mg/L; turbidity- 10 units; pH- 7.4; TS- 387 mg/L; SS- 24 mg/L; settleable solids- <0.1 mg/L; volatile solids- 8 mg/L. No mention was made of other effluent characteristics such as dissolved oxygen or iron and manganese concentrations.

No studies have been published modelling lagoons receiving alum sludge or what changes this sludge undergoes when it is stored in clarifiers. It is possible that it exhibits behavior similar to lake sediments, of which considerable material has been published. Iron and manganese are quickly oxidized in waters with a high dissolved oxygen content and tend to form hydroxides that become part of the bottom sediments of a lake. When a lake stratifies and forms an oxygen-deficient hypolimnion, the iron

and manganese often become reduced and solubilize into the water. Iron has been found to become reduced at redox levels of between 200 to 300 mV while manganese is found to become reduced at higher redox levels (Cole, 1979). This same phenomena may occur in clarifiers and lagoons when oxygen concentrations and redox levels drop.

CHARACTERISTICS OF ALUM SLUDGE

Alum sludge behaves as a non-Newtonian fluid (AWWA, 1971; Gates and McDermott, 1968). The BOD ranges from 36-90 mg/L but the COD is generally much higher varying from 500-15,500 mg/L (Neubauer, 1969; AWWA, 1971). Specific resistance values have been reported by various sources to be between 1.0 to 53.0×10^{13} m/kg (King et al., 1975; AWWA, 1969; Vesilind, 1969).

Several investigators have shown that particle size and particle-size distribution have a major effect on the dewatering characteristics of sludge (Karr and Keinath, 1978; Knocke et al., 1980). It appears that the larger the particle size and the narrower the particle size distribution, the easier a sludge is to dewater. This phenomenon can be explained in that there are less fines in the sludge to clog up the interstitial voids. Rudolfs and Heukelekian (1934) reported that fines are initially created in anaerobic digestion which causes the sludge to become more difficult to dewater. They also reported that as digestion proceeds the fines are destroyed and the dewatering characteristics improve.

There is practically no published literature on the effects of aging sludge on its dewatering characteristics. Calkins and Novak (1978) reported that after a period of a few months the sludge of the lagoons he sampled had higher specific resistances, varying from 50% to 100% increase in measured specific resistance (SR).

SUMMARY

The discovery of THM's in drinking water has stimulated major changes in water treatment processes. A modification which has gained wide acceptance is the discontinuation of prechlorination in favor of chlorinating at a later point. There has been no published research on the effects of this treatment change on the clarifier removal efficiencies and the sludge characteristics. Extensive research has shown that sludge dewaterability is a function of particle-size. What effect sludge age has on dewatering characteristics has also not been fully determined. The purpose of this study was to investigate the effects of the discontinuation of prechlorination on clarifier removal efficiency and sludge characteristics.

III. METHODS AND MATERIALS

In order to determine the changes in alum sludge characteristics over time as well as to analyze the sludge's effect on the overlying water column, it was necessary to conduct experiments on the sludge in a controlled environment and to evaluate the water quality and sludge characteristics in the actual WTP basins. Therefore, a series of fresh sludge samples were obtained and aged in a controlled laboratory environment. At the time of sludge collection, water samples from the basins were collected for analysis while the basins were in service and selected water-quality characteristics were described. The final aspect of the research, which was to determine the effects on the removal efficiencies of the clarifiers and the characteristics of the sludge generated when using chlorine dioxide as a preoxidant, involved obtaining sludge samples and water-quality data at several basin depths immediately prior to and throughout the period of preoxidant addition at the plant.

LABORATORY SAMPLES

Collection and Storage of Samples

Fresh alum sludge was collected on March 19, April 29, and June 17, 1985 for use in the investigation of the effect of seasonal changes. Sludge was collected from the discharge of Lee Hall clarifiers that were equipped with continual sludge removal mechanisms. These clarifiers were

cleaned daily, making it possible to obtain sludge that was approximately one day old. The sludge was collected and transported in clean, five gallon carboys packed in ice. Once they arrived at Virginia Tech the samples were transferred to half gallon Mason jars equipped with Teflon lids. In the first set of samples, an airspace of about an inch was provided, while subsequent samples were filled completely and tightly sealed. The samples were then stored in the dark, one set being stored in a 30°C incubator and another set stored in a 20°C constant temperature room. The jars were left undisturbed until, one by one, they were periodically sacrificed for analysis.

Analyses

During storage the samples separated such that a sludge layer was formed which occupied the bottom three to five inches of the jar and a clear to yellowish supernatant occupied the remaining five to seven inches of the jar. The supernatant and the sludge layer in each jar were tested and sampled in their undisturbed state. Then the contents were gently mixed and other tests were performed characteristics were monitored each time a jar was sacrificed:

1. The overlying supernatant liquor
 - dissolved oxygen
 - oxidation-reduction potential
 - soluble manganese
 - soluble iron

- total organic carbon
2. The sludge layer
 - oxidation-reduction potential
 3. The mixed contents of the jar
 - pH
 - particle count
 - specific resistance
 - capillary suction time

MONITORING AND SAMPLING OF CLARIFIERS WHILE IN SERVICE

Sampling and Analysis

Clarifiers from both the Lee Hall and Harwood's Mill treatment plants were profiled for dissolved oxygen (DO) and temperature and sampled weekly over a six month period. The profiles were taken at the influent, middle, and effluent ends of the clarifiers at one-foot intervals of depth. At the Lee Hall treatment plant, it was possible to evaluate two clarifiers that received the same influent, one of which was equipped to continually remove sludge while the other was not. At the Harwood's Mill treatment plant, none of the clarifiers were equipped with sludge-removal mechanisms. Samples taken and tests performed on the clarifiers at both plants were as follows:

1. Raw water (plant influent)
 - soluble manganese

- soluble iron
 - total organic carbon
2. Influent, middle, and effluent of clarifiers
 - dissolved oxygen profile
 - temperature profile
 3. Clarifier effluent
 - soluble manganese
 - soluble iron
 - total organic carbon

EVALUATION OF THE EFFECTS OF CHLORINE DIOXIDE ON WATER AND SLUDGE

CHARACTERISTICS

Sampling and Analysis

In order to observe the effects of chlorine dioxide as a preoxidant at the Harwood's Mill treatment plant, an extensive sampling program was undertaken immediately prior to the time chlorine dioxide was first added and again after chlorine dioxide had been fed for about two to four weeks. Sludge samples were taken from the influent portion of the clarifier basins by coring the sludge at the bottom of the clarifier using a one inch diameter PVC pole. Water samples were taken at different depths throughout the basin with a portable submersible pump. Because there were continual breakdowns of the chlorine dioxide feed equipment, it was not possible to test basins that had continually received influent that had been treated with chlorine dioxide. Clarifier characteristics were not

evaluated unless chlorine dioxide had been fed continuously for at least 48 hours. The evaluation period spanned the months of August and September, 1985.

The following analyses were performed:

1. Raw plant influent

- soluble manganese
- soluble iron
- total organic carbon

2. Influent, middle, and effluent of clarifiers

- dissolved oxygen profile
- temperature profile
- oxidation-reduction profile (before chlorine dioxide addition only)
- soluble manganese profile
- soluble iron profile
- total organic carbon profile

3. sludge from clarifiers

- specific resistance
- capillary suction time

ANALYTICAL PROCEDURES

Glassware Preparation

All glassware used to store samples, with the exception of that used for THM formation potential determination, was washed with soap and water, acid washed, rinsed with tap water, rinsed again with distilled water, and oven dried. The glassware used for THM formation potential determination was washed with soap and water and oven dried.

Dissolved Oxygen

Dissolved Oxygen (DO) concentrations were determined with a Yellow Springs Instrument Company (Yellow Springs, MD) Model 51B Oxygen Meter. The meter was air calibrated and the probe was gently stirred and allowed to equilibrate before readings were taken.

Oxidation Reduction Potential

Oxidation reduction (redox) potentials were determined using a Fisher Scientific (Raleigh, N.C.) Accumet Model 620 pH meter. An Orion (Cambridge, MA) double junction, silver chloride reference electrode and a Fisher Scientific bright-platinum, indicating electrode were used to determine redox potential. The probes were submersed approximately two inches into the supernatant and one inch into the sludge layer and allowed

to equilibrate for five minutes before readings were taken. Redox potential values are generally adjusted to reflect the difference from a standard hydrogen electrode at a temperature of 20°C and a pH of 7. This value is referred to as E_7 . The following formulae were used to convert the readings into standard form (Vassos and Ewing, 1983, p.44):

$$E_7 = E(\text{ref}) + E(\text{ind}) \quad [1]$$

where: $E(\text{ref}) = 222 \text{ mV}$ (value for Ag/AgCl electrode)

. $E(\text{ind}) = \text{mV reading of the meter}$

The E_7 reading was also corrected by subtracting 59.2 mV for every pH unit the sample was below 7. A full explanation of redox measurements can be found in Vassos and Ewing (1983).

Soluble Iron and Manganese

Soluble iron and manganese concentrations were determined using a Perkin-Elmer (Norwalk, CT) Model 760 Atomic Absorption Spectrophotometer (AA). All samples were acidified at the time of collection and refrigerated until analyzed.

Total Organic Carbon

Total organic carbon (TOC) concentrations were determined using a Dohrmann/ Envirotech (Santa Clara, CA) DC-54 ultra-low-level TOC analyzer. This system utilizes a UV-promoted, wet-chemical oxidation method with subsequent reductive pyrolysis and flame ionization detection to determine the TOC of the sample.

pH

Determinations of pH were made with a Fisher-Scientific Accumet Model 620 pH meter equipped with a Fisher Scientific combination electrode (Cat. No. 13-69-97).

Particle Count

Particle counts were performed using a HIAC (Menlo Park, CA) Model PC-320 particle size analyzer. The stirred samples were diluted tenfold to provide the proper density of particles such that the counts were accurate. Particle counts were performed over a range from 5 to 200 μm .

Particle counts were used to calculate a cumulative surface area of the particles. It was assumed that each particle was approximately spherical and the particle diameter was used to calculate what the surface area of a sphere would be. These data were then used to determine the percent surface area each discrete particle size category comprised.

Specific Resistance

Specific resistance (SR) measurements were performed as outlined by Vesilind (1979). A 100 mL sample sample was filtered through a No. 40 Whatman filter by applying a constant vacuum of 20 psig. Time was recorded for every 10 mL that was filtered. The results were plotted as time/volume versus volume. The slope b , was then obtained for the linear portion of the graph and was substituted into the following equation:

- . $SR = r^* = 2 b P A^2 / u w$ [2]
- . where; P = vacuum applied
- . A = surface area of the filter
- . u = viscosity
- . w = cake deposited / unit filtrate

Capillary Suction Time

Capillary suction time (CST) measurements were performed using a Triton (Essex, England) Type 165 CST apparatus and using Whatman No. 17 Chromatography paper. The procedure is outlined by Vesilind (1979). The CST is a measure of the time required for the liquid fraction of a sludge to travel one cm on a piece of blotter paper. A small portion of sludge is poured into a cylinder set on top of the paper and a timer measures the time required to travel between two concentric circles that are separated by one centimeter. It can provide a rough approximation of the SR for a particular sludge.

IV. RESULTS AND DISCUSSION

LABORATORY STUDIES

Water Quality

The sludge collected from the Lee Hall WTP was stored in Mason jars to simulate the conditions that would be encountered in a lagoon receiving sludge on an intermittent basis. These microcosms did not simulate conditions in a clarifier exactly because in the clarifiers there is a continual deposition of newly generated sludge.

The sludge appearance changed over time. All but one of the first set of samples that were collected on March 19th remained light brown during the 120-day storage period. After a period of a month a very thin, light orange/rust-colored layer developed about one a centimeter under the sludge surface. It was thought at that time to be an oxidized microzone; however, no analyses were performed to confirm the nature of this zone.

Figures 1 and 2 depict the temporal changes in TOC and soluble iron and manganese concentration in the water above the sludge. The redox potential of the sludge is also shown. It can be observed that the graphs are remarkably similar even though one set of samples was kept at 20°C while the other was kept at 30°C. In the 30°C sludge, however, the redox potential initially declined by 150 mV in a four week period and remained at approximately +100 mV for three weeks. At this time the lower three

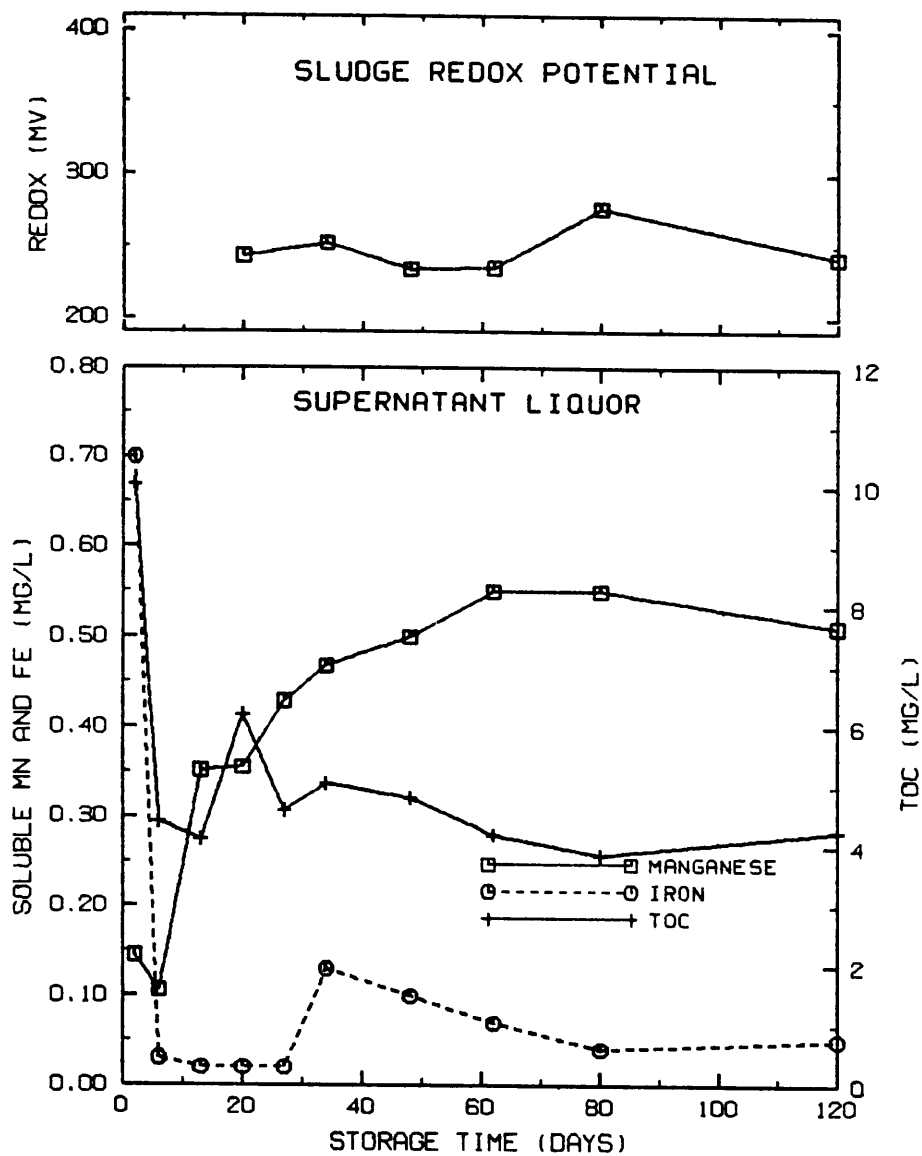


Figure 1. Variations in Aqueous Mn, Fe, and TOC above Sludge Layer. Sludge Redox Potential also Shown. Sample Collected on March 19, 1985. Storage Temperature, 20°C.

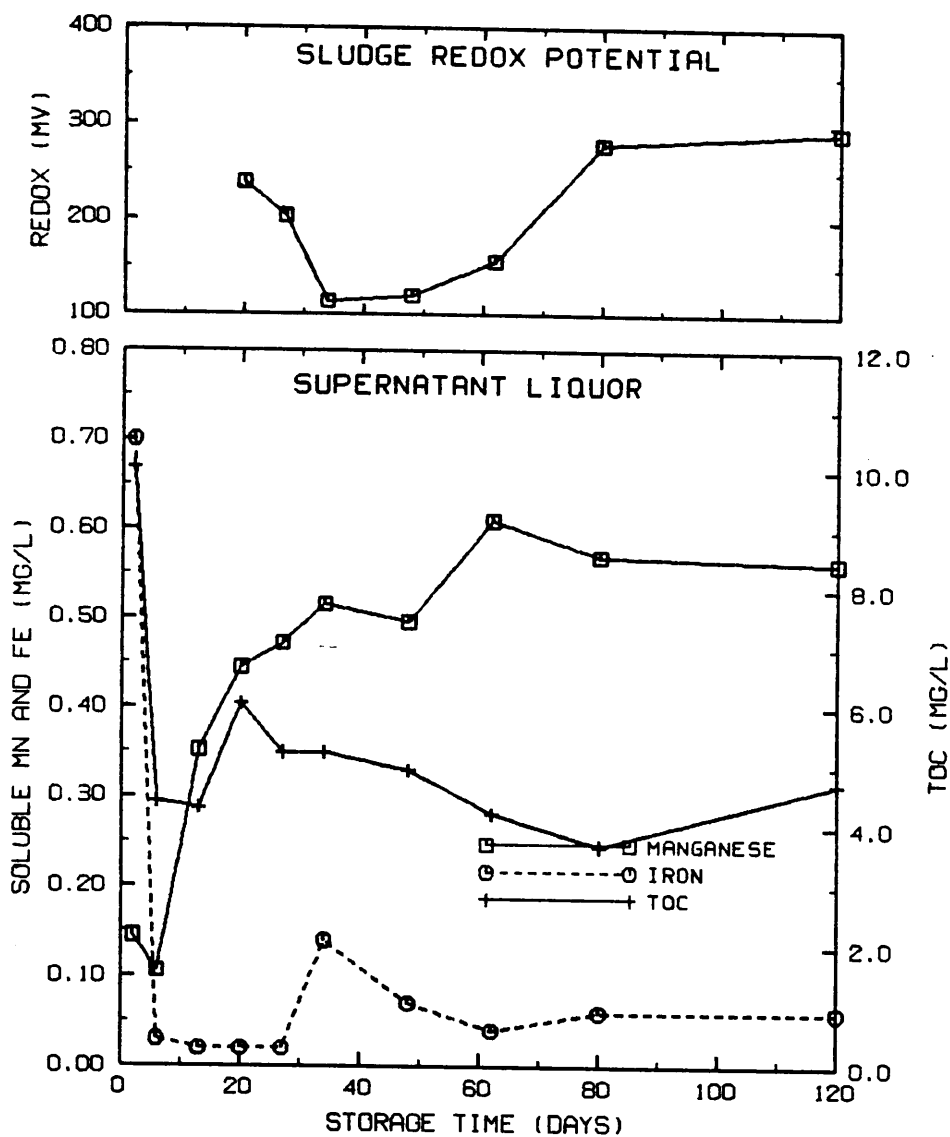


Figure 2. Variations in Aqueous Mn, Fe, and TOC above Sludge Layer. Sludge Redox Potential also Shown. Sample Collected on March 19, 1985. Storage Temperature, 30°C.

centimeters of the sludge turned black while the upper five centimeters of the sludge layer remained brown. The sludge then increased to the initial reading of 250 mV after it had been stored for 100 days. During the time period when the sludge redox potential decreased to 100 mV it was observed that the bottom two or three centimeters of the sludge turned black, while the upper five or six centimeters remained brown. No major change was noted in the quality of the overlying water, possibly because this black sludge was separated from the water by an overlying light-brown sludge layer that prevented release of much iron and manganese from sludge into the water.

After an initial peak, the TOC concentration remained fairly constant over time. The iron concentration remained near the detection limit of the AA (0.02 mg/L) except during the period between 30 and 60 days. Manganese levels, however, increased steadily during the first 40 days, then stabilized at approximately 0.5 mg/L. These data conform well to those observed in classical limnological studies of lake sediments (Cole, 1979). Manganese is released from lake sediments before iron and is oxidized and precipitated back into the sediments more slowly than iron. Iron reduction occurs at a redox potential of between 200 and 300 mV, a range which also seems to occur in the microcosms. A small amount of airspace (two to three centimeters) was inadvertently left in the jars and this air may have provided enough oxygen to reaerate the water and the sludge. This could be one explanation for why the DO of the water remained relatively constant. It is also possible that there was not enough organic material present to be degraded by microorganisms to cause much oxygen depletion.

