AMMONIA REMOVAL FROM A LANDFILL LEACHATE BY BIOLOGICAL NITRIFICATION AND DENITRIFICATION

by

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ABSTRACT

The discharge of a landfill leachate to a receiving water body can cause a serious pollution problem. One component of leachate that can have a severe impact on a receiving water body is ammonia and its oxidized form, nitrate.

This study investigated the biological treatibility of a high ammonia leachate, with specific regard to nitriification and denitrification. A continuous-feed, single sludge denitrification system with recycle was used. Leachate ammonia concentrations of up to 288 mg/L-N were reduced to less than 1 mg/L. The ammonia was removed by nitrification and bacterial uptake. About 25% of the incoming ammonia was taken up by the bacteria in the anoxic reactor; the rest was subsequently nitrified in the aerobic reactor. The nitrates produced in the aerobic reactor were recycled back to the anoxic reactor to undergo denitrification. Glucose was added directly to the anoxic reactor; however, 100% denitrification was achieved on several occasions. The influent leachate COD removal was 20%; however after the addition of glucose to the system, a mean COD removal of 74% was obtained. Of the COD removed across the system, 85% was used in the anoxic reactor. The four metals monitored regularly, zinc, manganese, nickel and iron were removed by the biomass, but not to the same extent.

During the latter part of the study, the system was first spiked with manganese, and then - zinc, to try and induce an inhibitory effect on the nitrification process. The manganese had no detectable effect on the system. However, total zinc (>95% soluble) levels of between 14.9 and 17.6 mg/L caused substantial inhibition of the nitrification process, resulting in approximately 70 mg/L ammonia in the effluent (feed = 216 mg/L). This inhibition was also evident from the lower percent nitrification values and the unit nitrification rates. This high influent zinc concentration also caused deflocculation, resulting in the loss of significant quantities of biomass with the effluent. The high zinc concentrations also inhibited the deniurifiers, resulting in a decrease in the ammonia uptake, as well as an increase in the COD (used)/Nitrate + Nitrite (NOT) (reduced) ratios in the anoxic

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reactor. The zinc levels were then lowered to allow the system to return to normal; after this state had been reached, the influent total zinc (>95% soluble) levels were again increased up to 19.5 mg/L. This concentration of zinc did not result in any ammonia appearing in the effluent; thus, it is possible that the bacteria had acclimitized to these high influent zinc concentrations.

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1. INTRODUCTION

Landfills and garbage dumps have been in existence for a long time, in fact, the land was probably the first and most convenient site for the disposal of man's wastes. However, it is only recently that we are realizing some of the potential hazards associated with land disposal, the primary one being leachate.

Leachate is generated when water enters the landfill, percolates through it, and picks up soluble materials, some of them soluble products of biological and chemical reactions. The water can enter a fill by such means as precipitation or by drainage of flood waters, springs, or the passage of groundwater through the fill (Patel, Hoye and Toftner, 1979). A four year study of the amount and characteristics of leachate at the Boone County Field Site found a direct correlation between the cumulative precipitation and cumulative volume of leachate produced (Wigh and Brunner, 1979).

Numerous surveys have noted that there are wide variations in the composition of Municipal Solid Waste Landfill leachate (Fuller, Alesii and Carter, 1979; McDougall, Fusco and O'Brien, 1980; Chian, 1977). The variability in composition of leachate from a Municipal Solid Waste Landfill to landfill, is due mainly to the quality and quantity of industrial wastes often included. The variation in leachate composition within a given landfill is due largely to the age of disposal and amount of rainfall contacting the solid waste (Fuller, Alesii and Carter, 1979). Municipal leachates are typically anoxic, contain reduced species and are buffered to a neutral pH. The major inorganic constituents in leachate include chlorides, sulphates, bicarbonates, ammonia , iron(II), manganese II, sodium, potassium, calcium, chromium, copper, nickel, lead and zinc, most of which are found in low concentrations (Jasper, Atwater and Mavinic, 1984).

In a new landfill, aerobic conditions will exist from a few weeks to approximately six months, depending on the fill material. Thereafter, conditions favour autotrophic, facultative anaerobic bacteria, which degrade the organic matter to produce volatile fatty acids (eg. acetic acid,

butyric acid). This degradation does not change the BOD much, but the acids can lower the pH in the landfill to about 4.5 or 5. This low pH increases the solubility of many inorganics in the landfill, and is toxic to the methane producing bacteria; therefore little methane is produced. This is known as the first stage of anaerobic decomposition and is characterized by: high volatile fatty acid production, low pH, high BOD/COD, low methane production and high conductivity. Organic carbon values of up to 25,000 mg/L have been reported during the early months after first establishment of the landfill. The volatile acids were found to be most prominent early in the biodegradation process (Chian, 1977).

The second stage anaerobic decomposition takes place when the methane producing bacteria become established. This stage is characterized by higher pH's and lower COD's and BOD's. The methane producing bacteria degrade the volatile fatty acids to methane (CH₄) and carbon dioxide (CO₂) in approximately a 50%– 50% ratio. The degradation of the acids allows the pH to remain around pH 7. This pH level will decrease the solubility of some of the inorganics. This decrease and the decrease in the volatile fatty acids results in a decline in conductivity (Chian, 1977). A by–product of methane generation is ammonia which is released by the biomass. Therefore, an older landfill will produce a leachate that is characteristically high in ammonia and low in BOD and COD.

Discharge of landfill leachates to receiving waters are posing problems in areas such as aquatic life toxicity, potable water contamination, bioaccumulation of toxic metals, color and odor. One component of leachate that can have a severe impact on a receiving water body is ammonia (NH_4^+) and its oxidized form, nitrate (NO_3^-) . A high ammonia content in the effluent leachate can be toxic to aquatic life. There also exists the potential for dissolved oxygen (D.O.) reduction (through ammonia oxidation) and the potential for eutrophication as a result of nitrate accumulation. Land disposal of the effluent could also result in nitrate contamination.

The purpose of this investigation was to study the biological treatability of a leachate from an "older" landfill, with specific regard to nitrification and denitrification. A continuous-feed, single sludge denitrification system was used. The parameters monitored were ammonia (NH_4^+) , nitrate and nitrate (NOT), influent and effluent solids, mixed liquor solids, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD₅), Total Kjheldal Nitrogen, pH, ORP and trace metals. The system was operated at two solids retention times (also called sludge age) during the study. The system was also spiked with specific trace metals to try and induce a toxic effect on the process. Since the nitrifiers are very sensitive to some heavy metals, knowledge of what metals inhibit the nitrifiers, and in what concentrations, is essential for successful treatment of landfill leachate.

2. LITERATURE SEARCH

The potential problem of leachate formation from landfills would seem to be a long term one. This is due to the fact that no matter what mode of refuse disposal is used, there will always be a residue remaining, which will have to be disposed of at a landfill. Furthermore, it would seem that a landfill site will always be required as a standby disposal method in case of interruption of operation of whatever disposal method is being used (eg. incineration).

With proper planning, good engineering design and adequate monitoring of a landfill site, the problem of leachate contamination of ground and surface waters can be reduced and, in some cases, eliminated. Unfortunately this does not prevent the formation of leachate. Therefore, when direct discharge to a water body causes a pollution¹ problem, collection and treatment of the leachate is required. This section will cover some leachate treatment methods, as well as review the treatment method used for this investigation.

Although leachate is biodegradable, it has a large range of refractory organic components. The soluble organic content of leachate is made up of three groups, in order of decreasing biodegradability:

1. Short chain fatty acids of low molecular weight, which accounts for up to 90% of the soluble organic content.

2. Humic – carbohydrate like substances of high molecular weight, constituting the next highest fraction.

3. Fulvic – like substances accounting for only a small proportion of the total.

In older landfills, the more readily degradable organics have already been removed by natural biological processes within the landfill, so that the humic – carbohydrate like substances and to a lesser extent the fulvic – like substances make up the bulk of the organic content. Therefore biological treatment will generally be effective in removing most of the organics from leachate from

¹"Pollution" is that which is in excess of what the natural environment can assimilate.

recently placed refuse. Biological treatment will not remove the smaller fulvic – like component, or be effective in removing the organics in leachates from older landfills where fulvic – like substances comprise the bulk of the organics. In such cases, physical – chemical treatment may be more effective (Chian and DeWalle 1976).

The high ammonia content in leachates from older landfills can be reduced by physical – chemical means (eg. stripping) or by aerobic biological processes (eg. nitrification). The biological ammonia removal method will be discussed in greater detail later on in this chapter.

Some heavy metals in the leachate can be removed by both physical-chemical and biological processes.

2.1 TREATMENT PROCESSES

2.1.1 SANITARY LANDFILL AS A REACTOR

Several researchers have suggested that recirculation of leachates through a landfill could be used as a method of leachate treatment. Pohland et al; in Jasper Atwater and Mavinic (1984), worked with lab – scale treatment cells and found that after 2 – 3 years, the cells with recycle produced leachate with markedly reduced BOD₅, TOC and COD concentrations.

Robinson and Maris (1982), also conducted experiments to assess the effects of recirculation of leachate and found that leachate produced from natural test cells after 18 months had a low BOD₅, but the COD, ammoniacal– N and chloride remained relatively high, as did the concentrations of some metals; notably iron, manganese, sodium and potassium.

Although both these studies indicate that recirculation of leachate might be a viable option as a first step in some treatment scheme, recirculation at a full – scale site might present difficulties in achieving the high rates of liquid flow found in lysimeters, and consequently making some of the benefits of recirculation observed on a small scale, more difficult to obtain. Robinson and Maris (1985) however, conducted experiments at a full scale landfill site and demonstrated that the benefits of recirculation of leachate, found in smaller studies, can be obtained on a larger scale; however, longer recycle periods may be needed. Nevertheless, these researchers felt that recirculation alone would not provide complete treatment and that a combination of recirculation and aerobic biological treatment may be the most effective option.

2.1.2 PHYSICAL – CHEMICAL TREATMENT

Leachates from older landfills, which have a smaller biodegradable organic component, are more amenable to Physical/Chemical treatment. Physical and or chemical treatment may consist of equalization, lime and polymer treatment, air stripping, precipation, filtration, activated carbon adsorbtion, reverse osmosis, ion exchange and break point chlorination.

Chian and DeWalle (1976) state that physical chemical treatment processes are most effective in treating leachate from stabilized landfills, or in further removing organic matter in the effluent of biological units treating leachate. Of all the physical – chemical processes evaluated, activated carbon and reverse osmosis give the most effective removal of residual organic matter.

Bjorkman and Mavinic (1977) used lime and ozone to treat a high strength leachate, which was typical of leachates from newer landfills. These researchers found effective removal of some metallic ions as well as effective reduction in color and turbidity. The main components of the COD (consisting of mostly organic carbons) however, were not efficiently removed. They also reported that sludge from a physical – chemical treatment process may present a disposal problem.

Cook and Foree (1974) also found that the use of physical – chemical treatment was effective for color removal, but, with the exception of activated carbon, was relatively ineffective for total COD removal.

Ammonia air stripping is the physical/chemical method of removing or reducing the ammonia content in leachates. Keenan et. al. (1984) reported on a leachate treatment facility in Bucks County, Pa. The plant included both physical/ chemical and biological processes, and incorporated air stripping to reduce the ammonia concentration into the biological system to non inhibitory levels (300 mg/L NH_4^+). The physical/ chemical ammonia treatment provided ammonia removals of approximately 50%; however the biological process was needed to further reduce the

ammonia concentrations to dischargable levels, through the process of assimilation and nitrification.

2.1.3 ANAEROBIC TREATMENT

Anaerobic treatment of leachate is a process in which complex organic molecules in the influent are bacteriologically fermented to volatile fatty acids. These acids are then converted to methane and carbon dioxide by methanogenic bacteria, resulting in low production of biological solids requiring disposal. The methane is a useful source of energy and if collected and sold, could reduce the overall cost of the treatment plant.

Wright et. al. (1985) used a 640 litre, anaerobic downflow, stationary, fixed film reactor of National Research Council Design, to treat a landfill leachate with a COD of 22900 mg/L. The reactor was loaded at 1, 2 and 4 Kg COD/m³/day and achieved COD reductions exceeding 92%. Higher loadings and shock loadings resulted in failure. In these cases it is suspected that phosphorus additions may have been helpful in preventing failure. Gas production rate approached the theoretical rate of 0.39 litres of methane per gram of COD removed. The raw leachate had a mean ammonia concentration of 363 mg/L. This treatment system did not remove any of the influent ammonia; infact the ammonia concentration in the reactors increased as a result of nitrogen being provided by the sludge in the reactor (as a result of previous experiments on fish waste).

Boyle and Ham (1974) investigated anaerobic treatment of leachate and found greater than 90% BOD reduction for hydraulic retention times greater than 10 days and temperatures in the range of 23 to 30° C.

Henry et. al. (1982) utilized an anaerobic filter to treat a high strength leachate. These researchers obtained 90% COD removal with a 12 hour detention time at 25° C and with a 72 hour detention time at 10° C. The gas produced was comparable to that produced by conventional anaerobic sludge digestion, but had a higher methane content at 77 – 84%. Regardless of the potential advantages of anaerobic treatment, it still leaves the need for additional treatment for the removal of ammonia.

Austin, et al. (1984) studied the anaerobic treatment of a landfill leachate using anaerobic fixed film reactors. The leachate was a high-strength leachate with a COD of 23000 mg/L and a BOD of 17500 mg/L. The reactors provided better than 98.5% BOD removal and 96.9% COD removal. However, these reactors provided negligble ammonia removal; infact, one reactor showed an increase in ammonia. These researchers also found that the best treatment of this leachate was established with chemical pretreatment, followed by the anaerobic fixed film reactor, plus an aerated lagoon. The pretreatment step was used to buffer the pH so as to enhance methane generation in the anaerobic reactor, as well as precipitate out some metals, namely zinc, that could be toxic to the anaerobic bacteria. The aerated lagoon removed 99.7% of the ammonia.

Since anaerobic treatment of leachate does not remove the ammonia component of leachate, this treatment method does not seem feasible for "older" leachates which have a high ammonia concentration. However, this method has been quite successful in treating high strength leachates from "young" landfills.

2.1.4 AEROBIC TREATMENT

This form of treatment has been shown to be most effective in the removal of organic constituents of leachates from "young" landfills. These leachates contain high concentrations of readily biodegradable short chain fatty acids.

Cook and Foree (1974), Uloth and Mavinic (1977) and Zapf – Gilje and Mavinic (1981) (amongst many), treating high strength leachate, found greater than 95% COD removal was achieved for detention times of 10 days and greater. Cook and Foree (1974) found that for detention times of less than 5 days, the system failed.

Aerobic biostabilization has also been effective in removing a considerable portion of the metals found in high concentrations in "young" or high strength leachates. Zapf Gilje and Mavinic (1981) found that most metals were reduced in concentration by more than 90%, although further polishing was required to meet local effluent pollution control objectives. Since almost all metals accumulate in the sludge, overall successful treatment of leachates must include adequate control of

the resultant sludge.

The proper nutrient balance must be considered in any biological treatment process. Most leachates lack phosphoros; therefore, in order to achieve adequate treatment, it must be added in some form or another. Stegmann and Ehrig (1980) reported that a lack of phosphoros inhibited the biological degradation process, to a certain degree. Generally BOD:N:P ratios should be maintained at 100:5:1, although Temoin (1980), reported that the most effective treatment of a leachate was achieved with a nutrient loading of 100:3.2:1.1. Wong and Mavinic (1982) investigated the treatment of a municipal landfill leachate by aerobic biostabilization. They reported that a BOD₅:N:P loading of 100:3.2:1.1 was "adequate" for treatment.

Aerobic biodegradation must also be capable of treating leachate at cold winter temperatures. In fact, leachate production at a landfill on the West Coast, is often greatest during the winter due to heavier precipitation. Robinson and Maris (1985) treated leachate aerobically at temperatures of 10 and 5° C, and obtained better than 92% COD removal. However substantial phosphoros additions and SRT's of greater than 10 days were required. Lower retention periods produced adverse effects, particularly on clarifying properties of the effluents.

Leachates from "older" landfills (stabilized landfills) are less amenable to aerobic biological treatment as they contain more refractory, fulvic like compounds. Therefore the COD from these leachates is effectively removed using physical – chemical methods, especially activated carbon and reverse osmosis. "Older" leachates are also characteristically high in ammonia. Aside from air stripping (physical – chemical treatment), the only other viable treatment scheme for a high ammonia waste is aerobic nitrification and denitrification.

2.1.4.1 Nitrification

The principal agents of nitrification are considered to be the chemoautotrophic bacteria, which oxidize ammonia sequentially to nitrite and nitrate according to Equations 1 and 2.

$$NH_{4^{+}} + 1.5O_{2^{-}} - - - - \rightarrow NO_{2^{-}} + H_{2}O + 2H^{+} + (240 - 350 \text{ kJ})$$
 (1)

$$NO_2^- + 0.5O_2^- - - - - - NO_3^- + (65 - 90 \text{ kJ})_2$$
 (2)

The energy released in these reactions is used by the nitrfying organisms in synthesizing their organic requirements from inorganic carbon sources, such as carbon dioxide, bicarbonate and carbonate (Barnes and Bliss 1983). Ammonia oxidation is carried out principally by organisms of the genera *Nitrosmonas (N.europaea* and *N.monocella)* and *Nitrosococcus*. Nitrite oxidation is effected principally by members of the genera *Nitrobacter (N.agilis* and *N.winogradskyi)* and *Nitrosocystis*. Oxygen is involved in ammonia oxidation not only by incorporation into the energy substrate as implied by Equation 1, but also in the acceptance of electrons during electron transfer through the cytochrome system. Because the net energy produced in nitrite oxidation is so much less than that produced in ammonia oxidation, the cell yield for *Nitrobacter* is less than that of *Nitrosomonas*, for each unit of nitrogen oxidized. For this reason, *Nitrosomonas* are expected to be present in greater numbers than *Nitrobacter* in nitrifying environments (Barnes and Bliss 1983).

On the assumption that the gross composition of *Nitrosomonas* and *Nitrobacter* can be represented as $C_5H_7NO_2$, the overall reaction for nitrifier synthesis is expressed as Equation 3 (Barnes and Bliss 1983).

Equation 3 shows that nitrification has a very low cell yield per unit of ammonium nitrogen oxidized. It also shows that the requirement for oxygen in nitrification is significant, approximately 4.2g oxygen for each g NH_4^+ -N removed. Approximately 7g of alkalinity are also needed to buffer the system against hydrogen ions produced during nitrification.

The principal problem with effecting nitrification in aerobic biological treatment systems is that nitrifying bacteria are very much slower growing than the heterotrophic organisms involved in carbon removal, and the reaction rate of nitrification is correspondingly slower. This means that in order to maintain a population of nitrifiers in a growth system, the mean sludge age must be long enough to avoid "wash out" of nitrifying organisms from the system. Generally about 5 days is considered a minimum sludge age necessary. (Winkler 1981). If nitrification is to be effected in a treatment plant, the metal concentrations in the waste must also be considered, as the nitrifiers are very sensitive to certain heavy metals. Martin (1979), from Martin and Richard (1982), found that zinc, lead, nickel, copper and chromium were toxic to *Nitrosomonas* at fairly low concentrations.

2.1.4.2 Denitrification

Denitrification is the process by which nitrate ions are reduced to nitrite ions and subsequently to nitrogen gas. Equation 4 represents the reduction of nitrate ions to nitrite ions; Equation 5 represents the reduction of nitrite ions to nitrogen; and Equation 6 represents the overall reaction. Several facultative heterotrophic micro-organisms can carry out these reactions, since it does not need specialist bacteria as is the case for nitrification.

$$NO_{3}^{-} + 0.33CH_{3}OH - --- NO_{2}^{-} + 0.33CO_{2} + 0.67H_{2}O_{2}$$
(4)

$$NO_{2}^{-} + 0.5CH_{3}OH - --- N_{2} + 0.5CO_{2} + 0.5H_{2}O + OH^{-}$$
(5)

$$NO_{3}^{-} + 0.83CH_{3}OH - --- N_{2} + 0.83CO_{2} + 1.17H_{2}O + OH^{-}$$
(6)

In the above equations, methanol (CH_3OH) was used as an electron donor. The denitrifying bacteria must have some chemical to oxidize, i.e. an electron donor, in order to use the nitrate ions as an electron acceptor. Many organic chemicals, for example acetic acid, acetone, glucose and methanol can be used. The organics present in the waste itself may be used; however, in many cases it is not enough for complete denitrification and must be augmented with an extra organic source.

The denitrification process uses nitrate as an electron acceptor and is the next most favoured to oxygen. Phosphate and sulphate can also act as electron acceptors; however, in a

wastewater which has undergone biological nitrification, the concentration of nitrate ions would be expected to be greater than the concentration of phosphate or sulphate ions. Therefore, under conditions of low oxygen concentration, biological denitrification can be expected to occur; these conditions are referred to as anoxic.

2.1.4.3 Biological Ammonia Removal From Leachate

Very little work has been done on biological ammonia removal from leachate, as most research on leachate treatment has concentrated on the removal of the COD and BOD components. This section will review some of the work done to date on biological ammonia removal.

Jasper, Atwater and Mavinic (1984) investigated the biological treatibility of leachate from the Port Mann landfill in Surrey, British Columbia. The treatment set up consisted of 3 single sludge denitrification systems, each operated at a different aerobic sludge age, 10, 15 and 20 days. The influent leachate had ammonia (NH_4^*) concentrations that ranged from 30 to 220 mg/L-N over the course of the study. The removal of ammonia was inconsistent, and the baseline goal of 10 mg/L effluent ammonia was not achieved with any degree of consistency. Nitrification efficiencies of at least 75% were initially obtained but subsequently fell to less than 10% by the end of the study. Metals accumulated fairly extensively in the sludge and it was postulated that this accumulation may have accounted, in part, for the failure of the nitrification/denitrification process. The authors concluded that the removal of nitrogen from raw leachate may not be possible using available biological techniques, at aerobic SRT's of less than 20 days. Some of the mean metal concentrations in the leachate were: zinc=0.55 mg/L, manganese=2.3 mg/L, chromium=0.006 mg/L, nickel=0.02 mg/L, iron=68 mg/L.