Figures 3 and 4 depict sludge redox potential and the manganese, iron, and TOC concentrations in the water overlying the sludge collected on April 29th and stored for 106 days. It should be noted that the scale for the concentrations of iron and manganese is an order of magnitude greater than in Figures 1 and 2. The redox potential scale was also shifted to reflect the negative values encountered. The sludges collected on April 29th turned black in one week whether they were stored at 20°C or 30°C but were with covered a thin bright, rust-colored precipitate. At times, the overlying water-column transparency changed from clear to a translucent yellow. The redox potential values of all samples of sludge were negative one week after collection and storage and remained negative throughout the study. These values are indicative of a strong reducing environment for iron and manganese. The concentration of manganese in the supernatant liquor indicated that the environment, at least in the sludge, was indeed conducive to the reduction of manganese even though the DO level in the water column never fell below 3 mg/L except on one occasion when it was 1.6 mg/L. Throughout the test period, iron concentrations were much lower than manganese concentrations. It is possible that once the iron was reduced and released from the sludge, the high DO concentration of the water caused it to oxidize and precipitate. The oxidized microzone could in turn have acted as a sealant preventing reducing conditions in the water column. The manganese concentration in the supernatant reached high levels probably because it was reduced more rapidly than the iron and entered the water column before the oxidized microzone was formed.

Throughout the testing it was found that the TOC of the water remained fairly constant and appeared not to be dependent on any other measured

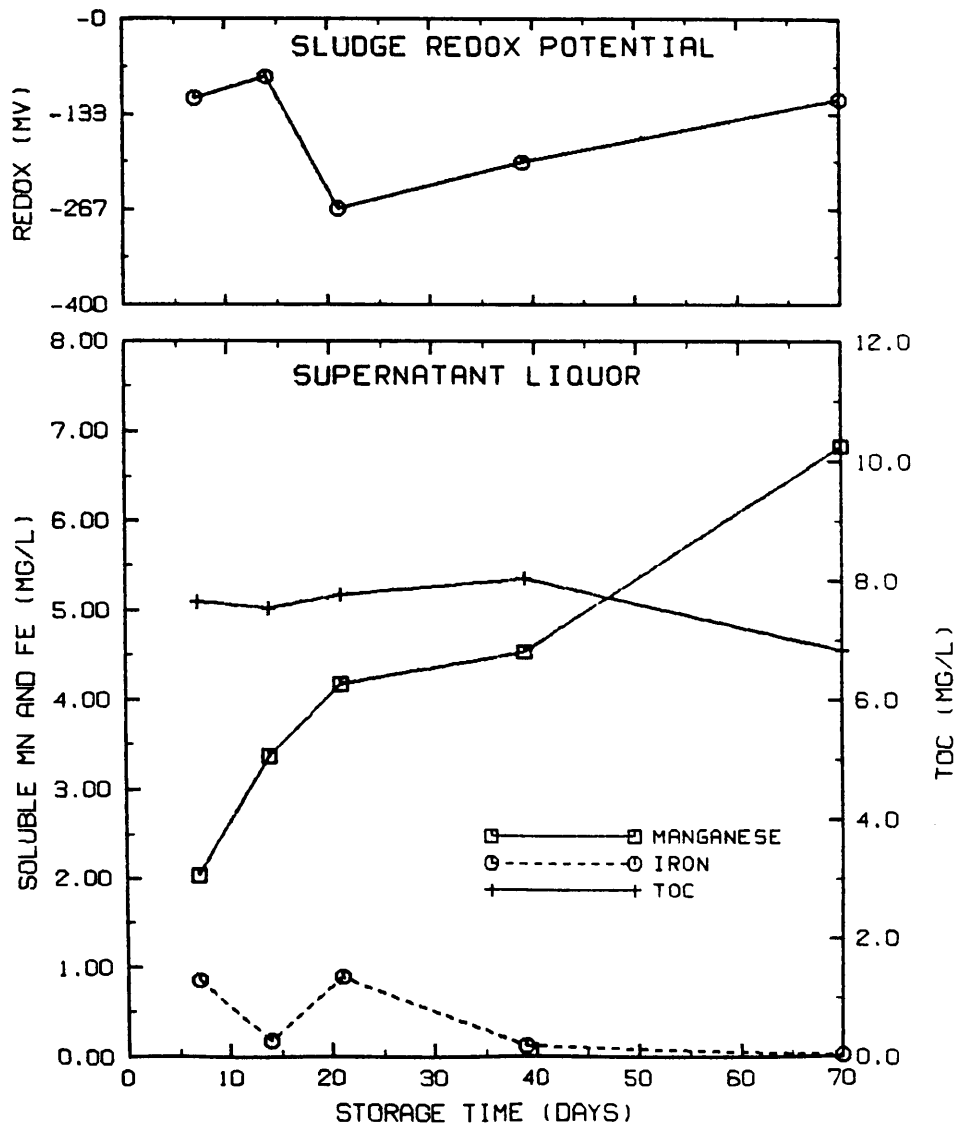


Figure 3. Variations in Aqueous Mn, Fe, and TOC above Sludge Layer. Sludge Redox Potential also Shown. Sample Collected on April 29, 1985. Storage Temperature, 20°C.

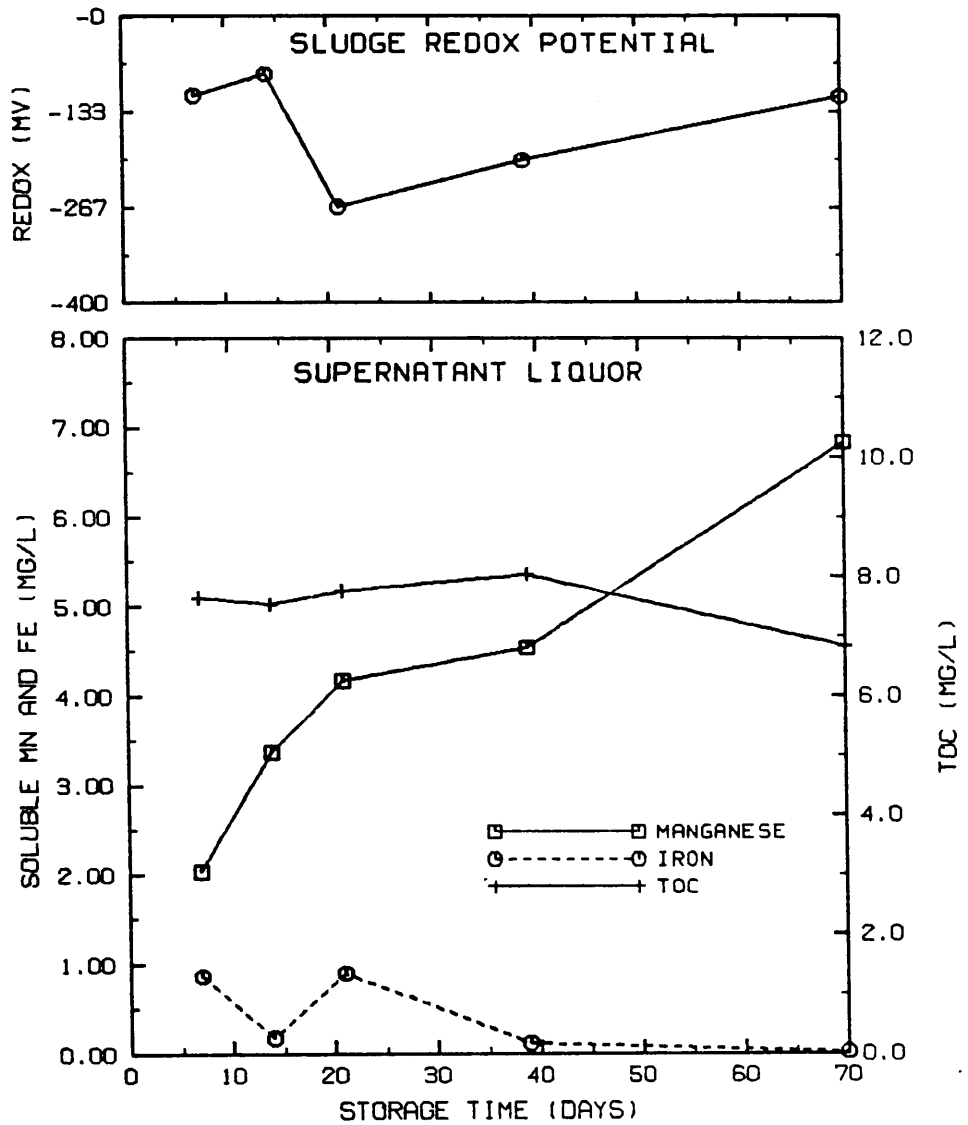


Figure 4. Variations in Aqueous Mn, Fe, and TOC above Sludge Layer. Sludge Redox Potential also Shown. Sample Collected on March 29, 1985. Storage Temperature, 30°C.

parameter. This could be the result of the oxidized microzone sealing the sludge from the supernatant such that soluble and colloidal organics that result from anaerobic decomposition, are not released into the overlying supernatant liquor.

Figures 5 and 6 show the water quality characteristics for the set of samples which were collected on June 17th. These samples turned black within a week. They differed from the earlier samples in that some of the jars were found to have rust colored precipitate on top of the sludge while others did not. Thus, some of the samples had oxidized microzones when tested and others did not. This explains some of the anomalies in the data presented in Figures 5 and 6. Whenever a sample that had an oxidized microzone was tested, it was found to have a very low concentration of iron in the supernatant liquor. Conversely, when an oxidized microzone was absent, the iron concentrations were found to be of the same order of magnitude as the manganese concentrations. DO concentrations averaged 0.5 mg/L in the samples that did not have a microzone and the sludge of these samples had a lower redox potential than the samples that did have a precipitate layer.

The effects of the microzone on overlying water quality can be illustrated by observation of the sludge stored at 30°C. A precipitate was found on the sludge that was tested at 15, 30, and 38 days. The levels of iron in the water columns for these jars averaged 0.08 mg/l compared to 4.18 mg/l for the jar tested at 21 days.

The TOC concentration in the supernatant liquor also increased at approximately the same rate as that of manganese. The similar rate of

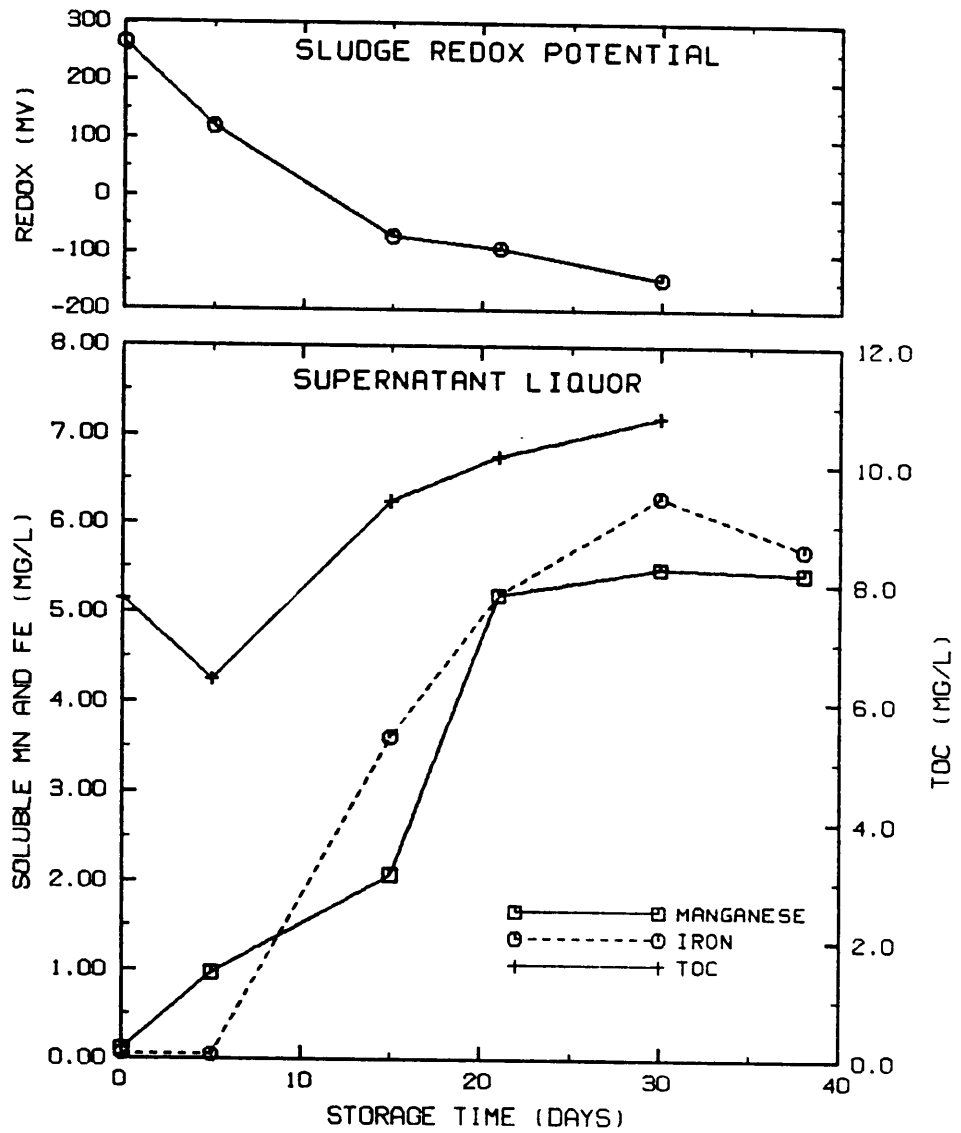


Figure 5. Variations in Aqueous Mn, Fe, and TOC above Sludge Layer. Sludge Redox Potential also Shown. Sample Collected on June 17, 1985. Storage Temperature, 20°C.

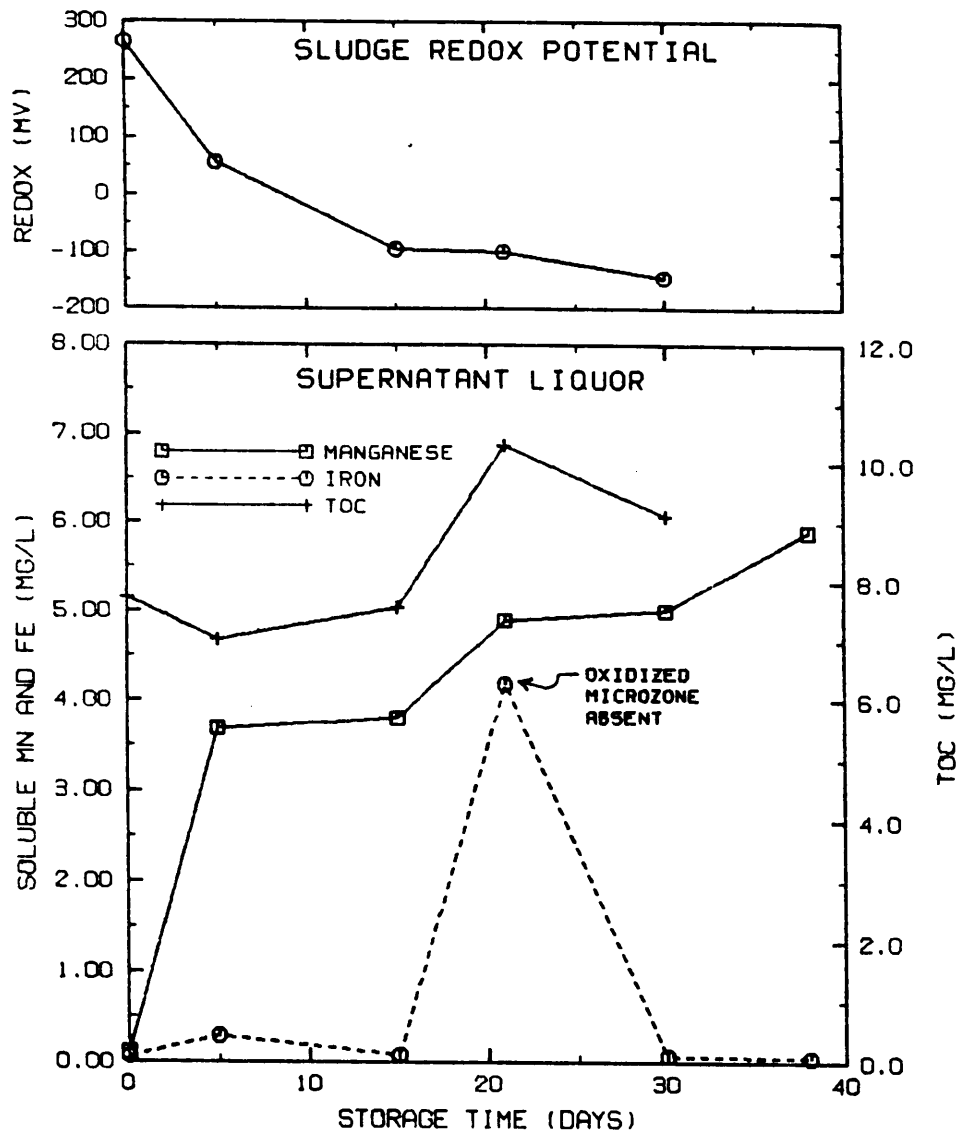


Figure 6. Variations in Aqueous Mn, Fe, and TOC above Sludge Layer. Sludge Redox Potential also Shown. Sample Collected on June 17, 1985. Storage Temperature, 30°C.

increase in both the TOC and manganese could have been caused by an organic-manganese colloid being formed.

Figure 7 is similar to Figure 6 except that the iron data from the jars with an oxidized microzone is excluded and all data from microcosms with no microzones are included. This figure clearly shows that the formation of an oxidized microzone and the concentration of iron in the water column are closely related. Table 1 shows the result of a number of jars that were tested at the same time. Some of these samples had an oxidized microzone while others did not. It can be seen that the presence of a microzone resulted in low concentrations in the supernatant liquor and in lower TOC levels in all of the samples but one.

The following observations can be made about the supernatant liquor of the microcosms. It appeared that the character of the sludge changed markedly between March 19th and April 29th. Figures 8 and 9 summarize previously presented manganese concentrations in the

three microcosms. The second and third set of samples exhibit similar concentrations of manganese while the first set of samples is extremely low by comparison. Similar results would be noted if the iron levels of the samples were compared, taking care to exclude the samples with an oxidized microzone. The sludge from the second and third set of samples also displayed characteristics of anaerobiosis after a week, while only one jar of the first set of samples showed any signs of anaerobiosis during the 120 day test period. A possible explanation for this marked change could be that the reservoir underwent a spring overturn which caused organic material and iron and manganese to be suspended in the

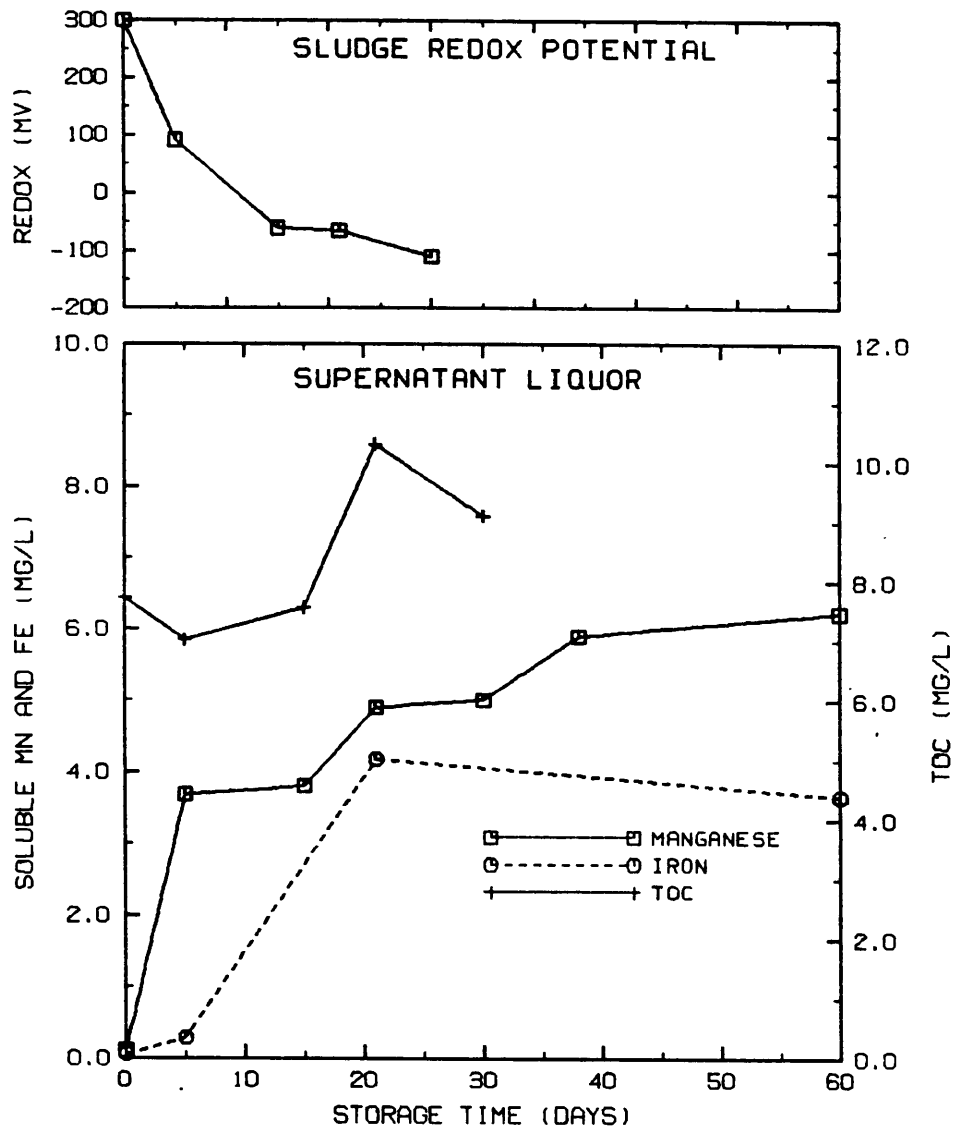


Figure 7. Variations in Aqueous Mn, Fe, and TOC above Sludge Layer. Sludge Redox Potential also Shown. Sample Collected on June 17, 1985. Storage Temperature, 30°C. No Microzone Present in Samples.

Table 1

Comparison of TOC, and Soluble Iron and Manganese in Microcosms with and without Oxidized Microzones.

Date Sample Collected	Storage time (days)	Storage Temp (°C)	Oxidized Microzone Present?	Fe (mg/L)	Mn (mg/L)	TOC (mg/L)
4/29/85	106	20	yes	0.02	5.20	5.5
4/29/85	106	20	yes	0.02	5.13	5.7
4/29/85	106	20	yes	0.02	4.56	5.2
4/29/85	106	30	yes	0.02	4.91	6.6
4/29/85	106	30	yes	0.02	4.01	6.3
4/29/85	106	30	yes	0.02	4.72	6.1
6/17/85	57	20	no	3.71	5.87	10.4
6/17/85	57	20	yes	0.02	3.86	7.0
6/17/85	57	20	yes	0.02	5.43	6.8
6/17/85	57	30	yes	0.02	6.1	10.1
6/17/85	57	30	no	3.57	5.37	9.8
6/17/85	57	30	no	3.76	7.28	10.7

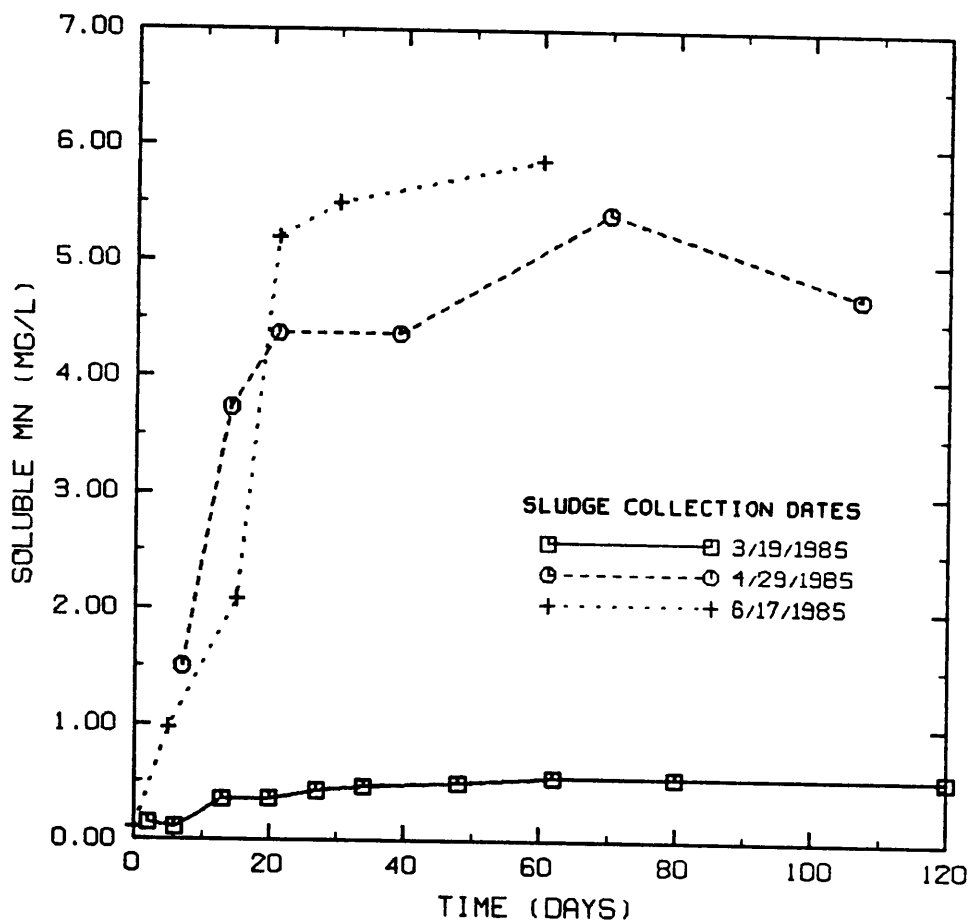


Figure 8. Comparison of Aqueous Manganese in Supernatant Liquor for Samples Collected at Different Dates. Storage Temperature 20°C.

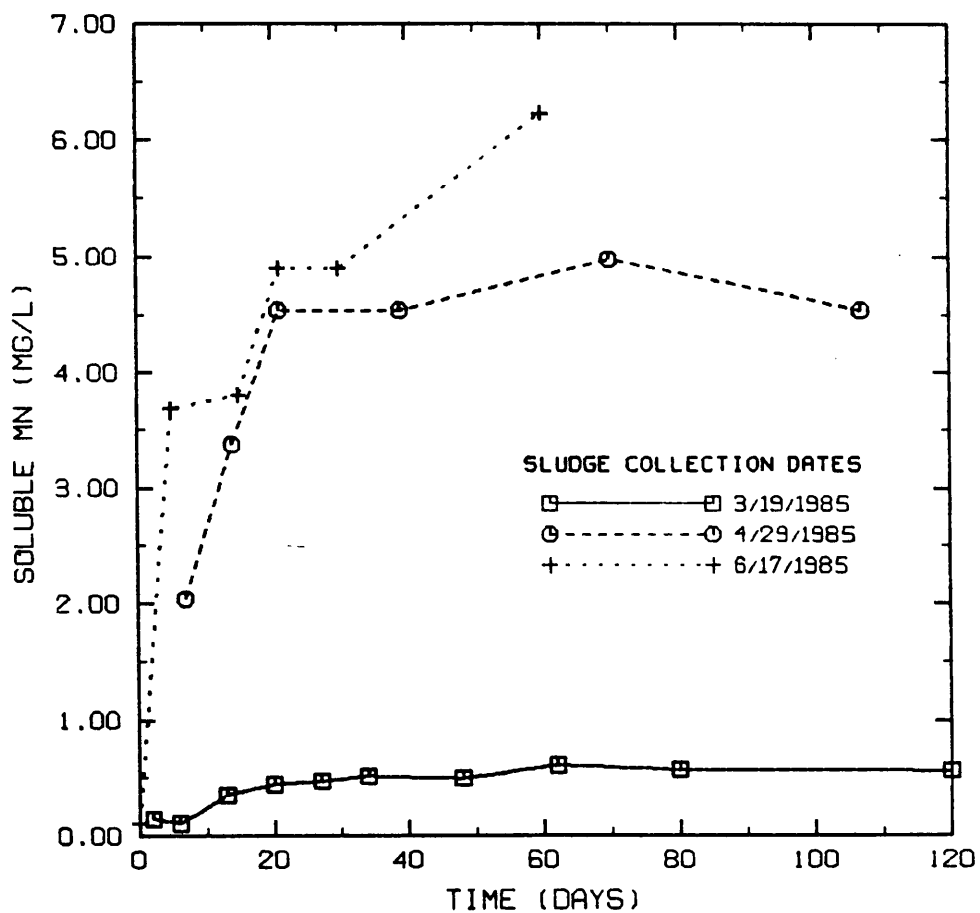


Figure 9. Comparison of Aqueous Manganese in Supernatant Liquor for Samples Collected at Different Dates. Storage Temperature 30°C.

water, to enter the influent of the treatment plant, and to be incorporated into the sludge.

It is quite possible that the precipitate observed in the jars was an artifact of the testing procedure (holding the sludge in jars). In a clarifier, the continual deposition of sludge probably would prevent the formation such a layer. However, in a lagoon that intermittently receives sludge, it is possible that such a layer could form. In any case, it appears that changes in raw water quality can alter the sludge that collects in the basin such that they have the potential to be anaerobic in less than a week. Once anaerobic conditions develop, previously bound iron and manganese can be released into the water column, causing the iron and manganese removal efficiencies of the clarifiers to deteriorate rapidly. In a lagoon that has a high proportion sludge to overlying water, high levels of iron and manganese might be found in the supernatant effluent discharge. The increase in TOC that was noted in the samples that had no oxidized microzone suggests that TOC might also increase once the sludge became anaerobic. The potential for deterioration in water quality caused by supernatant discharges from a lagoon might make it necessary to discharge the supernatant downstream from the raw influent or to pretreat the supernatant before it is discharged.

Sludge Dewatering Characteristics

Figures 10 and 11 show the variations in the specific resistance (SR) and the capillary suction time (CST) of the sludge samples during storage. The curves depicting the changes in both the SR and CST exhibit the same

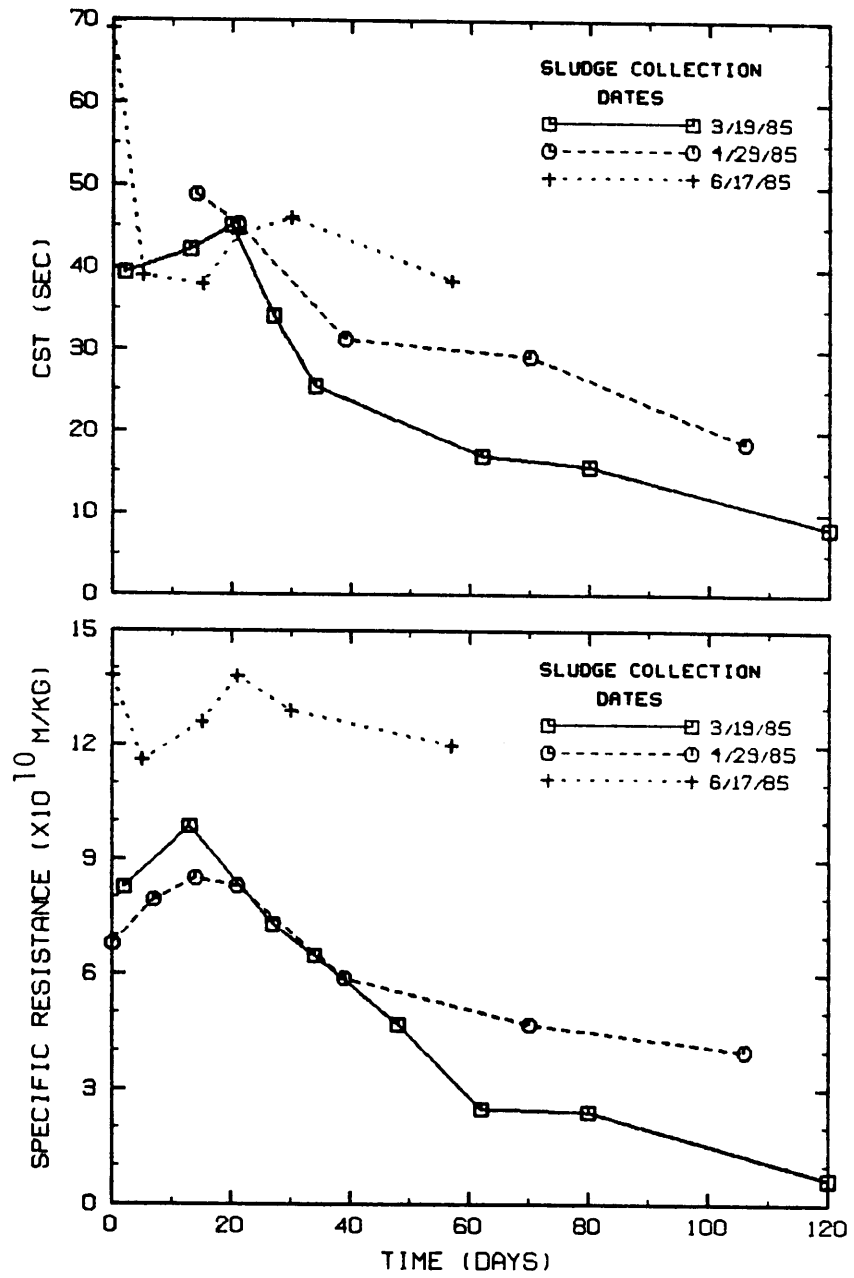


Figure 10. Comparison of Sludge Dewatering Characteristics. Storage Temperature, 20°C.

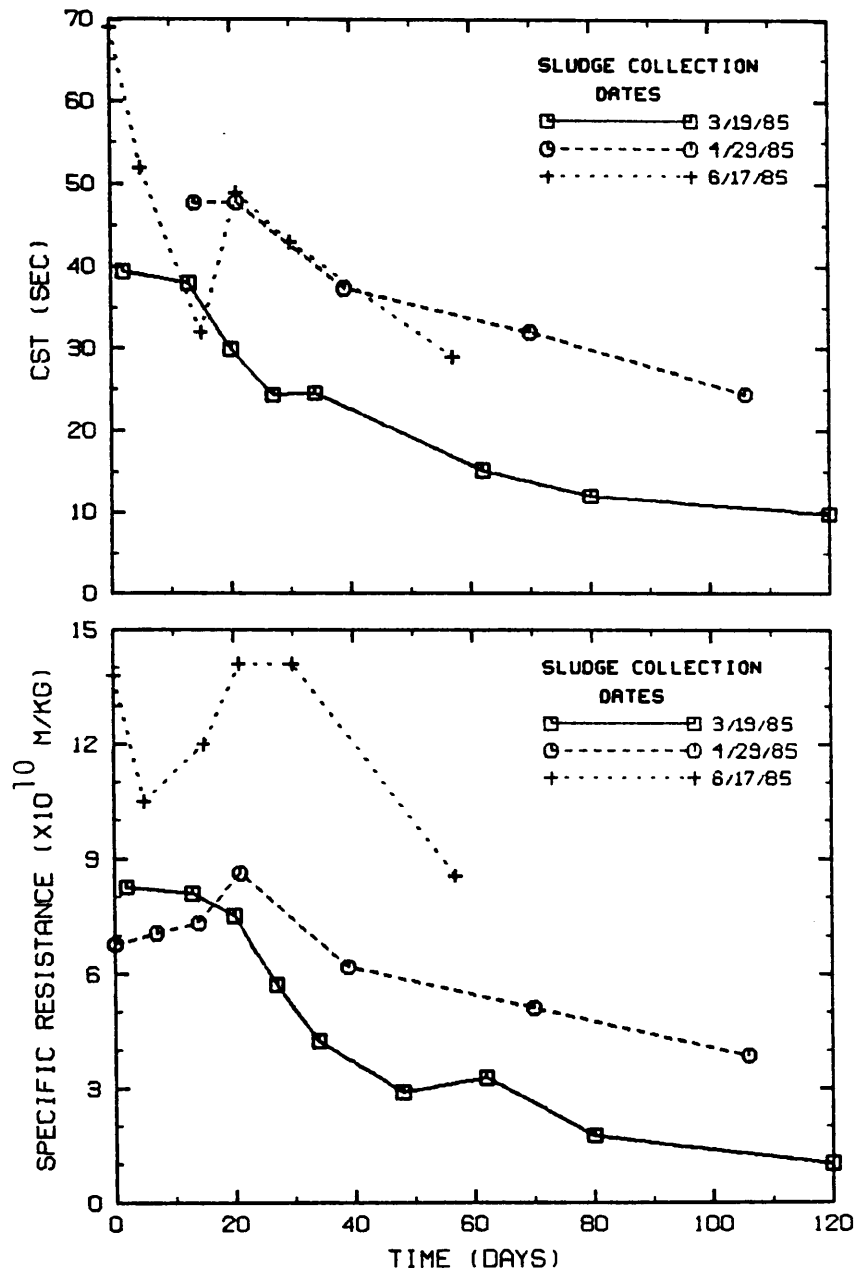


Figure 11. Comparison of Sludge Dewatering Characteristics. Storage Temperature, 30°C.

general trend for each sludge. Sludge in the the first and second sets of microcosms became easier to dewater as it aged. This trend was most noticeable in the first set of samples. A decrease of almost an order of magnitude in SR occurred during the 120 days of storage. The SR of the second set of sludges decreased by about 50% over a period of 106 days. Data from the third set of samples showed no clearly discernable trend but a well defined decrease in SR and CST with storage was not evident.

Sludge dewatering characteristics appear in part to be related to the sludge redox potential. When the redox potential declined, the sludge became more difficult to dewater. It appears that as the sludges became anaerobic, they were increasingly difficult to dewater. If this is so then sludges with a high organic content may ultimately be harder to dewater after being stored than a sludge with a low organic content.

The trend for the sludge samples to become easier to dewater could be due to chemical changes that result in particle growth over time. This was particularly evident in the sludge samples collected in the early spring. If particle growth was occurring it should be reflected by changes in the particle size distribution as storage time increased. Figure 12 shows that the mean particle size did increase with storage for the sludge collected April 29th. that represents the cutoff point has become 65 μm . At the same time the specific resistance decreases from 8.3 to 4.7×10^{10} m/kg. The specific resistance of the sludge did not have a well defined trend nor did it have a well defined shift in particle size distribution. Figure 12 depicts the overlap of the particle counts from sludge collected June 17th.