Knox (1983) operated an aerobic "fill and draw" bench scale treatment system, to treat a leachate with an ammonia concentration ranging from 200 to 600 mg/L as N. This was a leachate from an "older" landfill and was typically low in BOD and COD (80–250 mg/L and 850–1350 mg/L, respectively). The system proved capable of completely nitrifying the ammonia in the leachate. The metal concentrations in the leachate, however, were very low.

(e.g. zinc=0.16 mg/L, manganese=0.5 mg/L, chromium=0.05 mg/L, nickel=0.04mg/L)

Robinson, Barber and Maris (1982) ran laboratory – scale, aerobic units at a temperature of 10° C for the treatment of leachate. Nominal retention periods of 5, 10, 15 and 20 days were used. They observed that the removal of ammonia resulted entirely from conversion to organic nitrogen during reduction of COD, and no nitrification occured. The reasons given to explain the absence of nitrification were combined effects of sludge age and temperature, the low ratio of nitrogen to BOD in the influent and possible inhibitory substances in the leachate. Some of the metal concentrations in the leachate were: zinc=13.6 mg/L, manganese=21.6 mg/L, chromium=0.08 mg/L, nickel=0.17 mg/L, iron=48 mg/L.

Stegmann and Ehrig (1980) also reported on a lab – scale, activated sludge plant treating leachate. These researchers found that full nitrification was achieved and an influent NH_4 *-N concentration of 973 mg/L was reduced to an effluent concentration of less than 8 mg/L. No influent metal data was presented.

Keenen, Steiner and Fungaroli (1984) reported on a full scale leachate treatment plant located at a landfill in Falls Township, Bucks County, Pa. The leachate had a mean ammonia concentration of 758 mg/L–N. Since this high ammonia concentration was believed to be toxic to nitrifiers, chemical/physical treatment was used to reduce the ammonia concentration to a level suitable for biological treatment, as well as precipitating out the metals. The influent ammonia into the biological units had a mean concentration of 350 mg/L–N, and the effluent had a mean concentration of 75 mg/L–N. This reduction was primarily due to nitrifying organisms. Some of the mean metal concentrations into the biological units were: zinc=0.53mg/L, chromium=0.07 mg/L, nickel=0.75 mg/L, iron=2.71 mg/L. These metal concentrations were very low compared to the raw leachate influent metal concentrations. The authors also reported that the cold winter temperatures inhibited the biochemical oxidation of ammonia, resulting in severe operating problems.

The best treatment method suited to "older" leachates, which have a high ammonia content, would seem to be aerobic nitrification and denitrification. Researchers who have

investigated this method of leachate treatment have had varied success with the removal of ammonia. The purpose of this study was to determine conclusively, whether or not a high ammonia leachate could be treated successfully with this method, as well as to determine what metals in the leachate, and in what concentration, would inhibit this process.

3. EXPERIMENTAL SET-UP AND OPERATION

3.1 TREATMENT SCHEME

The reactor set up used was a single sludge denitrification system with recycle, shown schematically in Figure 1. This system, supplied by Wastewater Technology Center, EPS, Burlington Ontario, will be called "system 1". A second system was set up during the second half of the study to act as a control to system 1, which was to be spiked with trace metals. The control set up will be known as "system 2", schematically shown in Figure 2. The process for system 1 is described in detail below.

3.1.1 BIOLOGICAL TREATMENT SYSTEM 1.

3.1.1.1 Leachate Feed

The leachate used for this study was obtained from the Port Mann landfill in Surrey, British Columbia (Figure 3), and is classified as an "older" leachate. The basic characteristics of this leachate are shown in Table 1. Fresh leachate was obtained from 2 different wells at the landfill every 2 weeks, well #2 and well #3, which are shown on Figure 3. The only measured difference between the leachates from the two wells was that well #3 produced a leachate that had a consistently higher ammonia (NH₄⁺) concentration. The leachate was stored in closed containers and at a temperature of 4° C, until used. Chian and DeWalle (1976) state that storage under anaerobic conditions and at low temperatures is necessary to avoid a decrease in COD and an increase in suspended solids. Leachate feed was continuously added to the anoxic reactor at a rate of approximately 10 litres a day, from a constantly mixed supply contained in a plastic tank. The tank was covered with a lid to prevent excess aeration of the feed.

3.1.1.2 Anoxic Reactor

The main function of the anoxic reactor was to denitrify the highly nitrified return sludge from the clarifier, according to Reaction step 7.

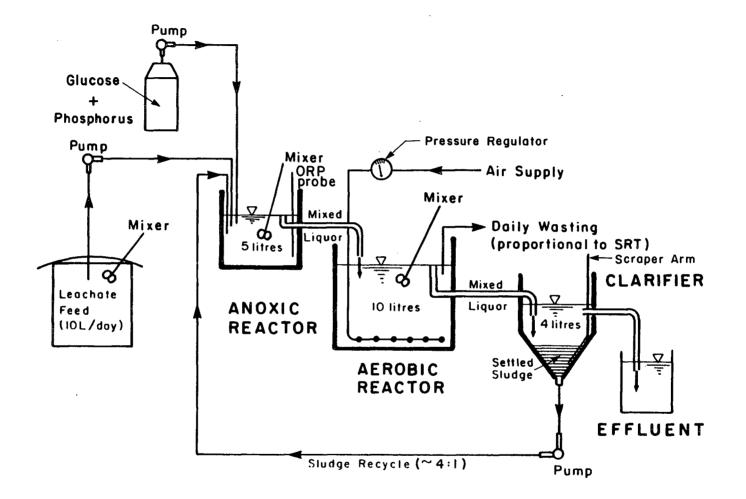


Fig. 1: LABORATORY BIOLOGICAL TREATMENT SYSTEM 1.

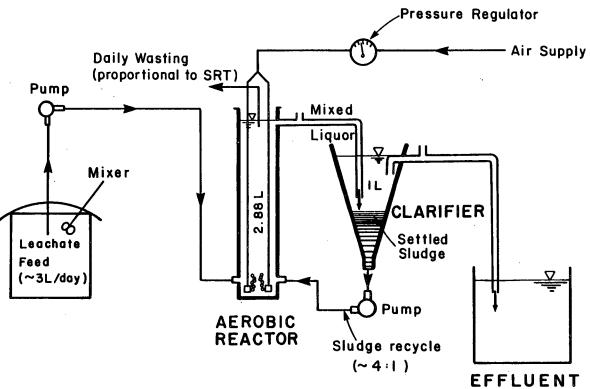


Fig.2: LABORATORY BIOLOGICAL TREATMENT SYSTEM 2 (control).

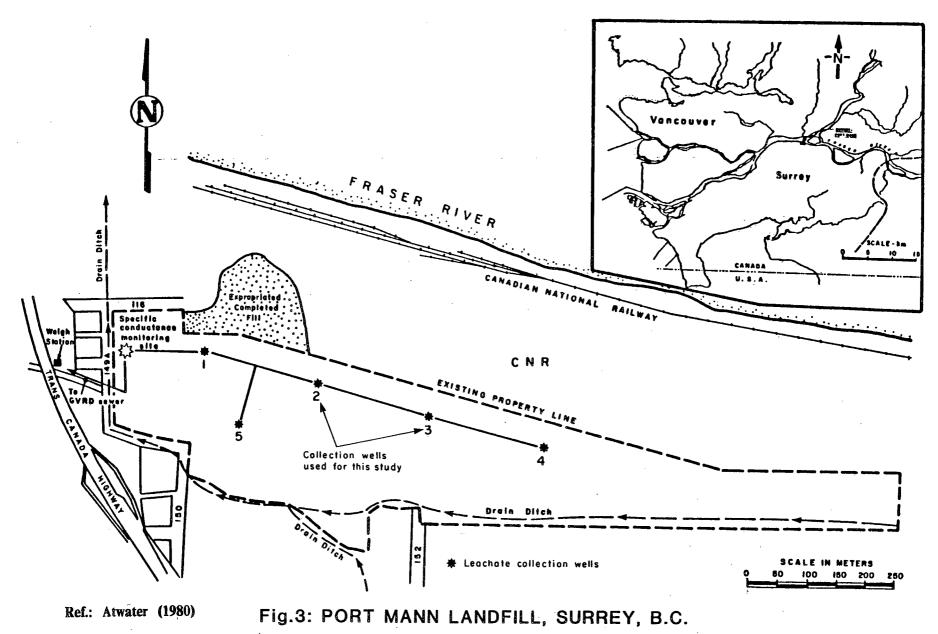


Table 1. Basic Characteristics of Port Mann Leachate

Parameter	Concentration*
COD	217 - 318
BOD5	6 - 24
Ammonia-N	122 - 288
pH	7.5 - 8.3
Zinc	0.018 - 0.179
Manganese	0.024 - 0.286
Iron	3.70 - 36.25
Nickel	0.022 - 0.066

* All values expressed as mg/L, except pH in pH units.

 $NO_3^- - - - - NO_2^- - - - - N_2(g)$ (7)

This reduction of nitrates to nitrogen gas is carried out by heterotrophic bacteria. The reactor was a plexiglas tank with a liquid volume of 5 litres and a mechanical mixer. In addition to receiving fresh leachate continuously, the anoxic reactor also received a solution of glucose and sodium phosphate tribasic (Na_3PO_4 .12H₂O). Phosphorus was added to prevent nutrient limitation. Several measurements of phosphorus were carried out on the clarifier effluent to ensure that it was not limiting. Since the BOD, of the influent leachate was very low, it was necessary to provide an additional carbon source (electron donor) for the denitrification process. Therefore, glucose was added to the sodium phosphate tribasic solution. Methanol is a common carbon source used for denitrification, but was not used for this study since it has been found to inhibit ammonia oxidation (Hooper and Terry 1973). Barnes and Bliss (1983) state that, although many organic compounds are inhibitory to nitrifiers, especially *Nitrosomonas*, glucose is one compound that is not. In the latter part of the study, trace metals, namely manganese and zinc, were added directly to the anoxic reactor, in order to induce inhibition of the nitrification system. An ORP probe was also installed in the anoxic reactor in the latter part of the study, to ensure that there was a reducing environment to facilitate denitrification.

3.1.1.3 Aerobic Reactor

This reactor was a large, polythelene carboy with a liquid volume of 10 litres, and was gravity fed from the anoxic reactor. The tank was aerated by a perforated pipe diffuser, fitted to the bottom of the tank. A mixer ensured that the contents were well stirred. A residual (D.O.) of between 1 and 3 mg/L provided sufficient oxygen for carbonaceous oxidation and nitrification of ammonia. The nitrification process itself involves the oxidation of ammonia to nitrates by chemoautrophic bacteria, according to Reaction step 8.

 $NH_4^+----> NO_2^----> NO_3^-$ (8)

In order to maintain a desired SRT, Mixed Liquor Suspended Solids (MLSS) was wasted directly from the aerobic reactor in proportion to the SRT.

3.1.1.4 Final Clarifier

A conical, plexiglas tank with a 4 litre capacity, was used as the clarifier. Mixed-liquor from the aerobic reactor was fed to the clarifier, by gravity, where it was settled and gravity thickened for approximately 2 hours. The supernatant overflowed a weir and then flowed by gravity into a collection tank. The nitrified settled sludge was recycled back to the anoxic reactor at a rate of approximately 4:1. The recycle pump was operated on a cycle of 15 minutes on and 15 minutes off. This combination was necessary to clear the recycle line of mixed liquor solids, as well as to provide proper volumetric thoroughput. Nevertheless, over time, the insides of the recycle line became coated with bacterial growth, and it was necessary to "pinch" the line every so often, to free it of the attached growth. One problem that was encountered with the clarifier operation was that the sludge tended to adhere to the sides of the clarifier. In order to alleviate this problem, a scraper mechanism was installed on day 72 of steady state; this kept the clarifier sides free of sludge. The scraper mechanism was operated on a cycle of 1 minute on and 15 minutes off.

3.1.2 BIOLOGICAL TREATMENT SYSTEM 2

3.1.2.1 Leachate Feed

The leachate used was the same as the one used for system 1. The leachate feed was fed continuously to the aerobic reactor at a rate of approximately 3 litres a day, from a constantly mixed supply contained in a plastic tank. The tank was covered with a lid to prevent excess aeration of the feed.

3.1.2.2 Aerobic Reactor

The reactor was a plexiglas cyclinder, with a liquid volume of 2.88 litres. The reactor was aerated with 2 stone diffusers. Due to a lack of mixers, the diffused air was utilized to keep

the mixed liquor completely mixed. The D.O. provided sufficient oxygen for carbonaceous oxidation and nitrification of ammonia. In order to maintain a desired SRT, MLSS was wasted directly from the aerobic reactor in proportion to the SRT.

3.1.2.3 Final Clarifier

A conical, plexiglas cyclinder with a 1 litre capacity, was used as the clarifier. Mixed liquor from the aerobic reactor was fed to the clarifier, by gravity, where it was settled and gravity thickened for approximately 2 hours. The supernatant flowed by gravity into a collection tank. The nitrified sludge was recycled back to the aerobic reactor at a rate of approximately 4:1. The recycle pump was operated on a cycle of 15 minutes on and 15 minutes off.

3.2 OPERATION

3.2.1 BIOLOGICAL TREATMENT SYSTEM 1

The treatment system was started up on February 23rd, 1984 with 15 litres of sludge from a sewage treatment, pilot plant operating at the University of British Columbia. Continuous leachate feed was also started at this time. Mixed liquor wasting was started a few days later. April 26th, 1984 was regarded as day 1 of steady state, although full nitrification had already been reached in early March. Mixed liquor was wasted from the aerobic reactor in order to maintain a 13 day aerobic SRT. The amount wasted was changed on day 54 in order to obtain a 15 day aerobic SRT. This change was made to enable comparison with results obtained from Jasper, Atwater and Mavinic (1984), in an earlier study. Addition of glucose to the anoxic reactor was started on day 11. The amount of glucose entering the system varied overtime. This was due, primarily, to the variation in the speed of the pump, that was used to feed glucose to the anoxic reactor. Metal addition to the anoxic reactor with the glucose solution. However, both metals formed a precipitate with the phosphate, also in solution, and it was therefore necessary to add the phosphate to the

anoxic reactor, separately, on a daily basis.

3.2.2 BIOLOGICAL TREATMENT SYSTEM 2

This treatment system was set up on October 8th, 1984 with 2.88 litres of sludge from system 1. At this point in the study, it was planned to add metals to system 1, to try and induce an inhibitory effect on the nitrifiers. In response to this, system 2 was set up to act as a control. Both systems were receiving the same leachate, and both were operating at the same SRT and recycle rate, the only difference being that system 1 was receiving a higher metal concentration, as well as employing an anoxic basin for denitrification. Therefore, any change detected in system 1 and not in system 2, could then be attributed to the metal spiking. System 2 did not include an anoxic reactor in the belief that the most susceptible bacteria to high metal concentrations in the biological ammonia removal process were the nitrifiers, and these bacteria need only an aerobic environment. Mixed liquor was wasted from the aerobic reactor at a rate of 192 ml per day, in order to maintain a 15 day aerobic SRT. Phosphate was added to the aerobic reactor every few days to ensure that nutrient limitation did not occur.

4. ANALYTICAL METHODS

All tests were carried out on system 1, with the exception of nitrate + nitrite and ammonia, which were done on both systems.

4.1 <u>SOLIDS</u>

Suspended Solids (SS) and Volatile Suspended Solids (VSS) tests were performed on the influent leachate and effluent, once a week. Mixed Liquor Suspended Solids (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS) tests were performed on the contents of the anoxic and aerobic reactors, once a week. All analysis of solids was done conforming to the procedure outlined in Standard Methods (1980).

4.2 DISSOLVED OXYGEN AND PH

pH measurements were taken on filtered samples of influent, effluent and anoxic and aerobic MLSS. These measurements were done twice a week for the first half of the study. Occasional checks were made during the latter half of the study to ensure that the pH was in the right range (pH 7.5–8.5) for nitrification and denitrification. The pH meter used was a Fisher Accumet Model 320, Expanded Scale Research pH meter.

Dissolved oxygen values were spot checked during the entire study to ensure that D.O. levels of between 1 and 3 mg/l were maintained in the aerobic reactor, as well as ensuring that negligble D.O. was being entrained in the anoxic reactor. A Yellow Springs Instruments Co. Ltd., Model 54A Oxygen meter was used for measuring the D.O. levels.

4.3 ORP (OXIDATION-REDUCTION POTENTIAL)

An ORP probe was installed in the anoxic reactor during the second half of the study, to ensure that reducing conditions were present. ORP was measured using a Cole Parmer Digi phase pH Meter, with platinum probe electrode and a calomel reference electrode. ORP was reported as Ecal, that is, millivolts with respect to the calomel electrode.

4.4 BOD (BIOCHEMICAL OXYGEN DEMAND)

BOD₅ measurements were carried out on filtered samples from the influent, effluent and anoxic and aerobic contents. The filter paper used was a Whatman #4. These measurements were made once a week during day 70 to 120 of steady state. BOD₅ was determined by the procedure in Standard Methods (1980). A Y.S.I. Model 54 oxygen meter was used to measure the initial and final dissolved oxygen. The azide modification of the Winkler titration (Standard Methods 1980) was used to standardize the dissolved oxygen probe. The dillution water was seeded (5 mls seed per litre of dilution water) with influent from a UBC campus pilot treatment plant.

4.5 COD (CHEMICAL OXYGEN DEMAND)

The COD test was performed on filtered samples from the influent, effluent and anoxic and aerobic reactors. The filter paper used was a Whatman #4. The test was done twice a week until the latter half of the study, when it was performed only once a week. The procedure followed was as outlined in Standard Methods (1980). Mercuric sulphate was added to the samples to remove any chloride interference.

4.6 TKN (TOTAL KJELDAHL NITROGEN)

TKN on the influent and effluent were run during the first quarter of the study. The effluent was filtered on a Whatman #4 filter paper. This test was carried out to determine what the ratio of TKN to ammonia was. It was determined that the ammonia comprised greater than 70% of the TKN, and this was found to be consistent for the duration of the testing. The method of analysis

used is outlined in the Technicon Manual (1974), and the instrument used was a Technicon Auto Analyser 2 S.C. Colorimeter.

4.7 TP (TOTAL PHOSPHOROS)

TP was run on effluent samples from time to time, to ensure that enough phosphoros was being added to the system, and nutrient limiting was not occuring. The method of analysis used is outlined in the Technicon Manual (1974), and the instrument used was a Technicon Auto Analyser 2 S.C. Colorimeter.

4.8 <u>AMMONIA NITROGEN</u>

This test was run twice a week for the duration of the study; however ammonia testing on system 2 was started during the latter half of the study. Ammonia was run on filtered (Whatman #4 filter paper) samples from the influent, effluent, and anoxic and aerobic reactors, for system 1. Only the effluent samples were tested for system 2. This was done to check and ensure that the nitrification process was working well, and that no ammonia was escaping into the effluent. The testing method used was the distillation process. In this method, the sample is buffered at a pH of 9.5 with a borate buffer and distilled into a solution of indicating boric acid. The ammonia is then determined titrimetrically with standard sulfuric acid. Buffering decreases hydrolysis of cyanates and organic nitrogen compounds. Ammonia was analysed immediately after sample collection.

4.9 NITRATE AND NITRITE

Nitrate + nitrite were run on filtered samples (Whatman #4 filter paper) from the influent, effluent and anoxic and aerobic reactors. During the letter half of the study, nitrate + nitrite testing was also done on the filtered effluent of system 2. These tests were run twice a week. Nitrite itself was also run occasionally on both systems, although this testing was done more frequently towards the end of the study. The tests were carried out according to the Technicon Manual (1974), and the instrument used was a Technicon Auto Analyser 2 S.C. Colorimeter. One change made to the

Technicon procedure for nitrates + nitrites was that, instead of using cadmium granules, a cadmium-silver alloy wire in teflon tubing was used as a column. The column was prepared according to a method outlined in Anal. Chem. 1980, 52, 1376–1377.

4.10 TRACE METALS

Weekly analyses were done for four metals: zinc, manganese, iron and nickel. Metal monitoring was started around day 50 of steady state. Lead and chromium concentrations were also monitored during certain periods. Influent, effluent, anoxic and aerobic samples were checked. Since the metal concentrations in the influent and effluent were low, it was necessary to concentrate these samples. 500 mls of unfiltered influent, and 500 mls of filtered (on Whatman #4 filter paper) effluent were digested down to 50 mls. The digestion method follows closely the method in the recommended EPA procedure (Methods for Chemical Analysis of Water and Wastes, 1979). The anoxic and aerobic mixed liquor samples were first centrifuged, after which the seperated liquid was wasted. The remaining solids were dried at 105° C, ground up and then digested. The digestions, the EPA recommendation to omit HCl from the digestion and use only HNO₃ was followed, since it was intended to use the graphite furnace for lead detection. The graphite furnace used was a Perkin Elmer HGA 500 703 Atomic Absorption Spectrophotometer. All other metal analyses were done on another Atomic Absorption Spectrophotometer, a Jarrell Ash AA (Model 810).

5. RESULTS AND DISCUSSION

All data presented in this section was obtained on system 1, unless otherwise specified. Steady state was defined as complete nitrification and no presence of ammonia in the effluent.

5.1 CARBON REMOVAL

The influent leachate COD was relatively low and ranged between 217 and 318 mg/L. The treated effluent COD concentrations were also in the same range. Before the addition of extra carbon to the anoxic reactor, a 20% removal of the leachate influent COD was obtained. This indicated that the refractory organic component of the influent leachate was about 80%, which is characteristic of older leachates. If no extra carbon had been added to the system, it is possible that the bacterial population might have developed the ability to degrade a larger portion of the refractory organics, but the probability is low. Chian and DeWalle (1976) reported on a study that tested the effectivness of activated sludge treatment on "old" leachate. Results also showed no decrease in COD after an aeration period of 184 hours, due to the refractory nature of the organics.