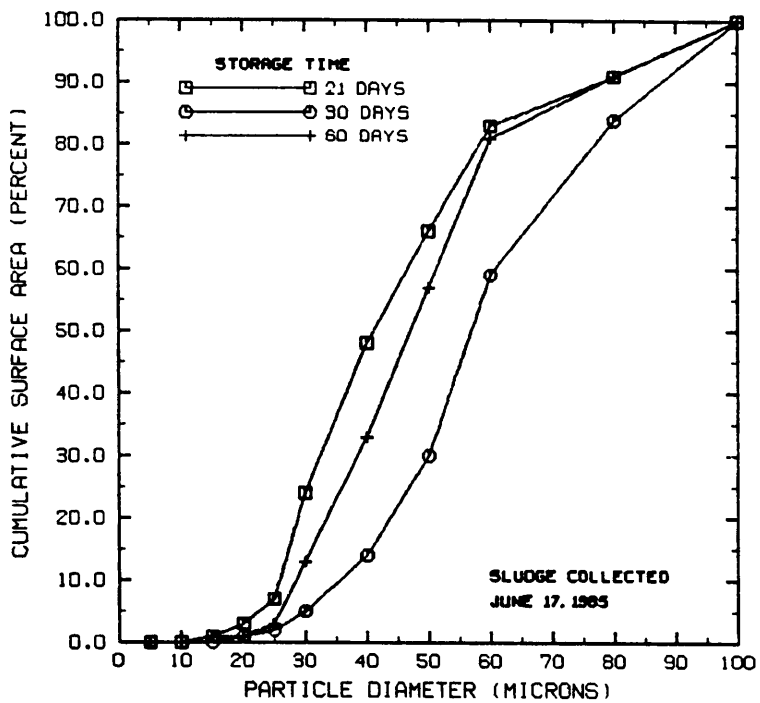
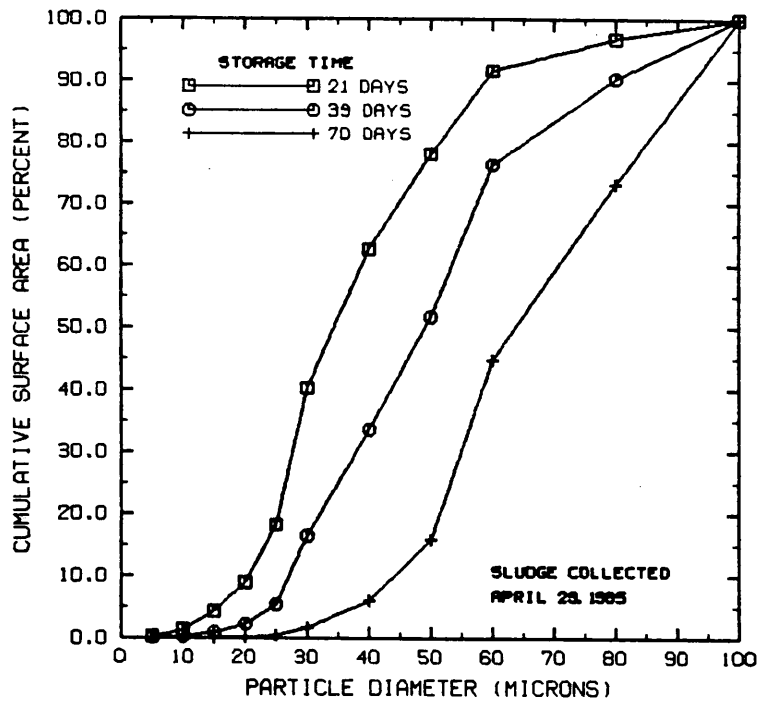


Figure 12. Comparison of Cumulative Surface Area Distributions. Samples Collected April 29 and June 17, 1985. Storage Temperature, 20°C.

In no case was there a clearly discernible increase in SR or CST with time. Samples 1 and 2 tended to become easier to dewater over time, while sample 3 showed no well defined change. Increases in the organic content of sludge samples might lead to higher SR and CST values if anaerobic decomposition is an important factor in adversely impacting the dewatering characteristics of the sludge. It would also be likely that wide variations in the dewatering characteristics of samples would occur with high organic content because of differing rates of decomposition. This could explain the lack of a well defined trend in the SR and CST results obtained from the third set of samples. It would also explain why Calkins and Novak (1973) found that the specific resistance of lagooned alum sludge increased over time. Results of sludge samples that had been stored in a clarifier and which are presented later in this section also exhibit increases SR, possibly due to this phenomena.

What appears to be occurring is two separate changes which are influencing sludge dewatering characteristics. First, there is a chemical aging process resulting in particle growth as the sludge is stored. The second change is biological activity which is producing fines that cause a decrease in the sludge dewatering rate. In the sludge that was collected in the early spring it appears that the chemical aging process was the predominant factor. The sludge collected later in the year shows indications that biological activity was also influencing sludge properties.

If particle growth tends to occur with time when the sludge remains aerobic then processes which tend to keep a sludge aerobic should maintain or improve a sludge's dewatering characteristics. On the other hand, as

a sludge is exposed to anaerobic conditions it would become more difficult to dewater. Lagoons concentrate sludge and so would tend to promote anaerobic conditions by separating the sludge from an overlying column of oxygenated water. Therefore it would follow that sludges, especially with a relatively high organic content that were stored in lagoons would tend to become more difficult to dewater over time. Anything which could inhibit the onset of anaerobic conditions could have a beneficial effect on the dewatering characteristics of the sludge. In addition, if sludges are stored at low temperatures which would retard biological activity, the dewatering characteristics might improve. Winter storage of sludge might be acceptable even if summer storage were not. Also, the design of lagoons to maintain aerobic conditions might be a good policy. This could entail the use of chlorine to retard biological activity or the design of shallow lagoons to permit reaeration by the atmosphere.

MONITORING AND SAMPLING OF CLARIFIERS

Two clarifiers from the Lee Hall Treatment Plant and one from Harwood's Mill were monitored and sampled over a 108 day period. Dissolved oxygen and temperature profiles of the basins were determined at the influent, middle, and effluent portions of the clarifiers approximately once a week. In addition, raw influent and clarifier effluent samples were collected for analysis of soluble iron and manganese. Total organic carbon analyses were also performed on some of the samples.

Monitoring and sampling of the two clarifiers at the Lee Hall WTP permitted the direct comparison of the water in clarifiers with and

without sludge removal mechanisms. There were major differences in the dissolve oxygen profiles taken at the influent portion of the clarifiers. Profiles taken at the middle and effluent portions did not vary nearly as much, the most likely reason being that the majority of sludge settles out in the first half of the clarifier. Figures 13 through 16 compare the dissolved oxygen profiles of Clarifier 3, the manually cleaned basin, with those of Clarifier 5, which was equipped with a mechanical removal mechanism. These figures show that the dissolved oxygen levels remain the same in Clarifier 5 while there was a progressive decline and subsequent reestablishment of aerobic conditions in Clarifier 3 during a one month period. These profiles were representative of those observed at both the Lee Hall and Harwood's Mill WTP'S throughout the testing period.

Figure 13 depicts the DO condition of Clarifier 5 with that of Clarifier 3 four days after it had been cleaned and returned to service. It can be seen that the DO levels in the first ten feet of both clarifiers were not significantly different. At ten feet, the DO sharply decreased, and the bottom two feet of Clarifier 3 contains an oxygen concentration of less than 1 mg/L. Later studies at the Harwood's Mill WTP indicated that the decline of dissolved oxygen levels to less than 2 mg/L was coincidental to the presence of a sludge blanket. There was never a temperature gradient of more than two degrees in the clarifiers indicating that there was no thermal stratification. Figure 14 shows the condition of Clarifier 3 after it has been in service for 11 days. Dissolved oxygen levels began to decrease at the 8 foot level and were less than 2 mg/l for the bottom six feet. Figure 15 shows that after the basin had been in service for 24 days the DO levels had deteriorated to a point that the

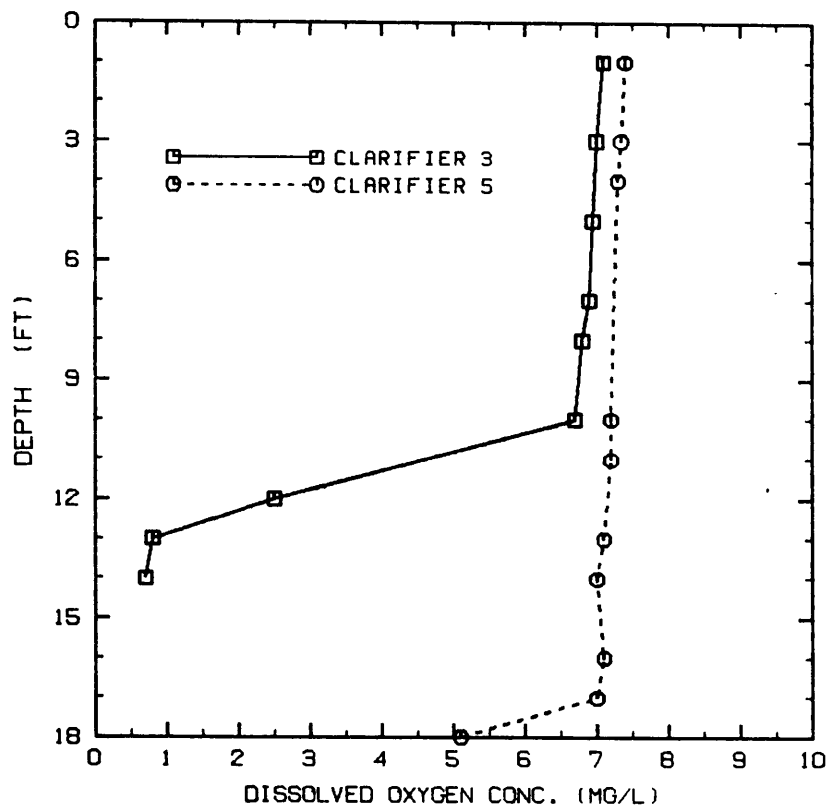


Figure 13. Dissolved Oxygen Profile at Influent End of Lee Hall Clarifiers. Influent of Lee Hall Clarifiers 3 and 5. June 28, 1985.

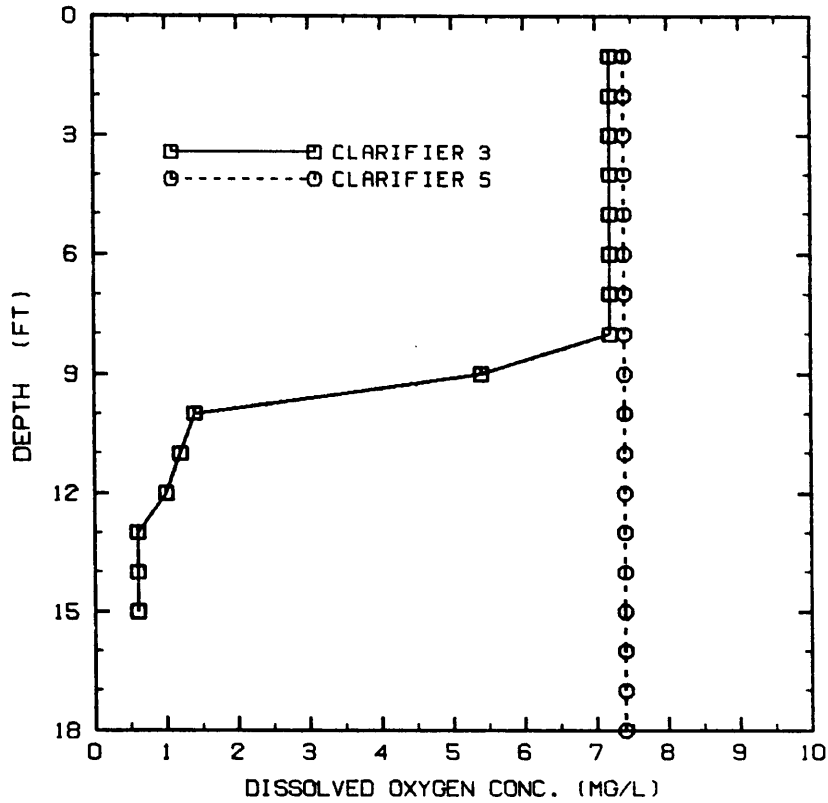


Figure 14. Dissolved Oxygen Profile at Influent End of Lee Hall Clarifiers. Influent of Lee Hall Clarifiers 3 and 5. July 5, 1985.

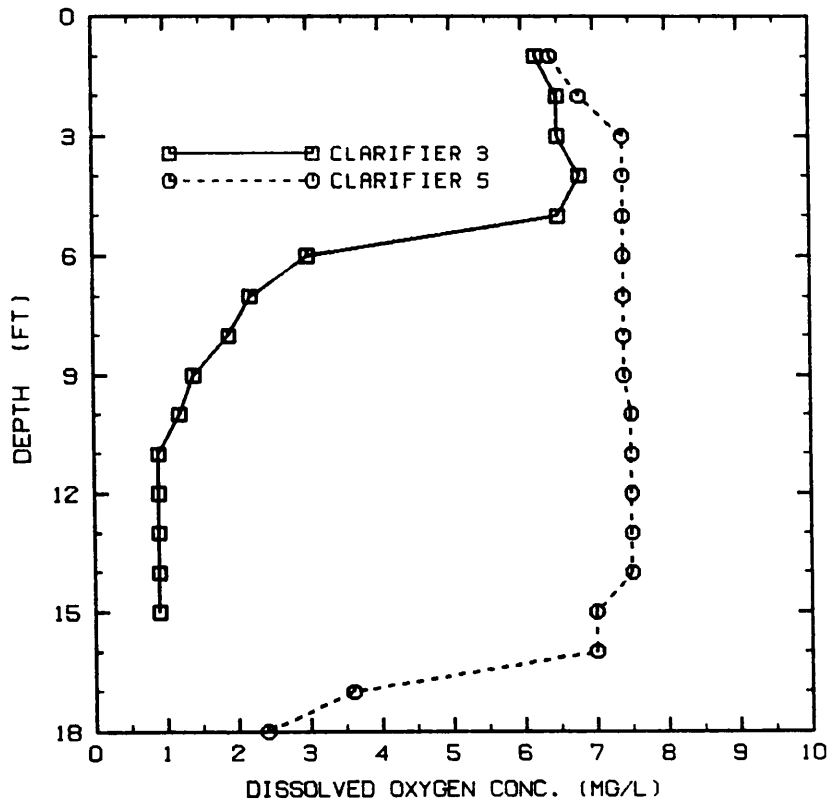


Figure 15. Dissolved Oxygen Profile at Influent End of Lee Hall Clarifiers. Influent of Lee Hall Clarifiers 3 and 5. July 18, 1985.

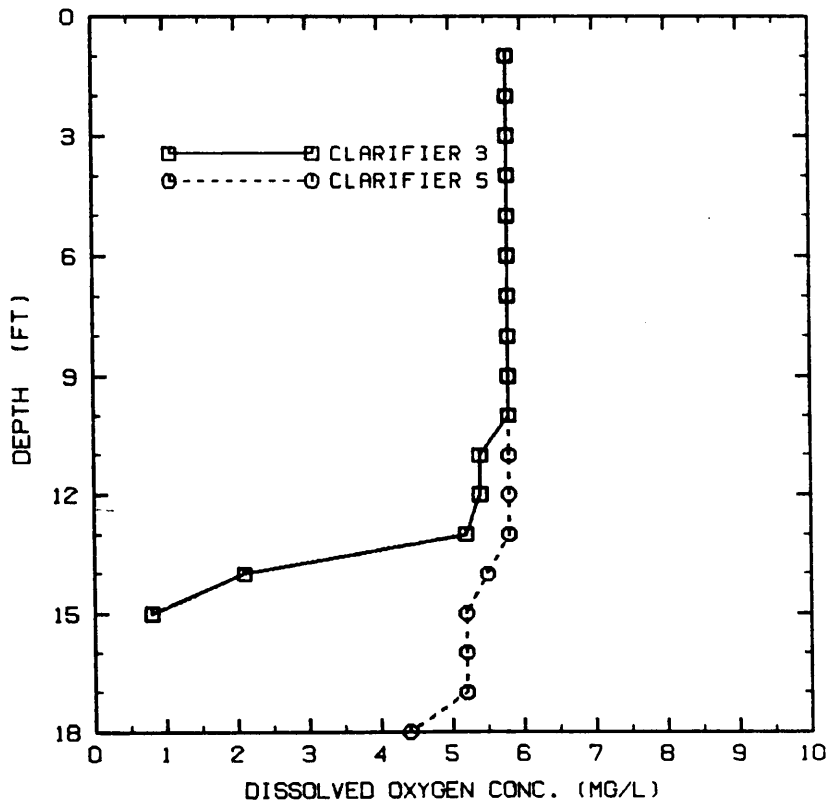


Figure 16. Dissolved Oxygen Profile at Influent End of Lee Hall Clarifiers. Influent of Lee Hall Clarifiers 3 and 5. August 2, 1985.

concentrations dropped sharply at the 5 foot depth, and levels of less than 2 mg/l were noted in the bottom seven feet of the clarifier. The clarifier was cleaned shortly thereafter, and Figure 16 shows the reestablishment of high DO levels in Clarifier 3 two days after it has been returned to service.

The decline in dissolved oxygen in Clarifier 3 indicates the presence of a reducing environment similar to the one found in the jars of sludge that were held in a controlled environment. One would expect, therefore, that iron and manganese would be released from the sludge. A comparison of the effluent iron and manganese levels with those of Clarifier 5 should show the difference in iron and manganese removal efficiencies over time in Clarifier 3.

Figures 17 and 18 show the levels of iron and manganese detected in the raw influent and in the effluent from clarifiers 3 and 5 from April 16th to August 2nd. No preoxidant was being added at this point. Figure 17 shows that the manganese removal efficiency was extremely erratic. Vertical lines have been drawn on the figures to indicate when Clarifier 3 was cleaned. From these data, it appears that there was little, if any, correlation between decreased manganese removal efficiencies and the accumulation of sludge in the clarifiers. Figure 18 indicates that the same trend was true for iron, with the removal efficiency remaining erratic and independent of any other measured parameter.

The lack of deterioration of the removal efficiency of Clarifier 3 with the accumulation of sludge indicates that there were factors other than sludge accumulation that were more important. Conditions such as varying hydraulic loading, the use of polymer, etc. could exert major

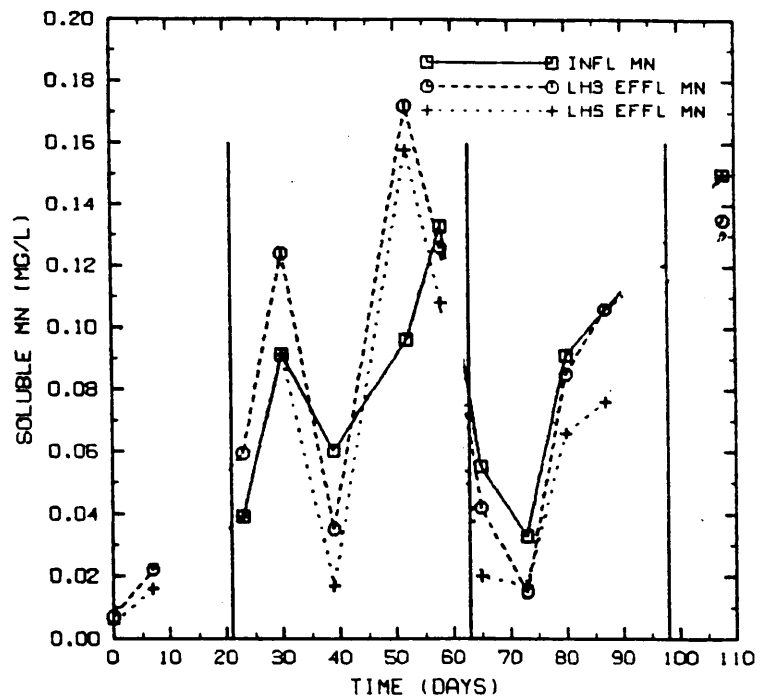
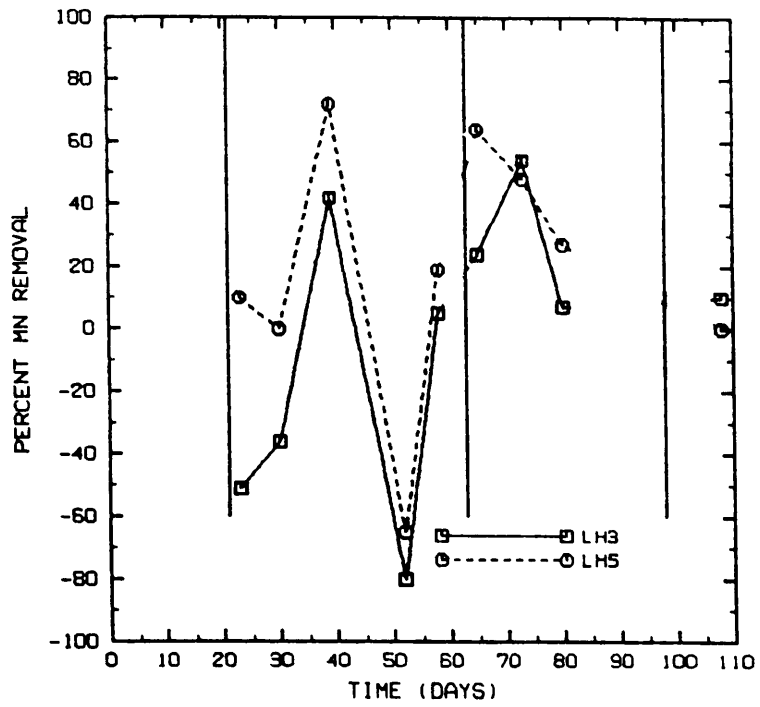


Figure 17. Manganese Removal in Lee Hall WTP Clarifiers 3 (LH3) and 5 (LH5) from April 16th to August 2nd. Vertical lines indicate when Clarifier 3 was cleaned.