The additional carbon (glucose) added to the system for denitrification formed a major component of the influent COD (shown in Figure 4). Because the leachate influent and effluent COD's were similar, it would seem that the glucose component of the COD was being completely removed. Since the flow rate for the influent varied, a more representative way of showing the influent COD would be in terms of mg/day (shown on Figure 5), rather than mg/L, although the two figures are not dissimilar. Even though there were large fluctuations in the influent COD, the effluent COD remained at a fairly constant level, thus proving the system capable of handling the shock loading with respect to COD. The COD removal is shown in Figure 6, with a mean removal efficiency of 73.9%. The metal spiking did not seem to have an effect on the COD removal efficiency of the system. Figure 7 shows that the percent COD removed also increased as the glucose component of the influent COD increased, an expected result.

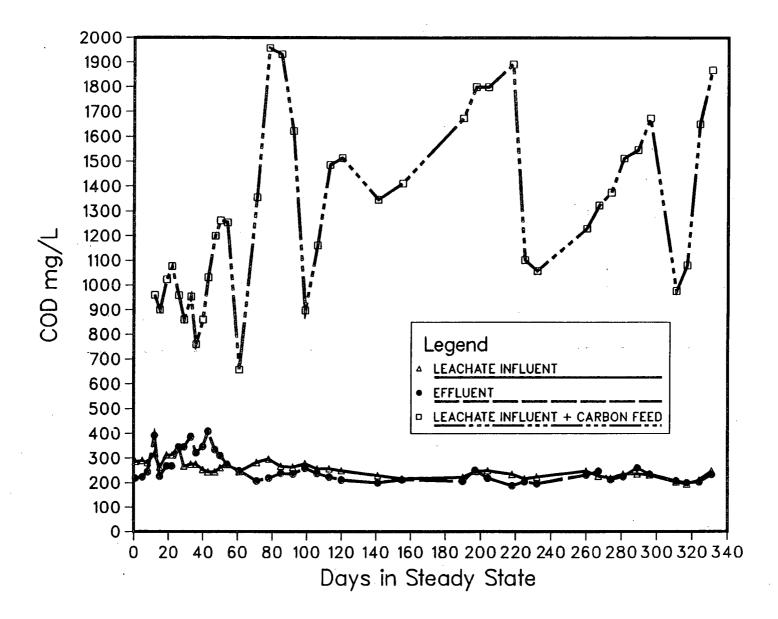


Figure 4.: Influent and Effluent COD Versus Time

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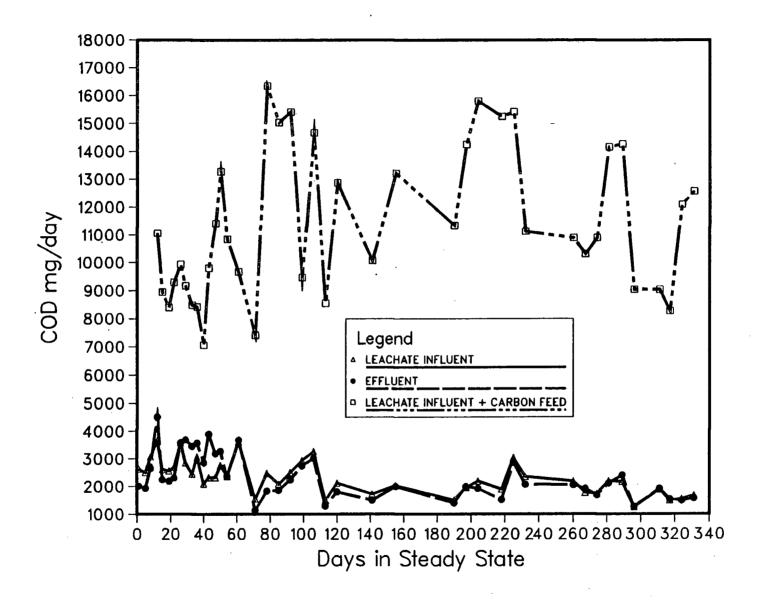
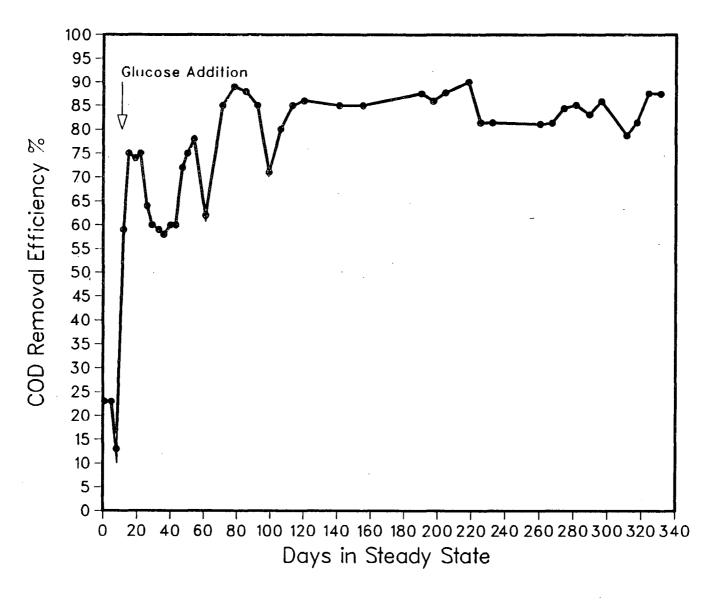


Figure 5.: Influent and Effluent COD Versus Time



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Figure 6.: COD Removal Efficiency Versus Time

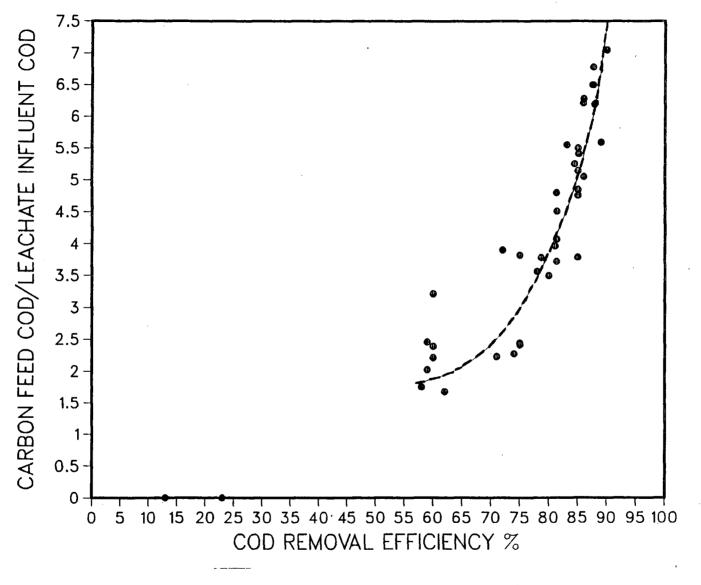


Figure 7.: Ratio of Carbon Feed to Leachate Influent COD Versus COD Removal Efficiency

An average of 85% of the destroyed COD was consumed in the anoxic reactor, presumably by the heterotrophic bacteria involved in the denitrifying process. The rest of the degradable carbon, 15%, was consumed by the heterotrophs in the aerobic reactor (shown in Figure 8).

BOD₅ measurements were made from day 70 to 120. The leachate influent BOD₅ was very low and varied from 8 to 24 mg/L as shown in Figure 9. The actual feed BOD₅ was high, as it was comprised mostly of glucose added for denitrification; however, the effluent BOD₅ was consistently below 25 mg/L (see Figure 9). A mean removal efficiency of 97.8% was obtained (see Figure 10).

5.2 SOLIDS (SS AND VSS)

The influent and effluent SS concentrations are shown in Figure 11. The effluent SS was usually lower than the influent; however, after the start of metal spiking on about day 220, the effluent SS concentration stayed high, and reached a peak on day 290. This peak also corresponded with the highest zinc concentration (Figure 12) added to the system, before inhibition of the nitrification system was detected. The influent zinc concentration to the system, during the spiking period, was at least 95% in soluble form. Since inhibition of the nitrification system was taking place at this time, there were a lot of stressed bacteria present, that simply deflocculated and went out with the effluent, thereby causing a rise in the effluent SS. From days 290 to 310, approximately, the zinc levels were brought down (Figure 12) and correspondingly the effluent SS values also decreased. However, after day 320, zinc spiking was again started; this time, however, a pronounced increase in the effluent SS values was not detected. The zinc spiking was stopped after day 335; therefore, it is difficult to tell if this trend would have continued.

It is speculated that the system became acclimitized to high influent concentrations of zinc, and the zinc no longer had the same effect of increasing the effluent SS, as was previously detected. Neufeld (1976) reported that shock loadings of heavy metals to activated sludge result in the formation of a highly stable pinpoint floc, and this condition termed "sludge deflocculation" has resulted in the loss of significant quantities of biomass over the effluent weir of continuous systems. He reported severe deflocculation when zinc levels exceeded 40 mg/L for a 20 day sludge age. This

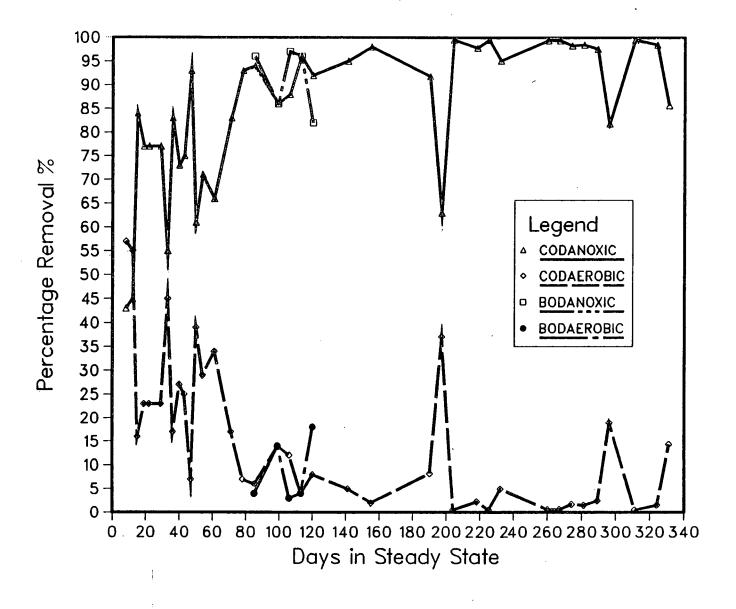


Figure 8.: Percentage COD and BOD₅ Removal Across the Reactors Versus Time

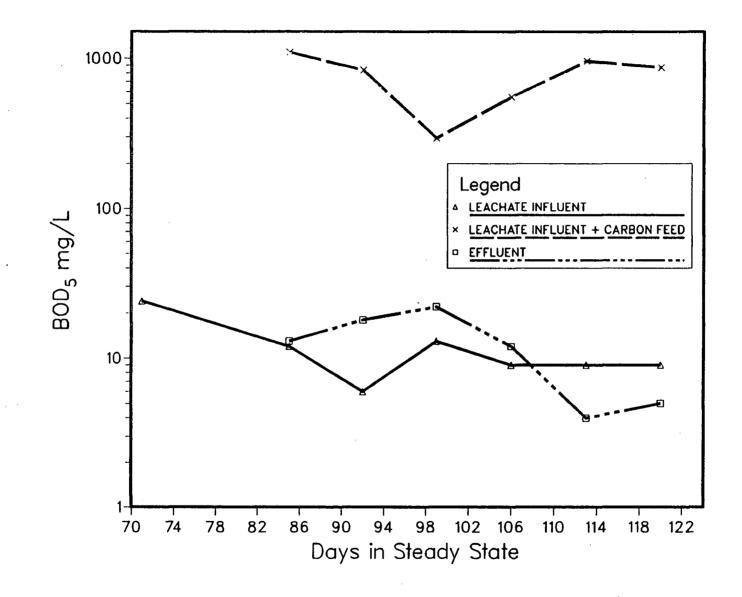


Figure 9.: BOD₅ Versus Time

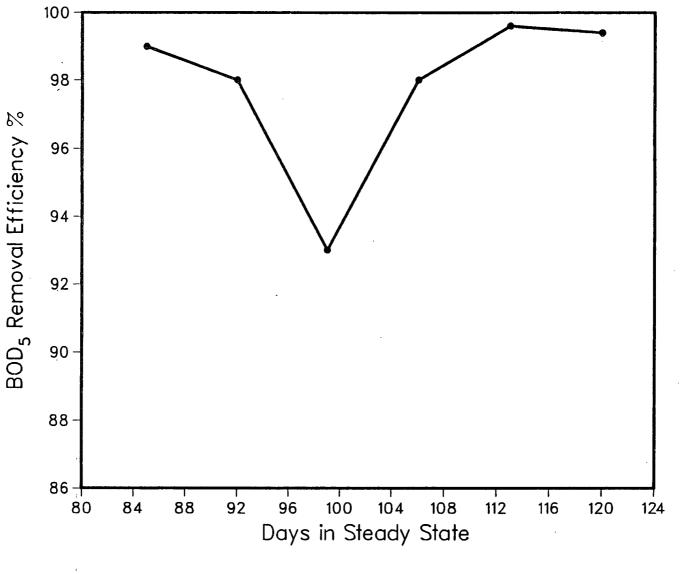
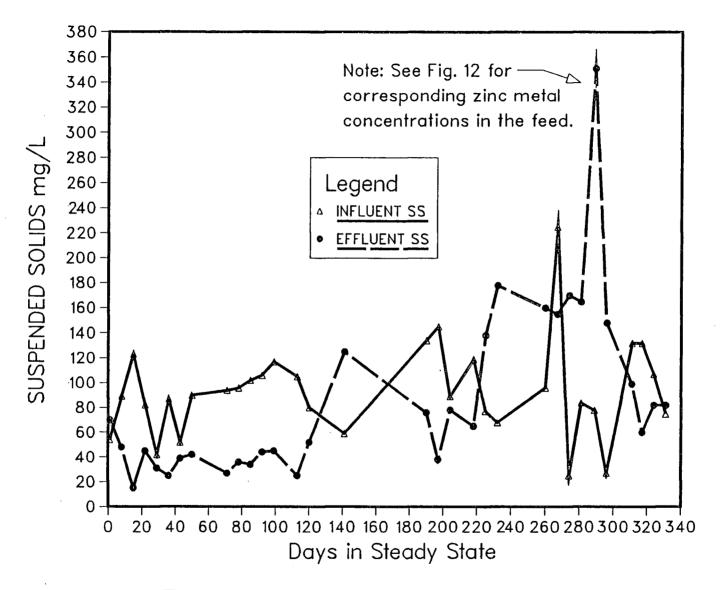


Figure 10.: BOD₅ Removal Efficiency Versus Time



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Figure 11.: Influent and Effluent SS Concentration Versus Time

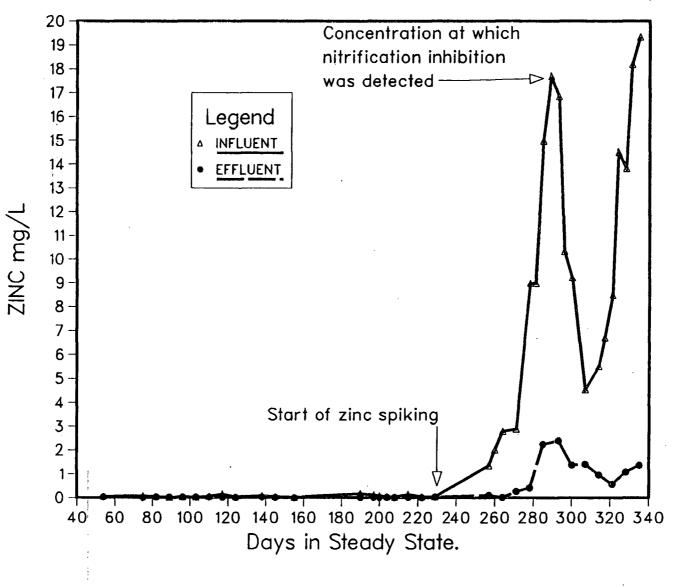


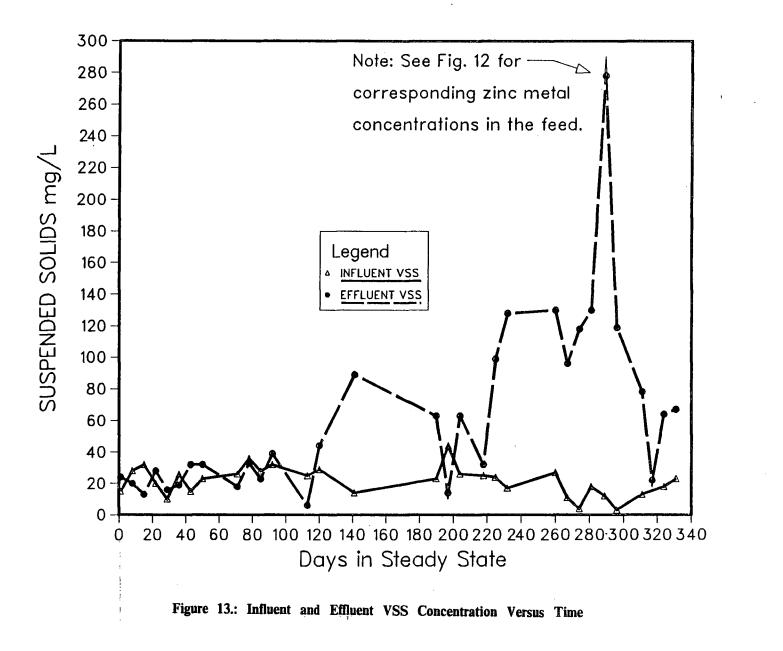
Figure 12.: Influent and Effluent Zinc Concentration Versus Time

is probably the same phenomena responsible for the high effluent SS in this system, prior to acclimitation.

The influent and effluent VSS concentrations followed a similar trend as the influent and effluent SS concentrations (Figure 13). Without the metal spiking, the clarifier produced an effluent with fairly low VSS, below 40 mg/L. This is clearly seen on Figure 13 from days 0 to 115. This level of suspended solids would enable discharge of the effluent (based on SS) to any receiving water body in British Columbia (Dept. of Lands, Forest and Water Resources (1975)). From days 120 to 190, the effluent VSS appears to have climbed to approximately 80 mg/L. However, this part of the curve was only based on two points, and may not be representative of the VSS values throughout that whole period. The influent VSS concentrations were consistently below 40 mg/L throughout the study (day 0 to 335).

The anoxic and aerobic MLSS concentrations are shown on Figure 14. From day 11, which was when glucose was first added to the anoxic reactor, to about day 54, the anoxic MLSS values were up to 20% greater than the aerobic MLSS values. On day 54, the aerobic SRT was changed from 13 to 15 days. After this time the aerobic MLSS values were greater than the anoxic values, remaining so for the duration of the study. This change is also apparent in Figure 15, which shows the anoxic and aerobic MLVSS concentrations. The anoxic and aerobic MLVSS closely follow the trends of the anoxic and aerobic MLSS. There is no apparent reason for the difference between the anoxic and aerobic values for both MLSS and MLVSS concentrations. This difference could be partially due to sampling technique, however, there are probably other explanations that are responsible. The fluctuations in the anoxic and aerobic MLSS and MLVSS are probably due to the variant carbon loading into the anoxic reactor. Figure 16 shows that, as the ratio of carbon feed COD to leachate COD increased, the MLVSS concentrations in both the reactors increased.

The MLVSS/MLSS ratios for the anoxic and aerobic reactors are shown in Figure 17. The average MLVSS/MLSS ratio for the anoxic and aerobic reactors are: 0.66 and 0.65 respectively. These values are a little higher than those reported by Jasper, Atwater and Mavinic (1984), who used a similar system to treat leachate from the same landfill.