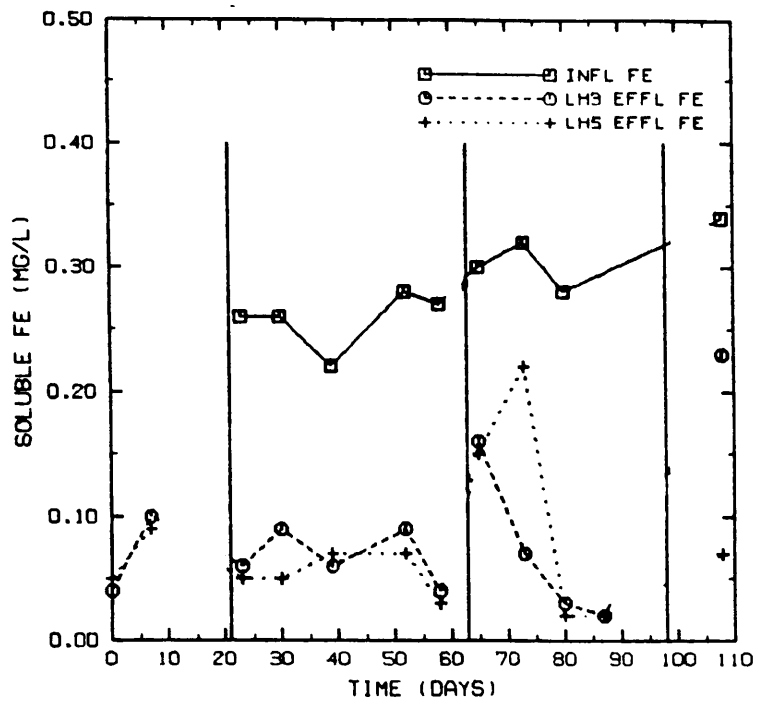
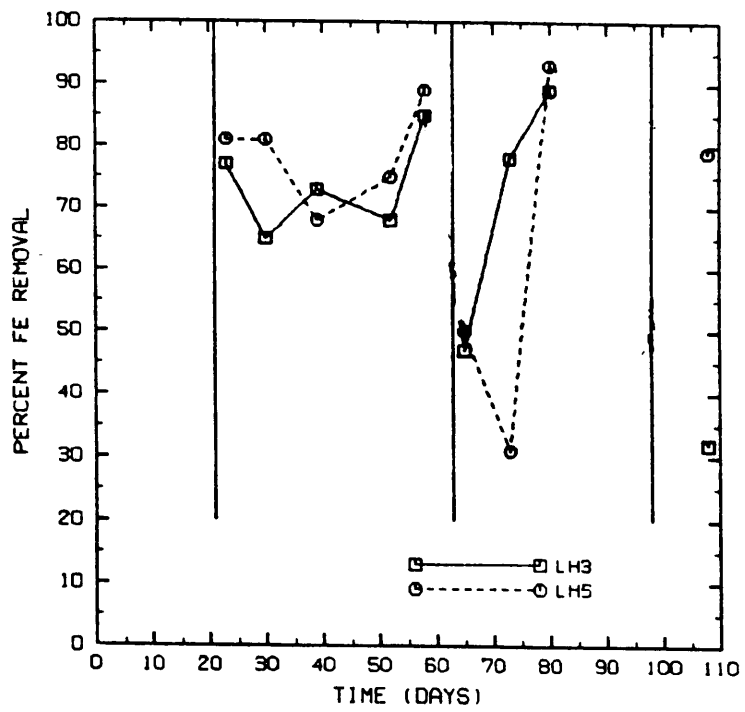


Figure 18. Iron Removal in Lee Hall WTP Clarifiers 3 (LH3) and 5 (LH5) from April 16th to August 2nd. Vertical lines indicate when Clarifier 3 was cleaned.

effects on the removal efficiencies of the clarifier. Another possible reason for the lack of an observable correlation between sludge accumulation and iron and manganese removal efficiency is that the sample collection procedures were not well standardized. Samples were taken by different plant personnel at different times of the day in order to accommodate their sampling schedule. Later, when an evaluation of chlorine dioxide as a preoxidant was made at Harwood's Mill WTP, a more standardized approach was adopted, and the correlation between sludge and the iron and manganese removal efficiencies were better. The data remain instructional, however, in that they show that perhaps other factors probably play a much more significant role in iron and manganese removal efficiencies than the accumulation of sludge alone.

High DO concentrations were observed in the middle and effluent portions of Clarifier 3 throughout its depth. It is likely that as the reduced iron and manganese released from the sludge was carried through these sections of the clarifier that they reoxidized and settled out before they reached the effluent weir.

EFFECTS OF CHLORINE DIOXIDE USED AS A PREOXIDANT

The final segment of research was an evaluation of the effect of chlorine dioxide on the sludge characteristics and the effluent quality from clarifiers that were not equipped with sludge-removal mechanisms. The three clarifiers at Harwood's Mill WTP were cleaned at staggered, one-week intervals prior to the beginning of the evaluation period. This made it possible to evaluate the effects of chlorine dioxide in all three

basins simultaneously and to obtain data when they contained different amounts of accumulated sludge. This was done in order to minimize the influence of other factors such as varying hydraulic loads, weather conditions, and raw-water quality.

Figures 19, 20, and 21 depict the results of the redox potentials and DO concentrations in the basins during August when no chlorine dioxide was used. It can be seen that as sludge accumulated the DO levels of the influent portion of the clarifier declined but the profiles at the middle and effluent portions of the clarifier remained relatively constant. The shape of the redox profiles are the same as the DO profiles and are indicative of conditions where iron and manganese can be reduced and released from the sludge that has accumulated at the influent of the clarifiers.

Figures 22, 23, and 24 depict the DO profiles in the clarifiers during a period in September when the Harwood's Mill WTP was using chlorine dioxide as a preoxidant. Data collected 6, 13, and 20 days into the study are shown. Because of breakdowns in the generating equipment, the clarifiers received chlorine dioxide only intermittently during the test period. Each of the clarifiers contained water treated with 1 mg/L of chlorine dioxide for 48 hours prior to the times data were taken. Comparison of these figures with the profiles taken before the addition of chlorine dioxide show that there was a marked increase of the DO levels at the influent portion of the clarifiers. It was also noted that the sludge blanket at the influent portion of the clarifiers was an average of two to three feet lower than it was when chlorine dioxide was not being

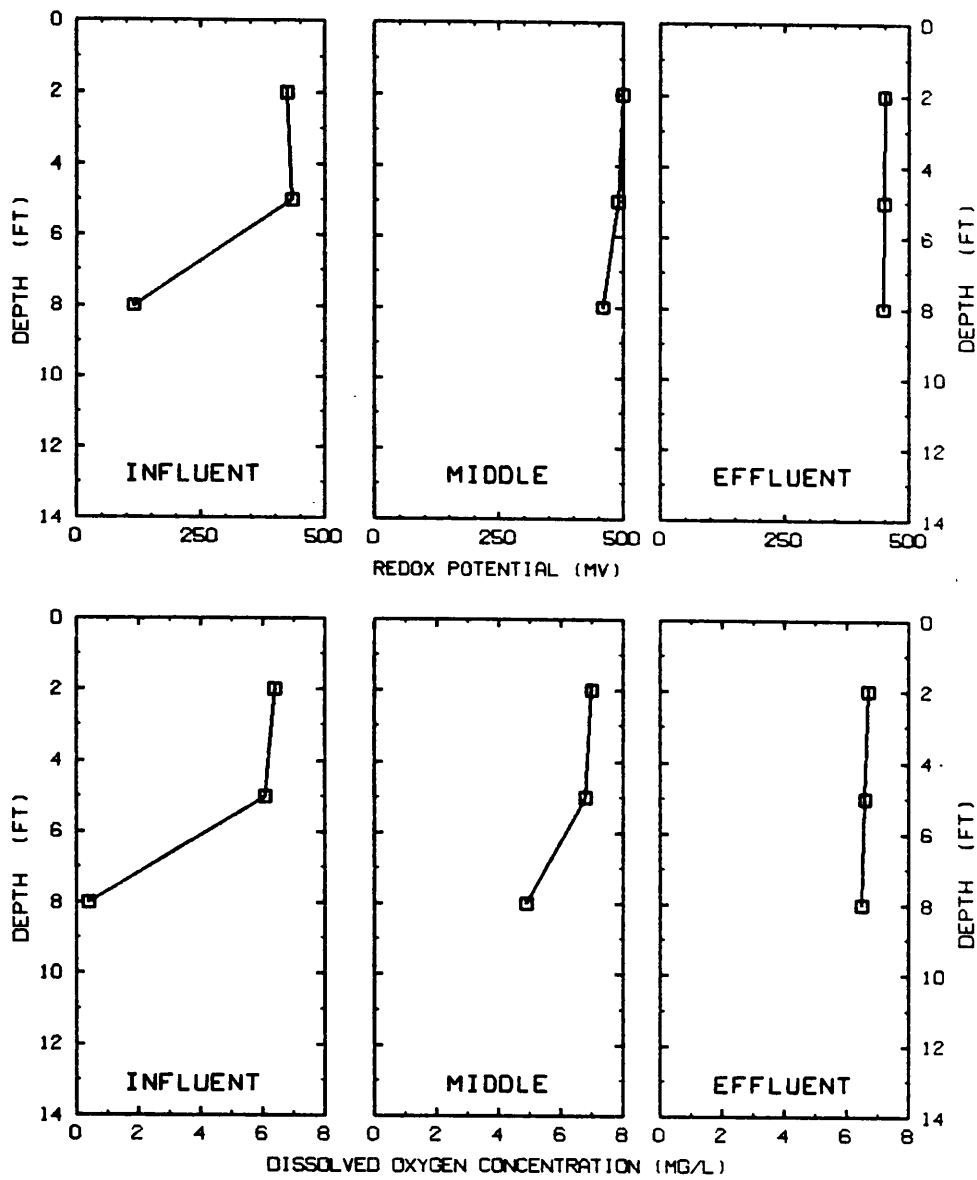


Figure 19. Dissolved Oxygen and Redox Potential Profiles Before Addition of Chlorine Dioxide. Clarifier in Service for 17 Days. August 23, 1985.

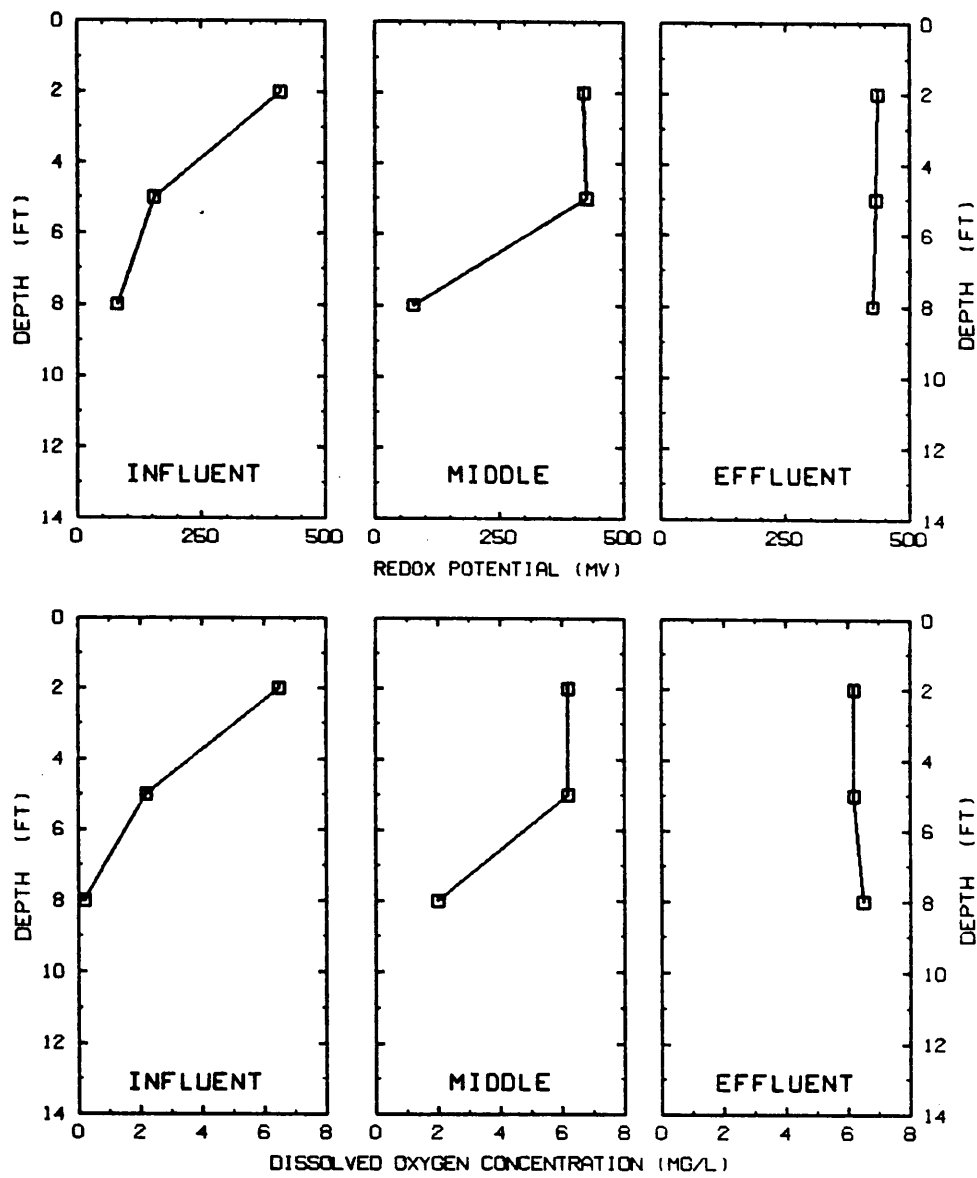


Figure 20. Dissolved Oxygen and Redox Potential Profiles Before Addition of Chlorine Dioxide. Clarifier in Service for 23 Days. August 23, 1985.

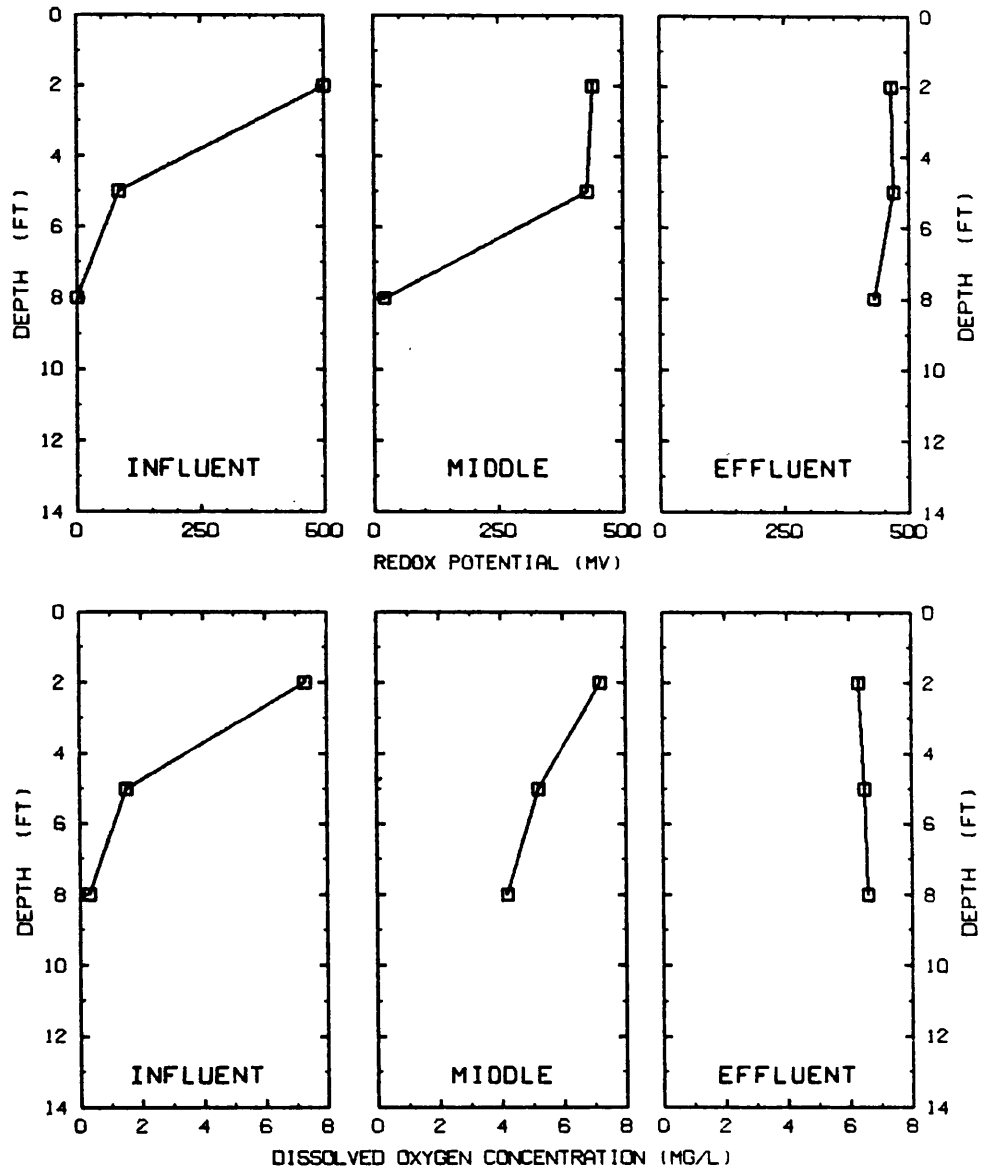


Figure 21. Dissolved Oxygen and Redox Potential Profiles Before Addition of Chlorine Dioxide. Clarifier in Service for 31 Days. August 23, 1985.

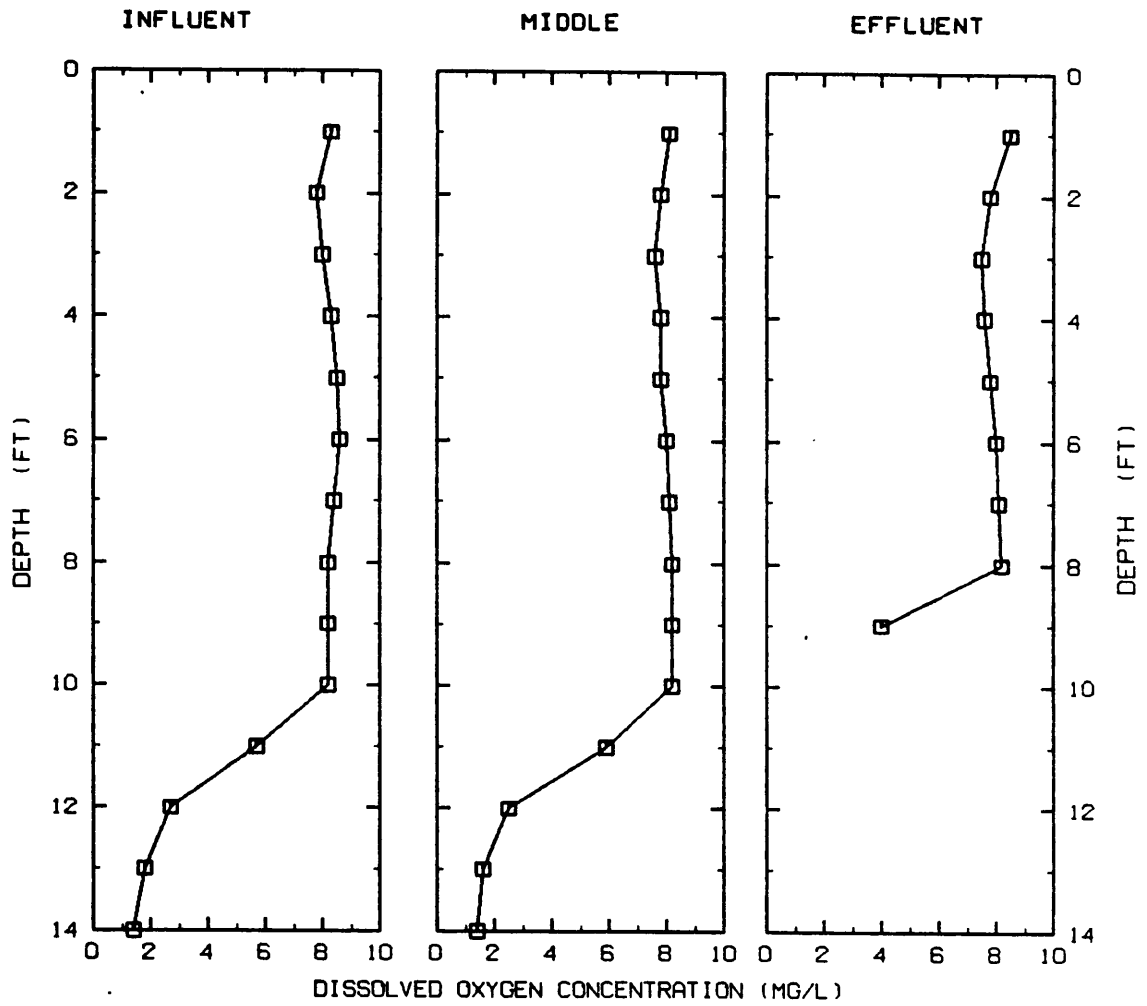


Figure 22. Dissolved Oxygen Profiles After Addition of Chlorine Dioxide. Clarifier in Service for 6 Days. September 24, 1985 .