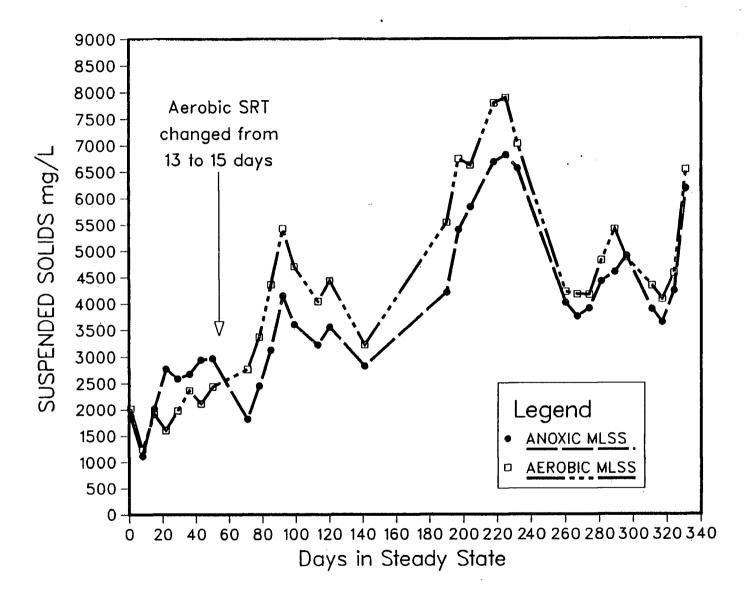


Figure 14.: Anoxic and Aerobic MLSS Concentration Versus Time

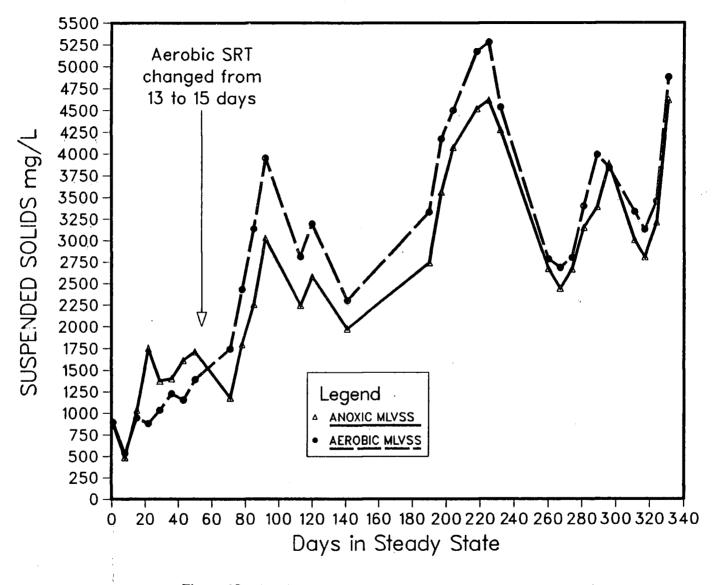


Figure 15.: Anoxic and Aerobic MLVSS Concentration Versus Time

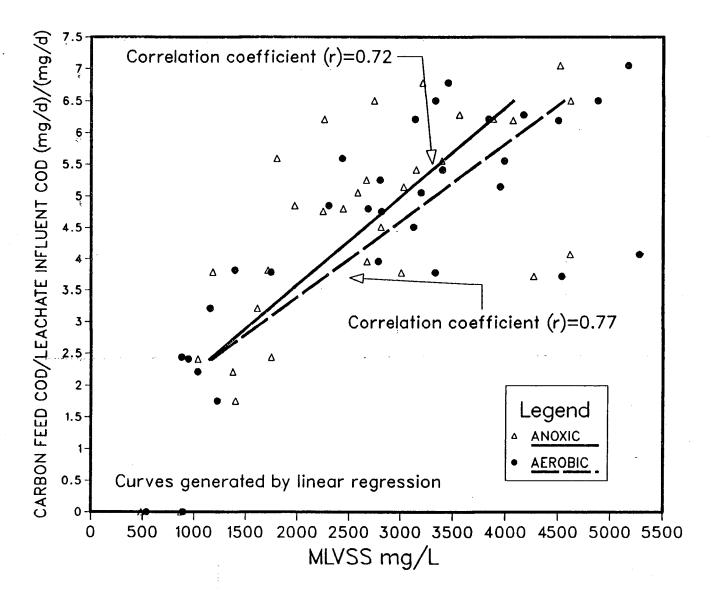


Figure 16.: Ratio of Carbon Feed to Leachate Influent COD Versus MLVSS Concentration

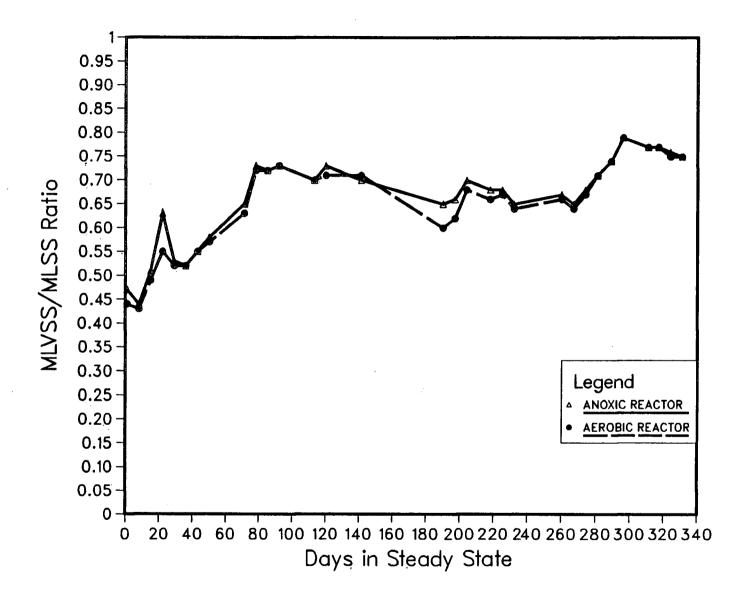


Figure 17.: MLVSS/MLSS Ratios in the Reactors Versus Time

5.3 AMMONIA REMOVAL

The primary objective of this study was to try and remove the ammonia from the leachate. The Port Mann leachate is relatively high in ammonia (NH_4^+) with concentrations ranging from 120 to 288 mg/L–N. As reported earlier, the ammonia formed a major component of the total kjeldahl nitrogen.

The influent, effluent and anoxic ammonia concentrations are shown in Figure 18. The aerobic and effluent ammonia concentrations were found to be the same, and are therefore represented as one curve. The influent ammonia concentrations were consistently above 200 mg/L-N, for the first half of the study. During this time, only well #3 at the landfill site was used for leachate collection. During the latter half of the study, operational problems were frequently encountered with well #3. Whenever this well could not be used, well #2 was utilized; however, well #2 produced a leachate with a relatively lower ammonia concentration. This also gave rise to fluctuations in the influent ammonia concentrations into the system. As shown in Figure 18, essentially complete ammonia removal was achieved, (except for days 200 and 290 to 315), and this was independent of fluctuations in the influent ammonia concentrations. A high effluent ammonia concentrations of less then 0.5 mg/L in the aerobic reacter. This low D.O. was caused by a leak in the air line to the aerobic reactor. This condition lasted about two days, before it could be rectified.

On approximately day 290, the effluent ammonia concentrations started to rise sharply, with a peak concentration of about 75 mg/L. This also corresponds to the period of initial highest influent zinc concentrations to the system. The system received a concentration 17.6 mg/L zinc on day 289. Since the effluent ammonia concentration was still approximately zero until this time, it would seem that the inhibition level of the nitrification system had been reached, with this concentration of zinc. No inhibition was observed at 14.9 mg/L zinc; however it is conceivable that the inhibitory level for this system could be between 14.9 mg/L and 17.6 mg/L of zinc.

It was obvious that this inhibition, in system 1, was being caused by the zinc spiking, since system 2, which was being fed the same leachate, showed no rise in the effluent ammonia

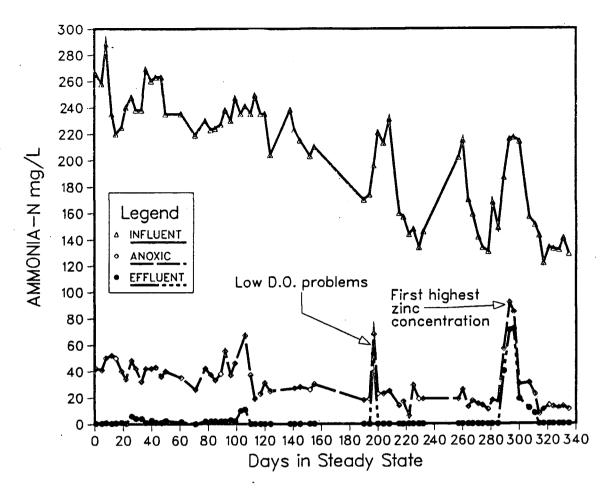


Figure 18.: Ammonia Concentration Versus Time

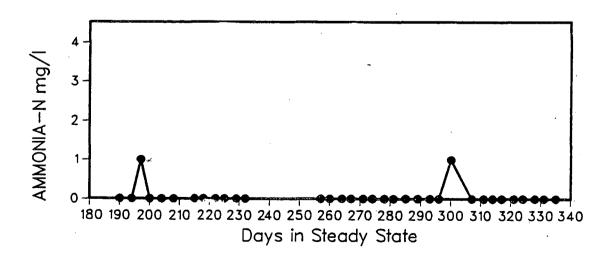


Figure 19.: Effluent Ammonia from System 2 Versus Time

concentrations (see Figure 19). In an attempt to discover if the system had the potential to recover from this inhibition, the influent zinc concentrations were promptly dropped, as shown in Figure 12. The influent zinc concentrations were systematically brought down until the ammonia concentration in the effluent was again at the zero level. This did not happen until day 314, when the influent zinc concentration was 5.5 mg/L. Since the lowering of the influent zinc concentration was started on day 296, this meant the system took 18 days to recover back to its stable state.

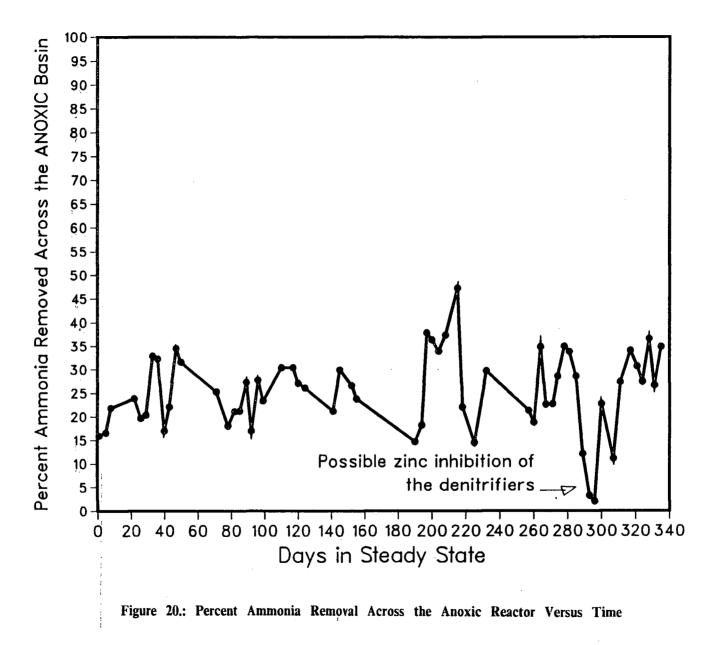
Once the system had recovered, the influent zinc concentrations were again raised (Figure 12) in order to narrow down the systems inhibitory concentration, assumed to be between 14.9 and 17.6 mg/L. The influent zinc concentration was steadily increased, over a 21 day period, until a concentration of 19.5 mg/L was reached on day 335. Up to this point, no rise in the effluent ammonia concentration was detected. From these results, it would seem that the nitrifiers were now acclimitized to these high levels of influent zinc. Unfortunately, the study had to be terminated on day 335, so the question of how much acclimation had taken place remained unanswered.

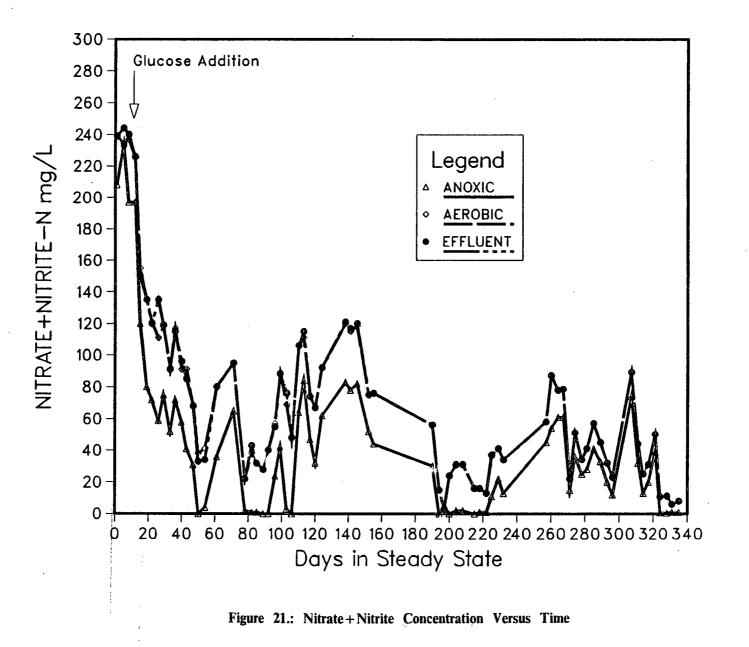
Most of the ammonia removed in the system was converted to nitrates in the aerobic reactor; however, some of the ammonia was taken up by the biomass. Figure 20 shows that a mean 25% of the influent ammonia was removed across the anoxic reactor by biomass uptake and perhaps, some stripping; however, because of anoxic conditions and pH's of 7.6–8.1, the component of ammonia removed by stripping would be very low. Therefore, the values shown in Figure 20 very closly represent the ammonia removed by the biomass in the anoxic reactor.

5.4 NITRIFICATION

The anoxic, aerobic and effluent NOT as N (nitrate + nitrite) concentrations are shown in Figure 21. Measurements for nitrite concentration were done occasionally and found to be negligible at most times; there were, however, instances where nitrite formed a substantial component of NOT, but this was only transient.

After the addition of glucose to the system on day 11, the pH in the anoxic and aerobic reactors was maintained around pH 8. According to Barnes and Bliss (1983), proportions of free

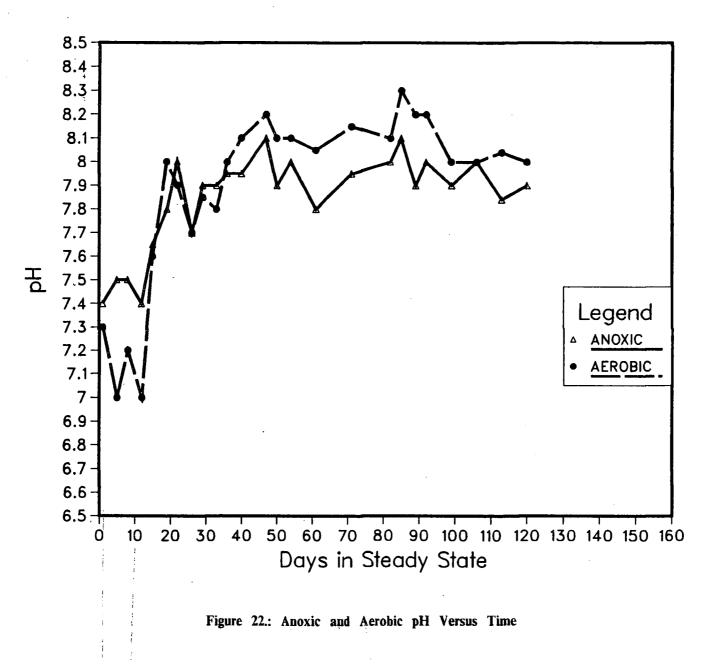




ammonia at a pH of 8 and a temperature of 25° C are about 5%, and 36% at a pH of 9 and a temperature of 25° C. The author mentions that inhibition of *Nitrosomonas* by free ammonia is likely in the range of 10 to 150 mg/l, but *Nitrobacter* is likely inhibited at much lower concentrations of 0.1 to 1.0 mg/L. This leads to the possibility that in wastes containing high concentrations of NH₄⁺/NH₃, inhibition of *Nitrobacter* may lead to the accumulation of nitrite. This could very well be the phenomena occuring in this system; as the pH goes up and down, even in a small range, there might be enough free ammonia produced to inhibit *Nitrobacter* and cause nitrite formation. Literature, however, places the optimum pH for *Nitrosomonas* and *Nitrobacter* between 7.5 and 8.5. Figure 22 shows that the pH in the anoxic and aerobic reactors were maintained in this range. The influent leachate had adequate alkalinity to buffer the H⁺ ions produced during the nitrification process.

Figure 23 shows the percent nitrification values obtained across the aerobic reactor. The calculation used is shown in Figure 23. Since there was little or no ammonia in the effluent leaving the clarifier and 25% (mean) of the incoming ammonia was used up by the biomass in the anoxic reactor, overall percent nitrification values of approximately 75% were expected. The higher percent nitrification values obtained are probably due to the nitrification of organic nitrogen (after conversion), as not all the TKN was made up of ammonia. Some nitrates were produced from the organic nitrogen as well as from the ammonia; therefore percent nitrification (based on incoming and outgoing ammonia in the aerobic reactor) of greater than 100% can be expected. Because of the probable variation in the TKN to ammonia ratio and the variation in the amount of ammonia uptaken by the biomass in the anoxic reactor, fluctuations in the percent nitrification across the aerobic reactor were expected, as shown clearly in Figure 23.

The effect of zinc inhibition on the nitrification system is more clearly seen in Figure 24. This shows percent nitrification values in system 1, based on the ammonia concentration into the aerobic reactor, not the difference between the incoming and outgoing ammonia concentrations. The percent nitrification dropped to 21% on day 289, which is when the system started to show signs of inhibition or failure. The percent nitrification values decreased to about 13%, but showed ŝ



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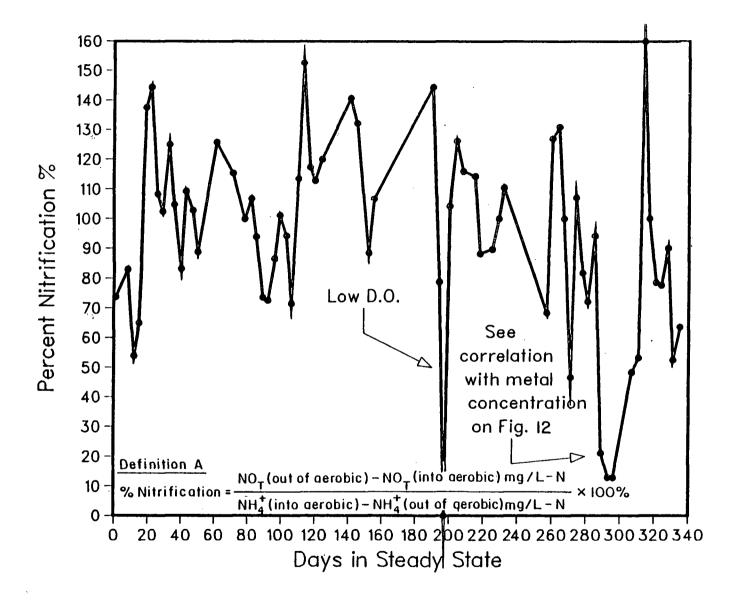


Figure 23.: Percent Nitrification Versus Time (Defn.:A)

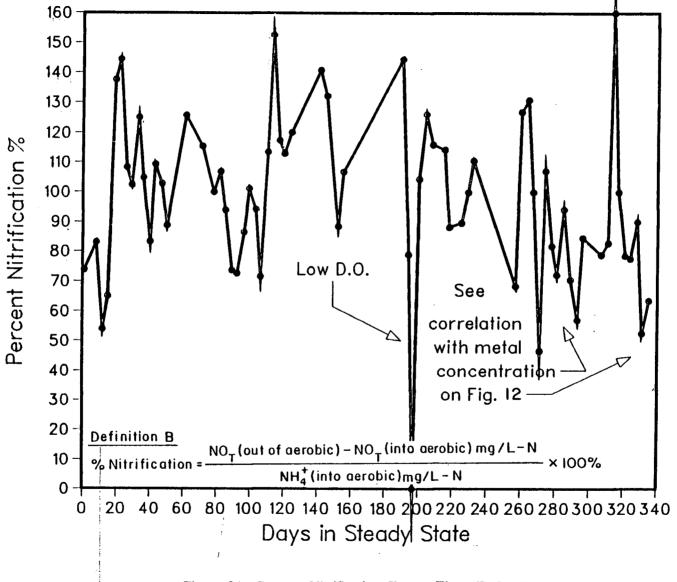


Figure 24.: Percent Nitrification Versus Time (Defn.:B)

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signs of increasing on day 307, with a value of 48%. At this point in time, the influent zinc concentrations were being lowered (see Figure 12). The percent nitrification values kept increasing and reached "normal" levels on day 314. This indicated that, as soon as the influent zinc concentrations dropped, the nitrification system started to return.

5.5 DENITRIFICATION

Figure 21 shows that after glucose addition to the anoxic reactor on day 11, a substantial decrease in nitrate concentration occured across the system; thus denitrification was improved. Fluctuations in the nitrate concentrations are more a function of the variant carbon loading to the anoxic reactor, than of the influent ammonia concentrations. The fact that 100% denitrification was achieved on several occasions, indicates that the system was not only capable of complete ammonia removal, but also complete denitrification. The COD used across the anoxic reactor varied from 2.8 to 50 mg COD/mg NOT reduced; this is shown in Figure 25. There are a number of possible explanations to account for this variation, however it is possible that a combination of the following scenarios are responsible.

Since 1 mg of nitrite exerts a 1.1 mg COD (Standard Methods 1980), transient nitrite concentrations in the recycle would result in an artificially high COD into the anoxic reactor, thus resulting in high COD/NOT ratios. Also any small error in the COD, nitrate and flow measurements could cause a large error in the COD (used)/NOT (reduced) ratios. However, these mechanisms alone cannot be responsible for the substantial increase in COD/NOT ratios about day 290.

This situation at day 290 onward, could be explained by the presence of facultative bacteria in the anoxic reactor (other than denitrifiers) that were utilizing some of the incoming glucose. Figure 8 shows that until day 90, the percentage COD used in the anoxic and aerobic reactors was increasing, indicating that after day 90, a stable bacterial population dominated. Figure 25 shows that about this time the COD (used)/NOT (reduced) ratios across the anoxic reactor increased, and averaged about 10:1, until day 270. During this period (after day 90), a certain type of bacteria

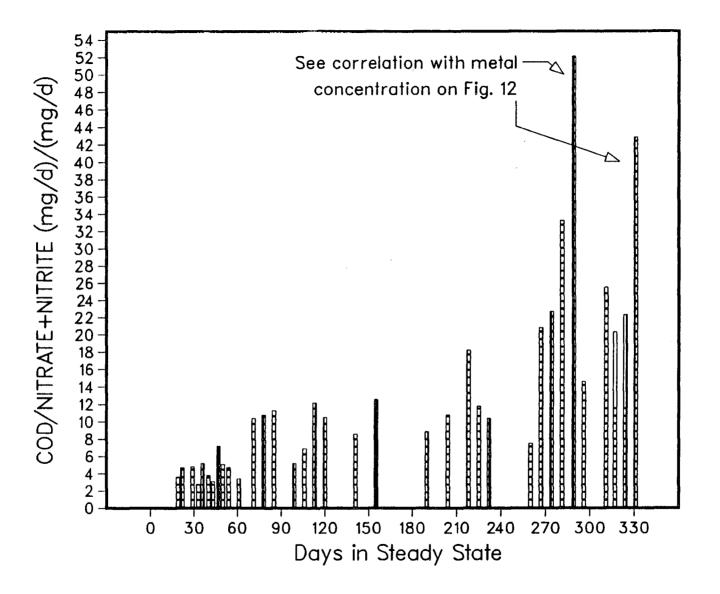


Figure 25.: Ratio of COD (used)/Nitrate+Nitrite (reduced) Versus Time

(other than denitrifiers) probably became established and consumed some of the incoming glucose, thereby increasing the COD/NOT ratios over what they were previously. During the period of zinc inhibition (about day 290) there was a decrease in the amount of nitrate reduced (Figure 26), therefore the carbon required for denitrification also decreased; however, the bacteria that were using the carbon for purposes other than denitrification, might have continued to use the same amount of carbon as before, thus giving rise to even higher COD/NOT ratios (Figure 25).

Another mechanism that could explain the variation in the COD/NOT ratios about day 290, is the formation (understress) of polysaccharides, by the bacteria, from the glucose. The large fluctuations in the COD/NOT ratios (Figure 25) correlate very well with the variation in the influent zinc concentrations (Figure 12).

There are a multiplicity of bacteria that produce extracellular polymers. These extracellular polymers play a vital role in activated sludge flocculation and the removal of metal by activated sludge (Brown and Lester, 1979). There is evidence to support the fact that the extracellular polymers are responsible for the adsorption of metal ions on to the biofloc. These extracellular polymers are also believed to protect the bacteria from metal ion toxicity (Brown and Lester, 1979). Bitton and Freihofer (1978), from Brown and Lester (1979), investigated the influence of bacterial extracellular polysaccharides on copper and cadmium toxicity to two strains of *K. aerogenes*, one capsulated strain and one non-capsulated strain. They found that the capsulated polysaccharide acted as a protective mechanism against copper toxicity and to a lesser extent, cadmium toxicity. In the current study, the viable bacteria possibly increased the production of polysaccharides as a protective measure, in response to the increasing influent zinc concentrations. This could, therefore, have resulted in an increase in the glucose used in the anoxic reactor, above and beyond the glucose that was required for denitrification. The glucose used for denitrification at this point was low, because of the decreased conversion of nitrates to nitrogen gas across the anoxic reactor (probably resulting from zinc inhibition of the denitrifiers).

Figure 26 shows that about day 290, when the influent zinc concentration was at its maximum, there was a marked decrease in the mg/day of nitrates reduced (independent of a

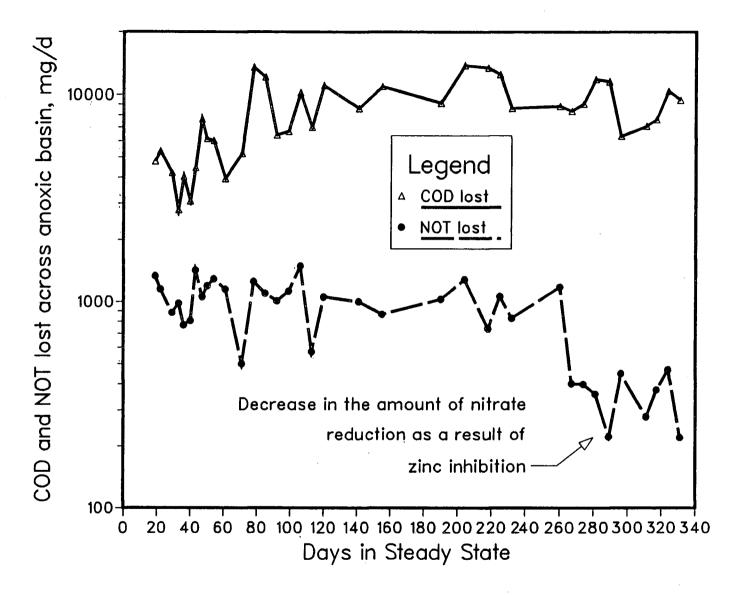


Figure 26.: COD and Nitrate+Nitrite Lost Across the Anoxic Reactor Versus Time

decrease in nitrate prodution) across the anoxic reactor. This indicated that both the heterotrophic denitrifying bacteria, and the nitrifiers were inhibited at these high influent zinc concentrations. Since the amount of nitrates reduced, decreased (Figure 26), the COD consumption across the anoxic reactor should have correspondingly dereased; however, it was high enough to produce COD/NOT ratios of about 50:1. Even though the glucose entering the system had decreased at this time, there was enough glucose available that could be used to produce extracellular polymers, because the glucose requirements for denitrification had also decreased. The formation of extracellular polysaccharides would then provide the bacteria with some protection against the influent zinc. The inhibition of the heterotrophic denitrifying bacteria is also indicated on Figure 20. About day 290, there was a marked decrease in the ammonia used across the anoxic reactor. This meant that there was less ammonia used as a nutrient source by the denitrifiers, probably as a result of decreased activity brought on by zinc inhibition.

The ORP in the anoxic reactor was monitored during the second half of the study, and is shown in Figure 27. From the ORP values, it is evident that the anoxic reactor had a good reducing environment necessary for denitrification. The ORP readings were also used as a rough indicator of the nitrate + nitrite concentration in the anoxic reactor; a low negative ORP reading indicating a high nitrate + nitrite concentration, while a very low reading indicating a relatively lower nitrate + nitrite concentration present.

5.6 REACTION AND UNIT REMOVAL RATES

5.6.1 <u>REACTION RATES</u>

The unit nitrification rates are shown in Figure 28. However, these rates are probably not the maximum rates achievable. The hydraulic retention time in the aerobic reactor was approximately 4.8 hours, and it is likely that most of the nitrates were produed in less time. Maximum rates would best be determined using batch tests, such that nitrate production data could be collected. Figure 28 shows the unit nitrification rates steadily dropping from day 1; this is due, in

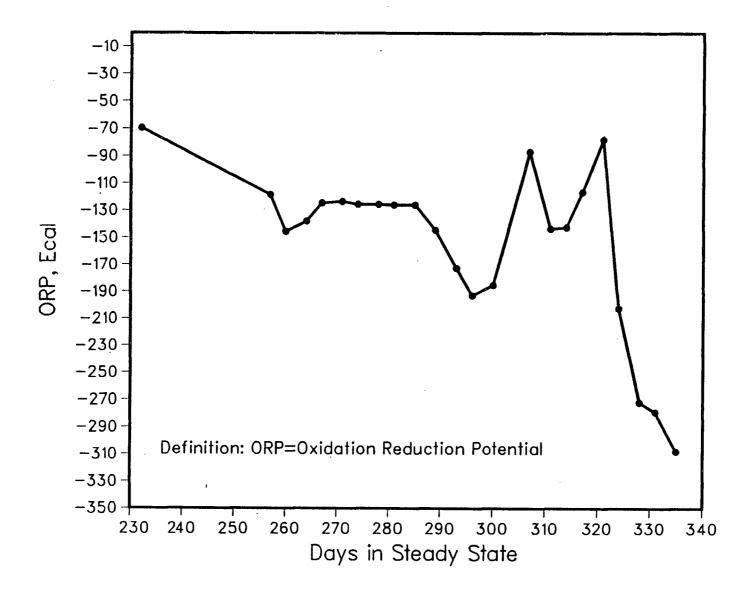


Figure 27.: ORP in the Anoxic Reactor Versus Time

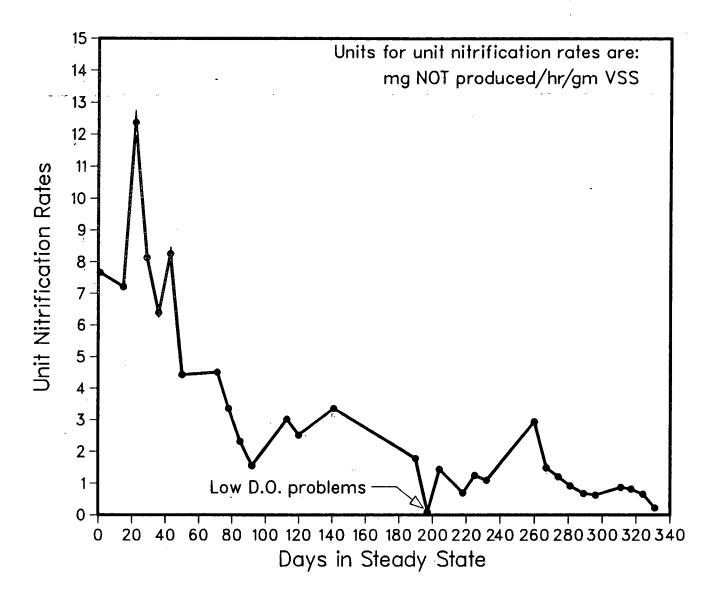


Figure 28.: Unit Nitrification Rates Versus Time

part, to the MLVSS increasing in response to an increased amount of glucose added. Unit nitrification rates are calculated as mg NOT produced/hr/gm VSS; therefore, any increase in the VSS will in turn produce lower values of unit nitrification rates. This drop in the rates is misleading, since it does not indicate a "real" drop in the nitrification rates; the major change in VSS is brought about by the carbon heterotrophs and not the nitrifiers. Since the percentage of nitrifiers in the MLVSS is not known, meaningful nitrification rates, which can be used to indicate changes in the performance of the nitrification system, can only be obtained if a constant MLVSS is maintained. In this study, the amount of glucose added to the system would have had to be constant, which it was not.

After about day 230, there was a fairly steady amount of glucose being fed into the anoxic reactor; therefore, the unit nitrification rates from this day onward could be used as a rough indicator of the nitrification process performance. About day 290, when inhibition was observed, the unit nitrification rates reached their lowest value, after steadily dropping, thus showing signs of inhibition. After day 290, when the zinc concentration was lowered, allowing the system to recover, the rates showed a slight increase. However, once the zinc conentration was again increased, the unit nitrification rates started dropping.

The unit denitrification rates are shown in Figure 29. These values also had a large variation because of the increasing carbon loading into the anoxic reactor. However, about day 290 and 330, which corresponds to the maximum influent zinc concentration into the system, a relative drop in the denitrification rates occured. This indicated that the denitrifiers were also understress.

5.6.2 UNIT REMOVAL RATES

The ammonia removal rates calculated as mg NH_{4}^+ removed/hr/gm VSS are shown in Figure 30. The aerobic ammonia removal rate shown in Figure 30 is very similar to the unit nitrification rates (Figure 28), as expected. The difference between the two curves is that the unit nitrification rate also includes nitrates produced from organic nitrogen, and the aerobic ammonia removal rate includes the ammonia consumed by the carbon heterotrophs, in the aerobic reactor.

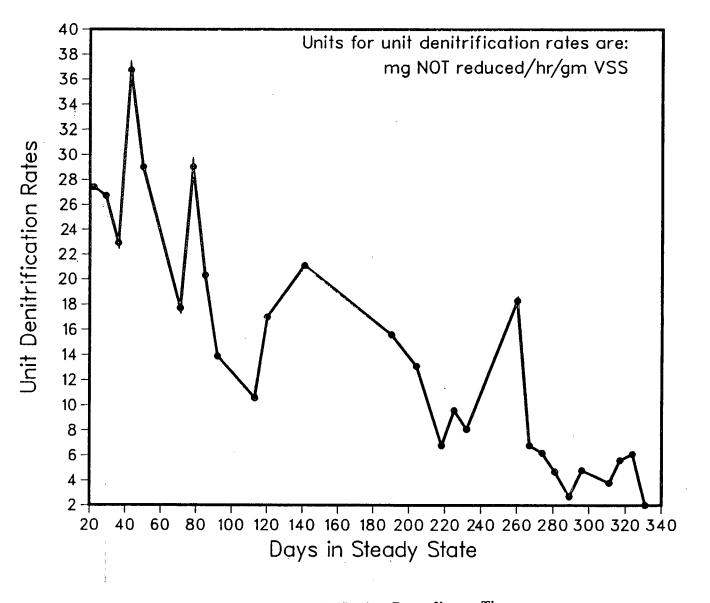
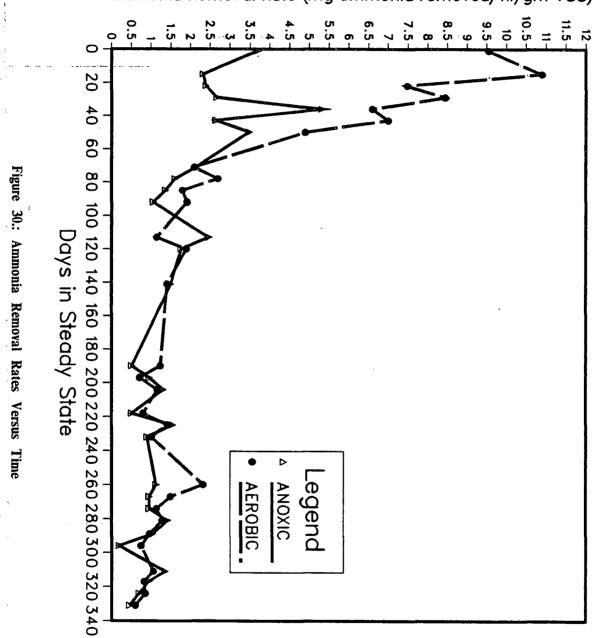


Figure 29.: Unit Denitrification Rates Versus Time

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Ammonia Removal Rate (mg ammonia removed/hr/gm VSS)

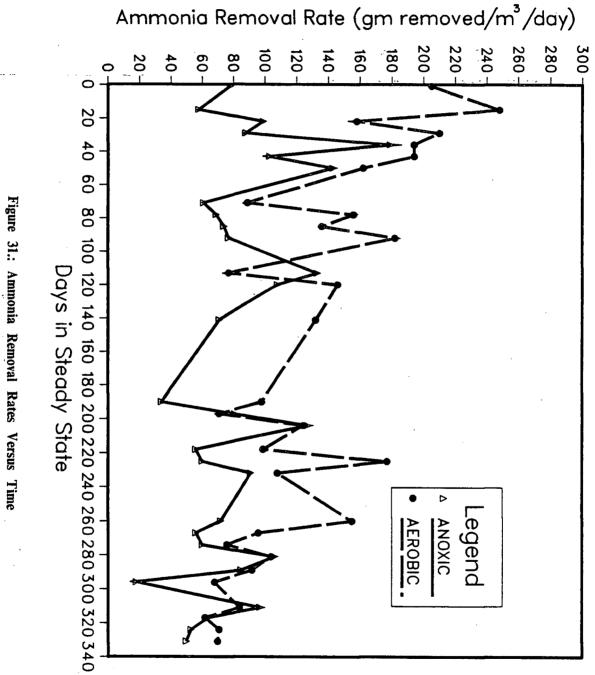
These differences and experimental error explain the slight variation between the two curves. Knox (1985) reported on a pilot-scale activated sludge plant treating a high ammonia leachate. He reported maximum ammonia removal rates of 5.5 mg-N/hr/gm VSS. In this study, values of up to 11 mg-N/hr/gm VSS were obtained in the initial phase of operation; however, after the MLVSS started to increase, due to glucose addition, the values started dropping. The anoxic ammonia removal rates are also shown in Figure 30, with a mean of 1.6 mg-N/hr/gm VSS. This removal rate was not dependent on nitrification, but on the activity of the denitrifiers. The anoxic ammonia removal rate also reached a minimum about day 290, indicating that the denitrifiers were probably inhibited by the high influent zinc concentrations.

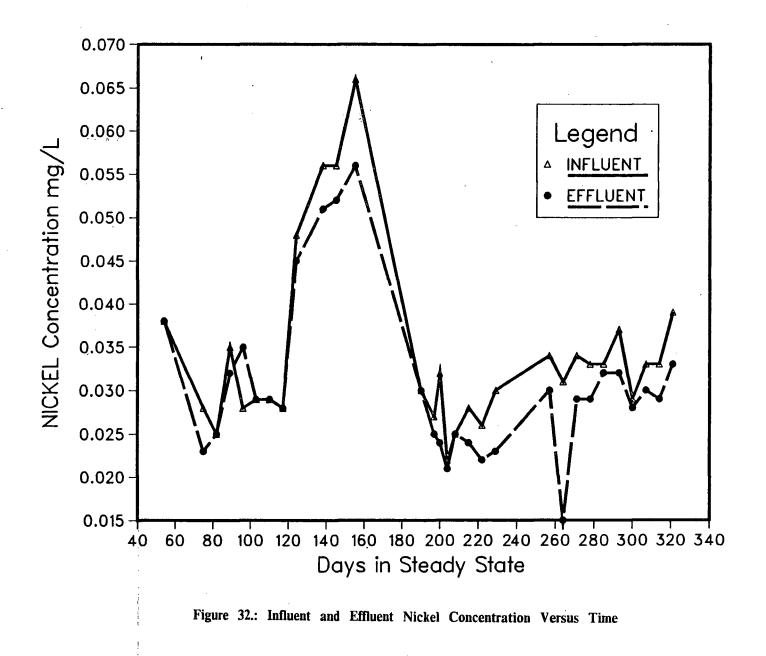
The ammonia removal rates calculated as gm NH_4^+ removed/m³/day are shown in Figure 31. The mean anoxic and aerobic removal rates are 82 and 132 gm-N/m³/day, respectively. The aerobic ammonia removal rates were slightly higher at the beginning of the study, probably because of the higher influent ammonia concentrations at that time. Knox (1985) obtained an ammonia removal rate of 418 gm-N/m³/day at a tempertaure of 21.3 °C and an influent ammonia concentration of 265 mg/L. The maximum aerobic ammonia removal rate obtained in this study was 248 gm-N/m³/day at room temperature, and an influent ammonia concentration of 220 mg/L.

5.7 METAL REMOVAL

Leachates contain a wide variety of metals, many of them in concentrations above discharge guidelines in British Columbia. The activated sludge process used to treat leachates, has also been effective in removing a considerable proportion of the metals entering treatment plants (Brown and Lester 1979). During this study, the four metals regularly monitored were zinc, iron, manganese and nickel. Chromium and lead were also measured on certain occasions. Metal spiking was carried out on system 1, while system 2 which was used as a control, received only leachate.

The influent and effluent nickel concentrations are shown in Figure 32. The influent concentrations are relatively low; these concentrations are generally lower than those reported by Jasper, Atwater and Mavinic (1984). The influent nickel concentrations were already consistently



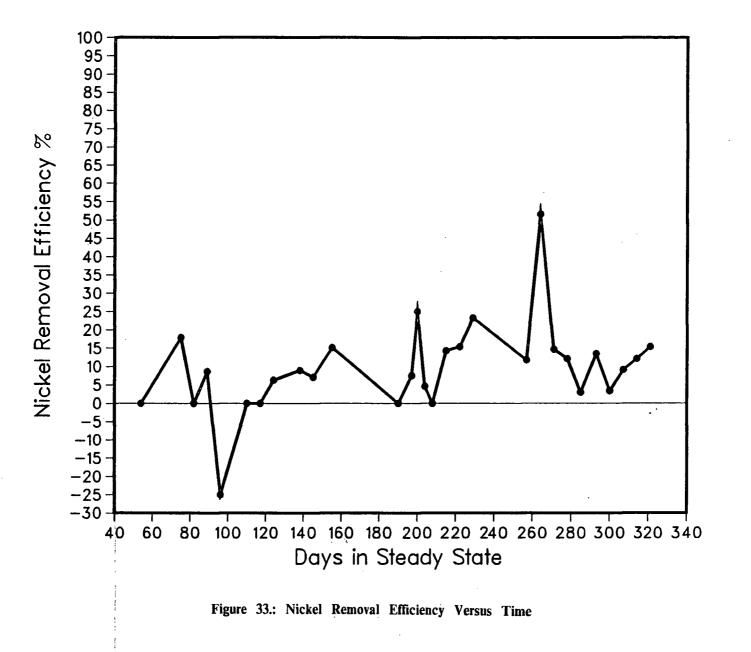


below the British Columbia discharge guidelines of 0.3 mg/L (Dept. of Lands, Forest and Water Resources 1975).

Sujarittanonta and Sherrard (1981) investigated the effect of nickel on the activated sludge process, and found that the effect of nickel on nitrification was significant. Nitrification was inhibited in reactors receiving Ni⁺² at 1 mg/L and COD at 396 mg/L. However, nitrification did proceed in the reactors receiving Ni⁺² at 1 mg/L and COD at 787 mg/L. This indicates that the increase in COD concentration could reduce the toxicity of the metal ion. These researchers showed that the toxicity of nickel is also a function of the MLSS:Ni⁺² ratio. This is due to the fact that as the influent COD increases, the MLSS will also increase. Since the influent nickel concentrations in this study were much lower than 1 mg/L, and the COD was much higher than 787 mg/L (due to the glucose addition for denitrification), it would seem that the system is capable of handling much higher influent nickel concentrations, before inhibition due to nickel would be expected. The ability of the bacteria to tolerate higher nickel concentrations at the higher COD loadings, may be due, in part, to protection by extracellular polymers, formed by the bacteria from the extra COD.

Huang and Sheikhdeslami (1982) also studied the effect of nickel on nitrification. These researchers used rate constants of both ammonia oxidation and nitrate formation under various influences of chromium, nickel and zinc, to evaluate relative inhibition of these metals. Nickel at concentrations of greater than 0.2 mg/L stopped ammonia oxidation completely at MLVSS concentrations of up to 1300 mg/L. The nickel concentrations encountered in this leachate were below 0.1 mg/L and MLVSS concentrations were much greater than 1300 mg/L.

From Figure 32, it is evident that not much of the influent nickel was taken up by the biomass, therefore resulting in poor nickel removals. Removal efficiencies ranged from -25% to +55%, as shown in Figure 33, with normal removals being less than 25%. Jasper, Atwater and Mavinic (1984) also found low nickel removals at 0 to 30%, in their Port Mann treatment study. Cheng et. al. (1975) studied metal uptake in the activated sludge process, and found that of the four metals studied (lead, copper, cadmium and nickel), nickel had the least uptake by the biomass. The negative removal efficiency shown in Figure 33, indicates that the influent nickel concentrations



had dropped low enough for nickel accumulated in the biomass to be released.

The influent and effluent iron concentrations are shown in Figures 34 and 35 (Log scale plot). Figure 34 shows that the iron concentrations in the landfill leachate gradually declined over the course of the study. This was partly due to the use of two different wells for leachate collection. This figure shows that for the latter part of the study period, the influent iron concentrations were lower than for the rest of the period; this is when well *#*2 was used exclusively. The iron concentration in the leachate was mostly in the suspended form as indicated by the filtered samples (see Figures 34 and 35). Both Figures 34 and 35 show that regardless of the fluctuations in the influent iron concentrations, the filtered effluent iron concentrations remained fairly low. However, the British Columbia discharge guideline of 0.3 mg/L (Dept. of Lands, Forest and Water Resources 1975) was not met consistently. Since no ammonia conversion inhibition was detected before the zinc spiking, it would seem that the influent iron concentrations in the leachate, even though they were high, had no adverse effect on the process.