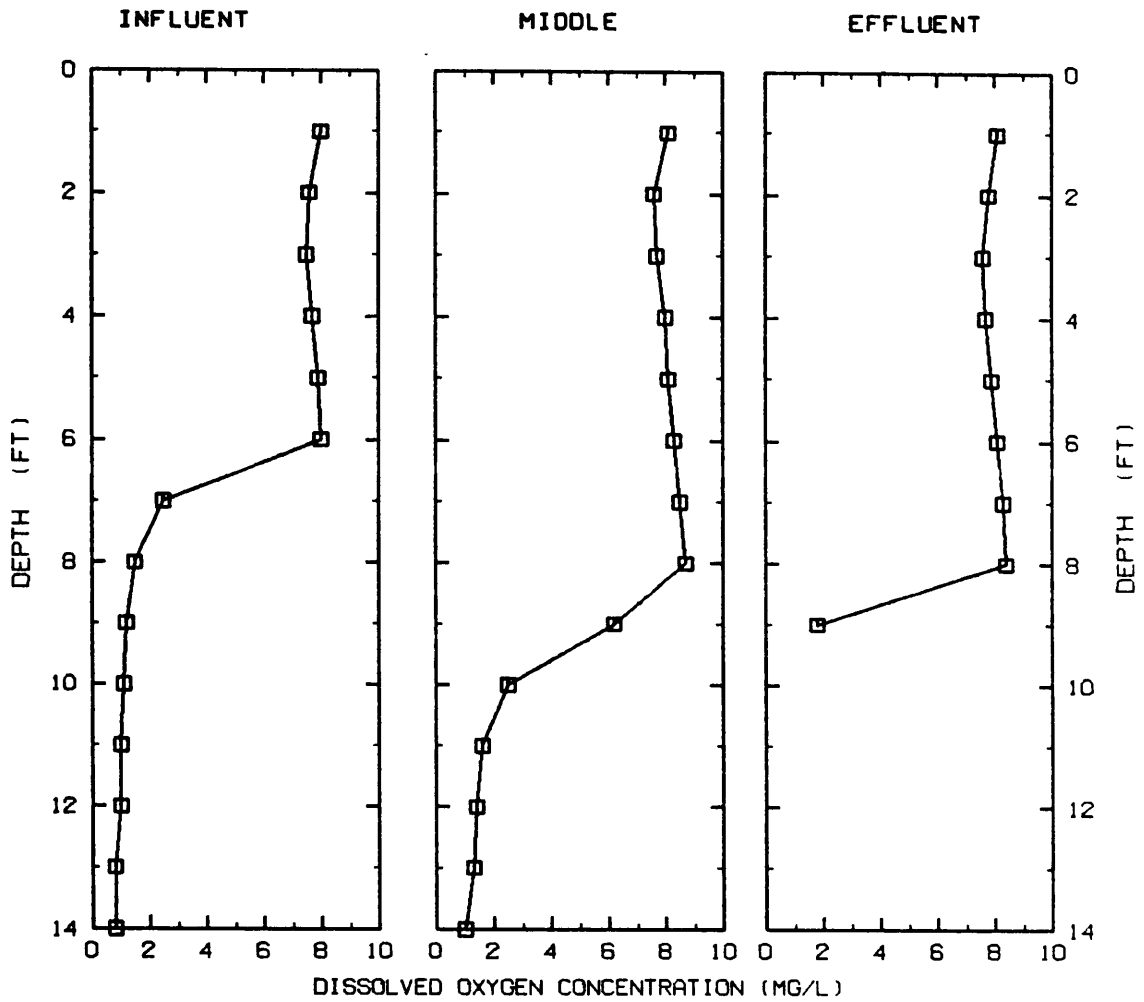


Figure 23. Dissolved Oxygen Profiles After Addition of Chlorine Dioxide. Clarifier in Service for 13 Days. September 24, 1985.

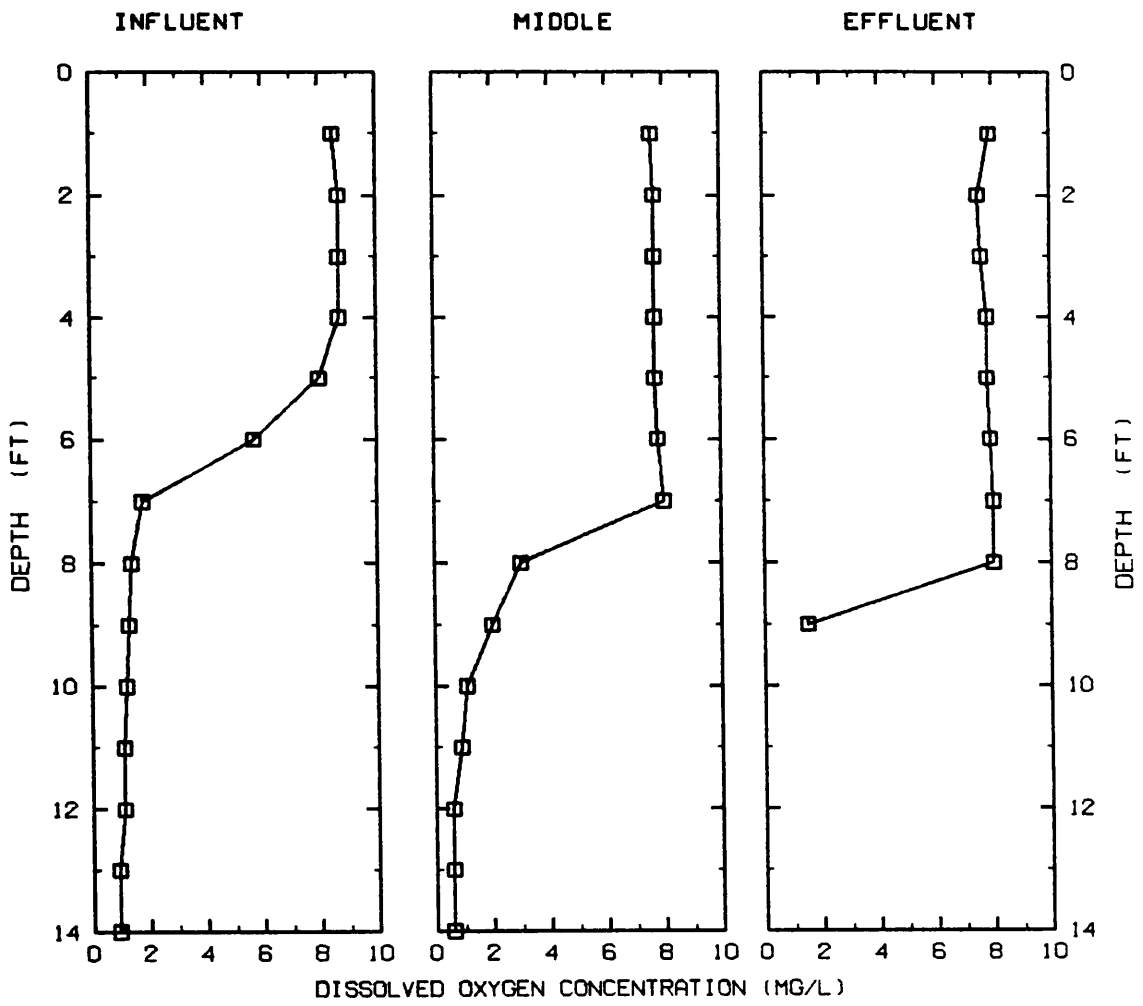


Figure 24. Dissolved Oxygen Profiles After Addition of Chlorine Dioxide. Clarifier in Service for 20 Days. September 24, 1985.

added suggesting improved settling characteristics of the sludge. The DO levels at the influent portion were still low enough, however, that iron and manganese could be reduced and released from the sludge. Redox potentials were not measured at this time because it was felt that the reaction of chlorine dioxide would be proceeding and that the system would therefore not be in equilibrium. This would make redox potential readings invalid.

Figures 25 and 26 show the effluent iron and manganese concentrations and the removal efficiencies of the clarifiers before and during the addition of chlorine dioxide. The effect of the storage of sludge is most apparent in Figure 25 which shows the manganese-removal efficiency to be negative when the clarifiers had been in service more than 23 days before chlorine dioxide was added. It can also be noted that the manganese removal efficiency decreased as more sludge accumulated, even when the clarifiers received chlorine dioxide. The removal efficiency was always better when a preoxidant was added. It is possible that the effluent would not have deteriorated at all if the chlorine dioxide feed had not been interrupted during the study.

Iron removal was also affected by the use of chlorine dioxide but to a lesser degree than manganese removal. This is probably because iron is harder to reduce and easier to oxidize. The trend remained the same, however, in that chlorine dioxide treatment markedly increased the iron-removal efficiency.

The TOC data from the study indicates that the effluent averaged 4 mg/ L for the test period when no chlorine dioxide was used and also when chlorine dioxide was added. The TOC in the effluent did not vary with

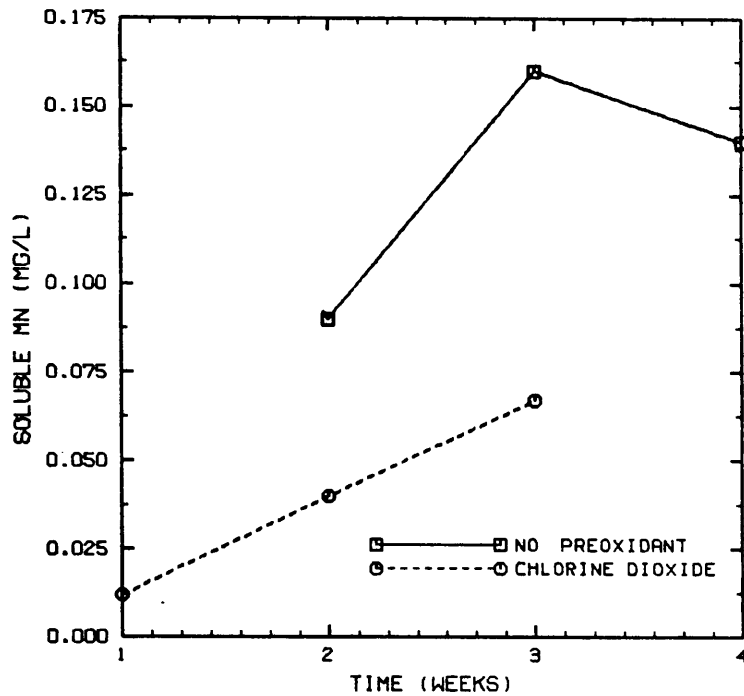
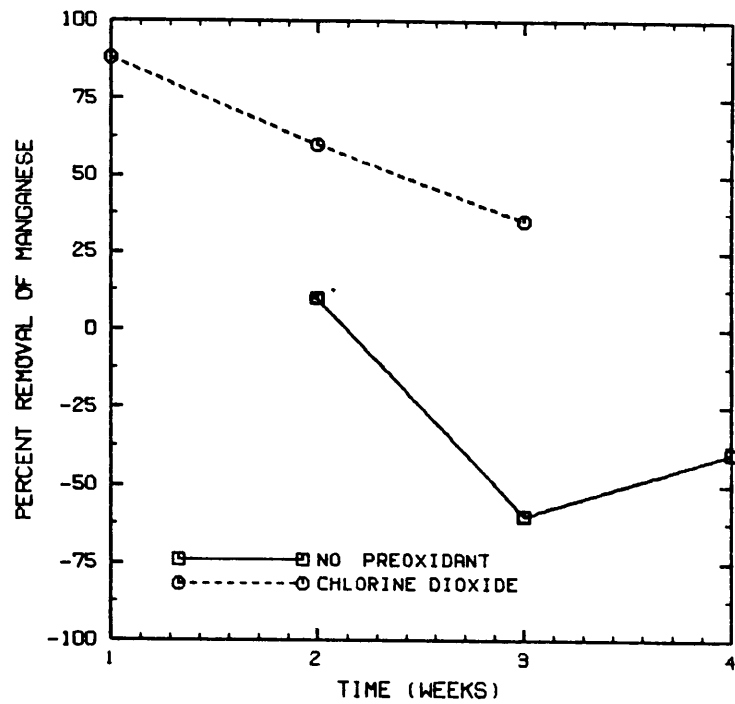


Figure 25. Comparison of Manganese Removal in Harwood's Mill WTP Clarifiers with and without the use of Chlorine Dioxide as a Preoxidant.

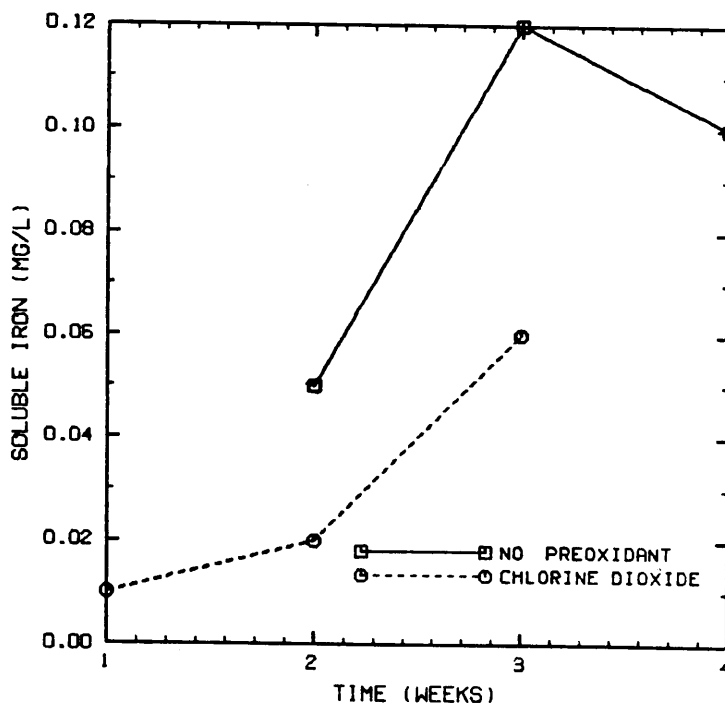
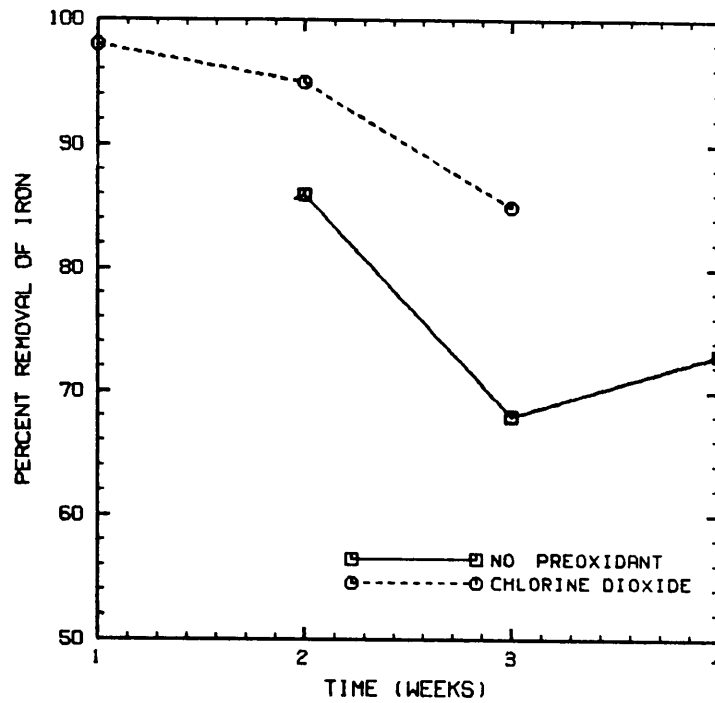


Figure 26. Comparison of Iron Removal in Harwood's Mill WTP Clarifiers with and without the use of Chlorine Dioxide as a Preoxidant.

the amount of sludge stored in the clarifiers. Different removal efficiencies would be calculated for the test period however because the influent TOC varied from 6 mg/L when no chlorine dioxide was used to 8 mg/L when chlorine dioxide was used as a preoxidant. It was found, however, that TOC in the supernatant liquor from the sludge samples was effected both by the accumulation of sludge in the clarifiers and by the use of chlorine dioxide. Figure 27 shows the concentrations of TOC that were found in the supernatant liquor. The high levels of TOC in the sludge generated without chlorine dioxide may be associated with biological activity in the sludge causing the production of soluble and colloidal organics. It appears, however, that these materials might be removed before reaching the effluent weirs.

Other qualitative differences were noted before and during the use of chlorine dioxide as a preoxidant. Prior to the addition of chlorine dioxide the clarifiers contained a large amount of floating bladderwort, a biofilm on the clarifier walls and effluent weirs, and a significant amount of algae. Laboratory culturing of bladderwort and the biofilm from the clarifier walls indicated that these growths can contribute TOC to the surrounding water. The impact of these growths would be reduced by dilution, however, under the continuous-flow conditions of a clarifier. Figure 28 shows the the TOC buildup in cultures of biofilm and bladderwort, indicating a significant increase in the TOC of the water over a 25-day period. Blue-green algae constituted part of the biofilm sample, and these organisms may contribute taste-and-odor substances to the drinking water. With the addition of chlorine dioxide, the biofilm

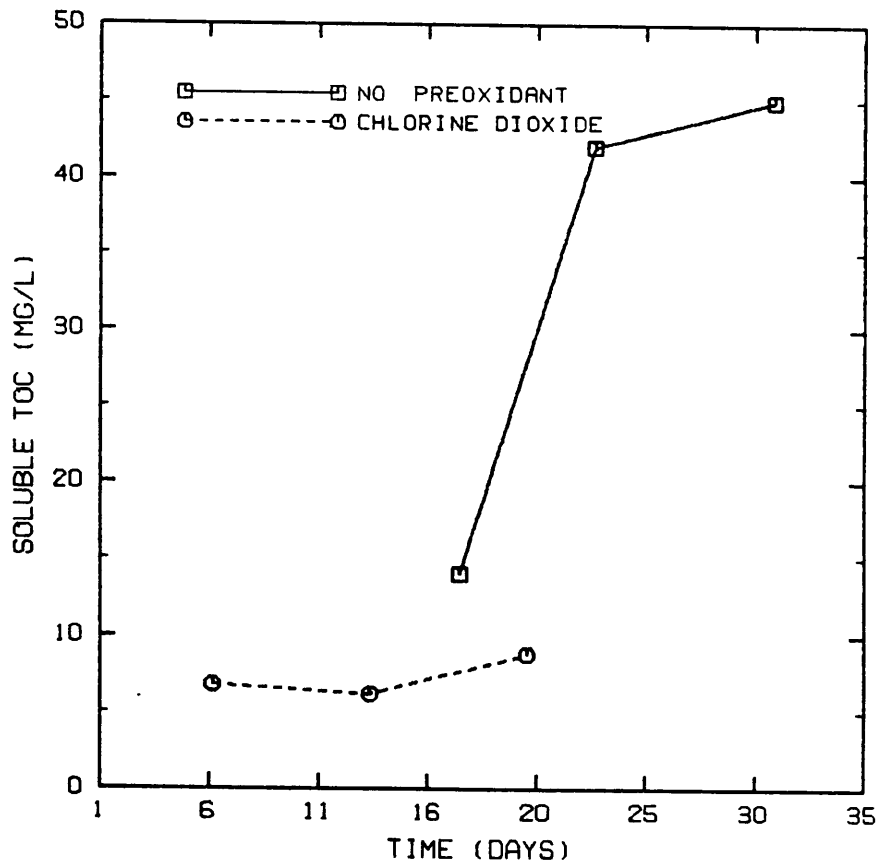


Figure 27. Total Organic Carbon Concentrations in Sludge Supernatant Liquor from Samples Collected at Harwood's Mill WTP.

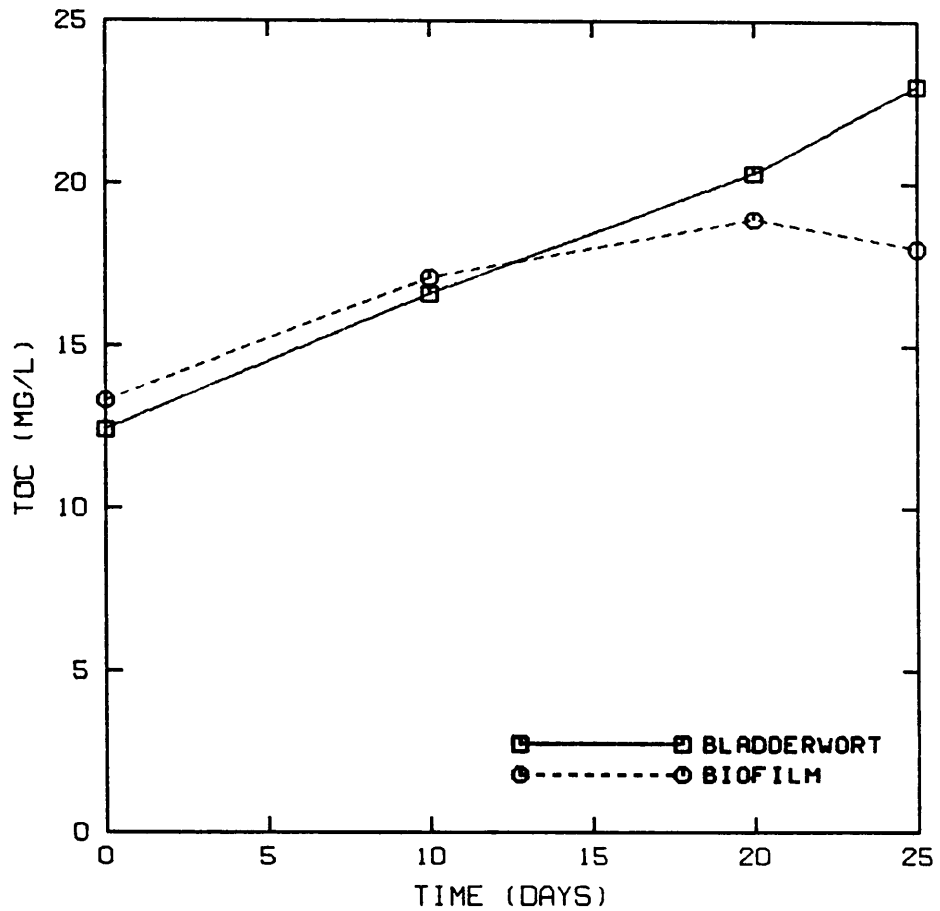


Figure 28. Increased TOC Concentrations in Laboratory Cultures of Bladderwort and Biofilm.

and algae growth were greatly reduced and bladderwort was almost entirely eliminated.

The visibility in the clarifiers also improved markedly. Before the use of chlorine dioxide it was possible to see objects only as deep as two to three feet below the water surface at the effluent end of the clarifiers. With the addition of chlorine dioxide, it became possible to clearly see the sludge layer ten feet down at the effluent end of the clarifier. The floc at the influent of the clarifier appeared larger and better defined when chlorine dioxide was being added, but whether this was a result of better flocculation or greater transparency is difficult to say.

Sludge samples were analyzed to determine if chlorine dioxide treatment significantly altered their dewatering characteristics. Figure 29 shows the change in specific resistance of the sludges formed before and during chlorine dioxide addition. Sludge formed during the chlorine dioxide treatment period dewatered significantly better than sludge that had not received chlorine dioxide. It can be seen from a comparison of SR values that sludge dewatering rates varied little during the 15 day period, perhaps because biological activity was inhibited.

Figure 30 is a comparison of the particle counts obtained from analysis of the sludge samples. The mean particle size in the two sets of sludge samples were significantly different. Figure 30 shows that half of the total surface area of the sludge was contained by particles 30 um and smaller before chlorine dioxide treatment while half of the surface area was contained by particles 65 um and smaller for the sludge when a preoxidant was added.

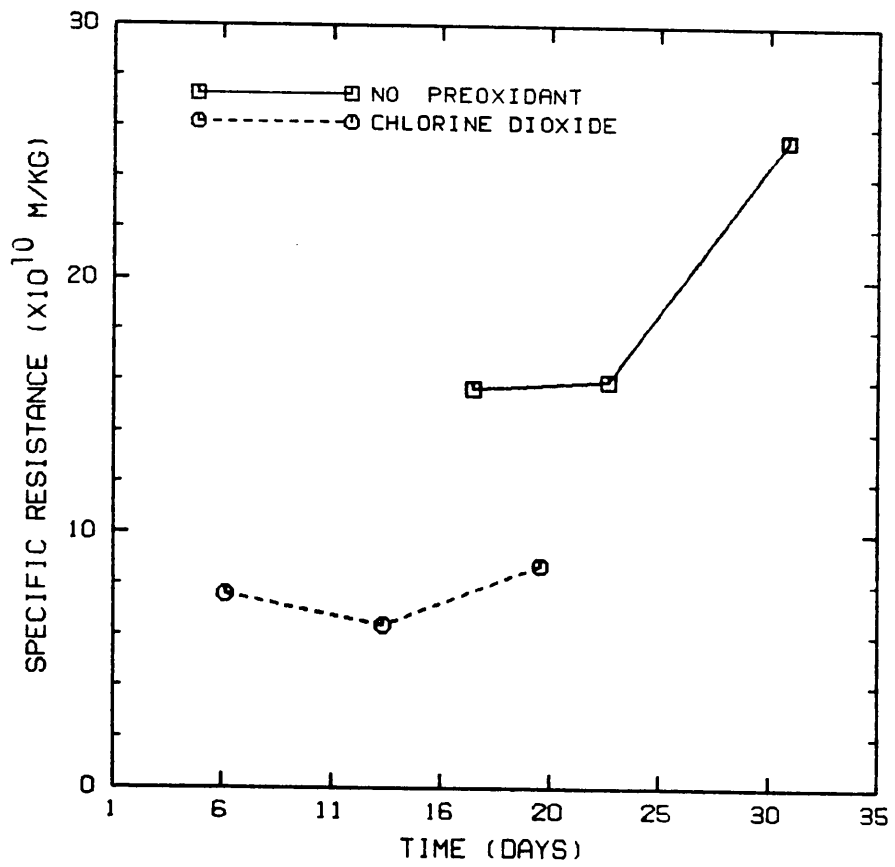


Figure 29. Comparison of Specific Resistance of Sludge with Storage.

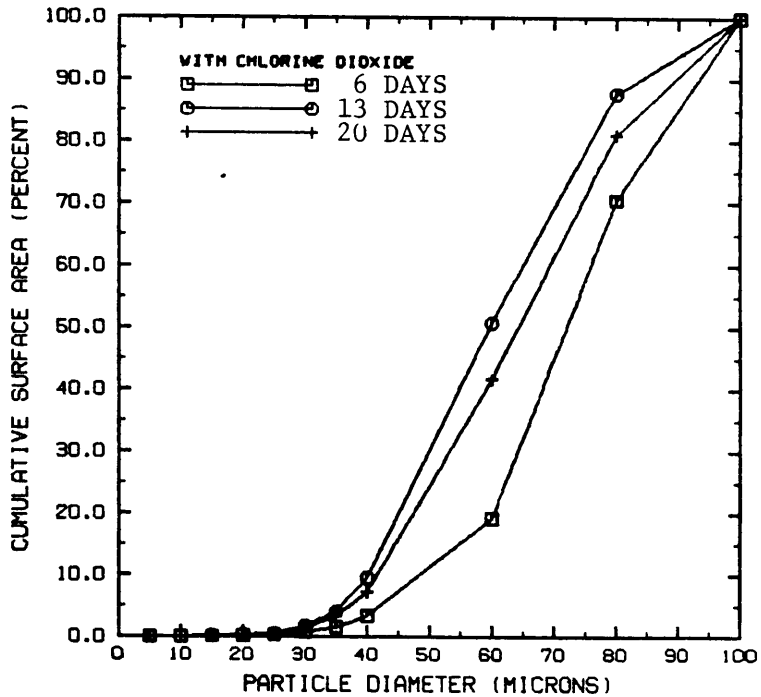
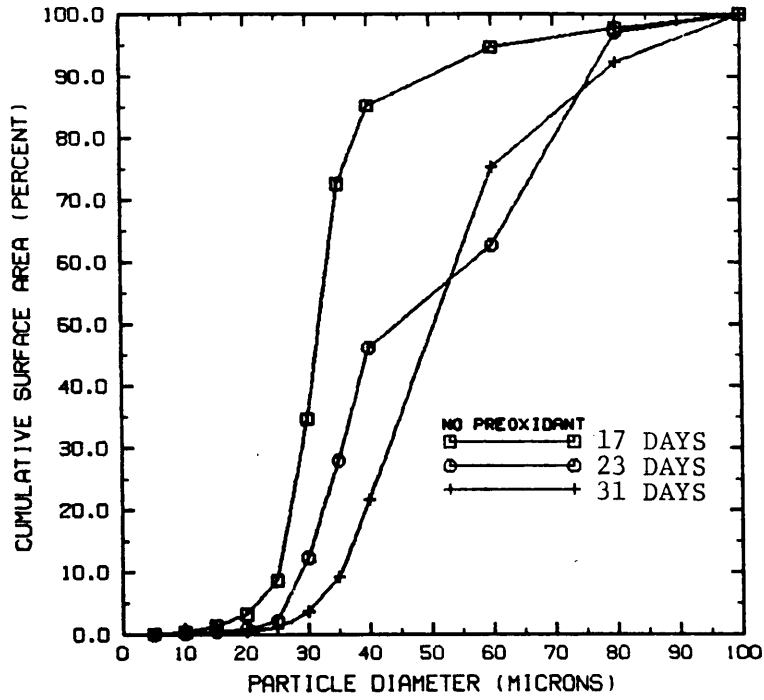


Figure 30. Cumulative Surface Area Distribution of Sludges Generated with and without Chlorine Dioxide.

Some of the supernatant liquor from a sludge sample that was collected during the test period before the addition of chlorine dioxide was chlorinated with 2 mg/L of chlorine. It was then gently stirred and particles counts were conducted over a 15 minute period. The results are shown in Figure 31. It can be seen that over a 15 minute time period there was significant particle growth. From the ten to fifteen minute time period, there was decrease in the number of smaller particles while the number of larger particles continued to increase. It could be that the improvement of dewatering characteristics that were observed in sludges formed during chlorine dioxide treatment were due to enhanced coagulation caused by chemical reaction in the presence of an oxidizing agent. This effect may be similar to the natural aging process which results in particle growth and improved sludge dewatering.

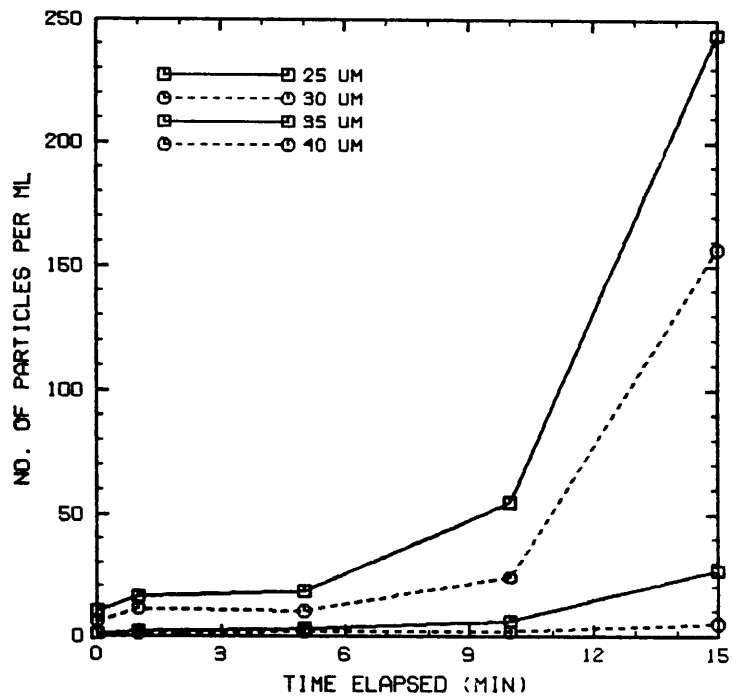
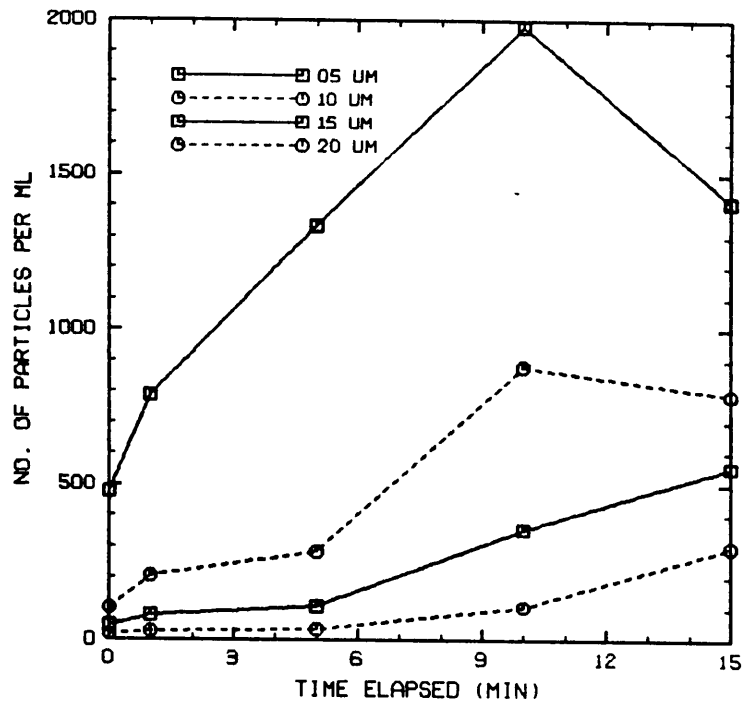


Figure 31. Growth of Particles in Sludge Supernatant Upon Chlorination with 2 mg/L Chlorine.

V.SUMMARY AND CONCLUSIONS

Each segment of the evaluation is summarized in the following paragraphs with a statement of conclusions following thereafter.

The release of iron and manganese from the alum sludge samples held in a controlled environment was found to be strongly correlated with the time of year during which the sample was collected. The amount of organic matter in the sludge appeared to play a significant role in whether the sludge remained aerobic or became anoxic. Redox potential proved to be a good measurement for predicting when conditions were present for reduction of iron and manganese. Extremely high levels of iron and manganese were found in the supernatant liquor of the samples that were collected in the late spring and throughout the summer. TOC appeared to remain constant in the samples collected in the early spring but was found to increase with storage in the samples collected in the late spring and early summer.

Dewatering characteristics of the samples collected in the early and late spring improved when stored. This was caused by particle growth and was probably a chemical phenomenon. The set of samples collected in the early summer did not exhibit any well defined trend in their dewatering characteristics. This was thought to be a result of competition of two phenomena. The first, mentioned above, is particle growth caused by a chemical reaction. The other appears to be the production of smaller particles by the process of anaerobic decomposition. The onset of

anaerobic conditions in the sludge probably adversely impacts the dewatering characteristics of the sludge.

Monitoring and sampling of the clarifiers from April to early August did not indicate that in-basin storage of sludge adversely impacts iron and manganese removal efficiencies. This conflicts with a later portion of the study which showed that storage of sludge significantly impacts the iron and manganese removal in the clarifiers. The disparity in results is thought to be due to nonstandard sample collection techniques that were used in the this portion of the study which did not minimize other factors that affect removal efficiency. Other factors apparently play a major role in the removal efficiency of clarifiers which obscure the impact of sludge storage. Factors that may have an impact on removal efficiencies include such things as raw water quality, weather conditions, hydraulic loading, alum dose, and the use of polymer. This does not mean that sludge storage does not affect removal efficiencies of the clarifiers but does point to the idea that other areas perhaps play a more significant role.

The final portion of the study evaluated the effect of using chlorine dioxide as a preoxidant. Treatment of the raw water with 1 mg/L of chlorine dioxide significantly improved the iron and manganese removal efficiencies of the clarifiers. Iron and manganese removal efficiencies were found to deteriorate as sludge accumulation in the clarifiers increased, regardless of whether or not chlorine dioxide was used. It is possible that if chlorine dioxide was fed on a continuous rather than an intermittent basis that the effluent would not have deteriorated.

The sludge that was generated from the influent treated with chlorine dioxide was significantly easier to dewater than the sludge with no chlorine dioxide. This was thought to be a result of inhibition of biological activity and by promotion of particle growth by the chlorine dioxide.

The significant conclusions of the study are:

1. Seasonal variations in water quality have a significant impact on how quickly a sludge becomes anaerobic and begins releasing iron and manganese.
2. Although iron and manganese and TOC are released by sludge as it goes anaerobic it appears to reprecipitate and settle in the clarifiers if there is sufficient detention time and oxygenated conditions in the overlying water.
3. The removal of TOC in clarifiers is not affected by storage of sludge in the clarifiers.
4. Chlorine dioxide can significantly improve the iron and manganese removal efficiencies of clarifiers.
5. Chlorine dioxide improves the dewatering characteristics of sludge.

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APPENDIX A. DATA FROM LABORATORY STUDIES OF STORED SLUDGE.

Table A1.

Supernatant Water Quality Data. Sludge Collected March 19, 1985.
Storage Temperature 20°C.

Supernatant Water Quality Data							
Sample Collected March 19, 1985. Storage Temp., 20°C							
Date	Storage Time (Days)	D.O. Water (mg/L)	Water Redox (mV)	Sludge Redox (mV)	Fe (mg/L)	Mn (mg/L)	TOC (mg/L)
3/21	2	--	--	--	0.70	0.145	10.04
3/25	6	--	--	--	0.03	0.106	4.42
4/1	13	--	--	--	<0.02	0.352	4.13
4/8	20	5.9	411	243	0.02	0.356	6.21
4/15	27	6.4	388	--	0.02	0.429	4.61
4/22	34	6.1	372	194	0.13	0.468	5.06
5/6	48	5.6	374	234	0.10	0.500	4.82
5/20	62	5.2	297	235	0.07	0.550	4.20
6/7	80	5.6	262	276	0.04	0.550	3.86
7/17	120	6.6	470	242	0.06	0.509	4.25
All Samples had an Oxidized Microzone							

Table A2.

Supernatant Water Quality Data. Sludge Collected April 29 and June 17, 1985. Storage Temperature 20°C.

Supernatant Water Quality Data							
Sample Collected April 29, 1985. Storage Temp., 20°C							
Date	Storage Time (Days)	D.O. Water (mg/L)	Water Redox (mV)	Sludge Redox (mV)	Fe (mg/L)	Mn (mg/L)	TOC (mg/L)
5/6	7	3.6	284	-26	0.19	1.50	7.88
5/13	14	4.1	536	-36	0.07	2.83	7.19
5/20	21	3.5	275	-322	0.06	3.73	6.65
6/7	39	4.2	263	-196	0.05	4.37	6.80
7/8	70	5.3	322	-88	0.02	5.41	6.23
8/13	106	--	--	--	<0.02	4.7	5.4
All Samples had an Oxidized Microzone							

Supernatant Water Quality Data							
Sample Collected June 17, 1985. Storage Temp., 20°C							
Date	Storage Time (Days)	D.O. Water (mg/L)	Water Redox (mV)	Sludge Redox (mV)	Fe (mg/L)	Mn (mg/L)	TOC (mg/L)
6/17	--	8.5	265	265	0.06	0.106	7.73
6/22	5	2.2	339	119	0.05	0.973	6.38
7/2	15	0.5	4	-71	3.61	2.080	9.38
7/8	21	0.5	1	-92	5.20	5.20	10.14
7/17	30	0.4	-98	-145	6.30	5.50	10.80
8/13	57	--	--	--	3.71	5.87	10.2
8/13	57	--	--	--	0.02	4.65	10.1
Samples with an Oxidized Microzone are in Bold Print							

Table A3.