The iron removal efficiency was quite high and averaged 95.6% for the period studied. The removal percentages are shown in Figure 36. Jasper, Atwater and Mavinic (1984) also reported high iron removals, at 90 to 98%. These researchers also had higher influent iron concentrations than those found in the leachate used for this study.

Most of the iron accumulated in the sludge, as indicated by the high removal efficiencies. The sludge iron concentrations are shown in Figure 37. There was little difference between aerobic and anoxic sludges. This figure also shows a decreasing trend in the sludge iron values, an expected result, since the influent concentrations were also dropping throughout the course of the study. During the first quarter of the study, the sludge iron values were comparable to those obtained by Jasper, Atwater and Mavinic (1984), and some values were higher than the maximum reported by Robinson (1980) from Jasper, Atwater and Mavinic (1984). By the study's end, the sludge iron values had dropped to below 15000 mg/Kg.

Chromium and lead were also measured on certain occasions during an eight month period. The concentrations found are shown in Table 2. Both chromium and lead have been found

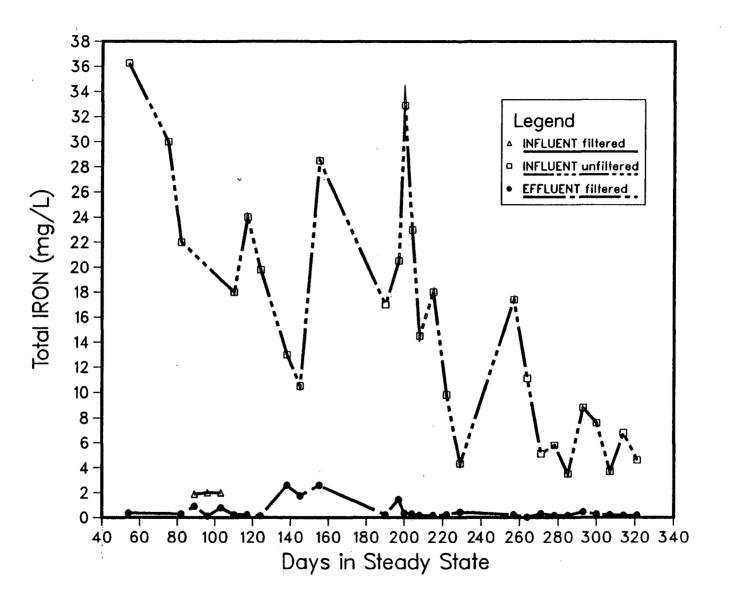


Figure 34.: Influent and Effluent Iron Concentration Versus Time

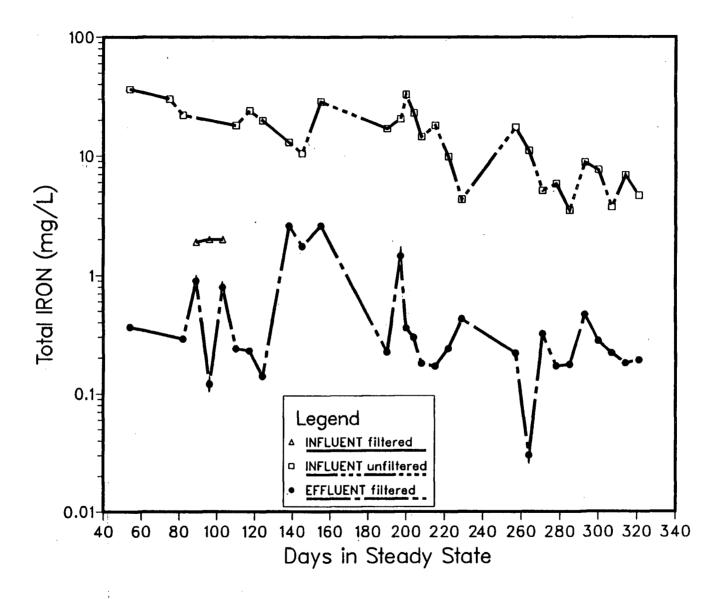


Figure 35.: Influent and Effluent Iron Concentration Versus Time - (semi-log plot)

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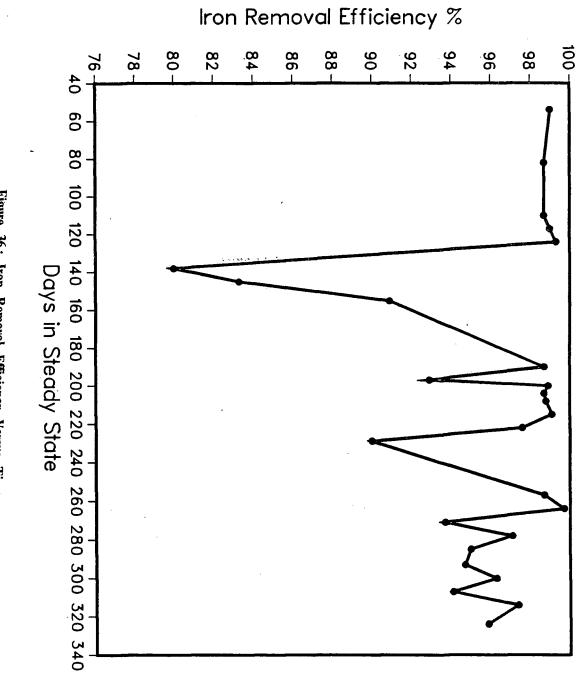


Figure 36.: Iron Removal Efficiency Versus Time

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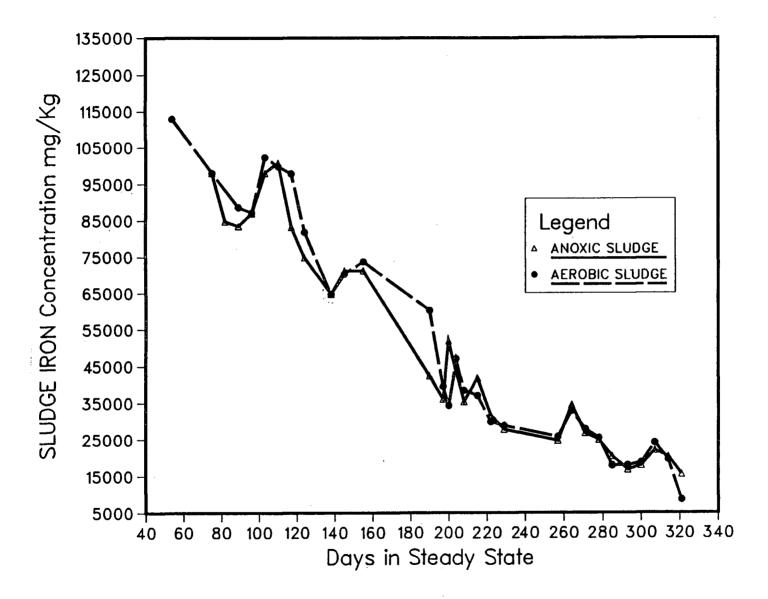


Figure 37.: Sludge Iron Concentration Versus Time

Day	Chromium		Lead	
	Influent	Effluent	Influent	Effluent
54	< 0.005	< 0.005	< 0.005	.016
75	< 0.005	< 0.005		< 0.005
82	< 0.005	< 0.005	.006	.006
89	< 0.005	< 0.005	< 0.005	
96	< 0.005	< 0.005	< 0.005	.006
103	< 0.005	< 0.005	.005	.006
110	< 0.005	< 0.005	< 0.005	
117	< 0.005	< 0.005	< 0.005	.010
124	< 0.005	< 0.005		.005
138	< 0.005	< 0.005	< 0.005	.006
145	< 0.005	< 0.005	< 0.005	< 0.005
152	< 0.005	< 0.005	< 0.005	< 0.005
169	< 0.005	< 0.005	.005	
190	< 0.005	< 0.005	< 0.005	< 0.005
197	< 0.005	< 0.005	< 0.005	< 0.005
204	< 0.005	< 0.005	< 0.005	< 0.005
208	< 0.005	< 0.005	< 0.005	< 0.005
215	< 0.005	< 0.005	< 0.005	< 0.005
222	< 0.005	< 0.005	< 0.005	
229	< 0.005	< 0.005	< 0.005	< 0.005
257	< 0.005	< 0.005	.008	< 0.005
264	< 0.005	< 0.005	< 0.005	< 0.005
271	< 0.005	< 0.005	< 0.005	< 0.005
278	< 0.005	< 0.005	< 0.005	< 0.005

Table 2. Chromium and Lead Concentrations*

* All concentrations in mg/L.

to be inhibitory to nitrifiers. Martin (1979), from Martin and Richard (1982), found toxicity thresholds for chromium (Cr^{+2}) and lead (Pb^{+2}) at 1 mg/L and 0.5 to 1 mg/L respectively. As shown in Table 2, the values encountered in the leachate during this study are much lower than the reported toxicity thresholds, therefore, the chromium and lead concentrations in this leachate were not high enough to induce inhibition of the nitrifiers.

The influent and effluent manganese concentrations are shown in Figures 38 and 39, the latter being a semi-log plot. The manganese concentrations in the leachate were low; however, they varied quite a bit, and ranged from 0.02 to 0.3 mg/L. Before metal spiking, the system had been working successfully at removing essentially 100% of the ammonia from the leachate, and it was obvious that no inhibition was taking place; in other words, no nitrification inhibition was being detected. A previous study conducted at the University of British Columbia by Jasper, Atwater and Mavinic (1984), used an almost identical system to treat leachate from the same landfill. This study found limited success with nitrification, and it was obvious that some sort of inhibition was taking place. Therefore, a comparison was made to find out what was in the previous leachate that was not in this leachate, something that could have caused nitrifier inhibition. The only detectable difference was the higher manganese and zinc concentrations in the previous leachate. In the previous study, the influent manganese concentration was higher than the level in this leachate for about fourteen weeks. Although manganese has not been reported to be inhibitory or toxic to nitrifiers, the influent manganese concentrations into the system were increased anyway, to see if inhibition would also take place.

On about day 190 of steady state operation, manganese in the form of manganous chloride was added to the system (system 1), with system 2 remaining as control. As noted in both Figures 38 and 39, the influent manganese concentrations increased substantially. The maximum influent concentration obtained was about 12.5 mg/L, which was greater than the maximum leachate concentrations observed by Jasper, Atwater and Mavinic (1984). Throughout the manganese spiking period, there was no nitrification inhibition detected, and it was concluded that manganese would not inhibit the nitrifiers. It was then decided to decrease the influent manganese concentrations and

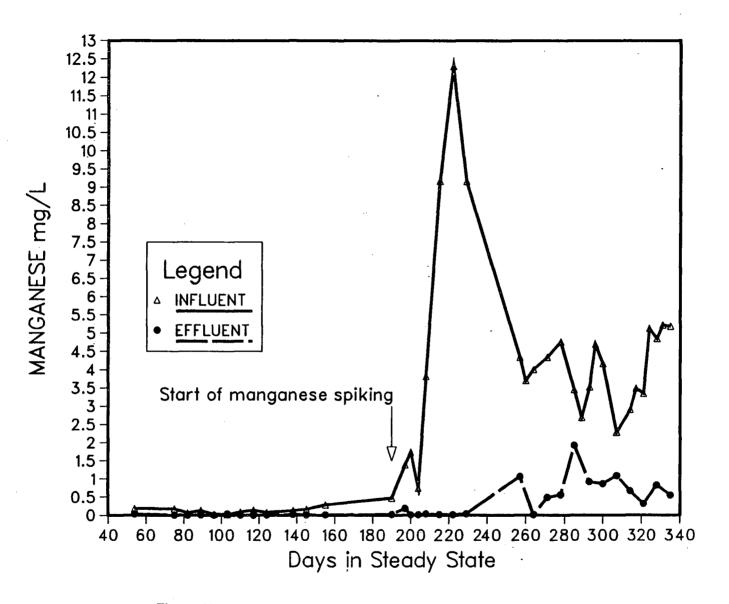


Figure 38.: Influent and Effluent Manganese Concentration Versus Time

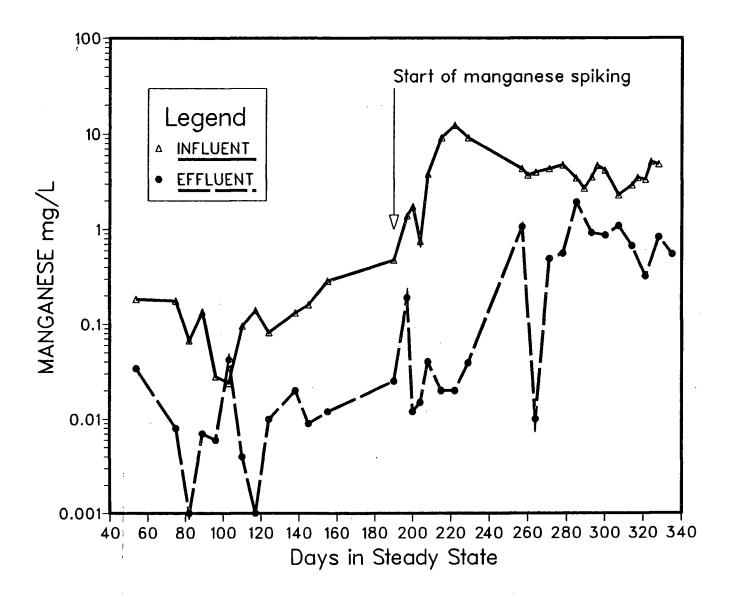


Figure 39.: Influent and Effluent Manganese Concentration Versus Time - (semi-log plot)

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start adding zinc. The influent manganese concentrations were still maintained at a comparatively high level of around 4 mg/L, for the duration of the study. If inhibition was due to a synergistic effect between zinc and manganese, then with this constant high influent manganese concentration, and zinc spiking, inhibition would still be detected.

Regardless of the large fluctuations in the influent manganese concentrations, a high removal efficiency was still maintained, although less so after zinc spiking commenced. The removal values are shown in Figure 40, with an overall average value of 87.6%. However, after zinc spiking began, the average removal dropped from 93.4% to 78.4%. High manganese removal efficiencies in the activated sludge process have also been reported by other researchers (Jasper, Atwater and Mavinic 1984). The effluent manganese values were below British Columbia discharge guidelines of 0.05 mg/L (Dept. of Lands, Forest and Water Resources, 1975) until day 190 of steady state operation. After this time, the system was spiked with manganese, and the effluent concentration was, for the most part, above the discharge guidelines.

For the most part, the manganese accumulated in the sludge, as indicated by the high removal efficiencies. The manganese sludge values are shown in Figure 41 and 42, the latter being a semi-log plot. There was little or no difference between anoxic and aerobic sludges. The sludge manganese plots parallel the influent and effluent plots quite well, and clearly depict the manganese spiking period. The sludge manganese values reached a maximum of 7700 mg/Kg dried sludge, which is far in excess of the values reported by Jasper, Atwater and Mavinic (1984); however, it is close to the high end of the range reported by Robinson (1980) in Jasper et. al. (1984).

Zinc was the only other metal monitored on a regular basis. Since an increase in the influent manganese concentrations had no detectable inhibitory effect on the nitrification system, the next step was to spike with additional zinc. The previous study by Jasper et. al. (1984) which reported nitrifier inhibition, had influent zinc concentrations of up to 4 mg/L, higher than in the leachate used herein. Thus, zinc additions to system 1, in the form of zinc chloride, were started about day 230. This is clearly shown in Figure 12 as well as Figure 43, the latter being a semi-log

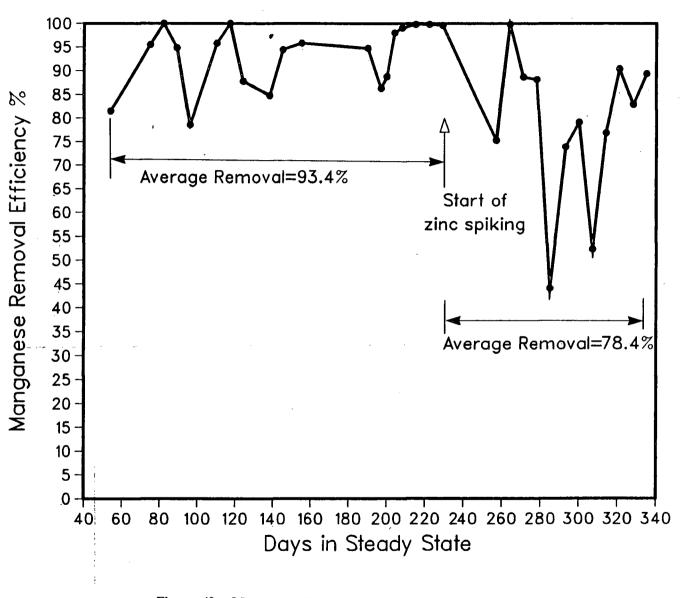


Figure 40.: Manganese Removal Efficiency Versus Time

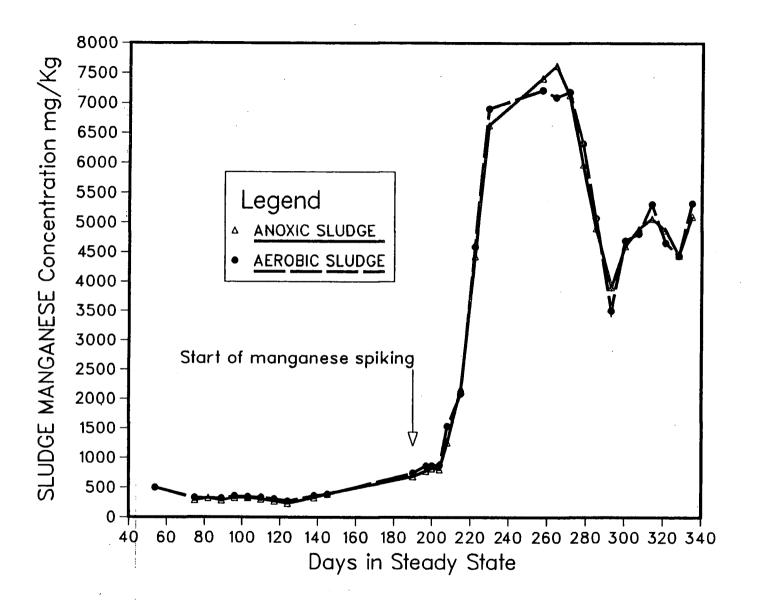
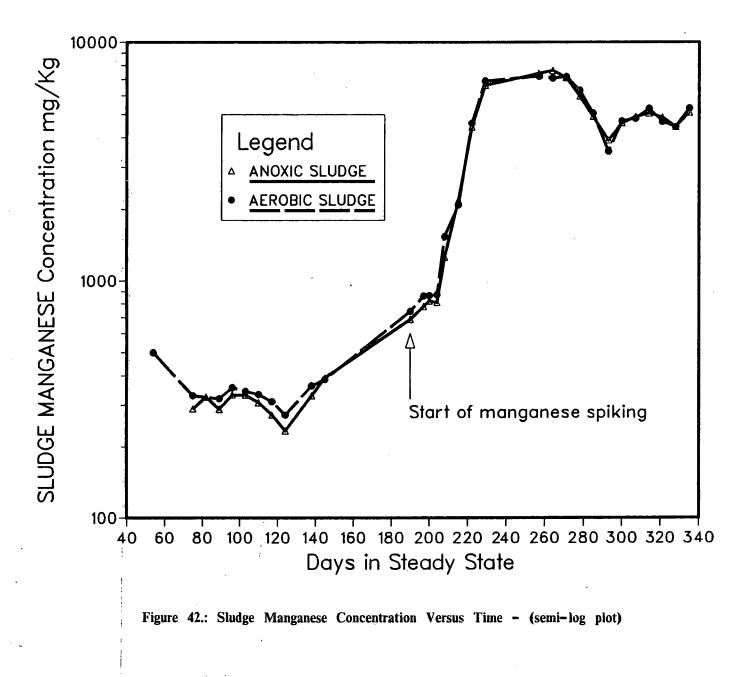


Figure 41.: Sludge Manganese Concentration Versus Time



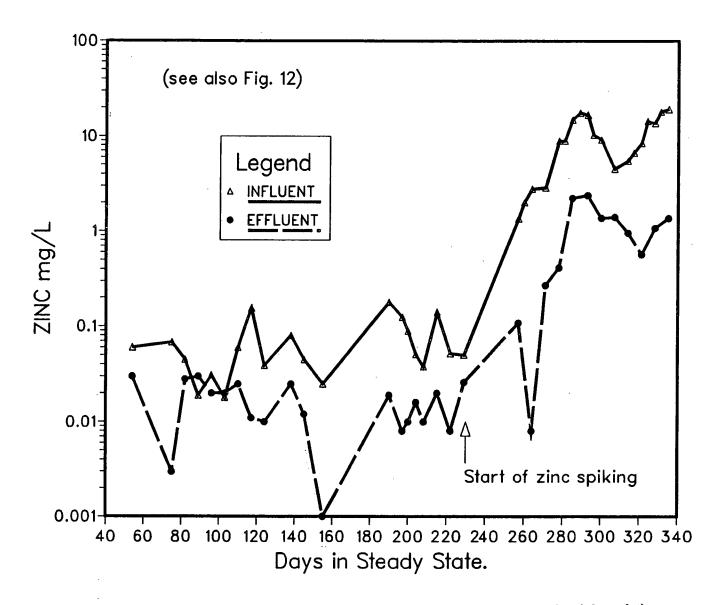


Figure 43.: Influent and Effluent Zinc Concentration Versus Time - (semi-log plot)

plot. The influent zinc concentrations were brought up to 14.9 mg/L by day 285, over a 55 day period. Up to this point in time, no inhibition was detected, in other words, there was no ammonia in the effluent from the treatment system (see Figure 18). The influent zinc concentration was subsequently brought up to 17.6 mg/L by day 290, which is when ammonia was first detected in the effluent (see Figure 18). At this time, a substantial drop in percent nitrification was also observed, as shown in Figure 24. However, the percent nitrification (based on percent nitrification as defined in Figure 24) had dropped to about 13% and not to zero; therefore, this concentration was inhibitory and not toxic. The control system (system #2), which was being fed leachate, but no additional metals, showed no signs of inhibition from the time it was started.

At this point in time, it was decided to decrease the influent zinc concentrations, to see if the system could recover. The concentrations were dropped until there was no ammonia detected in the effluent, that is, the system was back at "steady state". The concentration of zinc had to be dropped to about 5.5 mg/L (Figure 12 and 43), before there was no detectable ammonia in the effluent (Figure 18); this was reached about day 305. Figure 24 also shows that when the influent zinc concentrations were being dropped, the percent nitrification values started increasing. Because the influent zinc concentrations were increased from 14.9 mg/L, at which concentration no inhibition was observed, to 17.6 mg/L, when inhibition was observed, the inhibitory concentration for this system was thought to be anywhere between these two concentrations. Therefore, it was decided to increase the influent zinc concentrations again, in system 1, in order to identify the inhibitory zinc level for this system. The influent zinc concentration was subsequently increased to 19.5 mg/L, over a 30 day period, but there was no ammonia in the effluent. This indicated that the bacteria were now acclimitizing to the high influent zinc concentrations. Unfortunately, the study had to be terminated on day 340, and therefore, it is not known whether this trend would have continued.

Knoetze, et al. (1980) studied the inhibitory effects of various heavy metals on a nitrification-denitrification activated sludge process. These researchers reported that for a 10 day sludge age, nitrification was not inhibited at zinc (Zn^{+2}) concentrations below 10 mg/L. This is in

agreement with the work done for this study.

Robinson and Maris (1982) reported on laboratory-scale biological units treating leachate. The leachate used had fairly low concentrations of ammoniacal nitrogen (76 mg/L); however, no nitrification took place. In units where SRT was greater than 5 days, effluent ammonia values were below 1 mg/L. This removal of ammonia was due principally to bacterial uptake. These researchers, at first, postulated that the lack of nitrification was a result of the combined effects of low temperature (10° C) and low SRT. The SRT however, was subsequently taken as high as 20 days, and still no nitrification occured. The mean influent zinc concentration encountered by these researchers was 17.6 mg/L. It may very well be that this high zinc concentration was indeed responsible for the lack of nitrification, observed by Robinson and Maris. In fact, coincidentally, the zinc concentration at which inhibition first occured in the current study was also 17.6 mg/L, at a 15 day aerobic SRT.

Zinc toxicity was also reported by Martin (1979) from Martin and Richard (1982). The *Nitrosomonas* toxicity threshold for zinc was 10 mg/L; however, the authors add that this value is illustrative only, because it was not determined under specific conditions and did not take into account the possible synergistic effect due to the presence of other inhibitors.

Basically, the information available in literature on zinc inhibition is inconsistent. Huang and Sheikhdeslami (1982) also studied the metal inhibition of nitrification using rate constants of both ammonia oxidation and nitrate formation. They found that zinc concentrations of 0.6 mg/L (probably soluble) with an MLVSS of up to 2133 mg/L, reduced the rate constants to lower than 20% of the control. In this case, a fairly low concentration of zinc caused substantial inhibition.

Despite the problems associated with zinc and nitrification, the system utilized in this study was quite effective in removing zinc, and the removal efficiencies are shown in Figure 44. The negative removal efficiency obtained around day 90 was probably due to the low influent zinc concentrations at that time; in other words, some of the zinc adsorbed onto the biomass went back into solution to maintain equilibrium. The high influent zinc concentration did not seem to affect the zinc removal as it did the removal of manganese. A mean zinc removal efficiency of 75% was

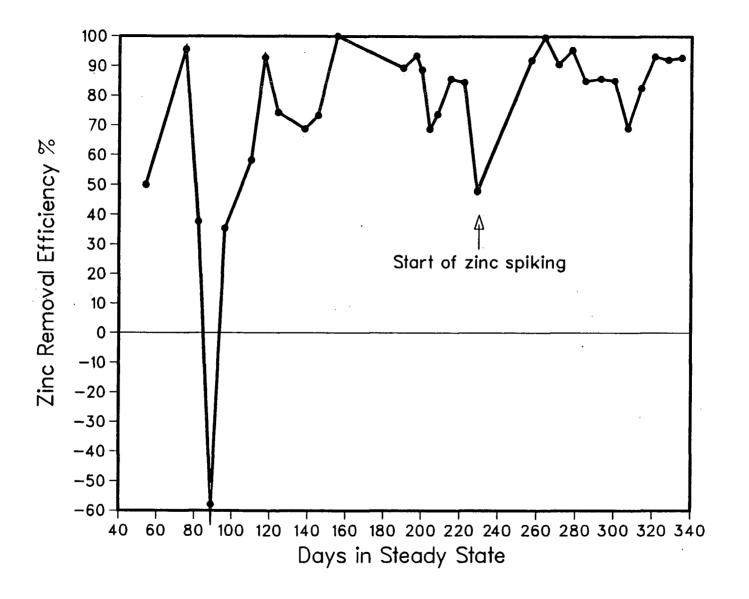


Figure 44.: Zinc Removal Efficiency Versus Time

obtained. The effluent zinc concentration was below the British Columbia discharge guideline of 0.5 mg/L (total zinc) (Dept. of Lands, Forest and Water Resources, 1975) up to about day 280, even though the influent concentrations were around 4 mg/L. However, after day 280, the influent concentrations were increased to fairly high levels, thus increasing the effluent zinc levels to over 0.5 mg/L.

The sludge zinc concentrations are shown in Figure 45. There was little difference between the anoxic and aerobic sludges. The increase in sludge zinc concentrations when zinc spiking was initiated on day 230 is clearly depicted. The sludge zinc values reached a maximum of over 10000 mg/Kg dried sludge. The maximum sludge zinc concentrations obtained by Jasper, et al. (1984) was 1800 mg/Kg dried sludge. It is interesting to note that when inhibition was detected on about day 290, the sludge zinc values were at their maximum of over 10000 mg/Kg, but when the influent zinc levels were reduced and "steady state" (zero ammonia in the effluent) was reached again, the sludge zinc concentrations were still at the previously established inhibition level. This seems to indicate that inhibition of the nitrifiers was due more to the influent zinc concentrations than the zinc adsorbed by the biomass. It also seems to indicate a relatively slow "flushing out" phenomenon between the active biomass and the zinc metal species.

These results appear to be contradictory to conclusions made by Martin and Richard (1982) as well as others, who studied the toxic effects of several heavy metals (nickel, cadmium, copper and zinc) on nitrification. These researchers reported that inhibition of nitrification by metallic ions is attributable to adsorption of the metallic ions on the flocs containing the nitrifying bacteria, and thereby partially or completely blocking the enzyme mechanisms. There was no indication, by these authors, that actual influent metal concentrations affected any change in performance by the nitrifying organisms. Because of the "apparent" contradiction between published data and the results of this research, especially as it pertains to zinc, and because of the importance of expanding the knowledge associated with nitrification–denitrification toxicity, it is obvious that much more work is needed in this vital research area.

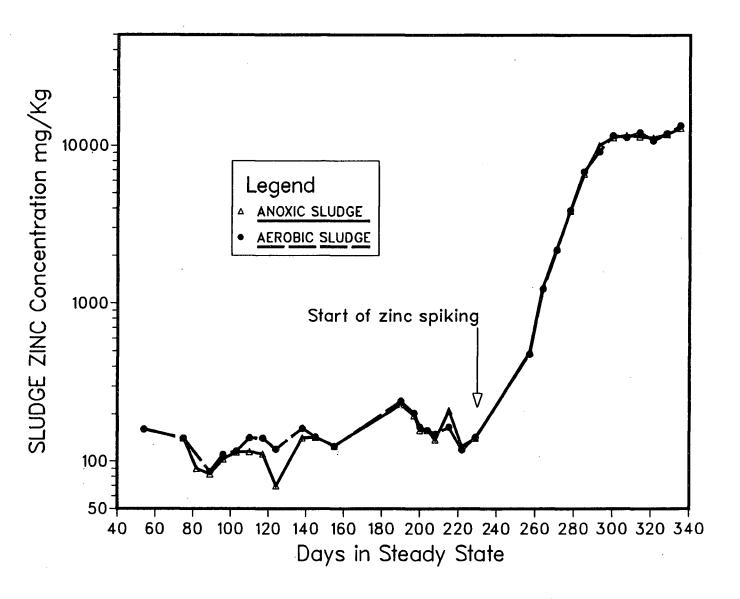


Figure 45.: Sludge Zinc Concentration Versus Time

The purpose of this study was to determine conclusively whether or not a high ammonia leachate could be treated successfully, using a nitrification–denitrification activated sludge system. This study has 340 days of "steady state" operation data, that shows that the ammonia in a high ammonia leachate can be removed, by essentially 100%. The leachate contains a wide variety of metals, many of which are known to inhibit the nitrification process. This study showed that influent zinc severely inhibited the nitrification process, although bacterial acclimitization appeared to be possible. Chromium, lead and nickel are some of the other metals known to inhibit the nitrification process. Studies to determine the inhibitory concentration of these other metals are vital if treatment of a high ammonia leachate, on a full scale, is to be successful.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

Municipal leachate, obtained from the Port Mann landfill site near Vancouver, was treated in a biological treatment system, consisting of an anoxic basin (for denitrification), an aerobic basin (for carbon and ammonia removal) and a final clarifier (with provision for recycle back to the anoxic basin). Solids wasting, to control SRT, was carried out directly from the aerobic reactor. This unit ran for a total of 340 days and based on the operational procedure and time, the following conclusions can be made:

1. Overall COD removal was excellent and averaged 73.9%; however, this was dependent on the amount of glucose entering the system for denitrification, since most of the influent leachate COD consisted of refractory organics. However, before the addition of glucose, a 20% removal of the leachate influent COD was obtained. Of the COD removed across the system, 85% was used in the anoxic reactor for denitrification, and the remaining 15% was used up by the heterotrophs in the aerobic reactor. The COD (used)/NOT (reduced) ratio averaged 13:1 in the anoxic reactor, and ranged from 2.8 to 50:1. The COD used across the anoxic reactor was probably made up of COD used for denitrification, COD used by bacteria other than denitrifiers, and COD used to produce polysaccharides.

2. Essentially 100% of the ammonia in the influent leachate was removed. The effluent from the system averaged less than 1 mg/L most of the time. Approximately 25% of the incoming ammonia was utilized as a nutrient source by the bacteria in the anoxic reactor; the rest of the ammonia was successfully nitrified, assimilated and stripped in the aerobic reactor. The mean anoxic and aerobic ammonia removal rates are 82 and 132 gm-N/m³/day, respectively.

3. Since the influent leachate had very low biodegradable carbon, an extra carbon source (glucose) was added to aid in denitrification. Essentially complete denitrification was obtained at various

times in the study. Only partial denitrification was obtained the rest of the time, because of the variant carbon loading to the anoxic reactor.

4. For the four metals monitored regularly, the mean removal efficiencies were: zinc = 75%, iron = 95.6%, manganese = 87.6% and nickel = 9.5%. The effluent iron values were not consistently below the B.C. discharge guidelines. Before additional metal spiking, the rest of the metals in the effluent were always below the B.C. discharge guidelines. After deliberately increasing the zinc and manganese influent levels, the respective effluent concentrations were consistently above the B.C. discharge guidelines. Other metals in the leachate were of little consequence, since they were of low influent concentration to begin with.

5. Three of the metals monitored regularly, zinc, iron and manganese, accumulated extensively in the sludge. For all these metals, the sludge metal concentration followed closely the trend of the influent metal concentration. The sludge iron levels reached a maximun of about 115000 mg/Kg at the beginning of the study, and continued decreasing from then on. The sludge zinc and manganese values were also high, due to spiking, and reached values of 13400 mg/Kg and 7600 mg/Kg respectively. Nickel removal was very low and therefore resulted in very low (non detectable) nickel sludge values.

6. When the manganese influent concentrations were elevated, no inhibition to nitrification was observed. Throughout this period, nitrification took place, and all of the influent ammonia was removed. However, zinc spiking caused substantial inhibition of the nitrification system. The "inhibition concentration" appeared to be between 14.5 and 17.6 mg/L total zinc (95% soluble), resulting in approximately 70 mg/L of ammonia in the effluent (feed = 216 mg/L). There is also a possibility that this inhibition was due to a synergistic effect between manganese and zinc, since the manganese concentration was also maintained at a fairly high level during zinc spiking. The high zinc concentration also resulted in a MLSS concentration of about 355 mg/L in the effluent.

Note: After the initial inhibition, the zinc concentration was subsequently decreased, thus allowing the nitrification system to recover. When the system returned to normal, the influent zinc concentrations were again increased; however, no inhibition was detected this time, even up to total zinc (>95% soluble) influent levels of 19.5 mg/L. This seems to indicate that the system had acclimitized to the high concentrations of zinc. At this point, the study was terminated and, therefore, the extent of acclimitization could not be determined.

6.2 <u>RECOMMENDATIONS</u>

Based on the results of this study, it is recommended that:

1. A study be carried out whereby the zinc concentration in the system is again increased to the inhibition point (w.r.t. nitrification), then decreased, so that the system can recover. Following this, the zinc levels should be increased again, to see if acclimitization can be achieved. In this manner, the extent of acclimitization might be determined. This study would be a direct continuation from this thesis, at the point of termination.

During the last phase of this work, a high influent manganese concentration was also maintained during the zinc spiking period; therefore, the inhibition caused could have been a synergistic effect between zinc and manganese. In the next phase of research, only the zinc concentration would be increased and the influent manganese concentrations left as found in the leachate (relatively low levels). If inhibition did occur this time, it would prove that inhibition to nitrification was caused only by zinc and not a synergistic effect between zinc and manganese.

2. A study be undertaken whereby the aerobic SRT is varied when the system is receiving a zinc concentration close to the inhibitory concentration for nitrification, to see what effect SRT might have on system recovery at sustained zinc levels. If inhibition could be controlled by SRT, then this information would be invaluable in the operation of a full-scale treatment plant, since SRT is easy to control and change in response to influent metal levels. This would also indicate if the sludge

zinc concentration is directly related to SRT manipulation. Work done for this thesis has indicated that, with respect to zinc, it might be the influent concentration, rather than the sludge concentration, that causes inhibition of the nitrification system. However, the data base is inconclusive at this point and needs expansion.

3. A study be carried out where nitrification rates would be measured while increasing the zinc concentrations to the system (mg NH_4 oxidized/time/gVSS). This would indicate relative inhibition to the nitrifiers for different zinc concentrations, and this information could be used for any nitrification system. However, the system used for this research, should maintain a constant MLVSS concentration, otherwise the nitrate rates measured would be misleading.

4. Cold temperature work should also be done in conjunction with the three studies discussed above. In the northern hemisphere, liquid waste temperatures in the winter can drop quite low; this low temperature also stresses the nitrifiers, causing temperature inhibition. Therefore, the cumulative effect of cold temperature and metal inhibition must be determined. This information would be very useful for successful "high ammonia leachate" treatment during the winter.

5. A study be undertaken to determine the effect and inhibitory concentration (to nitrification) of other heavy metals found in leachate. Nickel, cadmium, chromium and copper have also been postulated as being inhibitory/toxic to nitrifiers.

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APPENDICES (DATA FOR FIGURES)

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Nitrate + Nitrite - Anoxic, Aerobic and Effluent	
Influent, Anoxic and Effluent Ammonia (system 1)	
Influent and Effluent COD	101
Influent and Effluent BOD ₅ BOD ₅ Removal Efficiency	
Percent COD Removed Across the Anoxic and Aerobic Reactors Percent BOD ₅ Removed Across the Anoxic Reactor	
COD (used)/NOT (reduced) Across the Anoxic Reactor COD Removal Efficiency MLVSS/MLSS (Aerobic)	
Carbon Feed COD/Leachate Influent COD Versus COD Removal Efficiency, Anoxic MLVSS and Aerobic MLVSS	105
Percent BOD ₅ Removed Across the Aerobic Reactor Anoxic and Aerobic pH	106
ORP in the Anoxic Reactor Unit Nitrification and Denitrification Rates	107
Anoxic and Aerobic Ammonia Removal Rates (mg NH ₄ ⁺ removed/hr/gm VSS) Anoxic Ammonia Removal Rates (gm NH ₄ ⁺ removed/m ³ /day)	108
Percent Nitrification (system 1) Defn. A and B Percent Ammonia Removal Across the Anoxic Reactor	109
Metals	
Influent and Effluent SS Influent VSS	

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Effluent VSS	
Anoxic and Aerobic MLSS	
Anoxic and Aerobic MLVSS	
MLVSS/MLSS (Anoxic)	
Aerobic Ammonia Removal Rates (gm NH4 ⁺ removed/m ³ /day)	

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DAY	NITRATE + NITRITE (ANOXIC) (mg/L)	NITRATE + NITRITE (AEROBIC) (mg/L)	NITRATE + NITRITE (EFFLUENT) (mg/L)
DAY 1 5 8 12 15 19 22 26 29 33 40 43 47 54 61 78 85 89 96 99 103 106 113 117 120 124 138 141 155 190 204 205 215 200 204 205 205 205 205 205 205 205 205	NITRITE (ANOXIC)	NITRITE (AEROBIC)	NITRITE (EFFLUENT)
257 260 264	45 54 61	58 87 78	58 87 78

DAY	NITRATE + NITRITE (ANOXIC) (mg/L)	NITRATE + NITRITE (AEROBIC) (mg/L)	NITRATE + NITRITE (EFFLUENT) (mg/L)
267	61	78	78
271	15	22	22
274	36	51	51
278	25	34	34
281	28	41	41
285	41	57	57
289	33	45	45
293	20	32	32
296	12	23	23
307	74	89	89
311	32	44	44
314	13	25	25
317	20	31	31
321	39	50	50
324	1	11	11
328	1	11	11
331	1	6	6
335	1	8	8

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$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	DAY	INFLUENT AMMONIA (SYSTEM 1) (mg/L)	ANOXIC AMMONIA (SYSTEM 1) (mg/L)	EFFLUENT AMMONIA (SYSTEM 1) (mg/L)
5 258 41 0.3 8 288 50 0.8 12 235 52 0.3 15 220 50 0.6 19 225 40 1.0 22 240 34 0.4 26 248 48 5.8 29 238 32 4.0 33 238 32 4.0 36 269 42 1.0 40 260 42 2.6 43 263 33 1.1 47 263 36 1.0 50 235 40 2.3 61 235 35 1.5 71 219 26 0 78 230 42 2.0 89 227 38 2.0 92 238 55 2.0 92 238 55 2.0 92 238 37 30 103 235 </td <td></td> <td></td> <td></td> <td></td>				
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15 220 50 0.6 19 225 40 1.0 22 240 34 0.4 26 248 48 5.8 29 238 42 4.0 33 238 32 4.0 36 269 42 1.0 40 260 42 2.66 43 263 43 1.1 47 263 36 1.0 50 225 40 2.33 61 235 35 1.5 71 219 26 0 78 230 42 2.0 82 223 37 2.0 85 224 33 2.0 89 227 38 2.0 96 230 37 3.0 99 247 46 2.0 103 235 $ 10.0$ 106 241 67 11.0 110 235 37 0 1117 235 23 0 124 204 25 0 138 238 $ 0$ 141 223 27 0 144 174 19 0 190 170 18 0 194 174 19 0 225 244 23 0 225 223 26 0 225 223 26 0 225 144 </td <td>12</td> <td></td> <td></td> <td></td>	12			
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DAY	INFLUENT AMMONIA (SYSTEM 1) (mg/L)	ANOXIC AMMONIA (SYSTEM 1) (mg/L)	EFFLUENT AMMONIA (SYSTEM 1) (mg/L)
267	159	17.5	0
271	142	15	0
274	134	14	0
278	131	11	0
281	168	18	0
285	149	17	0
289	187	57	40
293	216	92	71
296	217	85	72
300	214	30	19
307	157	31	12
311	151	22.5	8
314	143	7.5	0
317	122	11	õ
321	134	14	õ
324	133	13	õ
328	132	12	ŏ
331	141	13.3	Ŭ ·
335	129	11	õ
000			v

(CONTINUED)

DAY	LEACHATE INFLUENT COD (mg/day)	EFFLUENT COD (mg/day)	LEACHATE INFLUENT + CARBON FEED COD (mg/day)
· 1	2631	2015	
5	2506	1935	_
8	3074	2660	
12	3663	4516	11058
15	2624	2256	8944
19	2570	2200	8400
22	2704	2316	9296
26	3588	3588	9935
29	2857	3688	9171
33	2456	3453	8487
36	3061	3571	8426
40	2085	2857	7061
43	2328	3886	9802
47	2328	3183	11402
50	2754	3267	13268
54	2367	2367	10836
61	3614	3673	9665
71	1548	1138	7411
78	2480	1837	16342
85	2085	1859	15030
92	2508	2242	15405
99	2936	2746	9467
106	3261	3008	14662
113	1486	1290	8556
120	2125	1802	12860
141	1723	1505	10078
155	2031	1994	13207
190	1509	1401	11333
197	1956	1996	14248
204	2195	1923	15795
218	1894	1523	15250
225 232	3038	2870	15414
252	2354 2197	2070	11120
267	1776	2056 1932	10889
274	1742	1695	10306 10890
281	2209	2115	14152
289	2176	2406	14152
296	1253	1274	9040
311	1889	1926	9038
317	1501	1540	8273
324	1552	1493	12078
331	1673	1572	12553

 DAY	LEACHATE INFLUENT BOD5 (mg/L)	LEACHATE INFLUENT + CARBON FEED (mg/L)	EFFLUENT BOD5 (mg/L)
71	24	_	_
85	12	1091	13
92	6	835	18
99	13	295	22
106	9	553	12
113	9	956	4
120	9	868	5