Supernatant Water Quality Data. Sludge Collected March 19, 1985.
Storage Temperature 30°C.

Supernatant Water Quality Data							
Sample Collected March 19, 1985. Storage Temp., 30°C							
Date	Storage Time (Days)	D.O. Water (mg/L)	Water Redox (mV)	Sludge Redox (mV)	Fe (mg/L)	Mn (mg/L)	TOC (mg/L)
3/21	2	--	--	--	0.70	0.145	10.04
3/25	6	--	--	--	0.03	0.106	4.42
4/1	13	--	--	--	<0.02	0.352	4.31
4/8	20	5.4	366	238	0.02	0.445	6.06
4/15	27	5.2	395	203	0.02	0.472	5.23
4/22	34	6.1	377	114	0.14	0.516	5.24
5/6	48	5.4	319	120	0.07	0.496	4.94
5/20	62	4.5	302	156	0.04	0.610	4.22
6/7	80	6.3	284	278	0.06	0.570	3.68
7/17	120	5.8	443	292	0.06	0.563	4.72
All Samples had an Oxidized Microzone							

Table A4.

Supernatant Water Quality Data. Sludge Collected April 29 and June 17, 1985. Storage Temperature 30°C.

Supernatant Water Quality Data							
Sample Collected April 29, 1985. Storage Temp., 30°C							
Date	Storage Time (Days)	D.O. Water (mg/L)	Water Redox (mV)	Sludge Redox (mV)	Fe (mg/L)	Mn (mg/L)	TOC (mg/L)
5/6	7	3.0	282	-111	0.87	2.04	7.65
5/13	14	3.5	314	-81	0.18	3.37	7.54
5/20	21	1.6	209	-266	0.90	4.17	7.76
6/7	39	3.7	439	-201	0.12	4.54	8.03
7/8	70	4.5	329	-113	0.02	4.98	6.83
8/13	106	--	--	<0.02	<0.04	4.54	6.30
All Samples had an Oxidized Microzone							

Supernatant Water Quality Data							
Sample Collected June 17, 1985. Storage Temp., 30°C							
Date	Storage Time (Days)	D.O. Water (mg/L)	Water Redox (mV)	Sludge Redox (mV)	Fe (mg/L)	Mn (mg/L)	TOC (mg/L)
6/17	--	8.5	265	265	0.06	0.106	7.73
6/22	5	1.2	251	56	0.29	3.686	7.02
7/2	15	3.0	336	-96	0.08	3.805	7.57
7/8	21	0.5	-52	-100	4.18	4.90	10.31
7/17	30	3.1	406	-145	0.07	5.01	9.11
7/25	38	--	--	--	0.05	5.90	--
8/13	57	--	--	--	<0.02	6.10	--
8/13	57	--	--	--	3.66	6.23	--
Samples with an Oxidized Microzone in Bold Print							

Table A5.

Dewatering Characteristics of Stored Sludge. Sludge Collected March 19, 1985. Storage Temperature 20°C.

Sludge Characteristics						
Sludge Collected March 19, 1985. Storage Temp., 20°C						
Date	Storage Time (Days)	Initial Solids (%)	Final Solids (%)	Slope (s/mL ²)	Specific Resistance (x10 ¹⁰ m/kg)	CST (sec)
3/21	2	0.17	15.03	0.0165	8.26	39.4
4/1	13	0.14	6.35	0.0164	9.86	42.2
4/8	20	0.17	8.88	0.0049	2.40	45.1
4/15	27	0.14	11.91	0.0120	7.29	34.1
4/22	34	0.14	13.43	0.0099	6.49	25.5
5/6	48	0.15	10.25	0.0083	4.69	--
5/20	62	0.14	13.03	0.0041	2.49	17
6/7	80	0.13	7.66	0.0037	2.41	15.7
7/17	120	0.14	11.01	0.0011	0.65	8.2

Table A6.

Dewatering Characteristics of Stored Sludge. Sludge Collected April 29 and June 17, 1985. Storage Temperature 20°C.

Sludge Characteristics						
Sludge Collected April 29, 1985. Storage Temp., 20°C						
Date	Storage Time (Days)	Initial Solids (%)	Final Solids (%)	Slope (s/mL ²)	Specific Resistance (x10 ¹⁰ m/kg)	CST (sec)
4/29	0	0.22	9.60	0.0181	6.79	--
5/6	7	0.21	12.79	0.0197	7.94	--
5/13	14	0.23	9.02	0.0233	8.50	48.9
5/20	21	0.20	4.35	0.0202	8.32	45.2
6/7	39	0.22	6.11	0.0156	5.89	31.3
7/8	70	0.21	14.44	0.0116	4.69	29.2
8/13	106	0.21	7.66	0.0100	3.98	18.6

Sludge Characteristics						
Sludge Collected June 17, 1985. Storage Temp., 20°C						
Date	Storage Time (Days)	Initial Solids (%)	Final Solids (%)	Slope (s/mL ²)	Specific Resistance (x10 ¹⁰ m/kg)	CST (sec)
6/17	0	0.19	9.68	0.0310	13.8	69
6/22	5	0.15	7.86	0.0206	11.6	39
7/2	15	0.15	8.64	0.0224	12.6	38
7/8	21	0.16	5.56	0.0265	13.8	44
7/11	30	0.15	13.9	0.0228	12.95	46
7/25	38	0.14	4.94	0.0222	13.3	50
8/13	57	0.15	6.40	0.0214	12.0	38.5

Table A7.

Dewatering Characteristics of Stored Sludge. Sludge Collected March 19, 1985. Storage Temperature 30°C.

Sludge Characteristics						
Sludge Collected March 19, 1985. Storage Temp., 30°C						
Date	Storage Time (Days)	Initial Solids (%)	Final Solids (%)	Slope (s/mL ²)	Specific Resistance (x10 ¹⁰ m/kg)	CST (sec)
3/21	2	0.17	15.03	0.0165	8.26	39.4
4/1	13	0.14	5.72	0.0135	8.10	38.0
4/8	20	0.14	10.57	0.0124	7.52	29.9
4/15	27	0.14	13.12	0.0094	5.72	24.4
4/22	34	0.15	13.56	0.0075	4.25	24.6
5/6	48	0.15	5.26	0.0052	2.90	--
5/20	62	0.14	12.18	0.0054	3.28	15.2
6/7	80	0.14	10.47	0.0029	1.76	12.0
7/17	120	0.13	14.09	0.0016	1.02	9.8

Table A8.

Dewatering Characteristics of Stored Sludge. Sludge Collected April 29 and June 17, 1985. Storage Temperature 30°C.

Sludge Characteristics						
Sludge Collected April 29, 1985. Storage Temp., 30°C						
Date	Storage Time (Days)	Initial Solids (%)	Final Solids (%)	Slope (s/mL ²)	Specific Resistance (x10 ¹⁰ m/kg)	CST (sec)
4/29	0	0.22	9.60	0.0181	6.79	--
5/6	7	0.23	7.57	0.0195	7.08	--
5/13	14	0.22	7.78	0.0193	7.34	47.7
5/20	21	0.19	3.10	0.0203	8.63	47.8
6/7	39	0.21	4.80	0.0158	6.19	37.4
7/8	70	0.21	6.23	0.0129	5.11	32.0
8/13	106	0.26	9.27	0.0120	3.86	24.5

Sludge Characteristics						
Sludge Collected June 19, 1985. Storage Temp., 30°C						
Date	Storage Time (Days)	Initial Solids (%)	Final Solids (%)	Slope (s/mL ²)	Specific Resistance (x10 ¹⁰ m/kg)	CST (sec)
6/17	0	0.19	9.68	0.0310	13.8	69
6/22	5	0.20	8.14	0.0251	10.5	52
7/2	15	0.15	12.02	0.0212	12.0	32
7/8	21	0.13	15.72	0.0215	14.1	49
7/11	30	0.14	5.79	0.0229	13.7	43
7/25	38	0.20	7.29	0.0234	9.8	--
8/13	57	0.19	5.21	0.0196	8.56	29

Table A9.

Cumulative Surface Area of Particles. Sludge Collected April 29, 1985. Storage Temperature 20°C.

Percent of Surface Area Comprised by Particles of Specified Diameter or Smaller.			
Diameter	Storage Time (days)		
(um)	21	39	70
5	0	0	0
10	1	0	0
15	4	1	0
20	9	2	0
25	18	5	0
30	40	16	2
40	63	34	6
50	78	52	16
60	92	76	45
80	97	90	73
100	100	100	100

Table A10.

Cumulative Surface Area of Particles. Sludge Collected June 17, 1985.
Storage Temperature 20°C.

Percent of Surface Area Comprised by Particles of Specified Diameter or Smaller.						
Diameter	Storage Time (days)					
(μm)	0	5	15	21	30	60
5	0	0	0	0	0	0
10	0	1	1	0	0	0
15	1	2	2	1	0	1
20	1	5	5	3	1	1
25	3	14	13	7	2	3
30	11	40	40	24	5	13
40	30	64	64	48	14	33
50	54	78	78	66	30	57
60	80	90	90	83	59	81
80	90	95	95	91	84	91
100	100	100	100	100	100	100

Table A11.

Particle Counts from Chlorination of Sludge Supernatant with 2 mg/L of Chlorine.

Number of Particles per mL of the Specified Diameter.					
Diameter	Mixing Time (minutes)				
(μm)	0	1	5	10	15
5	477	788	1335	1978	1413
10	103	207	284	879	789
15	46	80	108	355	555
20	17	28	34	106	298
25	10	16	18	55	244
30	6	11	10	24	157
35	1	2	3	6	27
40	1	1	2	2	5

APPENDIX B. DATA FROM PROFILES AND SAMPLING OF LEE HALL CLARIFIERS.

Table B1.

Manganese Removal in Lee Hall WTP Clarifiers 3 and 5 from April 16 to August 2, 1985

Manganese Concentrations and Percent Removals at Lee Hall WTP					
Date	Raw Influent (mg/L)	Lee Hall Clar.3 (mg/L)	Percent Removal (%)	Lee Hall Clar.5 (mg/L)	Percent Removal (%)
4/16	--	0.007	--	0.005	--
4/23	--	0.022	--	0.016	--
5/9	0.039	0.059	-51	0.35	10
5/16	0.091	0.124	-36	0.005	95
5/28	0.060	0.035	42	0.017	72
6/7	0.096	0.172	-80	0.158	-65
6/13	0.133	0.126	5	0.108	19
6/20	0.055	0.042	24	0.020	64
6/28	0.033	0.015	54	0.017	48
7/5	0.091	0.085	7	0.066	27
7/18	0.138	0.097	30	0.085	38
8/2	0.150	0.135	10	0.150	0

Table B2.

Iron Removal in Lee Hall WTP Clarifiers 3 and 5 from April 16 to August 2, 1985.

Iron Concentrations and Percent Removals at Lee Hall WTP					
Date	Raw Influent (mg/L)	Lee Hall Clar.3 (mg/L)	Percent Removal (%)	Lee Hall Clar.5 (mg/L)	Percent Removal (%)
4/16	--	0.04	--	0.05	--
4/23	--	0.10	--	0.09	--
5/9	0.26	0.06	77	0.05	81
5/16	0.26	0.09	65	0.05	81
5/28	0.22	0.06	73	0.07	68
6/7	0.28	0.09	68	0.07	75
6/13	0.27	0.04	85	0.03	89
6/20	0.30	0.10	47	0.15	50
6/28	0.32	0.07	78	0.22	31
7/5	0.28	0.03	89	0.05	93
7/18	0.28	0.06	78	0.03	89
8/2	0.34	0.23	32	0.21	79

Table B3.

Dissolved Oxygen Profiles of Lee Hall WTP Clarifiers 3 and 5. June 28 and July 5, 1985.

June 28, 1985		
Depth (ft)	Lee Hall Clar.3 D.O. (mg/L)	Lee Hall Clar.5 D.O. (mg/L)
1	7.1	7.4
2	7.2	--
3	7.0	7.4
4	--	7.3
5	7.0	--
6	--	--
7	6.9	--
8	6.8	--
9	--	--
10	6.7	--
11	--	7.2
12	2.5	--
13	0.8	7.1
14	0.7	7.0
15	--	--
16	--	7.1
17	--	7.0
Clar.3 in service for 4 days		

July 5, 1985		
Depth (ft)	Lee Hall Clar.3 D.O. (mg/L)	Lee Hall Clar.5 D.O. (mg/L)
1	8.2	7.4
2	8.2	7.4
3	8.2	7.4
4	8.2	7.4
5	8.2	7.4
6	8.0	7.4
7	7.8	7.4
8	7.8	7.4
9	7.8	7.4
10	7.8	7.4
11	7.4	7.4
12	7.4	7.4
13	7.3	7.4
14	4.8	7.4
15	1.5	7.4
16	--	7.2
17	--	3.8
Clar.3 in service for 11 days		

Table B4.

Dissolved Oxygen Profiles of Lee Hall WTP Clarifiers 3 and 5. July 18 and August 2, 1985.

July 18, 1985		
Depth (ft)	Lee Hall Clar.3 D.O. (mg/L)	Lee Hall Clar.5 D.O. (mg/L)
1	6.2	6.4
2	6.5	6.2
3	6.5	7.4
4	6.8	7.4
5	6.5	7.4
6	3.0	7.4
7	2.2	7.4
8	1.9	7.4
9	1.4	7.4
10	1.2	7.5
11	0.9	7.5
12	0.9	7.5
13	0.9	7.5
14	0.9	7.5
15	0.9	7.0
16	--	7.0
17	--	3.6
Clar.3 in service for 24 days		

August 2, 1985		
Depth (ft)	Lee Hall Clar.3 D.O. (mg/L)	Lee Hall Clar.5 D.O. (mg/L)
1	5.8	5.8
2	5.8	5.8
3	5.8	5.8
4	5.8	5.8
5	5.8	5.8
6	5.8	5.8
7	5.8	5.8
8	5.8	5.8
9	5.8	5.8
10	5.8	5.8
11	5.4	5.8
12	5.4	5.8
13	5.2	5.8
14	2.1	5.5
15	0.8	5.2
16	--	5.2
17	--	5.2
Clar.3 in service for 2 days		

APPENDIX C. DATA FROM PROFILES AND SAMPLING OF HARWOOD'S MILL WTP
CLARIFIERS BEFORE AND DURING THE ADDITION OF CHLORINE DIOXIDE.

Table C1.

Dissolved Oxygen and Redox Profiles Prior to the Addition of Chlorine Dioxide to the Influent.

Depth (ft)	Influent		Middle		Effluent	
	D.O. (mg/L)	Redox (mV)	D.O. (mg/L)	Redox (mV)	D.O. (mg/L)	Redox (mV)
2	6.4	425	7.0	506	6.7	451
5	6.1	435	6.8	490	6.6	450
8	0.4	115	4.9	460	6.5	448
Clarifier in Service 17 days						

Depth (ft)	Influent		Middle		Effluent	
	D.O. (mg/L)	Redox (mV)	D.O. (mg/L)	Redox (mV)	D.O. (mg/L)	Redox (mV)
2	6.5	410	6.2	420	6.2	437
5	2.2	155	6.2	425	6.2	433
8	0.2	80	2.0	77	6.5	426
Clarifier in Service 23 days						

Depth (ft)	Influent		Middle		Effluent	
	D.O. (mg/L)	Redox (mV)	D.O. (mg/L)	Redox (mV)	D.O. (mg/L)	Redox (mV)
2	7.3	528	7.2	440	6.3	465
5	1.5	85	5.2	429	6.5	470
8	0.3	0	4.2	20	6.5	430
Clarifier in Service 31 days						

Table C2.

Dissolved Oxygen Profiles During to the Addition of Chlorine Dioxide.
Clarifier in Service 17 days.

Depth (ft)	Influent D.O. (mg/L)	Middle D.O. (mg/L)	Effluent D.O. (mg/L)
1	8.1	8.1	8.5
2	7.8	8.0	8.1
3	7.6	7.8	7.8
4	7.6	7.6	7.5
5	7.8	7.6	7.6
6	8.0	7.8	7.8
7	8.1	8.0	8.0
8	8.2	8.1	8.1
9	8.2	8.2	4.0
10	8.2	8.2	--
11	5.7	5.9	--
12	2.7	2.5	--
13	1.8	1.6	--
14	1.4	1.4	--

Table C3.

Dissolved Oxygen Profiles During to the Addition of Chlorine Dioxide.
Clarifier in Service 23 days.

Depth (ft)	Influent D.O. (mg/L)	Middle D.O. (mg/L)	Effluent D.O. (mg/L)
1	8.0	8.1	8.1
2	7.6	7.6	7.8
3	7.5	7.7	7.6
4	7.7	8.0	7.7
5	7.9	8.1	7.9
6	8.0	8.3	8.1
7	2.5	8.5	8.3
8	1.5	8.7	8.4
9	1.2	6.2	1.8
10	1.1	2.5	--
11	1.0	1.6	--
12	1.0	1.4	--
13	0.8	1.3	--
14	0.8	1.0	--

Table C4.

Dissolved Oxygen Profiles During to the Addition of Chlorine Dioxide.
Clarifier in Service 31 days.

Depth (ft)	Influent D.O. (mg/L)	Middle D.O. (mg/L)	Effluent D.O. (mg/L)
1	8.5	7.6	7.9
2	8.7	7.7	7.5
3	8.7	7.7	7.6
4	8.7	7.7	7.8
5	8.0	7.7	7.8
6	5.7	7.8	7.9
7	1.8	8.0	8.0
8	1.4	3.0	8.0
9	1.3	2.0	1.5
10	1.2	1.1	--
11	1.1	0.9	--
12	1.1	0.6	--
13	0.9	0.6	--
14	0.9	0.6	--

Table C5.

Manganese Data Prior to and During the Addition of Chlorine Dioxide to the Influent.

Mn Prior to the Addition of Chlorine Dioxide			
Time in Service (days)	Raw Influent (mg/L)	Clar. Effluent (mg/L)	Percent Removal (%)
17	0.100	0.090	10
23	0.100	0.160	-60
31	0.100	0.140	-40

Mn During the Addition of Chlorine Dioxide			
Time in Service (days)	Raw Influent (mg/L)	Clar. Effluent (mg/L)	Percent Removal (%)
6	0.101	0.012	88
13	0.101	0.040	60
20	0.101	0.067	35

Table C6.

Iron Data Prior to and During the Addition of Chlorine Dioxide to the Influent.

Fe Prior to the Addition of Chlorine Dioxide			
Time in Service (days)	Raw Influent (mg/L)	Clar. Effluent (mg/L)	Percent Removal (%)
17	0.37	0.05	86
23	0.37	0.12	68
31	0.37	0.10	73

Fe During the Addition of Chlorine Dioxide			
Time in Service (days)	Raw Influent (mg/L)	Clar. Effluent (mg/L)	Percent Removal (%)
6	0.40	0.01	98
13	0.40	0.02	95
20	0.40	0.06	85

Table C7.

Specific Resistance of Sludge and TOC of Supernatant Liquor Prior to and During the Addition of Chlorine Dioxide.

Time Service (days)	in	Supernatant TOC (mg/L)	Specific Resistance ($\times 10^{10}$ m/kg)
17		14	15.7
23		42	16.0
31		45	25.5
Prior to Chlorine Dioxide Addition			

Time Service (days)	in	Supernatant TOC (mg/L)	Specific Resistance ($\times 10^{10}$ m/kg)
6		6.8	7.6
13		6.2	6.4
20		8.8	8.7
During Chlorine Dioxide Addition			

Table C8.

Total Organic Carbon Data from the Culturing of Biofilm and Bladderwort.

Time Cultured (days)	Biofilm TOC (mg/L)	Bladderwort TOC (mg/L)
0	13.3	12.4
10	17.1	16.6
20	18.9	20.3
25	18	23

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