DAY	BOD5 REMOVAL EFFICIENCY (%)
85	99
92	98
99	93
106	98
113	99.6
120	99.4

DAY	PERCENT COD REMOVED ACROSS ANOXIC (%)	PERCENT COD REMOVED ACROSS AEROBIC (%)	PERCENT BOD5 REMOVED ACROSS ⁵ ANOXIC (%)
0	43.0	F7 0	
8		57.0	-
12	45.0	55.0	-
15	84.0	16.0	-
19 22	77.0 77.0	23.0	-
22 29	77.0	23.0 23.0	-
29 33	55.0	45.0	-
35	83.0	17.0	-
30 40	73.0	27.0	-
40 43	75.0	25.0	-
43 47	93.0	7.0	_
50	61.0	39.0	_
54	71.0	29.0	_
61	66.0	34.0	_
71	83.0	17.0	_
78	93.0	7.0	_
85	94.0	6.0	96
99	86.0	14.0	86
106	88.0	12.0	97
113	96.0	4.0	96
120	92.0	8.0	82
141	95.0	5.0	-
155	98.0	2.0	-
190	91.8	8.2	· _
197	63.0	37.0	_
204	99.5	0.5	_
218	97.8	2.2	-
225	99.5	0.5	-
232	95.1	4.9	-
260	99.4	0.6	-
267	99.4	0.6	-
274	98.3	1.7	-
281	98.5	1.5	-
289	97.6	2.4	-
296	81.8	18.9	-
311	99.5	0.5	-
324	98.5	1.5	-
331	85.7	14.3	-

DAY	COD (USED)/NO _{TT} (REDUCED) ACROSS ANOXIC (mg/d/mg/d)	COD REMOVAL EFFICIENCY (%)	MLVSS/MLSS (AEROBIC)
1	-	23.0	0.44
5 8 12	-	23.0 13.0	_ 0.43
12	-	59.0	0.49
15	-	75.0	
19	3.6	74.0	
22 26	4.7	74.0 75.0 64.0	0.55 -
20 29 33	4.8 2.8	60.0 59.0	0.52
36	5.2	58.0	0.52
40	3.8	60.0	
43	3.1	60.0	0.55
47	7.2	72.0	
50	5.1	75.0	0.57
54	4.7	78.0	
61	3.4	62.0	0.63
71	10.4	85.0	
78 85 92	10.8 11.3	89.0 88.0	0.72 0.72
92	_	85.0	0.73
99	5.2	71.0	
106	6.9	80.0	
113	12.2	85.0	0.70
120	10.5	86.0	0.71
141	8.6	85.0	0.71
155	12.6	85.0	
190	8.9	87.6	0.60
197	10.8	86.0	0.62
204	10.8	87.8	0.68
218	18.2	90.0	0.66
225	11.8	81.4	0.67
232	10.4	81.4	0.64
260	7.5	81.1	0.66
267	20.8	81.3	0.64
274	22.7	84.4	0.67
281	33.2	85.1	0.71
289	52.1	83.1	0.74
296	14.6	85.9	0.79
311	25.5	78.7	0.77
317	20.3	81.4	0.77
324	22.3	87.6	0.75
331	42.8	87.5	0.75

CARBON FEED COD/ LEACHATE INFLUENT COD (mg/d/mg/d)	COD REMOVAL EFFICIENCY (%)	ANOXIC MLVSS CONC' (mg/L)	AEROBIC MLVSS CONC' (mg/L)
 0	23 23	874 488	894 537
. 0	13		-
2.02	59	_	_
2.02	75	1036	944
2.27	74	1050	-
2.44	75	1748	879
2.21	90	1376	1034
2.46	59	-	_
1.75	58	1402	1225
2.39	60		
3.21	60	1612	1154
3.90	72		
3.82	75	1712	1393
3.56	78	-	-
1.68	62	-	-
3.79	85	1179	1742
5.59	89	1798	2430
6.21	88	2256	3136
5.14	85	3027	3948
2.23	71	-	· _
3.50	80	-	-
4.76	85	2245	2812
5.05	86	2580	3193
4.85	85	1972	2300
5.50	85	-	-
6.50	88	2740	3326
6.28	86	3558	4168
6.19	88 90	4069	4498
7.05	90 81	4516	5169
4.07	81	4614	5277 4535
3.72	81	4267 2672	2782
3.96 4.80	81	2672	2681
5.25	84	2441 2664	2797
5.41	85	3147	3395
5.55	83	3389	3987
6.21	86	3880	3836
3.78	79	3005	3328
4.51	81	2806	3123
6.78	88	3208	3449
6.50	88	4616	4875

DAY	PERCENT BOD5 REMOVED ACROSS AEROBIC (%)	ANOXIC REACTOR pH	AEROBIC REACTOR pH
1		7.40	7.30
5	-	7.50	7.00
5 8	-	7.50	7.20
12	· _	7.40	7.00
15	· _	7.65	7.60
19	-	7.80	8.00
22	-	8.00	7.90
26	_ · · ·	7.70	7.70
29	-	7.90	7.85
33	-	7.90	7.80
36	-	7.95	8.00
40	-	7.95	8.10
47	-	8.10	8.20
50	-	7.90	8.10
54	-	8.00	8.10
61	-	7.80	8.05
71	-	7.95	8.15
82	-	8.00	8.10
85	4	8.10	8.30
89 92	-	7.90	8.20
92 99	14	8.00 7.90	8.20 8.00
106	3	8.00	8.00
113	4	7.84	8.04
120	18	7.90	8.00

DAY	ORP IN THE ANOXIC REACTOR (Ecal.)	UNIT NITRIFICATION RATES (mg NO _T PRODUCED/ hr/gm VSS	UNIT DENITRIFICATION RATES (mg NO _T REDUCED/ hr/gm VSS
1	_	7.66	_
15	-	7.21	-
22	_	12.36	27.4
29	_	8.13	26.7
36	. –	6.39	22.9
43	_	8.25	36.7
50	-	4.43	29.0
71	-	4.51	17.7
78		3.36	29.0
85	-	2.32	20.3
92	-	1.56	13.9
113	· _	3.02	10.6
120	-	2.52	17.0
141	-	3.36	21.0
190	-	1.78	15.6
197 204	-	0.10	-
204 218	-	1.44 0.70	13.1 6.8
210	_	1.25	9.6
232	- 69.5	1.10	8.1
257	-118.5	-	-
260	-145.5	2.94	18.3
264	-138.0	_	_
267	- 124.5	1.49	6.8
271	-123.5	-	-
274	-125.5	1.21	6.2
278	-125.5		-
281	-126.0	0.92	4.7
285 289	-126.0	-	-
289	-144.5 -172.5	0.68	2.7
295	-193.0	0.63	- 4.8
300	-185.0	-	
307	- 87.0	-	_
311	-143.5	0.87	3.8
314	-142.5	_	_
317	-116.5	0.82	5.6
321	- 78.0	-	-
324	-202.5	0.66	6.1
328	-272.0	-	-
331 335	-279.0 -308.0	0.22	2.0
222	-300.0	-	-

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DAY	AMMONIA REMOVAL RATE (ANOXIC) (mg NH ₄ REMOVED/ hr/gm VSS)	AMMONIA REMOVAL RATE (AEROBIC) (mg NH4 REDUCED/ hr/gm VSS)	AMMONIA REMOVAL RATE (ANOXIC) (gm NH_4 REDUCED/ m^3/DAY)
1	3.70	9.55	78
8	-	19.10	-
15	2.33	10.90	58
22	2.33	7.48	99
29	2.40	8.45	88 .
36	5.32	6.60	179
43	2.65	7.00	103
50	3.48	4.90	143
71	2.14	2.10	61
78	1.61	2.70	69
85	1.37	1.80	74
92	1.06	1.92	77
113	2.47	1.14	133
120	1.76	1.90	108
141	1.50	2.40	71
190	0.51	1.23	34
197	0.95	0.71	81
204	1.30	1.15	127
218	0.51	0.80	56
225	0.54	1.40	60
232	0.89	1.00	91
260	1.12	2.32	72
267	0.95	1.49	56
274	0.95	1.13	60
281	1.41	1.28	106
289	1.04	0.96	85
296	0.19	0.74	18
311	1.35	1.05	97
317	0.94	0.82	64
324	0.69	0.85	53
331	0.45	0.60	50

DAY	PERCENT NITRIFICATION (SYSTEM 1) (%) (DEFN.: A)	PERCENT NITRIFICATION (SYSTEM 1) (%) (DEFN.: B)	PERCENT AMMONIA REMOVED ACROSS ANOXIC REACTOR (%)
1	73.8	73.8	15.9
5 8	-	-	16.6
8	83.0	83.0	21.8
12	54.0	54.0	-
15	65.0	65.0	-
19	137.5	137.5	-
22	144.4	144.4	23.9
26	108.3	108.3	19.7
2 9	102.4	102.4	20.4
33	125.0	125.0	32.9
36	104.8	104.8	32.3
40	83.3	83.3	17.0
43	109.3	109.3	22.1
47	102.8	102.8	34.5
50	88.8	88.8	31.6
61	125.7	125.7	-
71	115.4	115.4	25.3
78	100.0	100.0	18.1
82	106.8	106.8	21.1
85	93.9	93.9	21.2
89	73.7	73.7	27.3
92	72.7	72.7	17.0
96	86.5	86.5	27.8
99	101.1	101.1	23.4
103	94.2	94.2	
106	71.6	71.6	_
110	113.5	113.5	30.4
113	152.6	152.6	— .
117	117.4	117.4	30.4
120	112.9	112.9	27.1
124	120.0	120.0	26.1
141	140.7	140.7	21.2
145	132.1	132.1	29.9
152	88.5	88.5	26,6
155	106.7	106.7	23.8
190	144.4	144.4	14.7
194	78.9	78.9	18.2
197	0	0	37.8
200	104.3	104.3	36.3
204	126.1	126.1	33.9
208	116.0	116.0	37.3
215	114.3	114.3	47.2
218	88.2	88.2	22.0
225	89.7	89.7	14.5
229	100.0	100.0	-
232	110.5	110.5	29.7
257	68.4	68.4	21.3
260	126.9	126.9	18.8
264	130.8	130.8	34.8
267	100.0	100.0	22.6

(CONTINUED)

DAY	PERCENT NITRIFICATION (SYSTEM 1) (%) (DEFN.: A)	PERCENT NITRIFICATION (SYSTEM 1) (%) (DEFN.: B)	PERCENT AMMONIA REMOVED ACROSS ANOXIC REACTOR (%)
271	46.7	46.7	22.7
274	107.1	107.1	28.5
278	81.8	81.8	34.9
281	72.2	72.2	33.8
285	94.1	94.1	28.5
289	70.6	21.1	12.1
293	57.1	13.0	3.2
296	84.6	12.9	2.0
300	-	-	22.7
307	78.9	- 48.4	11.1
311	82.8	53.3	27.3
314	160.0	160.0	-
317	100.0	100.0	34.0
321	78.6	78.6	30.6
324	77.7	77.7	27.4
328	90.0	90.0	36.5
331	52.6	52.6	26.6
335	63.6	63.6	34.8

DAY	INFLUENT MANGANESE (UNFILTERED) (mg/L)	EFFLUENT MANGANESE (FILTERED) (mg/L)	IRON REMOVAL EFFICIENCY (%)
54	0.184	0.034	99.0
75	0.176	0.008	-
82	0.067	0	98.7
89	0.135	0.007	-
96	0.028	0.006	_
103	0.024	0.042	_
110	0.096	0.004	98.7
117	0.140	0	99.0
124	0.082	0.010	99.3
138	0.132	0.020	80.0
145	0.161	0.009	83.3
155	0.286	0.012	90.9
190	0.475	0.025	98.7
197	1.390	0.190	92.9
200	1.740	0.012	98.9
204	0.750	0.015	98.7
208	3.820	0.040	98.8
215	9.170	0.020	99.1
222	12.300	0.020	97.6
229	9.160	0.039	90.0
257	4.336	1.070	98.7
260	3.702	-	_
264	4.004	0.010	99.7
271	4.333	0.049	93.7
278.	4.757	0.560	97.1
285	3.453	1.930	95.0
289	2.691	-	-
293	3.527	0.920	94.7
296	4.688	-	-
300	4.162	0.870	96.3
307	2.287	1.090	94.1
314	2.907	0.670	97.4
317	3.490	-	-
321	3.345	0.320	-
324	5.123	-	95.9
328	4.840	0.830	-
331	5.210	-	-
335	5.180	0.550	-

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DAY	SLUDGE	SLUDGE	MANGANESE REMOVAL
	MANGANESE (ANOXIC)	MANGANESE (AEROBIC)	EFFIÇIENCY
	(tng/kg)	(mg/kg)	(%)
54	_	500	81.5
75	290	330	95.5
82	325	_	100.0
89	289	320	94.8
96	332	357	78.6
103	332	344	-
110	308	334	95.8
117	273	311	100.0
124	234	273	87.8
138	330	363	84.8
145	392	386	94.4
155	-	-	95.8
190	687	743	94.7
197	778	`862	86.3
200	821	866	88.8
204	808	873	98.0
208	1259	1573	99.0
215	2181	2086	99.8
222	4432	4593	99.8
229	6629	6905	99.6
257	7415	7214	75.3
264	7620	7097	99.8
271	7133	7186	88.7
278	5974	6321	88.2
285	4906	5077	44.1
293	3903	3503	73.9
300	4605	4698	79.1
307	4896	4813	52.3
314	5068	5310	76.9
321	4877	4663	90.4
328	4446	4442	82.9
335	5104	5324	89.4

DAY	INFLUENT IRON-FILTERED (mg/L)	EFFLUENT IRON-FILTERED (mg/L)	INFLUENT IRON-UNFILTERED (mg/L)
54	—	-	36.2
75	-	-	30.0
82	-	-	22.0
89	1.9	0.9	-
96	2.0	0.12	· -
103	2.0	0.8	-
110	-	-	18.0
117		-	24.0
124	-	_	19.8
138	-	—	13.0
145	-	-	10.5
155	-	_	28.5
190			17.0
197	-	-	20.5
200	-	-	32.9
204		-	23.0
208	-	-	14.5
215	-	-	18.0
222	-	-	9.8
229	-	-	4.3
257	-	-	17.4
264	-	-	11.1
271	-	-	5.1
278	-	-	5.8
285	-	-	3.5
293	-	-	8.8
300	-	-	7.6
307	-	-	3.7
314	-	-	6.8
321	-	-	4.6

DAY	EFFLUENT IRON-UNFILTERED (mg/L)	SLUDGE IRON (ANOXIC) (mg/kg)	SLUDGE IRON (AEROBIC) (mg/kg)
54	0.365	_	113000
75	0.303	98000	98000
82	0.290	84746	98000
89	0.900	83476	88652
96	0.120	86996	88652
103	0.800	98039	87173
105	0.240	100781	99870
110	0.230	83185	97851
124	0.140	74836	81815
138	2.600	64825	64725
145	1.750	71191	70349
155	2.600	71179	73684
190	0.225	42204	6 <u>0</u> 240
190	1.450	36039	39435
200	0.360	51875	34295
200	0.300	43580	47001
204	0.180	35405	38425
215	0.170	41700	37012
222	0.240	31690	29837
229	0.430	27766	28838
257	0.220	24629	25723
264	0.030	34482	32843
271	0.320	26721	27834
278	0.170	24890	25420
285	0.175	20420	17894
293	0.470	16729	17932
300	0.280	17959	18750
307	0.220	21996	24067
314	0.180	20273	19502
321	0.190	15537	8608

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, DAY	INFLUENT NICKEL (mg/L)	EFFLUENT NICKEL (mg/L)	NICKEL REMOVAL EFFICIENCY (%)
54	0.038	0.038	0
75	0.028	0.023	17.9
82	0.025	0.025	0
89	0.035	0.032	8.6
96	0.028	0.035	-25.0
103	0.029	0.029	-25:0
110	0.029	0.029	0
117	0.028	0.028	õ
124	0.048	0.045	6 . 3
138	0.056	0.051	8.9
145	0.056	0.052	7.1
155	0.066	0.056	15.2
190	0.030	0.030	0
197	0.027	0.025	7.5
200	0.032	0.024	25.0
204	0.022	0.021	4.6
208	0.025	0.025	0
215	0.028	0.024	14.3
222	0.026	0.022	15.4
229	0.030	0.023	23.3
257	0.034	0.030	11.8
264	0.031	0.015	51.6
271	0.034	0.029	14.7
278	0.033	0.029	12.1
285	0.033	0.032	3.0
293	0.037	0.032	13.5
300	0.029	0.028	3.4
307	0.033	0.030.	9.1
314	0.033	0.029	12.1
321	0.039	0.033	15.4

DAY	INFLUENT ZINC (mg/L)	EFFLUENT ZINC (mg/L)	EFFLUENT AMMONIA (SYSTEM 2) (mg/L)
5.4	0.000	0.000	
54	0.060	0.030	-
75	0.068	0.003	-
82	0.045	0.028	. –
89	0.019	0.030	-
96	0.031	0.020	— .
103	0.018	0.020 0.025	-
110 117	0.060 0.155		-
117		0.011	-
138	0.039	0.010	-
138	0.080 0.045	0.025 0.012	-
145	0.025	0.001	-
190	0.179	0.019	0
190	0.179	0.019	0
194	0.124	0.008	1
200	0.089	0.010	0
200	0.051	0.010	õ
204	0.038	0.010	õ
200	0.140	0.010	ŏ
213	-	-	õ
222	0.052	0.008	ŏ
225	-	-	ŏ
229	0.050	0.026	õ
232	_	-	õ
257	1.356	0.108	Õ
260	2.012	-	0
264	2.791	0.008	0
267	_	-	0
271	2.890	0.270	0
274	-	-	0
278	8.990	0.415	0
281	8.990	-	0
285	14.966	2.240	0
289	17.678	-	0
293	16.838	2.390	0
296	10.337	-	0
300	9.238	1.380	1
307	4.545	1.410	0
311	_	-	0
314	5.512	0,960	0
317	6.701	-	0
321	8.493	0.570	0
324	14.493	-	0
328	13.820	1.080	0
331	18.190	-	0
335	19.330	1.370	0

DAY	SLUDGE ZINC (ANOXIC) (mg/kg)	SLUDGE ZINC (AEROBIC) (mg/kg)	ZINC REMOVAL EFFICIENCY (%)
-			
54	-	160	50.0
75	140	140	95.6
82	90	-	37.8
89	83	86	-57.9
96	103	110	35.5
103	114	116	-
110	115	141	58.3
117	111	140	92.9
124	70	119	74.3
138	141	162	68.8
145	142	143	73.3
155	125	124	100.0
190	229	241	89.4
197	195	202	93.5
200	157	165	88.8
204	157	157	68.8
208	137	149	73.7
215	210	165	85.7
222	124	118	84.6
229	140	142	48.0
257	490	478	92.0
264	1277	1236	99.7
271	2219	2176	90.7
278	3855	3890	95.4
285	6608	6825	85.0
293	10060	9118	85.8
300	11291	11595	85.1
307	11684	11321	69.0
314	11415	12148	82.6
321	11221	10736	93.3
328	11797	11953	92.2
335	12939	13405	92.9

DAY	INFLUENT SS (mg/L)	EFFLUENT SS (mg/L)	INFLUENT VSS (mg/L)
1	54	70	15
8	89	48	28
15	123	15	32
22	82	45	20
29	42	31	10
36	87	25	26
43	52	39	15
50	90	42	23
71	94	27	26
78	96	36	36
85	102	34	28
92	106	44	32
99	117	45	-
113	105	25	25
120	80	52	29
141	59	125	14
190	134	76	23
197	145	38	44
204	89	78	26
218	119	65	25
225	77	138	24
232	68	178	17
260	96	160	27
267	225	155	11
274	25	170	4
281	84	165	18
289	78	351	12
296	27	148	3
311	132	99	13
317	132	60	-
324 331	107 75	82	18
221	75	82	23

DAY	EFFLUENT VSS (mg/L)	ANOXIC MLSS (mg/L)	AEROBIC MLSS (mg/L)
1	24	1871	2016
8	20	1117	1251
15	13	2019	1912
22	28	2777	1607
29	16	2594	1980
36	19	2678	2367
43	32	2945	2115
50	32	2971	2439
71	18	1819	2770
78	33	2457	3370
85	23	3127	4361
92	39	4149	5424
99	-	3607	4704
113	6	3223	4050
120	44	3558	4435
141	89	2831	3227
190	63	4212	5536
197	14	5401	6744
204	63	5833	6621
218	32	6680	7797
225	99	6815	7894
232	128	6560	7035
260	130	4016	4223
267	96	3755	4174
274	118	3907	4169
281	130	4418	4813
289	278	4594	5406
296	119	4899	4864
311	78	3889	4336
317	22	3645	4082
324	64	4237	4572
331	67	6171	6531

DAY	ANOXIC MLVSS (mg/L)	AEROBIC MLVSS (mg/L)	MLVSS/MLSS (ANOXIC)
1	874	894	0.47
8	488	537	0.47
15	1036	944	0.51
22	1748	879	0.63
29	1376	1034	0.53
36	1402	1225	0.52
43	1612	1154	0.55
50	1712	1393	0.58
71	1179	1742	0.65
78	1798	2430	0.73
85	2256	3136	0.72
92	3027	3948	0.73
113	2245	2812	0.70
120	2580	3193	0.73
141	1972	2300	0.70
190	2740	3326	0.65
197	3558	4168	0.66
204	4069	4498	0.70
218	4516	5169	0.68
225	4614	5277	0.68
232	4276	4535	0.65
260	2672	2782	0.67
267	2441	2681	0.65
274	2664	2797	0.68
281	3147	3395	0.71
28 9	3387	3987	0.74
296	3880	3836	0.79
311	3005	3328	0.77
317	2806	3123	0.77
324	3208	3349	0.76
331	4616	4875	0.75

DAY	AMMONIA REMOVAL RATE
	(AEROBIC) (gm NH ₄ REMOVED/m ³ /DAY)
1	205
8	246
15	248
22	158
29	210
36	194
43	194
50 71	162 89
71	156
85	136
92	182
113	77
120	146
141	132
190	98
197	71
204	124
218	99
225	177
232 260	108 155
267	96
274	76
281	104
289	92
296	68
311	84
317	62
324	71
331	70